

KINETICS OF THE EMULSION POLYMERIZATION
OF STYRENE

BY
CLARK EDWARD ADAMS

B. A., Vanderbilt University, 1941

M. S., Vanderbilt University, 1942

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE UNIVERSITY
OF ILLINOIS, 1944

URBANA, ILLINOIS

RESTRICTED

547.25
Ad17k

UNIVERSITY OF ILLINOIS

THE GRADUATE SCHOOL

AUGUST 22, 1944

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY
SUPERVISION BY CLARK EDWARD ADAMS

ENTITLED KINETICS OF THE EMULSION POLYMERIZATION OF STYRENE

BE ACCEPTED* AS FULFILLING THIS PART OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY

Charles E. Rice

In Charge of Thesis

Wm. C. Rose

Head of Department

Recommendation concurred in†

H. E. Carter
T. J. Quirk
H. Snyder

Committee

on

Final Examination†

*Subject to successful final examination in the case of the doctorate.

†Required for doctor's degree but not for master's.

ACKNOWLEDGEMENT

The author wishes to express his sincere appreciation for the invaluable assistance of Dr. C. C. Price, who suggested and directed this research.

He also wishes to thank the Copolymer Research Branch of the War Production Board Rubber Research Program at the University of Illinois whose facilities were used in this work.

TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. HISTORICAL AND THEORETICAL	2
A. Solution Polymerization	2
B. Emulsion Polymerization	9
III. DISCUSSION OF RESULTS	18
IV. EXPERIMENTAL	31
Apparatus	31
Reagents	
Soap	32
Potassium Persulfate	33
Styrene	33
Addition of Reagents	36
Sampling	37
Styrene Determination	39
Persulfate Determination	40
pH Determination	42
Molecular Weight Determination	43
Rate Determination	45
Tables and Graphs	46
Molecular weight of the polymer at various conversions	46
Polymerizations 1 and 2	
Change in pH during the polymerization	49
Polymerization 3	
Potassium persulfate concentration during the polymerization	51
Polymerizations 4 and 5	

Effect of the purification of the styrene	53
Polymerizations 5-10	
Air atmosphere	60
Polymerizations 11 and 12	
Effect of the amount of alkali used to prepare the soap	63
Polymerizations 13-15	
Comparison of sodium and potassium soaps	67
Polymerizations 16 and 17	
Effect of soap having a high active oxygen content	70
Polymerizations 18 and 19	
Potassium dehydroabietate as the emulsifying agent	73
Polymerization 20	
Effect of mercaptan	75
Polymerization 21	
Effect of the variation of catalyst and monomer concentration on the rate of polymerization and the molecular weight of the polymer produced	
50°	77
Polymerizations 22-38	
60°	95
Polymerizations 39-41	
40°	99
Polymerizations 42-46	
Table I	105
Summary of polymerizations 5, 10, 22-38 (50°)	
Table II	107
Comparison of zero- and first-order rate constants with change of monomer concentration	
Table III	108
Summary of polymerizations 39-41 (60°)	

Table IV	109
Summary of polymerizations 42-46 (40°)	
Table V	110
Relationship of catalyst concentration and zero-order rate constant	
Table VI	112
Heat of activation	
Table VII	114
Evaluation of toluene constant for molecular weight determination	
V. SUMMARY	115
VI. BIBLIOGRAPHY	116

I. INTRODUCTION

Polymerization in emulsion has become an increasingly important subject for study because of its applicability to commercial production of synthetic rubbers and plastics. The theoretical aspects of this method of polymerization only recently have been investigated in connection with the rapidly increased production of synthetic rubber under the supervision of the United States Government. This problem includes the study of the emulsion polymerization of butadiene and styrene, which is more complex than the study of a single component. For the purpose of simplification, therefore, it was proposed to investigate the emulsion polymerization of styrene alone.

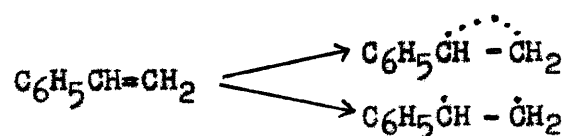
Polymerization of styrene has been intimately connected with the study of kinetics and mechanism of vinyl polymerization. Shortly after Bonastre first isolated styrene by the dry distillation of gum storax in 1831,¹ its reaction to form a high-molecular-weight compound was observed by E. Simon in 1839.² Since that time much data has been accumulated in the study of the polymerization reactions of styrene, so that this compound may be used advantageously in the investigation of the more recent emulsion polymerization technique, without the necessity of background research for comparison with solution polymerization.

II. HISTORICAL AND THEORETICAL

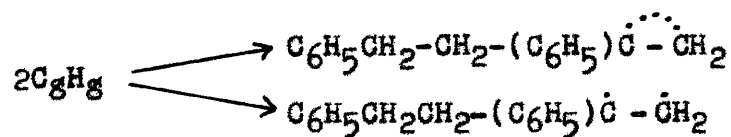
A. Solution Polymerization

The mechanism of the polymerization of styrene has been extensively studied in the gaseous phase,³ in bulk and in solution under many different conditions. It is not surprising that, under the variation of conditions used, the theories advanced by different chemists to explain the observed reactions are not in complete agreement. With time, it has become generally accepted that the course of vinyl polymerizations may be separated into three steps (A) initial activation of monomer molecules, (B) subsequent reaction of these molecules with other monomer molecules to form high-molecular-weight compounds by a chain mechanism, and (C) cessation of the chain reaction to form a stable polymer molecule.

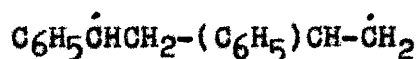
The initiation reaction consists of an activation of the ethylenic double bond. This activation may be brought about by heating, adsorption of light energy⁴ or by catalysts such as peroxides,⁵ metal halides,⁶ alkali metals⁷ or free radicals.⁸ This activation may be merely the formation of an activated state^{9,10} which renders the double bond especially capable of adding a normal molecule, thus forming an active dimer, capable of repeating this process. Initiation of the thermal polymerization of styrene has been explained by Staudinger¹¹ and Schulz and Husemann⁵ by cleavage of one of the bonds of the double bond forming a biradical. Both of these types of activation could be brought about by interference of vibrational energy within a single molecule, giving a monomolecular initiation,



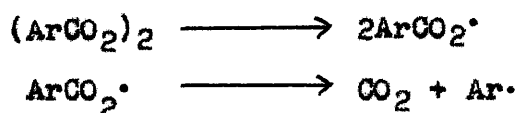
or by a bimolecular reaction.



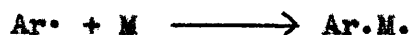
or



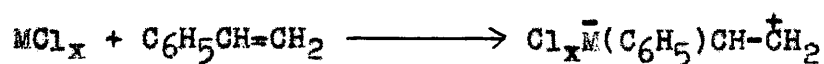
Benzoyl peroxide catalysts have been shown by Price and Kell¹² and S. Kamenskaya and S. Medvedev¹³ to initiate through the formation of free radicals.



Schulz and Wittig⁸ have clearly demonstrated the initiation of polymerization by free radicals from the dissociation of tetraphenylsuccinonitrile and benzeneazotriphenylmethane. Price and Kell¹⁴ used marked benzoyl peroxides to show that the presence of the free radical residue in the polymer is in a molar ratio. This is explained by the mechanism proposed,



and the observed unimolecular kinetics support the mechanism proposed for the reaction. The polymerization of styrene in the presence of electrophilic substances for catalysts, such as stannic chloride and antimony pentachloride, has been investigated by G. Williams.⁶ The initiating reaction of these substances has been explained^{15,16} as the acquisition by the catalyst of a pair of electrons from the double bond of the monomer



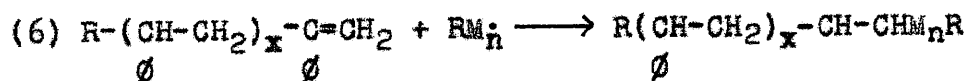
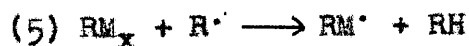
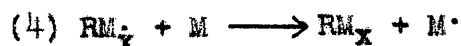
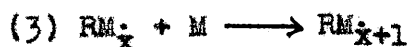
Impurities present in the polymerization are observed to "inhibit" the initiation reaction and cause an induction period. The presence of oxygen has been shown by W. Jorde¹⁷ in thermal polymerization and by H. E. Thompson and R. E. Burk¹⁸ in catalytic polymerization to be inhibitory. H. M. Stanley¹⁹ found that minute amounts of other substances, particularly phenylacetylene, affected the copolymerization of styrene and divinyl benzene. Quinoid, nitro, phenolic hydroxyl, amino and nitroso groups are effective²⁰ in inhibiting the polymerization of styrene.

The propagation reaction transforms the monomeric units into high-molecular-weight polymers. The mechanism generally accepted by most workers in the field is that this step is a chain reaction consisting of a great many reactions occurring in rapid succession. Every step of this reaction is exothermic and the state of the molecule remains the same as the activated monomer produced in the first step. This explanation is in closest agreement with the experimentally observed facts that propagation is extremely sensitive to small amounts of inhibitors²¹ and that the degree of polymerization is very nearly constant throughout the course of the polymerization.^{22,23}

G. S. Whitby¹⁰ holds that the stepwise-addition mechanism applies throughout the polymerization of polystyrene. This view is based on the bromine-adsorbing capacity of the polymerides and the increase of dipole moments of polystyrene with increase in molecular size. The work of R. C. Houtz and H. Adkins,²⁴ that precipitated and dried polystyrene preserves its capacity to

add further quantities of styrene and thus lengthen the chains under conditions of polymerization, supports this view. J. Risi and D. Gauvin,⁹ however, have concluded that low-boiling polymers are saturated and R. Signer and G. Weiller²⁵ found no frequencies corresponding to a double bond in the Raman Spectra of polystyrene. These facts materially weaken the argument of Whitby.

The reactions which take place during propagation by free radicals, though other means of activation give essentially the same reactions, are illustrated. The initiating molecule is represented by R, the monomer by M and the dot indicates the odd electron of the free radical.



Linear growth of the polymer proceeds by reactions (1), (2) and (3). Hydrogen transfer is involved in reaction (4), which does not destroy active centers or affect the rate of reaction. Reaction (4) is designated as chain transfer by H. Staudinger and A. Steinhofer.²⁶

Reactions (5) and (6) illustrate the theory of P. J. Flory²⁷ by which branched chains may be formed. An active radical may collide with a polymer chain at some distance from either end, forming a free radical, as in (5). This radical would be capable of adding monomer units and a branched chain would result. By reaction (6) a growing polymer may react with a "dead" polymer, having a

terminal double bond, in much the same way as it would react with a monomer unit. The active radical which is formed would have an active center in the middle of the polymer chain and further addition of monomer would result in a branched structure.

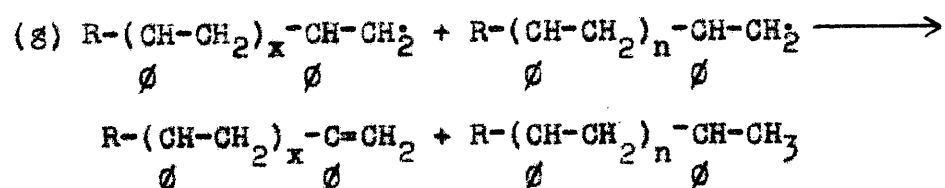
The kinetics for the reactions (3), (4), (5) and (6) are identical, and these mechanisms cannot be distinguished by rate studies. It is possible that all four reactions are involved in chain propagation. R. G. W. Norrish and E. F. Brookman²⁸ have concluded that the rate of the propagation reaction governs the rate of the polymerization and it is this rate which is determined in polymerization studies.

The work of H. Staudinger and A. Steinhöfer²⁶ indicates that the structure of the polystyrene is the regular head-to-tail structure, joining of one substituted and one unsubstituted carbon atom, which is to be expected from a monomer with a polarized double bond. T. Midgley, A. L. Henne and H. M. Leicester²⁹ from their investigations prefer the head-to-head, tail-to-tail structure, two carbon atoms of the same kind, both substituted or both unsubstituted, joined.

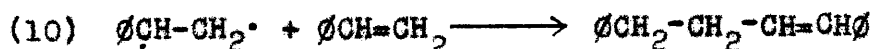
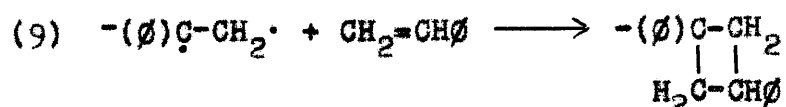
M. Koizumi and T. Titani³⁰ have conducted studies on polymerizations in the presence of heavy water and heavy alcohol. Their results showed no appreciable exchange of hydrogen and deuterium between styrene and the heavy water or alcohol and that there is no appreciable loosening or migrating of hydrogen atoms, at least with respect to the process of initiation and propagation.

Individual active polymeric chains may be deactivated and transformed into stable polymer molecules in several different ways.

Reactions (4), (5) and (6) form stable molecules but do not stop the chain reaction. The chain process may be stopped if two active molecules couple, (7), or disproportionate, (8).



Biradicals from the thermal initiation reaction may be terminated by an internal reaction similar to (8) according to H. Dostal and R. Raff,³¹ or the reaction of an activated molecule and a normal molecule as (9) or (10).



Solvents are known to influence the rate and degree of polymerization³² so that much of the data which has been obtained is complex and difficult to explain. The following equations generally are found to hold for polymerization of styrene in dilute solution.¹² The rate of chain growth is directly proportional to the concentration of active chains and the monomer.

$$(11) \quad \frac{-d[\text{M}]}{dt} = k_B[\text{A}\cdot][\text{M}]$$

The rate of formation of active chains, initiation, is dependent on the concentration of the catalyst.

$$(12) \quad \frac{d[\text{A}\cdot]}{dt} = k_A[\text{Cat}]$$

The rate of destruction of active chains, cessation, is proportional to the square of the concentration of active centers.

$$(13) \quad \frac{-dA}{dt} = k_G [A\cdot]^2$$

Applying the method of the stationary state, since the life of the active polymer, $A\cdot$, is undoubtedly short in comparison with the half life of the polymerization,³³ the rate of formation of active centers, equation (12), will be equal to the rate of their destruction, equation (13). Thus the concentration of active chains will be proportional to the square root of the catalyst concentration.

$$(14) \quad \begin{aligned} k_A [Cat] &= k_G [A\cdot]^2 \quad \text{or} \\ [A\cdot] &= (k_A/k_G)^{1/2} [Cat]^{1/2} \end{aligned}$$

Substitution of equation (14) in equation (11) gives equation (15).

$$(15) \quad \frac{-d[M]}{dt} = k [Cat]^{1/2} [M]$$

Schulz³⁴ found that the average degree of polymerization, $\bar{P}$, was inversely proportional to the square root of the catalyst concentration and directly proportional to the monomer concentration, if the monomer solvent and temperature are held constant. The degree of polymerization depends on the ratio of chain growth to the chain stopping reaction.

$$\bar{P} = \frac{k_B [A\cdot] [M]}{k_G [A\cdot]^2} = k \frac{[M]}{[Cat]^{1/2}}$$

B. Emulsion Polymerization

Attempts to simulate nature in the production of synthetic elastomers to give an artificial latex led to the investigation of polymerization in emulsion. From this work patents³⁵ were granted to the Fredrick Bayer and Company in 1912 for the polymerization of isoprene, butadiene and related compounds emulsified in water by egg albumin, starch or gelatine.

After the close of the first world war, interest in synthetic rubber lapsed as evidenced by a lack of patents for nearly seven years. The increase in price of raw rubber after 1922 again stimulated research in this field. Since 1927, a large number of patents have been granted for synthetic elastomers, especially to the I. G. Farbenindustrie.

Emulsion polymerization has been found to be superior to the use of massive processes. In emulsion polymerization, the reaction proceeds more rapidly and at lower temperatures, avoiding oily by-products, to give a better product than other methods. There is a much greater control of the process and handling of the product is greatly simplified. The toxic, inflammable and expensive solvents necessary for polymerization in solution are avoided. Because of these many advantages, emulsion polymerization is becoming ever increasingly used in commercial production of synthetic rubbers and plastics. Emulsion polymerization was first commercially used by E. I. du Pont de Nemours and Co. in the production of neoprene in 1931. Since this time the process has been extended to the commercial production of buna rubbers, Buna-S, Perbunan, Hycar, and Chemigum. Patents have been granted for the emulsion polymerization

of many other monomers and combination of monomers.

Mark and Raff³⁶ have given an excellent summary of the conditions of emulsion polymerization.

"Our experience so far may, perhaps, be summarized in the following general way:

"A series of components (between five and ten) are needed to build up the colloidal system in which the polymerization is expected to take place and to start and direct the reaction to its proper ending.

1. The basic phase, in which the emulsion is made. This is always, or mostly, water (free from iron, lime, and organic impurities). It is always in excess and represents between 60% and 80% of the weight of the total system.

2. The main monomer--butadiene, vinyl chloride, etc., to build up the backbone of the polymer to be produced. This will amount to about 60-80% of the final polymer or 15-30% of the emulsion.

3. The additional monomers--styrene, acrylonitrile, acrylic esters, vinylacetate, etc., which are present only if copolymers are to be produced. These will represent 20-40% of the weight of the final copolymer or about 5-15% of the initial colloidal system.

4. The emulsifying agent or agents, which enable us to produce colloidal dispersion of the monomers. Many different substances have been described and used and it seems that the actual choice of a special emulgator is of a certain importance for the success of the polymerization. Aliphatic long chain carboxylic and sulfonic acid salts, sulfonated long chain alcohols and amines as well as aromatic alkylated sulfonic acid salts have been applied with success. 0.2-2.0% of emulsifier, reckoned from the weight of the resultant polymer, is usually used.

5. The stabilizer, to prevent a premature precipitation of the emulsion. Various natural and synthetic protective colloids are recommended for this purpose, e.g. gelatine, glue, casein, starch, dextrans, methyl-cellulose, polyvinylalcohol, etc. The usual amount of stabilizer is between 2% and 5% of the weight of the polymer.

6. The regulator of surface tension, the action of which cannot yet be clearly defined. It seems, however, that these substances have to be present to obtain and maintain the most favorable average particle size of the emulsion and to narrow down as much as possible the distribution curve of the size of the dispersed particles of the monomer or mixture of monomers. Aliphatic alcohols of medium chain length C_5 to C_8 seem to serve this purpose best, but aromatic alcohols and amines have been recommended. They amount to between 0.1% and 0.5% of the polymer.

7. The catalyst, of which the main action is, presumably, the acceleration of the formation of polymerization nuclei without

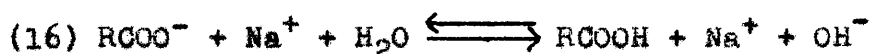
affecting the propagation process. It seems, however, that most substances which catalyze the starting reaction act similarly toward the cessation reaction and thus the addition of too much catalyst may result in a polymer of low molecular weight. Oxygen, ozone, hydrogen peroxide, organic peroxides and ozonides, persulfates, percarbonates, perborates and similar substances act as catalysts; they usually amount to between 0.1% and 1% of the weight of the resultant polymer.

8. The regulator, to direct the polyreaction and, presumably, to act mainly as an 'anti-knocking' agent, avoiding or cutting down branching and cross linking processes during the reaction. Very little is actually known about the action of these substances. Experience has shown, that chlorinated aliphatic hydrocarbons such as CCl_4 , C_2Cl_4 , C_2Cl_6 and similar aromatic compounds have a beneficial influence on the reaction, if about 2 to 5% of the weight of the polymer is added.

9. The pH adjuster or buffer. Most emulsions are very sensitive to the hydrogen ion concentration. The particle size and its distribution curve, the actual mechanism of the reaction and the stability of the final synthetic latex sometimes depend largely on the maintenance of the proper pH. Normal buffers such as phosphates, carbonates, acetates, etc., are usually applied in appropriate amounts (2-4% of the weight of the polymer)."

These conditions indicate that the process of emulsion polymerization is quite complex. Although emulsion polymerization has been in commercial use for over ten years, there has been almost no research on the theoretical aspect of the problem reported in the literature. Recently, however, intensive study of all aspects of emulsion polymerization has been stimulated by the loss of supply of natural rubber in the present war and the sponsorship of the United States Government and its program for research on synthetic rubber. Previous to this time it was generally assumed that the advantages of emulsion polymerization were due to dispersion of the monomer and the great surface of these particles, giving rise to a particularly reactive nucleus for promoting chain reactions and the process of polymerization. Thus it was believed that polymerization of the monomer droplets proceeded inward from the interface with the medium.

H. Finkentscher³⁷ in 1938 proposed that the course of the polymerization was not in the droplet, but in the monomer dissolved in the water which was continuously replaced by solution from the dispersed monomer. Since this time, all of the information obtained has supported this view. C. F. Fryling and E. W. Harrington³⁸ have summarized a number of points supporting the theory that initiation and locus of reaction of emulsion polymerization occurs in the aqueous phase. The observations of these authors on the change in pH during the course of the polymerization are explained on this basis. Considering the equilibrium (16),



the initial decrease in pH on addition of monomer is explained by formation of micelles in the aqueous phase shifting the equilibrium to the left. Addition of monomer removes the fatty acid by solution in the monomer phase, shifting the equilibrium to the right and increasing pH. During the polymerization process monomer is used up, releasing the fatty acid and decreasing the pH. It has also been observed in an undispersed monomer-water-persulfate system, that polymerization only occurs in the aqueous layer, causing cloudiness. This reaction does not occur at the interface for there is a clear layer for 5 mm. below the interface, in which space the monomer has not had time to polymerize. Reaction at the interface is further eliminated for polymerization may be effected in "emulsion" if the emulsion and monomers are separated, the only contact being the monomer vapors. This reaction is thus homogeneous. It is also pointed out that the best catalysts for emulsion polymerization are water soluble. The utility of various substances as emulsifiers in

emulsion polymerization is approximately the same order as their solubilizing action as found by J. W. McBain and A. W. Soldate,³⁹ and the rate of polymerization at low soap concentrations is linearly proportional to the soap concentration. Thus the soap must be intimately connected with the polymerization reaction and not just a means of dispersal. In fact, stable emulsification occurs only after the polymerization has started.

The supporting evidence presented by C. F. Fryling has been taken from the work of W. D. Harkins at the University of Chicago, J. W. McBain at Stanford University and W. B. Reynolds at the University of Cincinnati done in connection with the Copolymer Research Branch of the Rubber Director under the War Production Board. The investigations of these groups have more definitely defined the locus of the reaction in emulsion polymerization as occurring in the soap micelle and the polymer-monomer nuclei of the aqueous phase.

W. D. Harkins has based his conclusions on an intimate study of the emulsion, especially the micelles and polymer particles, throughout the course of the polymerization by means of X-rays and the electron microscope. Their work indicates that the micelles are plate-like, composed of three double layers of soap. Sandwiched between these soap particles are alternate layers of water and monomers, with the hydrocarbon chain of the soap oriented into the monomer and the polar carboxyl group toward the water. The monomer is in thin sheets of the order 6 to 15 Å in thickness, between two and four molecules thick. The water layers, presumed of the order of 35 to 50 Å thick, allow the water soluble catalyst to diffuse through the micelle.⁴⁰ From this data, it is calculated that the

initial surface of these monomer layers dissolved in the soap micelle is 13 square meters per cubic centimeter of water in the GR-S polymerization solution, compared with one square meter for the area of the interface of the monomer droplets.⁴¹ Both of these monomer surfaces are covered by a like monolayer of soap. Thus it is expected that about 13/14 of the initial reaction occurs in the micelle layers.

As the polymerization proceeds soap is adsorbed or incorporated in the growing polymer, so that most of the micelles have disappeared at a 13 per cent yield.⁴² After this time, the main reaction is in the polymer nuclei, which has been shown⁴³ in polystyrene polymerization to have adsorbed 50 per cent of the monomer at 13 per cent conversion and completely at yields greater than 50-60 per cent. Since the area of the monomer layers is greatest at the beginning of the reaction, it is considered that this is the period in which polymer particles are formed in greatest number and few nuclei will be formed after the micelles have disappeared. This was observed to be true and that after 25-30 per cent yield the number of nuclei is almost constant and at a nearly maximum value.⁴⁰

Harkins points out⁴¹ that the initial rate of reaction is more correctly proportional to the total area of the monomer layers in the micelles than to the concentration of the soap. In this way the effect of soap in low concentrations, especially of short chain soaps which do not form micelles, comparison of different soaps and the addition of salts, which increase the number of micelles, may be more correctly interpreted. According to this view, dilution will have no effect on the rate of reaction and Harkins showed this to be true.

The polymerization of monomer in true aqueous solution is not eliminated by this work, but this rate is observed to be quite slow in comparison with the overall reaction.⁴²

Harkins concludes⁴¹ from his work that the entire GR-S synthesis may be satisfactorily explained on kinetic grounds by the use of a second order rate equation as found in solution for styrene³² and by the assumption that the reaction at yields greater than 10-15 per cent takes place almost entirely within the monomer-polymer particle.

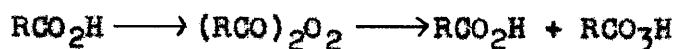
The work of McBain^{43,44} and Reynolds⁴⁵ on the solubilization and effect on rate of reaction of various soaps substantiates the loci of reaction as the soap micelles and the monomer-polymer particle. Low-molecular-weight soaps which are completely soluble and other emulsifying agents which do not form micelles do not promote polymerization in emulsion to the degree of even high-molecular-weight soaps which are insoluble in water at 50°. The addition of salts to the emulsion, which precipitates soap from solution to form micelles, thus promotes the reaction. McBain⁴⁶ demonstrated that the monomer phase was not necessary as polymerization occurred when monomers and emulsion were separated and the only contact was the vapor of the monomers.

The mechanism of the initiation of polymerization in emulsion is less well understood. It is believed that the action of modifiers is through the formation of free radicals by action of the persulfate or other oxidizing agent.^{47,48} Mercaptan, the modifier used in GR-S polymerization, has been found to be present in the polymer in a molar ratio which supports this theory.^{49,50}

W. J. Potter, A. M. Borders and H. J. Osterhof⁵¹ have observed that the polymerization proceeds in the absence of catalyst, if the soap used contains peroxides, and this has been substantiated by McBain.⁴⁴ The inhibitory effect of oxygen in polymerization of GR-S⁵² and styrene⁵³ is best explained by a free radical mechanism.

M. Corrin⁵⁴ has suggested that the soap may play an active role in the polymerization reaction through oxidation to peroxide by the persulfate. If peroxides are present in the soap used in high concentration with respect to the monomer and the active chain concentration, the observed inhibitory effect is explained by increased chain termination. The presence of peroxide in low concentration would have an accelerating effect on polymerization to form appreciable polymer chains. According to this view, a certain soap peroxide concentration would lead to a maximum production of un-terminated chains. This effect was experimentally verified by the use of oil soluble catalysts, benzoyl peroxide and ascaridol.

Fr. Fichter⁵⁵ has studied the reaction of persulfates on salts of low-molecular-weight fatty acids and has found that in boiling solutions alcohols and dicarboxylic acids are formed together with decomposition products such as carbon dioxide, oxygen, saturated and unsaturated hydrocarbons. He considers this reaction as similar to the Kolbe electrochemical synthesis of alcohols and dicarboxylic acids and proposes that the reaction proceeds through the formation of a diacyl peroxide to form an acyl peroxide which decomposes to form free radicals.



These observations directly support the active role of soap in poly-

merization proposed by Corrin and the work of this thesis in which styrene is polymerized in the absence of any intermediate catalyst. Although the temperature used in emulsion polymerization is not as great as that used by Fichter, a slower rate of reaction would be expected to occur. L. Green and O. Masson⁵⁶ have measured the decomposition of sodium persulfate at 70° C and found a unimolecular decomposition

$$\frac{dx}{dt} = k_1(a-x)$$

and k_1 to have a value of 0.0016 gram moles/liter/minute at 70° C and to be nearly independent of initial concentration or metallic portion.

The cessation reactions in emulsion polymerization are considered to be the same as solution polymerization discussed in part A. The effect of modifiers in reducing the molecular weight of the polymers in emulsion polymerization is believed due to their active participation in chain transfer.^{47,48,49}

Emulsion polymerization of styrene has been reported in the literature by H. Staudinger and E. Husemann⁵⁷ who showed that the particles formed in the latex were nearly spherical and followed the Einstein viscosity law for spheres, but were rod-like when dissolved in organic solvents. S. Yamamoto and S. Kawata⁵⁸ observed that the emulsion polymerization of styrene was affected by the use of different emulsifying agents.

III. DISCUSSION OF RESULTS

The kinetics of the emulsion polymerization of styrene under various conditions of temperature and concentration of monomer and catalyst has been studied. The reaction was followed by isolating and determining the amount of styrene remaining in the latex at various times.

A detailed description of the method of sampling and analyzing the latex is given in the experimental section. This consisted of withdrawing a definite volume of latex, and extracting the coagulated sample with chloroform. The styrene in the chloroform solution, containing styrene, polystyrene and fatty acid, was titrated with a standard solution of bromine in glacial acetic acid to an end-point of a permanent bromine color. This titration has been proposed by Uhrig and Levin,⁵⁹ who showed that this procedure was more than 99 per cent accurate in the determination of the bromine number of styrene. Care was taken so that all measurements and transfers were as nearly quantitative as possible. It was shown that with the method used, the amount of styrene found in the latex was greater than 98 per cent of the theoretical value. For example, in polymerization 8 (see experimental section), the amount of styrene in 10 cc. of latex was calculated to be 0.9811 g., and in two samples collected eighty minutes apart, but before the polymerization started, the styrene found was 0.9659 g. (98.4 per cent) and 0.9762 g. (99.5 per cent). It will be noted that similar values were obtained for the initial styrene concentration of other runs in which the quantities used were the same and care was taken that the styrene was added quantitatively. Polymerizations 11 and 12, where a number

of samples were taken over a period of more than twenty-four hours and the reaction mixture was open to the atmosphere, show that even under these extreme conditions, the determination of the styrene concentration is reproducible to within 96 per cent for polymerization 11 and 99 per cent for polymerization 12. Thus it is shown that the styrene can be determined within approximately 0.02 g. It is apparent that this error is quite appreciable in the analysis of the small amounts of styrene remaining in the latter part of the polymerization, but this region was not important in determining the rate of reaction which was to be studied.

It was found that the values for the styrene concentration, when plotted against time, lay very close to a straight line with few deviations. This was especially true for the first sixty to seventy per cent of the polymerization, which is most significant in rate determinations. The zero order rate constant for the reaction, found from the slope of this straight line, was readily reproducible within an error of about ten per cent. An examination of Tables I and II clearly shows this reproducibility between similar runs and series of runs. The absolute error is, of course, more appreciable in the polymerizations where the rate is lowest. The error found in the majority of the runs, however, is well within ten per cent. A few runs are obviously out of line with the normal and these may be explained by the complexity of the reaction studied and its great sensitivity to contamination. It was attempted, however, to conduct each polymerization, take samples, and determine the styrene in as nearly an analogous manner as possible.

Ten seconds were required for the collection of the sample of

latex. The time of sampling was averaged, however, and in every case the same procedure was used. The regularity and reproducibility of the results obtained indicate that the polymerization was stopped immediately as the sample was collected due to the contact of the latex with air. Our work in polymerizations 11 and 12 shows that air is an efficient inhibitor for the polymerization. Kolthoff and Dale⁵³ have also shown that air or oxygen is an effective inhibitor for the emulsion polymerization of styrene. It is thus believed that the error occurring in sampling is hardly appreciable. After collection, the samples were diluted with chloroform and kept in an ice-bath until extracted and titrated. No change in the styrene content of samples was noted dependent on the time of storage before titration and individual samples kept overnight in the icebox gave results consistent with the rest of the polymerization.

The concentration of potassium persulfate in the latex during the course of the polymerization was followed by a modification of the procedure proposed by Kolthoff and Guss⁶⁰ for analysis of GR-S latex. This method consisted in the reduction of the persulfate remaining in the latex after extraction of the fatty acid, styrene and polystyrene with chloroform, with an excess of a standard solution of ferrous sulfate. The amount of ferrous sulfate which remained after the reduction of persulfate was determined by titration with standard ceric sulfate and the amount of ferrous ion oxidized by the persulfate obtained by subtracting the amount of ferrous sulfate found from the amount added. The persulfate concentration of the sample could be calculated from this value. It was found (in polymerizations 4 and 5) that the concentration of potassium persulfate

remained more than 95 per cent of the theoretical value throughout the polymerization. This variation is hardly more than the experimental error, for samples differed by more than 3 per cent without regard for order. From these results it was concluded that changes in the concentration of persulfate during the course of the polymerization would have no appreciable effect on the rate of reaction.

The molecular weight of several polymer samples collected at various per cent conversions during polymerizations 1 and 2 was determined. The results of this investigation were not too consistent, but it is indicated that the average molecular weight changes very little during the course of the polymerization. These results are similar to those obtained in the polymerization of styrene in bulk and in solution and support the theory that emulsion polymerization proceeds by an addition mechanism similar to that proposed for solution and bulk polymerization. The observed decrease in average molecular weight in the last part of the polymerization is not believed to be significant, as it is within the experimental error of the determination of molecular weight.

The molecular weight of a purified sample of the polymer collected during the latter part of each polymerization was determined viscosimetrically. The equation relating the molecular weight and viscosity proposed by Kemp and Peters⁶¹ was used to calculate the molecular weight, M , from the relative viscosity, N_r , and the base molal concentration of the polymer, C .

$$M = \frac{\log. N_r}{C} \times K$$

The absolute molecular weights calculated from this equation are low in comparison to equations proposed by Staudinger⁶² and Alfrey,

Bartovics and Mark.⁶³ The determination of absolute molecular weight from viscosity data is as yet a controversial question, so the molecular weights recorded are not intended to be absolute, but only to give an indication of the relative degree of polymerization.

Tables I and III summarize the data obtained on molecular weights during the latter half of the study. These values are not very consistent, but they do show that the degree of polymerization is decreased as the temperature and catalyst concentration are increased. This variation is not very great in emulsion polymerization; most of the molecular weights were found to be between 200,000 and 300,000. This dependency between molecular weight and temperature and catalyst concentration has been generally observed in polymerization studies.⁶⁴

The changes in pH during the reaction were observed in polymerization 3. The results obtained were similar to those reported by Fryling and Harrington³³ and may be explained by their theory, discussed in the preceding section. The variation in the pH of the latex was not very large during the polymerization reaction and it was not considered necessary to use a pH regulator in this work.

The length of the induction period and the rate of reaction were found to be dependent on the purity of the styrene used. Styrene prepared by debromination of pure α,β -dibromoethylbenzene with magnesium was used as a basis of purity for styrene prepared by other methods. "Research styrene", obtained by distillation of purified styrene which had been partially polymerized by heat, was found to give the same results as the styrene prepared chemically. Partial polymerization and distillation of styrene otherwise puri-

fied by repeated distillation and/or washing with Nessler's reagent, potassium mercuric iodide dissolved in 10 per cent potassium hydroxide, reported by Johnson and McEwen⁶⁵ to remove phenylacetylene, increased the rate constant from 0.025 to 0.029 gram styrene/10 cc. latex/minute* and reduced the period before the start of polymerization two- to ten-fold. It appears that this method of preparing research styrene removes some inhibitor or retarder, such as phenylacetylene or traces of *t*-butylcatechol, which are not separated by washing or distillation. The impurities present in untreated styrene are not detectable by change in the index of refraction of the sample on purification.

Although specially purified styrene was used, the induction period could not be completely eliminated or controlled. Polymerizations 11 and 12 show that an air atmosphere completely inhibits the polymerization reaction. Kolthoff and Dale⁵³ have also observed this inhibitory effect of air and oxygen. The reaction flask was flushed with nitrogen before use and a nitrogen atmosphere was maintained at all times, but it is not unlikely that traces of oxygen remained in the flask and in the reagents used. These traces of oxygen could account for the induction periods observed. The rate of polymerization in polymerizations 11 and 12, where the induction period was over twenty-four hours, was only slightly different from similar runs conducted in a nitrogen atmosphere, 0.0318 compared with 0.0294. Although it would be preferable to eliminate the induction period, it does not appear to be important in determining the rate of polymerization.

* Hereafter the units gram styrene/10 cc. latex/minute will be implied in all rate values given.

The important role that soap plays in emulsion polymerization has been discussed in the preceding section of this thesis. Different samples of fatty acid, from which the soap used was prepared, were purified in the same way from the same starting material, U.S.P. stearic acid. Samples of the fatty acid prepared at different times were always checked by a trial polymerization against the former sample. Similar results were always obtained with the different samples. Soap prepared in situ, by the addition to an alkaline solution of the fatty acid dissolved in the monomer was found to give more reproducible results and a faster rate of polymerization than a previously-prepared soap solution of the same reagents. Polymerizations 6 and 7, rate 0.020 with soap solution, and polymerizations 8 and 9, rate 0.025 with soap prepared in situ, may be compared in this respect. The effect of the amount of alkali used to make the soap was studied in polymerizations 13, 14 and 15. The results from these polymerizations showed that the rate of reaction was slightly increased by the use of a 10 per cent excess of fatty acid, rate 0.0248, compared with a rate of 0.0208 for an equivalent amount of alkali and 0.0215 for a 10 per cent excess of alkali. These differences are not very great, but a 12.5 per cent excess of fatty acid was used in all of the runs and the amount of fatty acid and alkali used was accurately measured.

Potassium soap was found to be more easily handled than the sodium soaps which tended to form gels on cooling and gave a more viscous emulsion. The rates of reaction were the same when either sodium or potassium were used, as is shown in polymerizations 16 and 17. Although the active oxygen content of the fatty acid from which

the soap was prepared was increased from 3.3 to 848 parts per million by passing oxygen through the molten fatty acid at 120° C, neither the rate of reaction nor the induction period was greatly affected. These results are shown by comparing polymerizations 18 and 19. The differences observed are within the 10 per cent experimental error.

One polymerization, 20, was carried out using as the emulsifying agent highly-purified dehydroabietic acid, kindly furnished by the Hercules Powder Company. The results of this one experiment indicate that the rate of polymerization was less than one-third that of a similar run using fatty acid (see polymerization 32 or 33). The induction period was slightly longer, ten minutes compared with six, and the molecular weight of the polymer six-tenths of that produced by the controls. These observations seem to support the micelle theory of emulsion polymerization proposed by Harkins^{40,41,42,43} and others, for it appeared that the emulsion obtained was nearly as good as the soap emulsion, and that the solubilizing effect on styrene of the dehydroabietate should be at least as great as the soap.

Addition of 0.5 per cent, based on the weight of monomer, of dodecyl mercaptan to polymerization 21 had only a slight retarding effect on the rate of polymerization, giving a rate constant of 0.031 compared with 0.036 for the controls. The molecular weight of the polymer obtained in the presence of mercaptan, however, was reduced from 279,500 and 250,500 in polymerizations 32 and 33 to 15,400, or over seventeen times. The presence of mercaptan also appeared to eliminate the induction period. These observations

are in agreement with the generally observed effect of mercaptans as modifiers in emulsion polymerization. The action of mercaptans is believed to be due to their easy oxidation and reduction, and active participation in chain initiation and chain transfer.

Table I summarizes the data obtained in polymerizations 5, 10 and 22-37. An examination of the graphs of these polymerizations shows that the plot of the styrene concentration in 10 cc. of latex against time, for the first 60 to 80 per cent of the polymerization, follows a straight line. This plot is in agreement with the definition of a reaction of zero order, in which the rate of reaction is independent of the concentration of the substituent under observation.

$$-\frac{dC}{dt} = k_0$$

Integration and substitution, assuming the reaction starts at zero time, leads to the equation of this graph.

$$C_t = -k_0 t + C_0$$

It is also noted that a plot of the logarithm of the styrene concentration against time, "B" graphs of polymerizations 5, 10, and 28-31, also describes a straight line. This plot is in agreement with a first order reaction, in which the rate of polymerization is dependent on the first power of the concentration of the substituent. In this case it is observed that the straight-line agreement holds over a somewhat greater region than the zero order plot.

$$-\frac{dC}{dt} = k_1 C$$

Integration from zero time as before leads to the following equation.

$$\ln \frac{C_0}{C_t} = k_1 t \quad \text{or} \quad -\ln C_t = k_1 t + \text{const.}$$

From the individual graphs alone it is not possible to distinguish between the zero or first order reaction. However, it is observed in Table I that the zero order rate constant for the reaction is constant, for a given catalyst concentration, although the concentration of monomer is varied two-fold. Table II shows the effect of change of monomer concentration on the first order reaction rate. In this case the rate "constant" decreases as monomer concentration increases. This is the opposite effect that would be observed if the reaction were first order. The independence of the zero order reaction rate on monomer concentration substantiates that the reaction followed is of zero order.

This zero order reaction rate for styrene polymerization is peculiar to emulsion polymerization. Catalytic vinyl polymerization in solution was shown by Price and Kell^{1,2} to be a first order reaction based on monomer concentration. Since emulsion polymerization is believed to proceed by the same mechanism as polymerization in solution, the reaction kinetics observed in emulsion polymerization are probably limited by some factor other than the polymerization reaction.

These kinetics may be explained by the theory of Fikentscher³⁷ that emulsion polymerization proceeds in the monomer dissolved in the water. Thus the reaction would take place in a saturated solution of styrene which would be continually replenished from the monomer droplets as the styrene polymerized. This would be analogous to the initial polymerization rate of pure styrene, in which the concentration of the monomer is constant at 100 per cent, and was observed by Staudinger and Frost⁶⁴ to follow zero order kinetics.

The micelle theory of Harkins⁴³ is also consistent with the observed results, as the styrene which polymerizes in the micelles, or monomer-polymer particle, must pass through the water phase in solution to reach the locus of reaction. In this case the limiting reaction is also the solubility of the monomer in the water phase and the continuous rapid dissolution of the monomer from the droplets. As the rate of polymerization in emulsion is quite rapid, the process of solution of the monomer from the droplets must be extremely rapid, in order to maintain a constant concentration. This view is not improbable, as the very small droplets have a large and active surface.

The micelle monomer-polymer theory of Harkins is perhaps more consistent with the results obtained in this work, for after yields of the order of 80 per cent, the reaction no longer follows the zero order reaction curve. This portion of the curve more closely follows the first order kinetics as evidenced by agreement of the points in this region with the straight line for the first order reaction ("B" graphs of polymerizations 5, 10 and 28-31). This would be explained if, after this time all of the styrene was in solution in the monomer-polymer particles, as Harkins has shown, and the reaction would thus be expected to proceed as if in solution. McBain and Dean⁶⁶ have studied this slow rate of reaction in the latter part of emulsion polymerization, and give evidence that it is not caused by slow diffusion of the reactants or changes in pH or the concentration of catalyst and soap. If the main polymerization reaction takes place in the monomer dissolved in the water phase, this drop in reaction rate would not be expected, for the solubility

of styrene in water is very small and the water would not be expected to have dissolved all of the styrene at conversions within the region studied.

The similarity between emulsion and solution polymerization is substantiated by a study of the relationship of the rate of reaction and the catalyst concentration. Schulz⁵ and Husemann⁵ and Price and Kell¹² have shown that the rate of reaction for vinyl polymerization is proportional to the square root of the catalyst concentration, if the temperature and monomer concentration are held constant. Our data on this relationship is summarized in Table V and the corresponding graphs. In these graphs the logarithm of the zero-order rate constant is plotted against the logarithm of the catalyst concentration, and it is evidenced that a straight line of slope one-half is most consistent with the results. This slope of one-half corresponds to a relationship of the rate of reaction to the one-half power, or square root, of the catalyst concentration. This is to be expected from the mechanism discussed in the Historical and Theoretical section if the chain-initiating reaction is first order and the chain terminating reaction second order (see the discussion leading up to equation (15)).

The over-all energy of activation for the reaction studied was estimated graphically from the data summarized in Table VI. The energy of activation, E , is defined by the equation

$$\ln k = \text{const} - \frac{E}{RT}$$

and may be determined from values of the rate constant found under similar conditions at two different temperatures. The physical interpretation of this energy of activation is rather difficult, for

in polymerizations a number of reactions are proceeding at the same time. Our results, however, show that the natural logarithm of the rate constant is linearly dependent upon the inverse of the absolute temperature. The activation energy found, $18,900 \pm 2000$ calories per mole, is in good agreement with the values found for the catalytic polymerization of styrene by other techniques, about 20,000 calories per mole.⁶⁷

The purified polymers obtained in polymerizations 21, 26, 30, 33, 37 and 38 were analyzed for carbon and hydrogen. These analyses showed that the product was essentially pure polystyrene and the presence of end groups or foreign substituents in the molecule could not be detected in polymers of such high molecular weight. Snyder and Wall^{48,49} have reported that polymers formed in the presence of mercaptans contained sulfur in the ratio of one sulfur atom per molecule of polymer. An analysis for sulfur of the low-molecular-weight polymer produced in this way in polymerization 21 showed the presence of 0.018 per cent sulfur. Twenty-one-hundredths per cent sulfur would be expected in a polymer of molecular weight 15,400 containing one sulfur atom. It has been pointed out,⁶³ however, that this molecular weight used may be too low by a factor of ten, so this observation may be consistent with the work of Snyder and Wall.

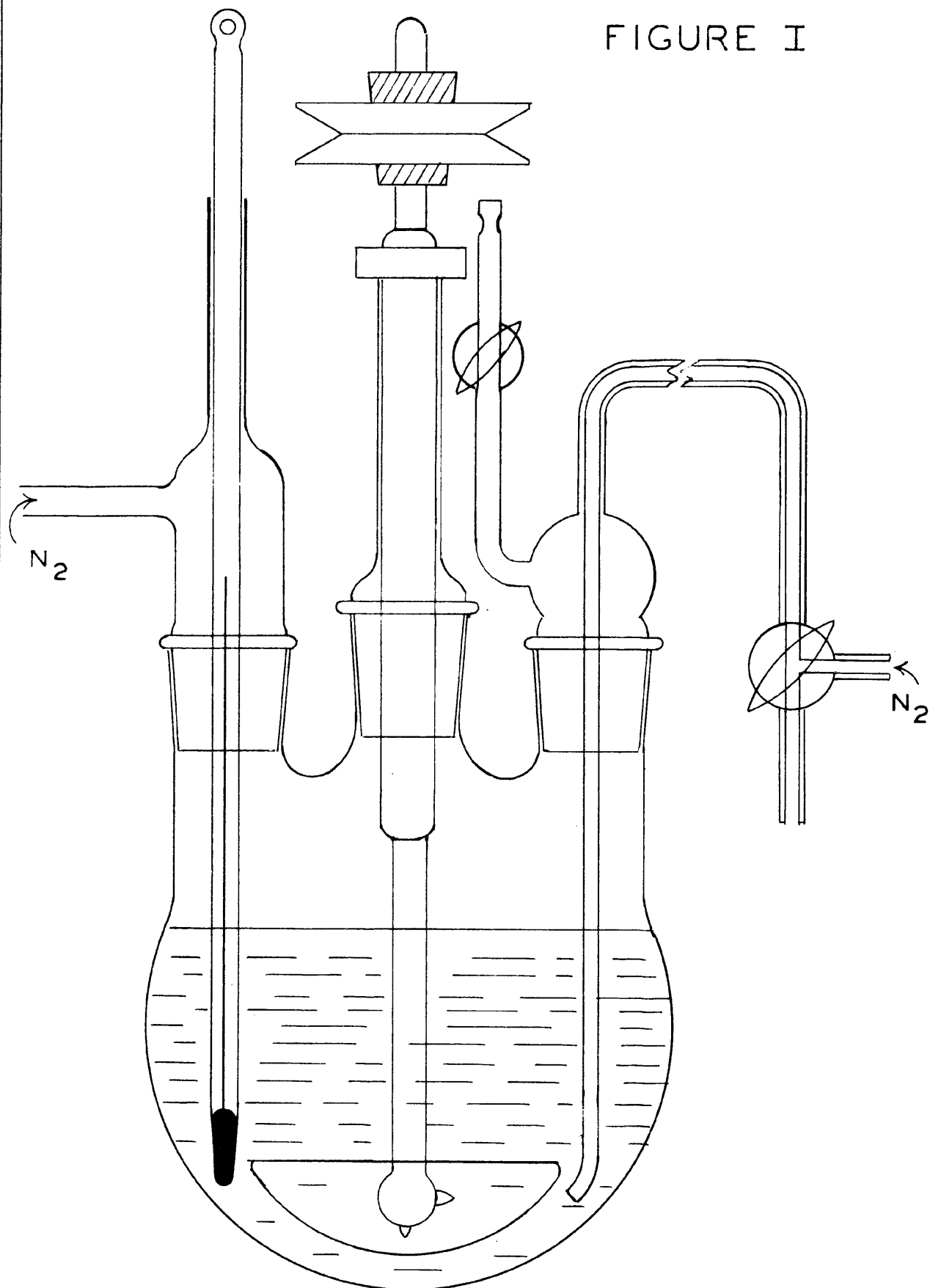
IV. EXPERIMENTAL

Description

Apparatus.--The apparatus used in the study of the emulsion polymerization of styrene is illustrated in Figure 1. The vessel was a 1-l. round-bottomed flask having three $\frac{3}{8}$ 24/40 ground-glass openings. In these openings were fitted, with corresponding ground-glass joints, a gas-inlet tube with thermometer (0-100° C), an all-glass stirrer with a close-fitting ground-glass bearing, and a sampling tube, as shown, with a stopcock to release the pressure in the flask. This apparatus allowed the reaction to be run under a nitrogen atmosphere with a pressure about 5 cm. of mercury above atmospheric. Under this pressure samples of the latex could be rapidly removed by opening the stopcock of the sampling tube. After the sample was collected, the pressure in the flask was released by opening the stopcock to the outside, and the sampling tube and its tip cleared by flushing with nitrogen from the three-way stopcock.

The polymerization apparatus was immersed in an oil-bath, which was well-insulated with asbestos and completely covered except for holes corresponding to the openings of the reaction vessel. The bath was maintained a few degrees less than the temperature desired by means of a "permanent heater", a thousand-watt, open-coil resistance controlled by means of a lamp bank connected in parallel. A similar heater, connected with a bimetallic thermo-regulator, controlled the temperature within $\pm 0.1^\circ$ C of that required. The oil in the bath was stirred mechanically so that constant temperature was maintained throughout the bath.

FIGURE I



Reagents

Soap.--Conductivity water was used to make all of the aqueous solutions reported. It was found to be impractical to prepare a stock soap solution, for at room temperature the soap used was quite insoluble and a homogeneous suspension could not be maintained. Soap in solution is also more subject to attack by atmospheric oxygen to form peroxides. For this reason the soap was made in situ, by addition of the fatty acid dissolved in the monomer to a standard alkali solution, which was stirred and heated to the temperature at which the polymerization was to be carried out. This method immediately gave a very finely dispersed and homogeneous suspension of styrene in water. A 400-cc. sample of 0.0666 N alkali (0.0266 mole), which had been standardized by titration against a standard hydrochloric acid, was accurately transferred to the vessel by means of a 100-cc. pipet. This solution neutralized 87.5 per cent of the 8.000-g. sample of fatty acid used (neutral equivalent 263 ± 2 , 0.0304 mole).

The fatty acid from which the soap was made was prepared by several crystallizations of A. S. LaPine and Company U.S.P. stearic acid. The melting point of the product used was $56-57^{\circ}$ C and the iodine number was less than one. Samples of considerable size were prepared at one time and stored in a vacuum dessicator under a pressure of 20 mm. of mercury. Thus oxidation by atmospheric oxygen was minimized. The active oxygen content of the fatty acid obtained and stored in this way was found to be negligible (3.27 parts per million). Comparable samples of fatty acid were used throughout this investigation and results which checked within the

experimental error were obtained using different samples prepared at different times.

Sodium soaps were prepared in the early polymerizations investigated. It was found that emulsions prepared with sodium soaps were more difficult to handle and transfer than when potassium soaps were used. The sodium soaps gave a more viscous solution and had a much greater tendency to gel when cooled during the collection and storing of samples, especially during the first part of the polymerization.

Potassium Persulfate.--It was found preferable to add the persulfate catalyst as a solution shortly before the styrene and fatty acid were emulsified in the reaction vessel. Standard solutions were prepared by weighing the calculated amount of potassium persulfate in a volumetric flask and making the solution up to volume. The potassium persulfate used was a good commercial reagent grade, Merck or Mallinckrodt, which had been recrystallized from water, ground to a fine powder and dried at room temperature in a dessicator to constant weight. The persulfate obtained by this method was free of sulfate and was found to be 100 per cent pure.

Styrene.--The results obtained in the polymerizations investigated were closely dependent on the purity of the styrene used. This dependency was investigated by the use of samples of styrene prepared in different ways. A commercial grade of styrene was available as a basis for these preparations. A limited supply of styrene of 99.8 per cent purity which had been obtained by a peculiar run in Monsanto's Texas City, Texas plant was also used. These

styrenes were inhibited during storage by a small amount, three parts per million, of t-butylcatechol.

Styrene designated as "research" was prepared in the following manner. Ordinary commercial styrene was washed with 10 per cent sodium hydroxide solution until the inhibitor was removed, as shown by the absence of color in the alkali layer on further washing. This styrene was then vigorously stirred mechanically for three hours with an equal amount of Nessler's reagent, potassium mercuric iodide, K_2HgI_4 , prepared by the addition of a solution of 245 g. of potassium iodide in 245 cc. of water to a mixture of 100 g. of mercuric chloride and 188 cc. of 10 per cent potassium hydroxide. This process removed the phenylacetylene present in commercial styrene as reported by Johnson and McEwen.⁶⁵ The yellow-orange precipitate which formed was removed by filtration and the styrene separated and dried with sodium sulfate. The commercial styrene prepared in this manner, or the pure Monsanto styrene, was distilled through a nine-inch all-glass fractionating column packed with glass beads. The center fraction, boiling at $46^\circ C$ (20 mm.) was collected in a receiver suitable for redistillation. This fraction was heated under a nitrogen atmosphere at $100 \pm 5^\circ C$ for about three hours. After this heating the styrene was quite viscous and 10 to 15 per cent had polymerized.⁶⁸ This partially polymerized styrene was again distilled through the column and the constant-boiling fraction collected. Other samples of styrene were prepared by various modifications of this process and are reported in the polymerizations where they were used.

A sample of styrene was prepared from highly purified α,β -

dibromoethylbenzene by the method of Braun and Moldanke.⁶⁹ Crude α,β -dibromoethylbenzene was purified by treating a boiling solution in high petroleum ether with Darco and recrystallizing this product from high petroleum ether. A solution of 396 g. (1.5 moles) of the pure dry α,β -dibromoethylbenzene, m. p. $73-74^{\circ}\text{C}$, in 1.25 l. of absolute ether was added slowly with stirring to 36.5 g. (1.5 moles) of magnesium turnings and 250 cc. of absolute ether in a 2-l. round-bottomed flask, equipped with three standard taper joints and a condenser, stirrer and dropping funnel. The solution was added over one and one-half hours so that gentle reflux was maintained. After the solution had been added, refluxing was continued for one hour by external heating. Water was added, with stirring, to the dark-brown reaction mixture until the white precipitate which first formed was dissolved. The ether layer was separated from the water in a separatory funnel and was washed twice with 400-cc. portions of water. The ether layer was dried over anhydrous calcium chloride and stored in the icebox until distilled. The ether was removed at atmospheric pressure and the styrene fractionated as described before, b. p. 43°C (17 mm.). The yield was 117.5 g. or 75 per cent of the theoretical amount.

The samples of styrene studied were stored in an icebox until used and no change was noted in the quality after several weeks' storage. For a particular series of runs, enough styrene was prepared so that the same sample was used for all of the polymerizations studied. No particular variations were observed, however, outside of the experimental error, when different batches of research styrene were compared under the same conditions.

Addition of Reagents

The polymerization reaction was always carried out in the same way except for changes noted in special runs. The bath and reaction vessel were heated to the temperature at which the polymerization was to be run. During this time the reaction vessel was flushed with commercial nitrogen which had been passed through two 125-cc. gas wash bottles filled with Fieser's solution⁷⁰ and through a gas wash bottle of lead acetate solution. As soon as the bath temperature was reached, 400 cc. of 0.0666 N potassium hydroxide solution was pipetted into the flask, while a stream of nitrogen was passed through the flask from the sampling tube. The alkali solution was then allowed to reach equilibrium with the bath, which was accomplished more rapidly when the bath was heated a few degrees above the temperature desired. After equilibrium had been attained for a few minutes, the desired amount of persulfate in 10 cc. of solution was pipetted into the flask. The 8.000-g. sample of fatty acid, weighed into a 125-cc. Erlenmeyer flask, was dissolved in a portion of styrene, transferred to the reaction vessel, and the remainder of the styrene used to rinse the Erlenmeyer flask and then added to the reaction mixture. This addition required about two minutes and the start of the polymerization was timed from one minute after the start of the addition of styrene and fatty acid. The styrene used was allowed to warm to room temperature before measurement, which was made immediately before addition either by a buret, for the 50-cc. portion, or by a combination of pipets. After the styrene had been measured, it was heated to approximately the temperature of the polymerization by an open flame in order that the

temperature of the reaction mixture would not be changed and to facilitate the dissolution of the fatty acid. The persulfate, fatty acid and styrene were added through the opening for the gas inlet tube and thermometer and during the addition nitrogen was passed through the flask from the sampling tube. After addition of the reagents, the gas inlet tube was set in place, the sampling tube was closed by means of the three-way stopcock, and the stopcock to the outside closed.

Sampling

A sample of the latex was taken shortly after all of the components had been added and as soon as the reaction mixture and bath had reached equilibrium. Samples were removed through the sampling tube by opening the stopcock to the tip, through which the latex was forced by the excess pressure of nitrogen in the reaction vessel. A few cubic centimeters of the latex was passed through the sampling tube as a rinse and was discarded. The sample then was collected in a 10-ml. volumetric flask which was filled slightly above the volume mark. The excess latex in the volumetric flask was removed by a small pipet. After the sample had been taken, the pressure in the flask was released through the stopcock to the outside, and the sampling tube and tip cleared of latex by flushing with nitrogen through the three-way stopcock. The sampling tube and the outside stopcocks were then closed. The collection of the sample required about ten seconds, and was started five seconds before the time reported, so that the average time of collection was that reported.

The sample, after it had been collected, was immediately and quantitatively transferred to a numbered 50-ml. Erlenmeyer flask by

washing with distilled water and chloroform, and the sample placed in an ice-bath. After this the volumetric flask and pipet were rinsed with water, alcohol and ether, consecutively, and set aside to dry at room temperature. By this procedure samples could be collected every four or five minutes.

Samples collected during the induction period showed that there was no change in the styrene titer of the latex during this time. Thus further samples were not taken until the start of the polymerization was noted by an increase in the temperature of the reaction mixture. After this time samples were collected after convenient time intervals and dependent upon the expected rate of the reaction. Sampling was continued until the polymerization reaction was nearly complete. This was determined by a drop in the temperature differential between the reaction mixture and the bath temperature to a negligible amount.

In order that the increase in temperature of the reaction mixture would be no larger than necessary, and the correction for temperature increase would be at a minimum, the bath heaters were turned off as soon as the polymerization started. The temperature of the reaction mixture and of the bath were noted and recorded before each sample was taken.

During the course of the polymerization, the appearance of the reaction mixture changed. At first the emulsion was quite white and opaque and foamed rather badly. After the polymerization had proceeded for some time the emulsion became more clear and limpid and there was much less tendency to foam.

A sample of latex for evaluation of the polymer was taken about

twenty seconds before the last quantitative sample. In this time approximately 25 cc. of the latex was collected in a 125-cc. separatory funnel. After the last sample had been taken, about 50 cc. of ether and 20 cc. of coagulant, 50 g. of sodium chloride and 12.5 cc. of concentrated sulfuric acid dissolved in 1 l. of water, were added to the separatory funnel and the mixture was shaken. The water separated as a clear lower layer and was discarded. The ether layer in which the polymer was suspended was diluted with an equal amount of 95 per cent ethanol and the polymer allowed to settle. The clear ether-ethanol solution was then decanted and the polymer was washed with a few cubic centimeters of 95 per cent ethanol. The hard and nearly powdery product thus obtained was collected by suction filtration and dried in air. This gradual exchange of alcohol for ether was necessary so that the polymer would be obtained in a finely divided condition and hard enough so that it would not stick together and form a solid mass when it was collected by filtration.

Styrene Determination

The rate of polymerization was followed by titration of the styrene remaining in the emulsion. This was accomplished by quantitatively transferring the samples which had been kept in 50-cc. Erlenmeyer flasks in an ice-bath, to a 75-cc. separatory funnel with water and chloroform. Chloroform was added so that a total of 25 to 30 cc. was present in the separatory funnel. The emulsion was then coagulated by a 10-cc. portion of the coagulant solution, described above, and the mixture well shaken. The chloroform-styrene-polystyrene layer was separated and the water layer extracted with two 20-cc. portions of chloroform. The chloroform extractions were

combined in a 200-cc. Erlenmeyer flask and the styrene present titrated by a solution of bromine in glacial acetic acid as described by Uhrig and Levin.⁵⁹ This bromine solution was standardized immediately before use in the following way. Five cubic centimeters of the bromine solution was accurately measured by a pipet into a 125-cc. Erlenmeyer flask containing 25 cc. of a 10 per cent potassium iodide solution and 5 cc. of chloroform. The iodine liberated in this way was titrated immediately with standard sodium thiosulfate solution, approximately 0.1 N. Starch was used as an indicator near the end-point. The bromine solution used was equivalent to approximately 0.04 g. styrene per cubic centimeter. The end-point in the styrene titration was taken as the yellow color of excess bromine which did not fade on standing. This end-point was somewhat difficult to attain in the titration of samples which contained considerable polymer and were quite viscous and cloudy. In these samples the color slowly faded on standing and it was necessary to add more bromine at intervals. A distinct end-point was obtained by the addition of less than 0.1 cc. of bromine solution in excess.

Persulfate Determination

In a number of runs the concentration of persulfate in the emulsion was also followed throughout the course of the polymerization. In this case the water layer, after the extraction with chloroform, was quantitatively transferred to a 200-ml. Erlenmeyer flask and the persulfate determined by a modification of the ferrous iron method reported by Kolthoff and Guss.⁶⁰ The sample was diluted to 100 cc., and 10 cc. of 6 N sulfuric acid was added. Nitrogen was bubbled through the solution for ten minutes to remove dissolved

oxygen. Ten cubic centimeters of a standard solution of ferrous sulfate was added accurately to the sample by means of a pipet and nitrogen passed through this solution for twenty minutes. At the end of this period, 2 cc. of 0.0005 molar ferrous-phenanthroline indicator was added, and the remaining ferrous sulfate immediately titrated with standard ceric sulfate to a colorless end-point.

The ferrous solution was prepared by dissolving 2.3 g. of ferrous sulfate heptahydrate in 500 cc. of water and 3 cc. of concentrated sulfuric acid and the solution diluted to one liter. This ferrous sulfate solution was standardized by adding 10.0 cc. of the solution to a 200-cc. Erlenmeyer flask containing 10 cc. of 6 N sulfuric acid and 100 cc. of water. Two cubic centimeters of the ferrous-phenanthroline indicator was added and the solution titrated to a colorless end-point with ceric sulfate solution.

Standard 0.01 M ceric sulfate, for standardization and titration of the ferrous solution, was prepared in the following manner. Six and three-tenths grams of ceric ammonium sulfate dihydrate was added to a solution of 50 cc. of sulfuric acid and 500 cc. of water. This solution was stirred until clear, filtered and made up to one liter. The ceric sulfate solution was standardized against standard arsenious oxide. The 0.1 N standard arsenious oxide solution was prepared by dissolving 2.4720 g. of pure dry arsenious oxide in 20 cc. of normal sodium hydroxide, making the solution just acid with normal sulfuric acid, and diluting to 500 cc. in a volumetric flask. Five cubic centimeters of this arsenious oxide solution was added to 10 cc. of 6 N sulfuric acid in a 200-cc. Erlenmeyer flask and diluted to 100 cc. Three drops of 0.01 M osmium tetroxide and 2 cc. of

0.0005 M ferrous-phenanthroline indicator were added and the solution titrated to a colorless end-point.

The number of milligrams of potassium persulfate in the samples titrated was calculated by the equation, $135 (V_0 - V)N$. In this equation V_0 is the milliliters of ceric solution equivalent to 10 cc. of ferrous solution, V the milliliters of ceric solution required for the titration of the ferrous sulfate remaining in the sample and N the normality of the ceric solution.

For the determination of persulfate, it was necessary to purify the chloroform used to extract the styrene and polymer from the emulsion. Ordinary chloroform contained preservatives which reduced the persulfate during the extraction. Technical chloroform was purified by vigorously shaking two liters with 200 cc. concentrated sulfuric acid in a large separatory funnel and separating the sulfuric acid layer. The process was repeated twice with fresh portions of acid. This chloroform was distilled through the nine-inch fractionating column described in the distillation of styrene. Chloroform prepared in this way was found to have no effect on the persulfate concentration of a standard potassium persulfate solution when shaken with the solution. This chloroform was not stable toward atmospheric oxygen, however, and after several weeks had a strong odor of phosgene.

pH Determination

The pH changes in the emulsion during polymerization were followed by withdrawing 15-cc. samples of the latex in 30-cc. beakers. The pH of these samples was determined at a definite temperature, using a commercial pH-meter, Hellige, model 7040, and with adequate

stirring. Glass and calomel electrodes were used. It was found that the latex tended to be coagulated in the capillary of the calomel electrode by the saturated potassium chloride solution. This disadvantage was eliminated by the use of a saturated potassium chloride bridge which could be readily cleaned by flushing with the saturated potassium chloride solution. This bridge consisted of a 50-cc. beaker which was closed by a rubber stopper through which passed the arm of the calomel electrode, a separatory funnel filled with saturated potassium chloride, and a capillary tube leading to the latex sample. The capillary tube could be kept from becoming clogged by opening the stopcock of the separatory funnel and allowing the potassium chloride solution to flow through it. This arrangement removed the determination from the surroundings afforded by the pH-meter and it was necessary to ground the surroundings of the new location. This was done by enveloping the place for the sample by a fine-mesh copper screen and grounding this to the pH-meter.

Molecular Weight Determination

Samples of the polymer which were used for determining the molecular weight were purified by being precipitated four times from a chloroform solution. A 0.5-g. sample was dissolved in about 75 cc. of technical chloroform in a 200-cc. Erlenmeyer flask by shaking for several hours on a mechanical shaker. This solution was diluted with an equal amount of diethyl ether and shaken by hand until any cloudiness which developed had disappeared. This solution was transferred to a 600-cc. beaker and was mechanically stirred while 200 cc. of 95 per cent ethanol was added very slowly from a

wash bottle. During the ethanol addition, the solution first became cloudy and then discrete particles began to appear in the clear solution. The particles were allowed to settle and the supernant solution was decanted and discarded. The polymer was washed with a few cubic centimeters of ethanol and was collected and dried by suction filtration. This precipitation was repeated three times. Before the last precipitation, the chloroform-ether solution was filtered into a clean beaker and the precipitation carried out with filtered ethanol. The polymer, purified in the last step, was collected on hardened filter paper and was dried in a vacuum dessicator under reduced pressure.

The molecular weight of a polymer was determined viscosimetrically in dilute toluene solution. The solutions were made up in volumetric flasks at 20° C with toluene which had been purified by stirring with concentrated sulfuric acid and distilled at 110-111° C, as described by Fieser.⁷¹ The relative viscosity of the solution was taken in an Ostwald viscosimeter immersed in a water-bath, the temperature of which was controlled at 25 ± 0.02° C.

The molecular weight was calculated from the relative viscosity by the relationship proposed by Kemp and Peters.⁶¹

$$M = \frac{\log. N_r}{C} \times K_{cm}$$

M = molecular weight

N_r = relative viscosity = $t(\text{solution})/t(\text{solvent})$

C = base molal concentration of the solution

K_{cm} = constant dependent on polymer and solvent. For

polystyrene and chloroform, $K_{cm} = 0.45 \times 10^{-4}$

The molecular weight of a number of polymer samples was calculated from the relative viscosity of their chloroform solutions, the constant for which was given by Kemp and Peters. The constant, 0.73×10^{-4} , was evaluated from the chloroform molecular weights and the relative viscosity of the same samples in toluene by the equation:

$$K = \frac{MW \text{ (chloroform)}}{\log N_r/C \text{ (toluene)}}$$

These results are summarized in Table VII.

Rate Determination

The rate of polymerization of the styrene in emulsion was determined by plotting on coordinate paper the weight in grams of styrene in a 10-cc. sample of latex, or the logarithm of this weight, against the time in minutes from the start of the polymerization. The slope of the straight line drawn through the points of the middle portion of the reaction was taken as the best measurement of the rate of reaction.

In polymerizations 1 and 2 the molecular weights of polymer formed at various conversions are tabulated. These results show that the molecular weight of the polymer remains essentially the same throughout the polymerization.

Polymerization 1

400 cc. 2 per cent soap solution

0.4393 g. $K_2S_2O_8$

50 cc. styrene, commercial, Nesslerized and distilled

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex	MW Sample
13	50.3	50.0	0.9674	
105	50.8	50.0	0.9416	
113	51.0	49.7	0.8847	
123	51.3	49.4	0.6*	I 180,680
131	51.8	49.2	0.3879	
140	51.2	49.8	0.1788	
148	51.0	50.0	0.1089	II 205,500
156	50.7	49.8	0.0865	
173	50.5	50.0	0.0603	
198	50.5	50.0	--	III 185,200

Rate: $k_0 = 0.0270$

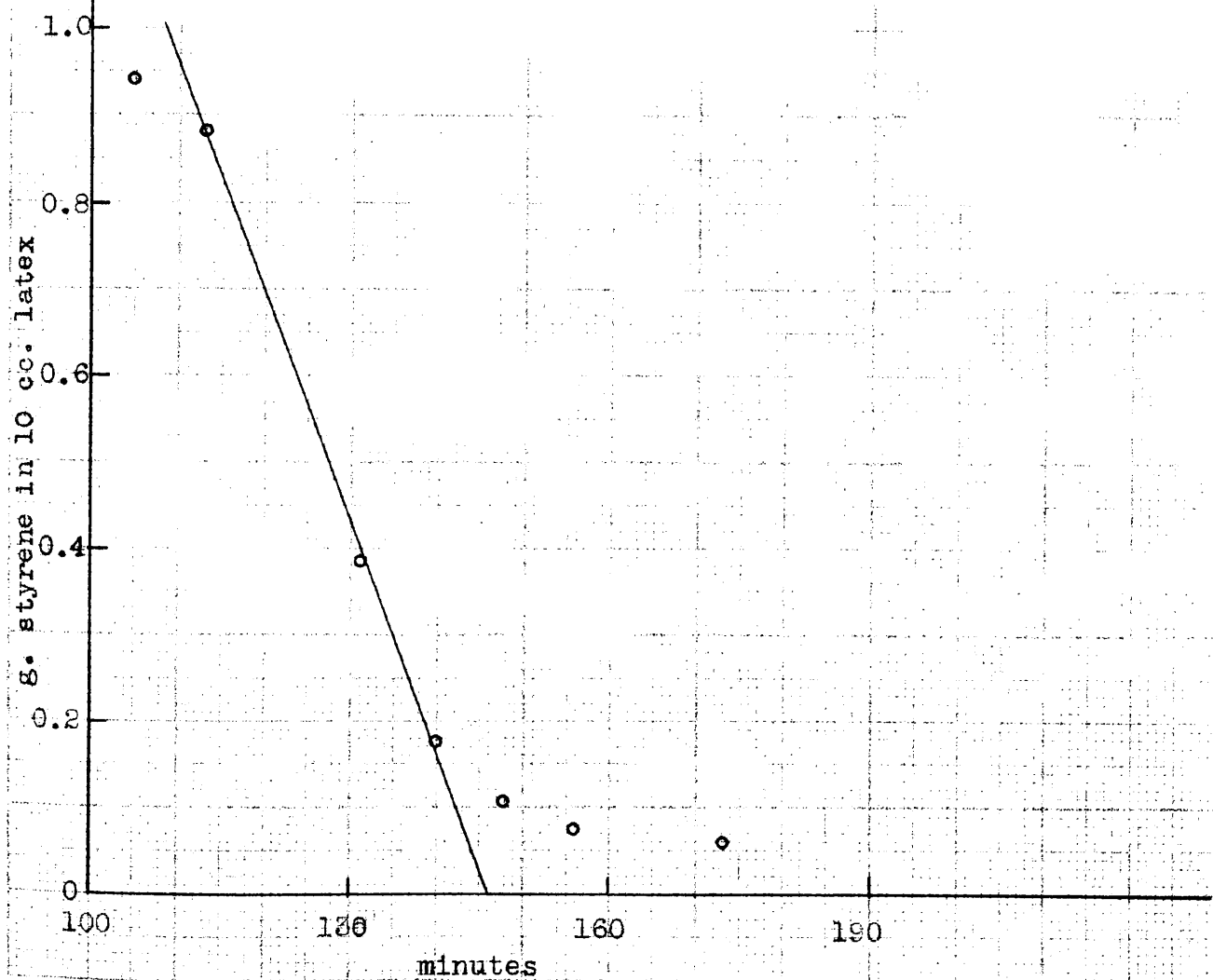
M.W. data ($CHCl_3$)	b.m.** conc.	rel. visc.
I	0.00316	1.323
II	0.00333	1.393
III	0.00316	1.331

* value estimated from graph

** base molal concentration = $\frac{\text{g. polymer}}{104.14} \cdot \frac{1000}{\text{g. solvent}}$

Polymerization 1

$$k_0 = 0.0270$$



Polymerization 2

400 cc. 2 per cent soap solution

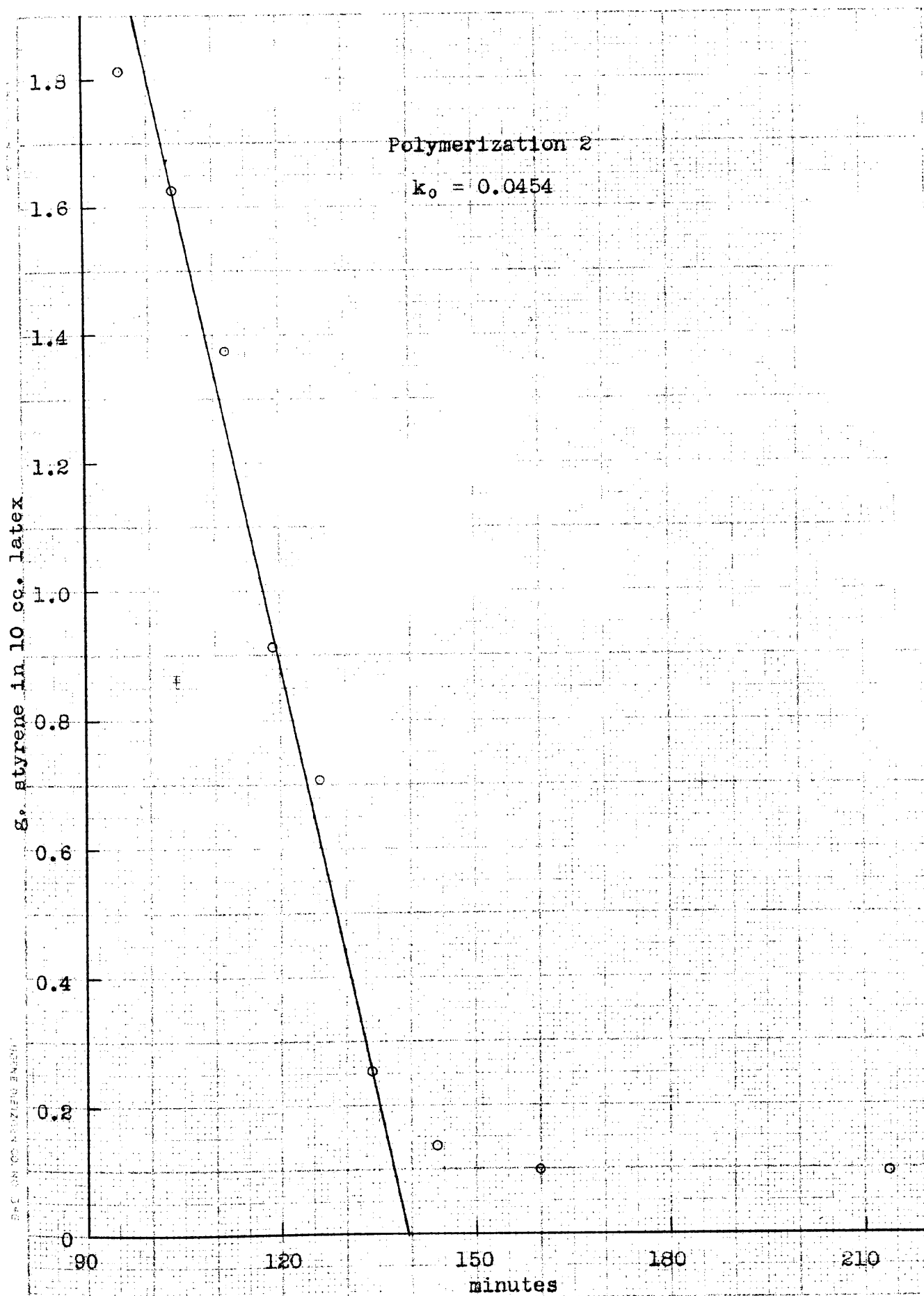
0.4840 g. $K_2S_2O_8$

100 cc. styrene, commercial, Nesslerized and distilled

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex	MW Sample
89	50.7	50.0	1.8133	
96	51.0	50.0	1.8120	
104	52.0	50.0	1.6265	
112	53.0	50.0	1.3781	I 224,500
119	53.2	49.8	0.9112	
126	53.5	49.8	0.5063	II 243,500
134	52.5	49.8	0.2548	
144	51.5	49.6	0.1385	III 252,700
159	50.2	49.5	0.0999	
214	50.5	50.0	0.0945	IV 222,300

Rate: $k_0 = 0.0454$

M. W. data ($CHCl_3$)	b.m. conc.	rel. visc.
I	0.00328	1.430
II	0.00308	1.440
III	0.00316	1.474
IV	0.00320	1.412



The change in pH of the latex during polymerization was observed in polymerization 3. The results are tabulated here and are discussed in Section III.

Polymerization 3

450 cc. 2 per cent soap solution pH = 9.68

0.2570 g. $K_2S_2O_8$ pH = 9.50

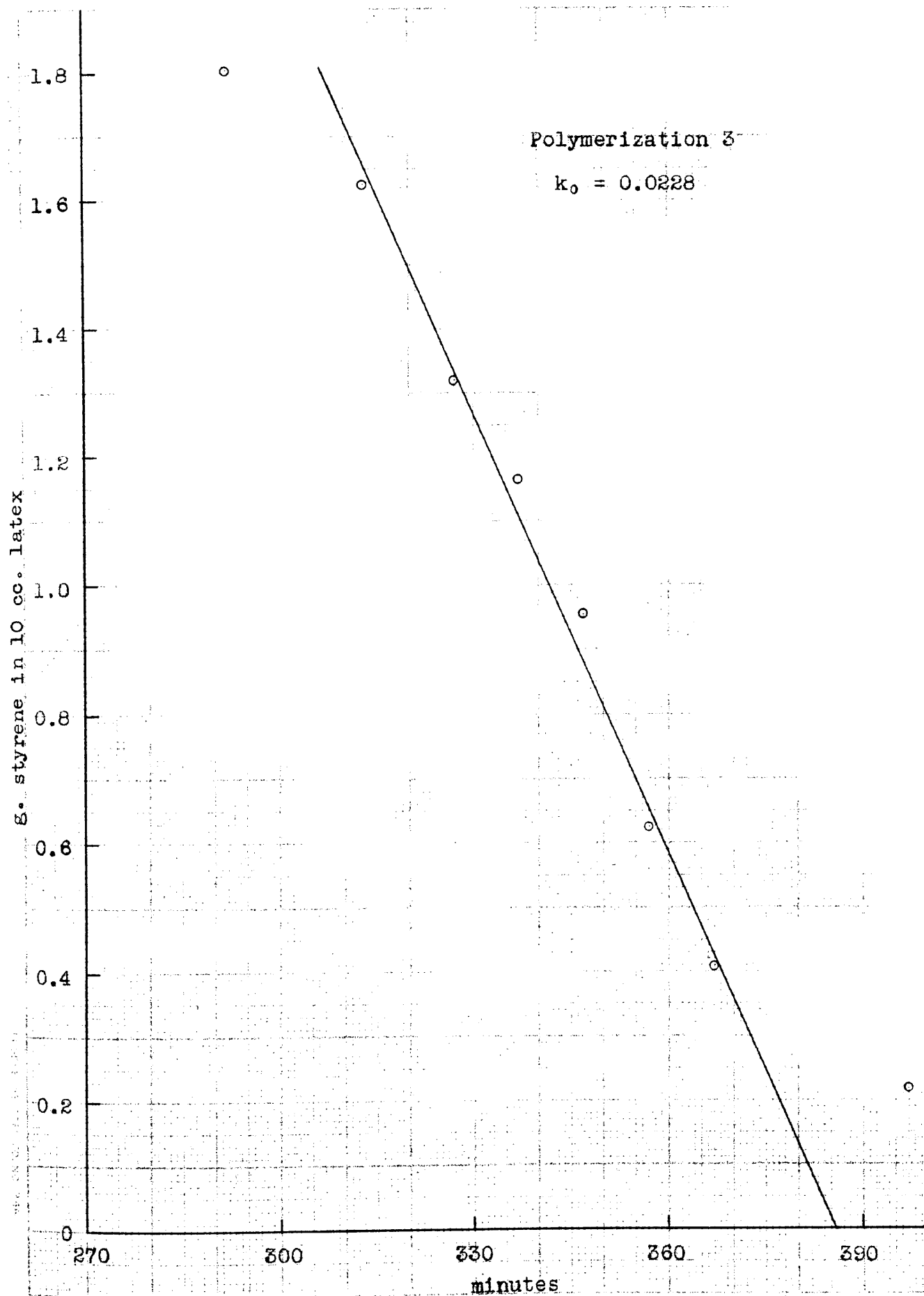
100 cc. styrene, commercial, Nesslerized and distilled

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex	pH latex 35° C
17	50.0	50.0	1.8888	
27	50.0	50.0	--	9.98
77	50.0	50.0	1.8200	
197	50.0	50.0	--	10.00
292	50.3	50.0	1.8036	
297	50.5	50.0	--	9.93
313	51.0	49.8	1.6242	
327	51.0	49.7	1.3196	
337	51.5	50.0	1.1635	
347	51.3	49.8	0.9533	
357	51.0	49.6	0.6240	
367	50.2	49.3	0.4082	
374	50.0	49.5	--	9.57
397	50.5	50.2	0.2197	
417	50.1	50.0	0.1993	
449	50.0	50.0	0.1421	
547	50.0	50.0	--	9.45

Rate: $k_0 = 0.0228$ MW($CHCl_3$) = 226,000

rel. visc. = 1.439

b. m. conc. = 0.00320



The concentration of potassium persulfate in the latex was followed in polymerizations 4 and 5. These results show no significant change in catalyst concentration during the polymerization reaction.

Polymerization 4

400 cc. 0.0665 N KOH
 10 cc. $K_2S_2O_8$ solution = 0.2197 g.
 8.000 g. fatty acid
 50 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex	mg. $K_2S_2O_8$ in 10 cc. latex
4	50.0	50.0	0.9428	4.380
35.2	50.2	50.0	0.9111	4.440
40	51.0	49.8	0.8366	4.425
45	51.3	49.7	0.7734	--
50	51.7	49.5	0.5697	4.395
55	51.7	49.4	0.4735	--
60	51.2	49.3	0.3639	4.425
65	51.0	49.1	0.2698	--
75	50.1	50.0	0.1820	--
85	50.1	50.0	0.1201	4.264
95.5	50.0	50.0	0.0908	--
				theoretical
				4.615

Rate: $k_0 = 0.0276$

MW(C_7H_8) = 257,300

rel. visc. = 1.543

b. m. conc. = 0.00555

Polymerization 4

$$k_0 = 0.0276$$

g. styrene 10 cc. latex

1.0
0.8
0.6
0.4
0.2
0

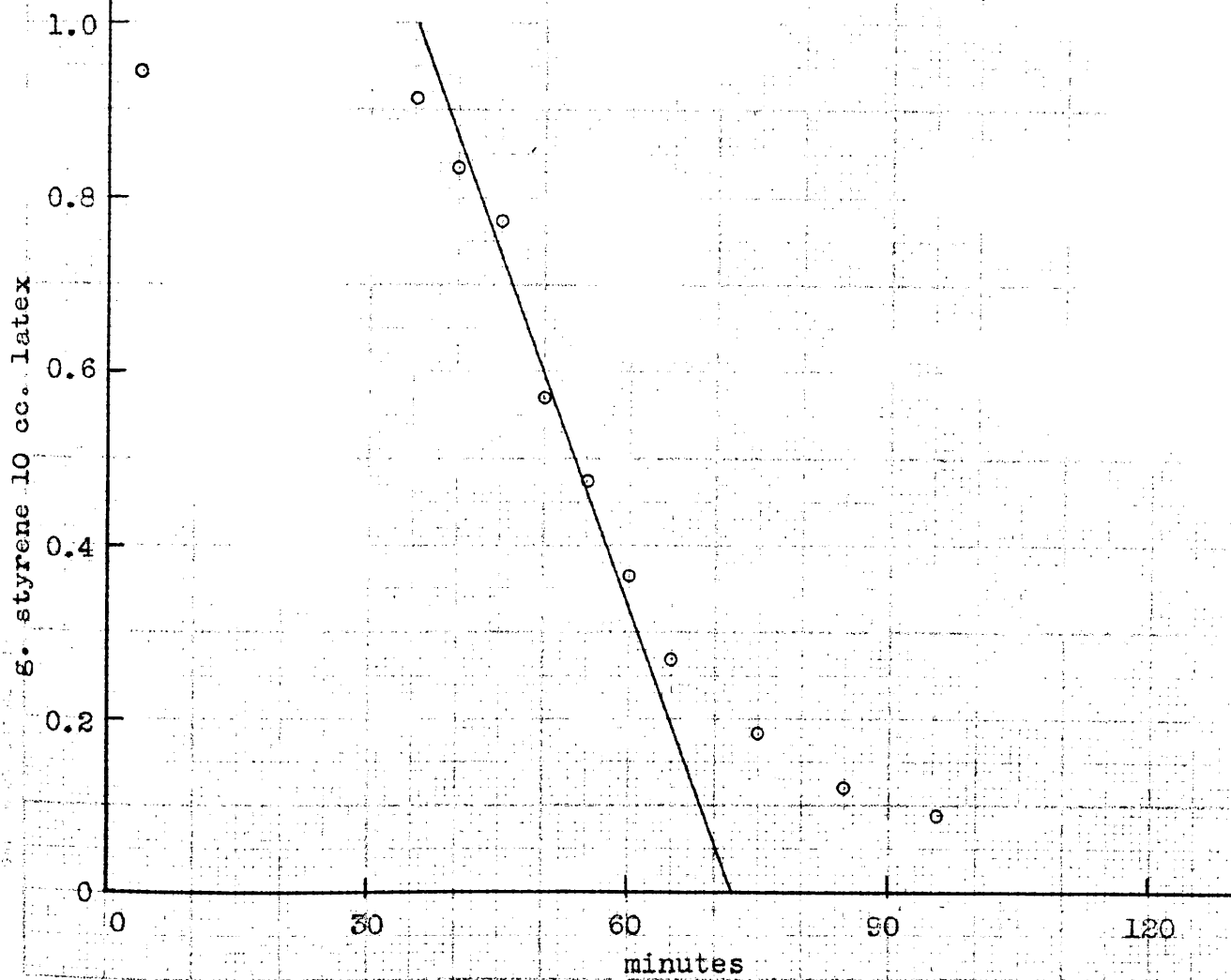
minutes

30

60

90

120



The effect of the purity of the styrene used was studied in polymerizations 5-10. The results of polymerization 5, run with styrene prepared chemically from pure α,β -dibromoethylbenzene, may be used as a basis for comparing the quality of styrene obtained by other methods of purification. Research styrene (see Experimental section for preparation) used in polymerization 10 gave results comparable with polymerization 5. Styrene purified by other methods gave longer induction periods and slower rates of polymerization than were found in polymerizations 5 or 10.

Polymerization 5

400 cc. 0.0665 N KOH
 10 cc. $K_2S_2O_8$ solution = 0.2197 g.
 8.000 g. stearic acid
 50 cc. styrene, from α,β -dibromoethylbenzene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex	log. styrene conc.	mg. $K_2S_2O_8$ in 10 cc. latex
7	50.0	50.0	0.9364	-0.03937	4.410
13	50.5	50.0	0.9093	-0.04129	4.560
18	51.3	49.8	0.7974	-0.09832	--
23	51.9	49.7	0.6417	-0.19267	4.515
28	52.0	49.5	0.5052	-0.29654	--
33	51.8	49.2	0.3649	-0.43783	4.541
38	51.3	49.1	0.2064	-0.68529	--
43	50.7	49.0	0.1386	-0.85824	--
52	50.0	50.0	0.0868	-1.06148	4.410
72	50.0	50.0	0.0611	-1.21396	4.440
					theoretical
					4.615

Rate: $k_0 = 0.0293$ $k_1 = 0.0260$

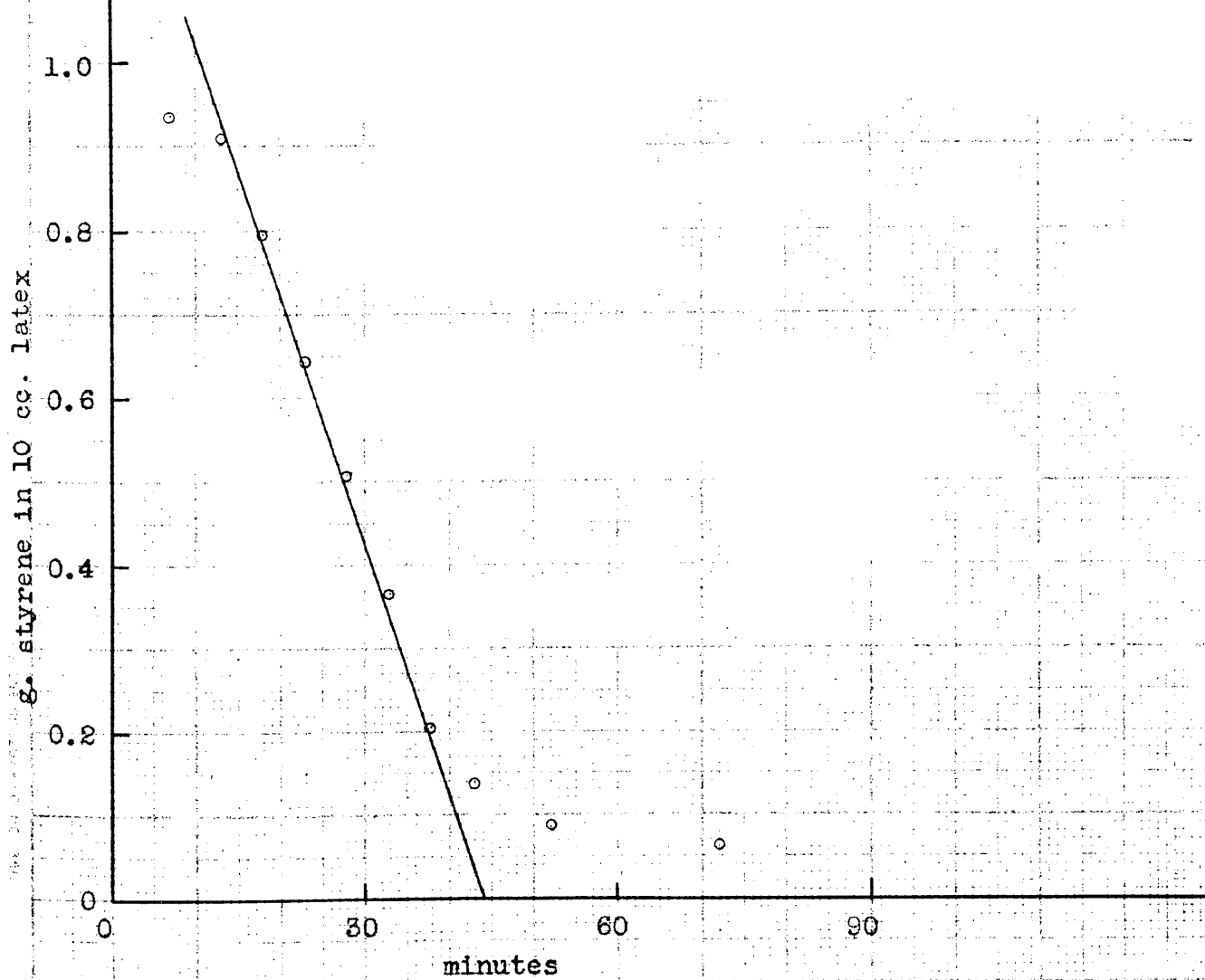
MW(C_7H_8) = 290,700

rel. visc. = 1.668

b. m. conc. = 0.00557

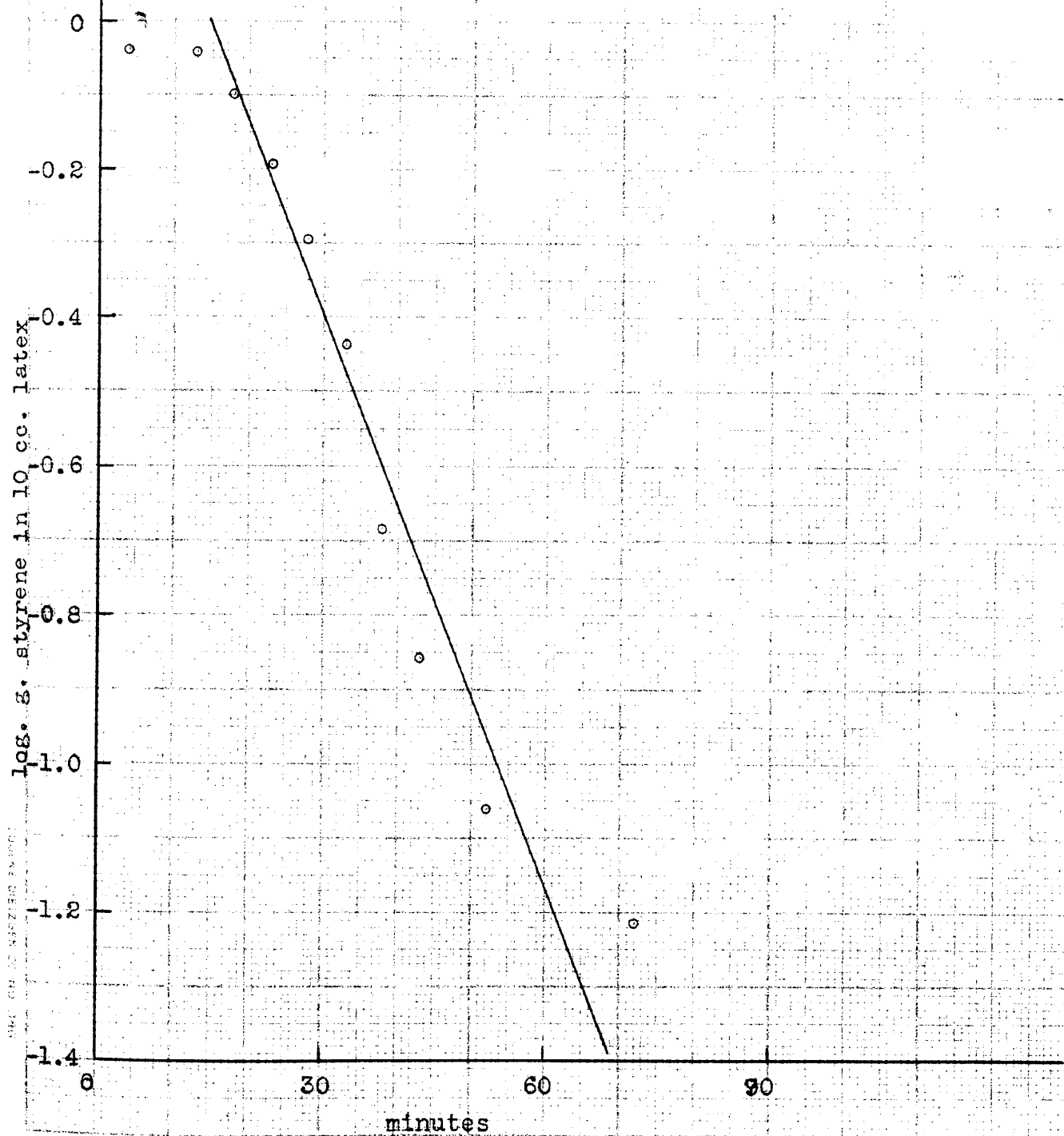
Polymerization 5

$$k_0 = 0.0293$$



Polymerization 5(B)

$$k_1 = 0.0260$$



Polymerization 6

400 cc. 2 per cent soap solution

0.2197 g. $K_2S_2O_8$

50 cc. styrene, commercial, Nesslerized and distilled

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
16	50.0	50.0	1.0267
120	50.0	50.0	1.0275
230	51.0	50.0	0.9222
240	51.5	50.0	0.7359
250	52.0	49.9	0.4853
260	51.4	49.8	0.3232
270	50.5	49.5	0.2453
280	49.9	50.0	0.0952
300	50.0	50.0	0.0853

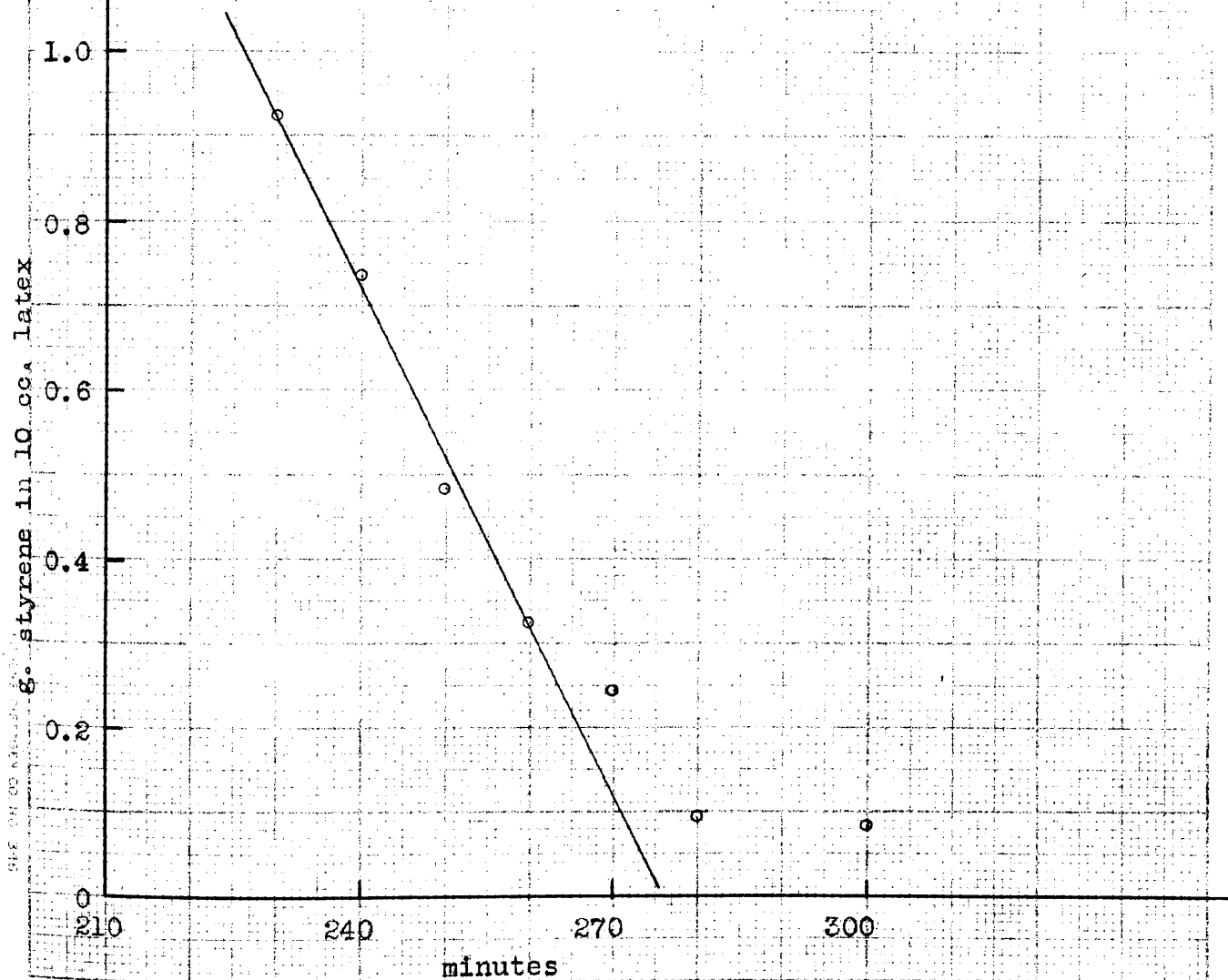
Rate: $k_o = 0.0200$ MW($CHCl_3$) = 248,200

rel. visc. = 1.476

b. m. conc. = 0.00323

Polymerization 6

$$k_0 = 0.0200$$



Polymerization 7

400 cc. 2 per cent soap solution

0.2197 g. $K_2S_2O_8$ 50 cc. styrene²²⁸, commercial, Nesslerized and distilled

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
55	50.0	50.0	1.0094
115	50.0	50.0	1.0376
159	51.3	49.7	0.7755
165	51.2	49.6	0.6660
172	51.0	49.5	0.5108
180	50.7	49.3	0.3343
187	50.0	49.5	0.2113
195	50.0	50.0	0.0830

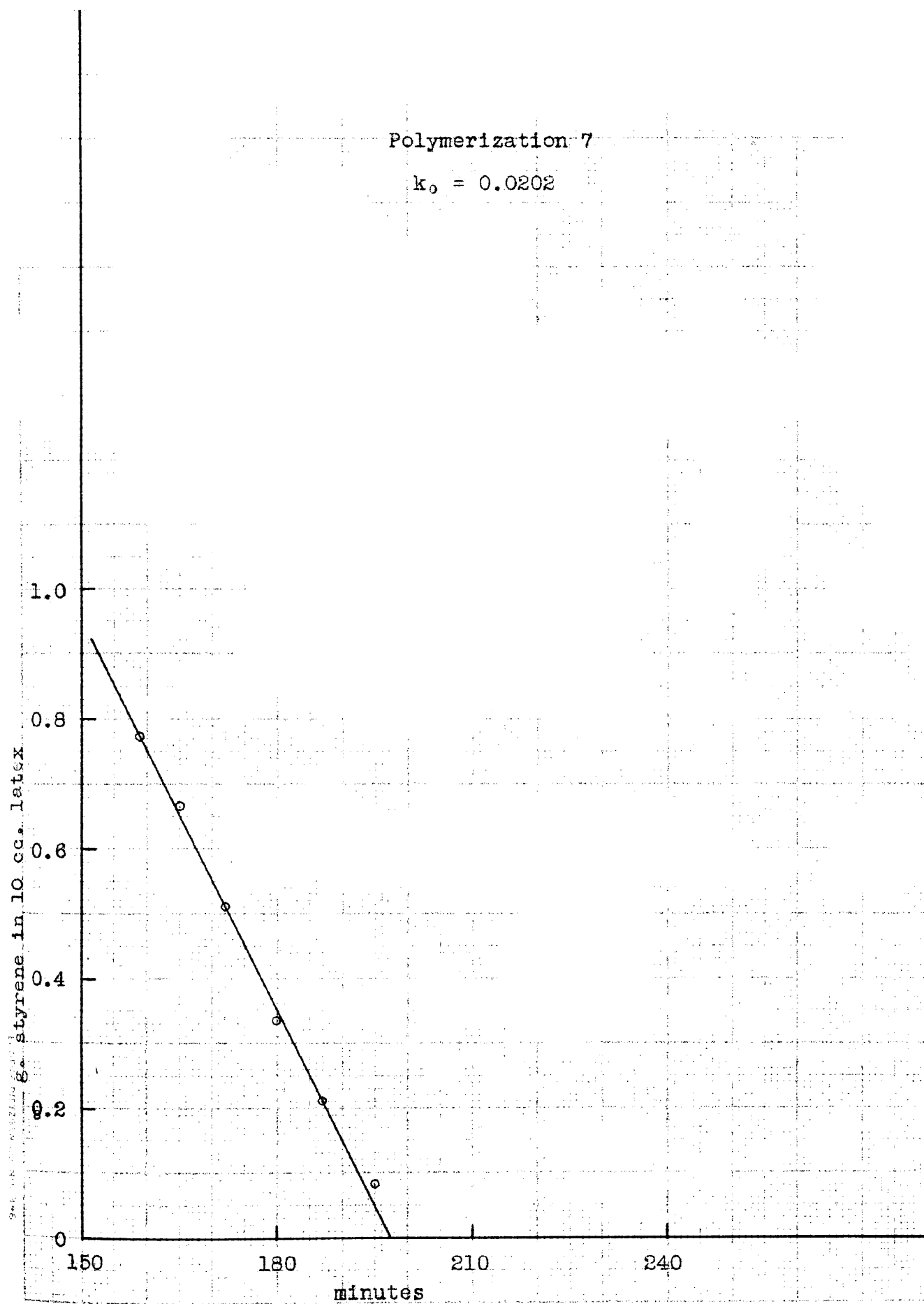
Rate: $k_0 = 0.0202$ MW($CHCl_3$) = 231,100

rel. visc. = 1.438

b. m. conc. = 0.00323

Polymerization 7

$$k_0 = 0.0202$$



Polymerization 8

400 cc. 0.0665 N NaOH0.2197 g. $K_2S_2O_8$

8.000 g. fatty acid

50 cc. styrene, Monsanto special, distilled

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
9	50.0	50.0	0.9659
89	50.0	50.0	0.9762
316	50.8	50.0	0.8783
323.3	52.8	50.0	0.7166
331	52.3	49.8	0.4791
338	51.5	49.8	0.2984
345	50.8	49.6	0.2202
359	50.0	49.5	0.1407

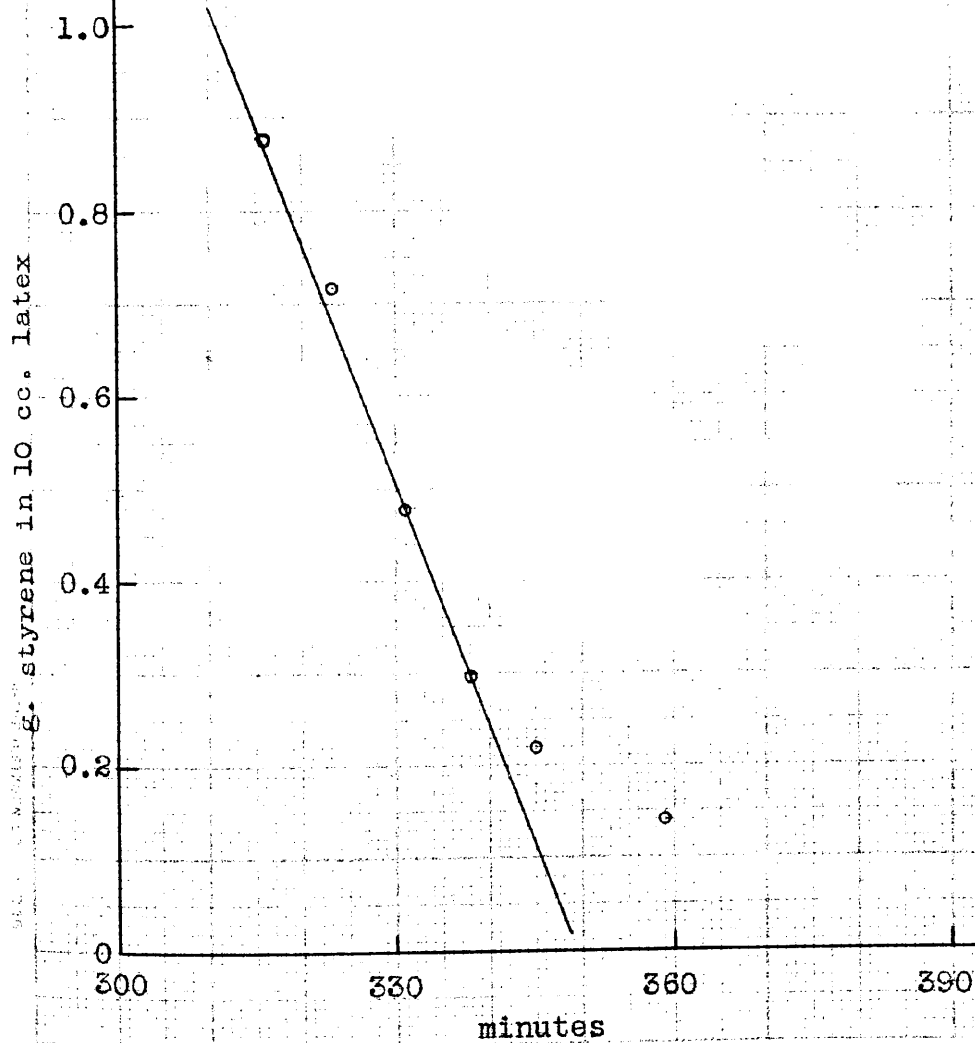
Rate: $k_p = 0.0262$ $MW(CHCl_3) = 237.400$

rel. visc. = 1.450

b. m. conc. = 0.00323

Polymerization 8

$$k_0 = 0.0262$$



Polymerization 9

400 cc. 0.0665 N NaOH
 0.2197 g. $K_2S_2O_8$
 8.000 g. fatty acid
 50 cc. styrene, Monsanto special, distilled

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
13	50.0	50.0	0.9857
46	50.5	50.0	0.9418
51	51.4	50.0	0.8120
56	51.8	49.8	0.6806
61	52.0	49.8	0.5705
66	51.9	49.8	0.3183
71	51.5	49.7	0.2629
76	50.9	49.6	0.2037
86	50.0	49.4	0.1318
96	50.0	50.0	0.1043

Rate: $k_0 = 0.0250$

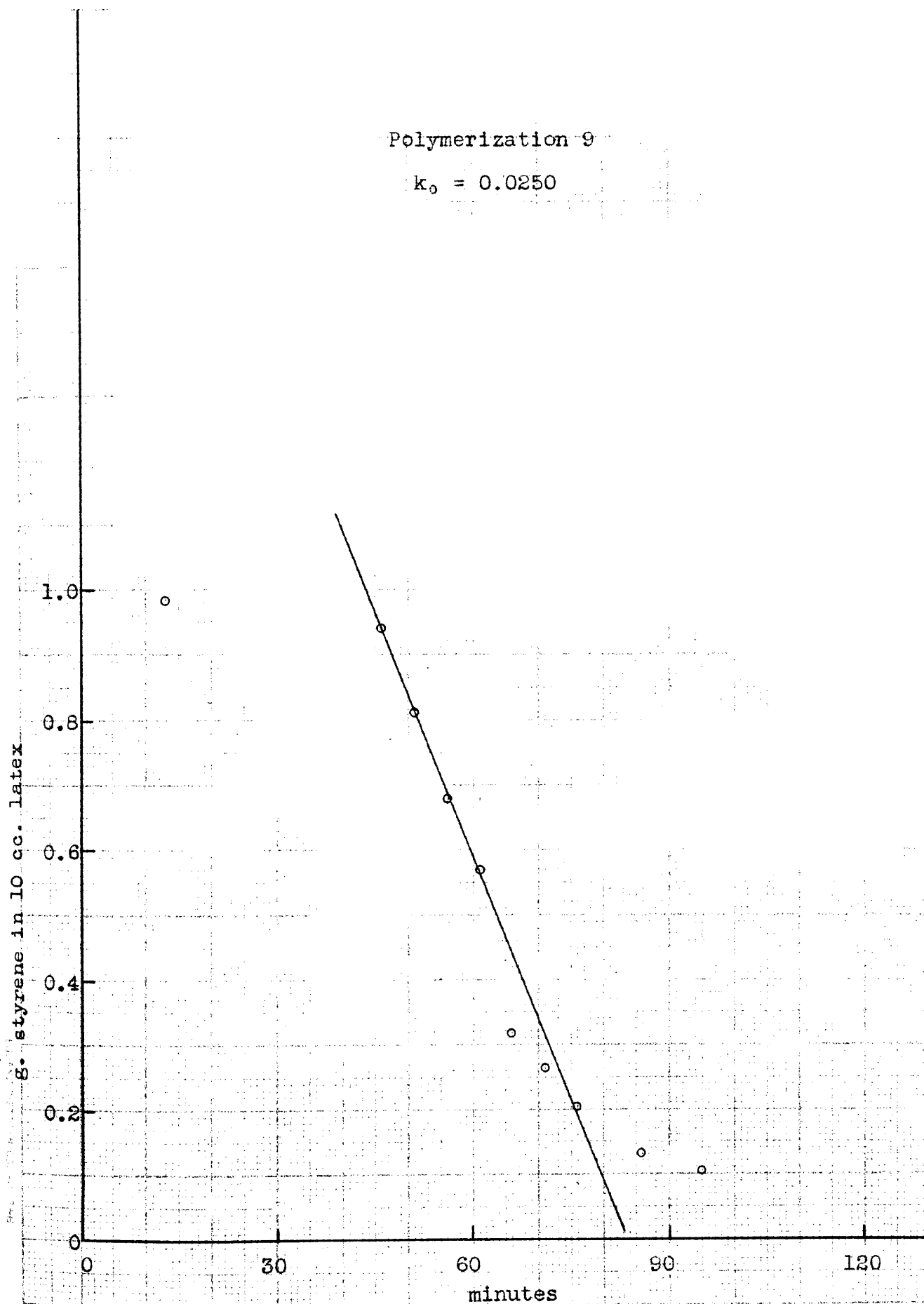
$MW(C_7H_8) = 256,700$

rel. visc. = 1.572

b. m. conc. = 0.00557

Polymerization 9

$$k_0 = 0.0250$$



Polymerization 10

400 cc. 0.0667 N KOH
 10 cc. $K_2S_2O_8$ solution = 0.2197 g.
 8.000 g. fatty acid
 50 cc. research styrene

Time. (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex	log. styrene conc.
6	50.0	50.0	0.9548	-0.02009
23	50.3	50.0	0.9270	-0.03298
27	51.0	49.8	0.8357	-0.07795
32	51.7	49.7	0.6930	-0.15927
37	52.0	49.6	0.5335	-0.27287
42	52.0	49.4	0.3624	-0.44081
47	52.5	49.3	0.2690	-0.57025
52	50.8	49.1	0.1910	-0.71897
62	50.3	50.0	0.1250	-0.90309
72	50.0	50.0	0.1025	-0.98928

Rate: $k_0 = 0.0294$ $k_1 = 0.0269$

$MW(C_7H_8) = 269,500$

rel. visc. = 1.602

b. m. conc. = 0.00555

Polymerization 10

$$k_0 = 0.0294$$

g. styrene in 10 cc. latex

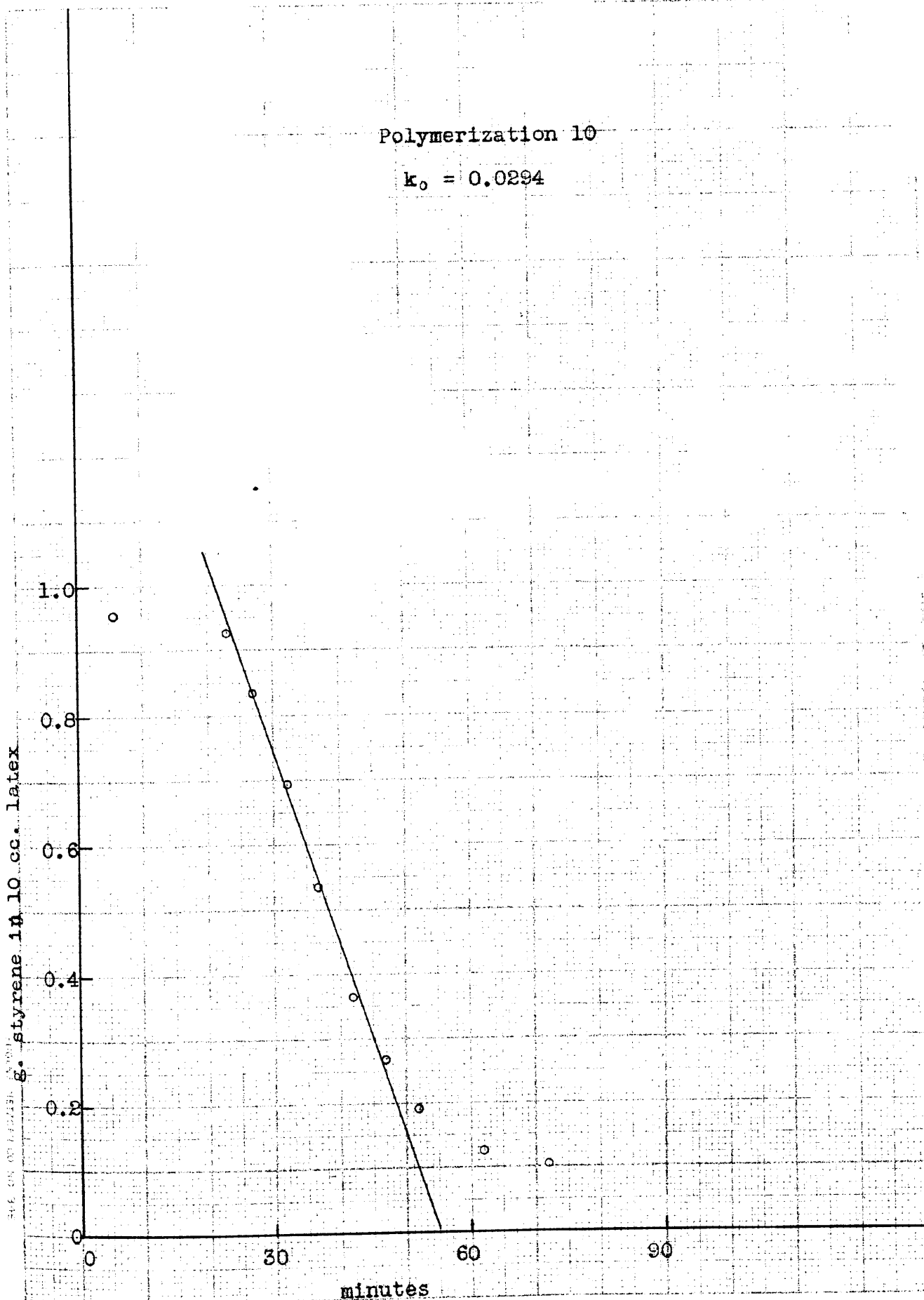
1.0
0.8
0.6
0.4
0.2
0

minutes

30

60

90

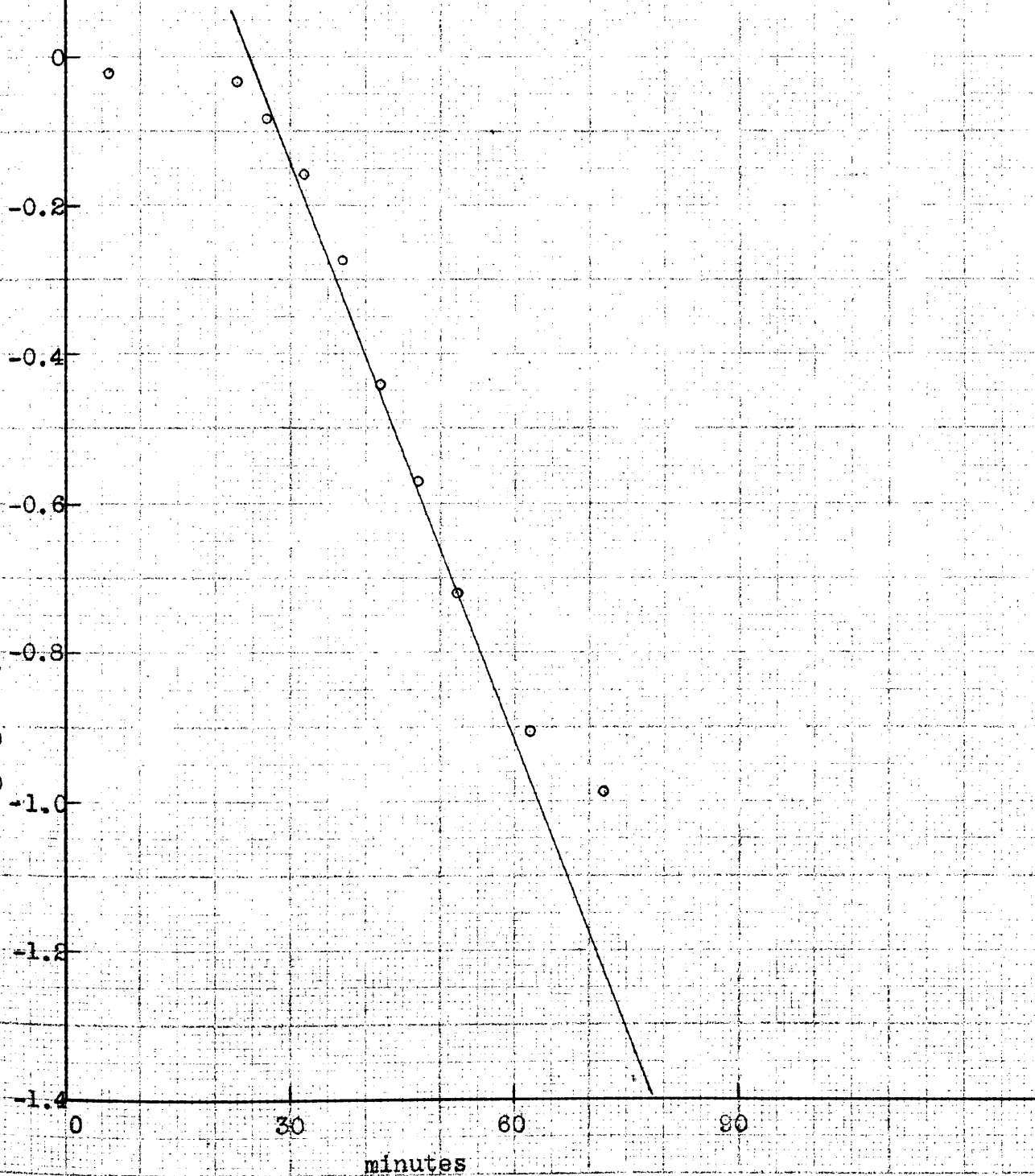


Polymerization 10(B)

$$k_1 = 0.0269$$

log. g. styrene in 10 cc. latex

ESTIM. POLYMER CO. INC. 1945



The presence of an atmosphere of air was found to completely inhibit polymerizations 11 and 12. When the air was replaced by nitrogen after a period of more than twenty-four hours, these polymerizations were found to proceed nearly normally.

Polymerization 11*

400 cc. 0.0663 N KOH
 0.2197 g. $K_2S_2O_8$
 8.000 g. fatty acid
 50 cc. research styrene

Time (min.)	Atmosphere	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
8	air	50.0	50.0	0.9533
71	"	50.0	50.0	0.9781
306	"	50.0	50.0	0.9633
466	"	50.0	50.0	0.9633
1096	"	50.0	50.0	0.9402
1451	"	50.0	50.0	0.9359
1461	nitrogen	50.0	50.0	--
1543	"	52.0	50.3	0.1939
1548	"	51.5	50.2	0.1351
1553	"	50.8	50.0	0.1081
1566	"	50.0	50.0	0.0915

* Rate and molecular weight were not determined

Polymerization 12

400 cc. 0.0663 N KOH
 0.2197 g. $K_2S_2O_8$
 8.000 g. fatty acid
 50 cc. research styrene

Time (min.)	Atmosphere	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
45	air	50.0	50.0	0.9368
690	"	50.0	50.0	0.9415
1365	"	50.0	50.0	0.9345
1665	"	50.0	50.0	0.9333
1675	nitrogen	50.0	50.0	--
1715	"	51.0	50.0	0.8167
1720	"	51.7	49.8	0.6779
1726	"	52.6	49.7	0.4190
1735	"	51.5	49.7	0.1610
1740	"	50.5	49.5	0.1153
1750	"	50.0	50.0	0.0844

Rate: $k_0 = 0.0319$

$MW(C_7H_8) = 218,400$

rel. visc. = 1.465

b. m. conc. = 0.00555

Polymerization 12

$$k_0 = 0.0319$$

g. styrene in 10 cc. latex

1.0

0.8

0.6

0.4

0.2

1650

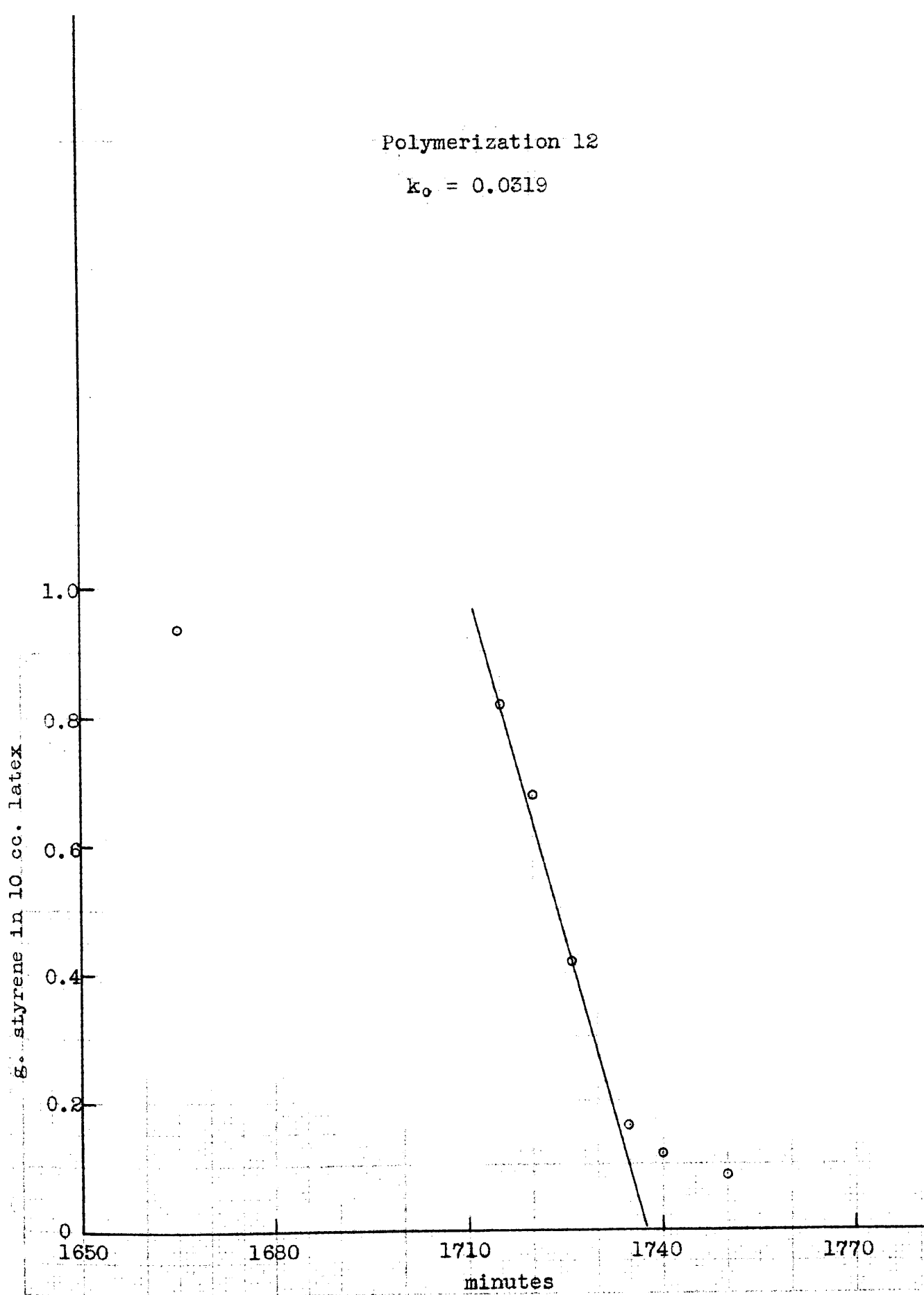
1680

1710

1740

1770

minutes



The effect of the amount of alkali used to prepare the soap in the emulsion was studied in polymerizations 13, 14 and 15. Alkali equivalent to or in 10 per cent excess of the fatty acid used, polymerizations 13 and 14 respectively, gave the same results but these rates of polymerization were slightly slower than polymerization 15, in which the alkali neutralized only 90 per cent of the fatty acid.

Polymerization 13

400 cc. 0.07656 N NaOH (amount equivalent to fatty acid)
 0.2197 g. $K_2S_2O_8$
 8.000 g. fatty acid
 50 cc. styrene, Monsanto special, distilled

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
8	50.0	50.0	0.9482
71	50.0	50.0	0.9783
129	50.3	50.0	0.8934
134	51.3	50.0	0.7901
139	51.5	49.8	0.6847
144	51.4	49.7	0.5748
149.4	51.2	49.6	0.4723
160	51.3	49.4	0.2607
167	51.0	49.1	0.1940

Rate: $k_o = 0.0208$

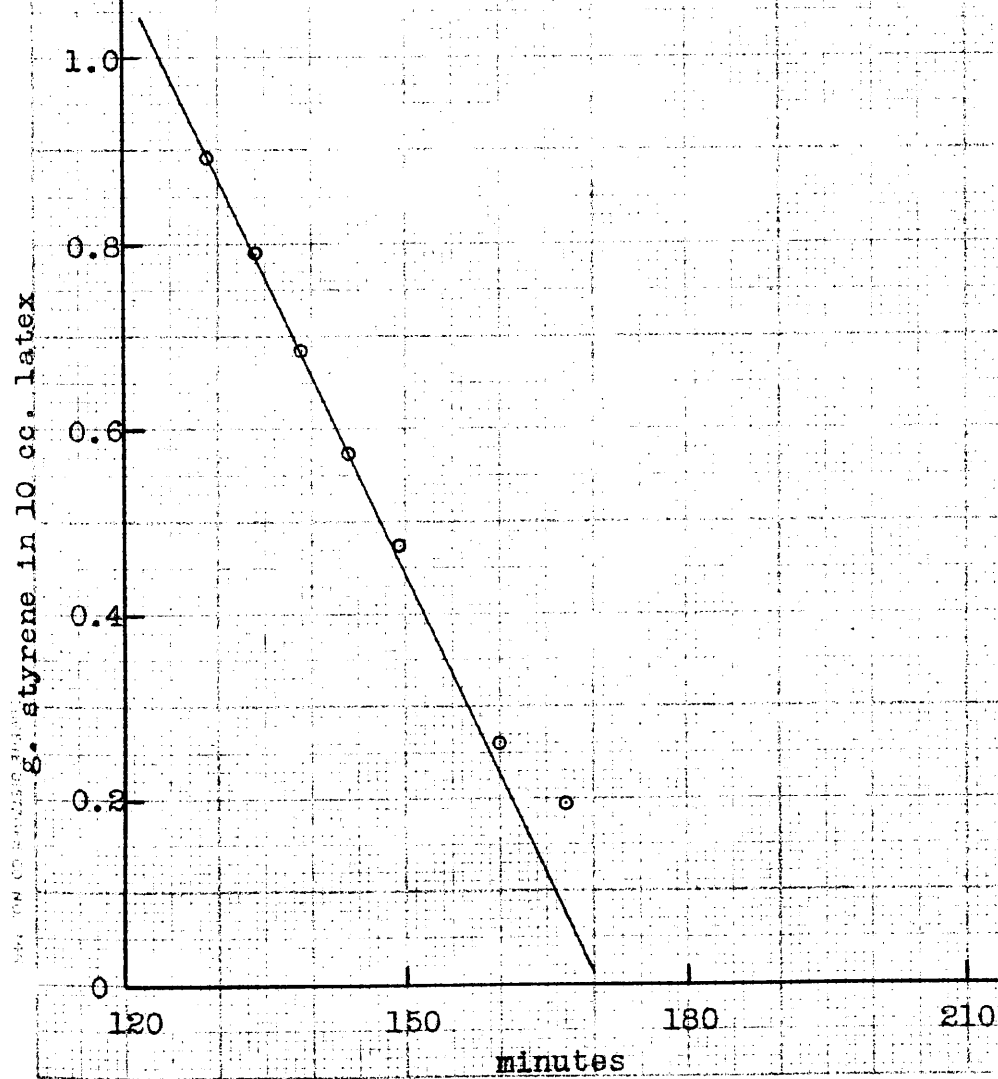
MW(C_7H_8) = 205,300

rel. visco. = 1.433

b. m. conc. = 0.00555

Polymerization 13

$$k_p = 0.0208$$



Polymerization 14

400 cc. 0.08416 N NaOH (in 10 per cent molar
excess of fatty acid)

0.2197 g. $K_2S_2O_8$

8.000 g. fatty acid

50 cc. styrene, Monsanto special, distilled

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
12	50.0	50.0	0.9693
33	50.5	50.0	0.9135
38	51.0	50.0	0.8283
45	51.3	49.8	0.7004
50	51.4	49.7	0.5892
55	51.5	49.6	0.4570
62	51.9	49.3	0.2920
89	49.2	49.0	0.1378

Rate: $k_0 = 0.0215$

$MW(C_7H_8) = 228,700$

rel. visc. = 1.492

b. m. conc. = 0.00555

Polymerization 14

$$k_0 = 0.0215$$

g. styrene in 10 cc. latex

1.0

0.8

0.6

0.4

0.2

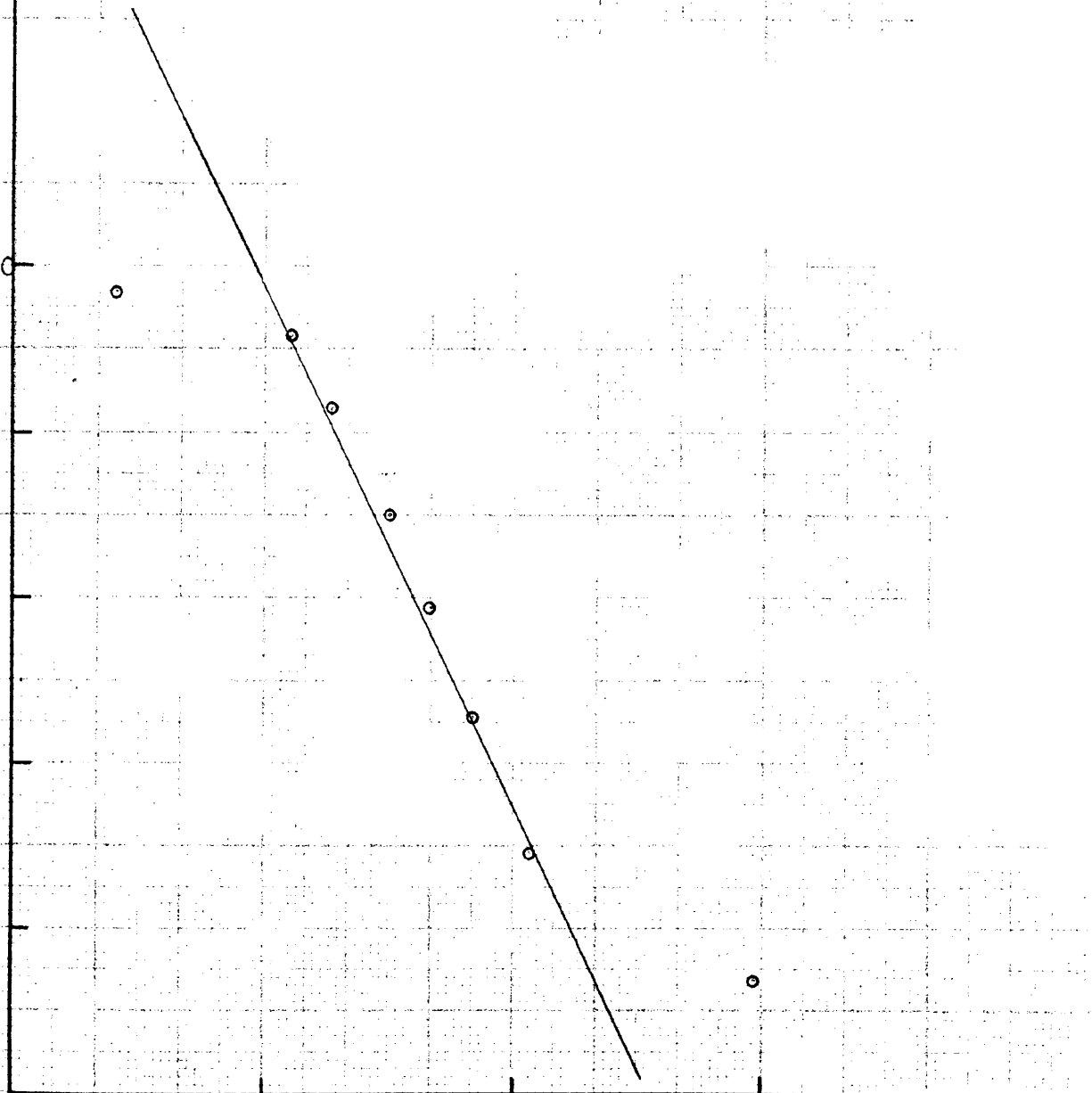
0

30

60

90

minutes



Polymerization 15

400 cc. 0.0688 N NaOH (90 per cent equivalent
to fatty acid)

0.2197 g. $K_2S_2O_8$

8.000 g. fatty acid

50 cc. styrene, Monsanto special, distilled

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
14	50.0	50.0	0.9652
72.5	50.4	50.0	0.9392
78	51.2	49.9	0.8188
83	51.7	49.8	0.6888
89	51.7	49.7	0.5372
93	51.5	49.4	0.4292
98	51.0	49.4	0.3720
107	51.3	49.2	0.2048
114	50.2	49.0	0.1584

Rate: $k_0 = 0.0248$

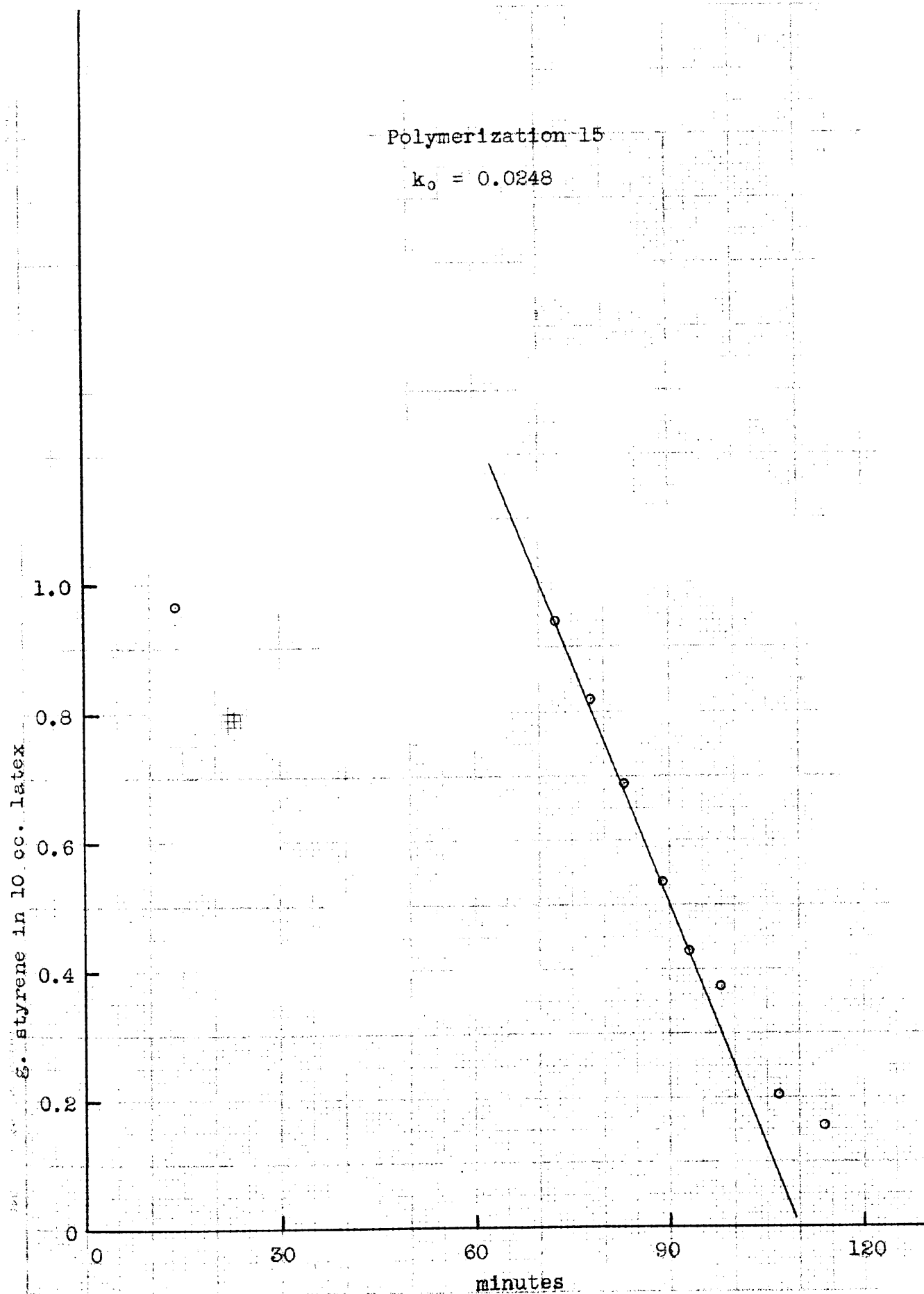
$MW(C_7H_8) = 218,400$

rel. visc. = 1.467

b. m. conc. = 0.00555

Polymerization 15

$$k_0 = 0.0248$$



Polymerizations 16 and 17 show that the same results were obtained when either sodium or potassium hydroxide was used to prepare the soap for the emulsion.

Polymerization 16

400 cc. 0.0665 N NaOH
 0.2197 g. $K_2S_2O_8$
 8.000 g. fatty acid
 50 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
9	50.0	50.0	0.9755
22	51.0	50.0	0.9035
27	51.4	48.8	0.7403
32	51.9	49.7	0.6002
37	52.0	49.6	0.4629
42	51.6	49.5	0.3371
47	51.1	49.3	0.2189
59	50.3	49.0	0.1234
69	49.5	50.0	0.0577

Rate: $k_0 = 0.0292$

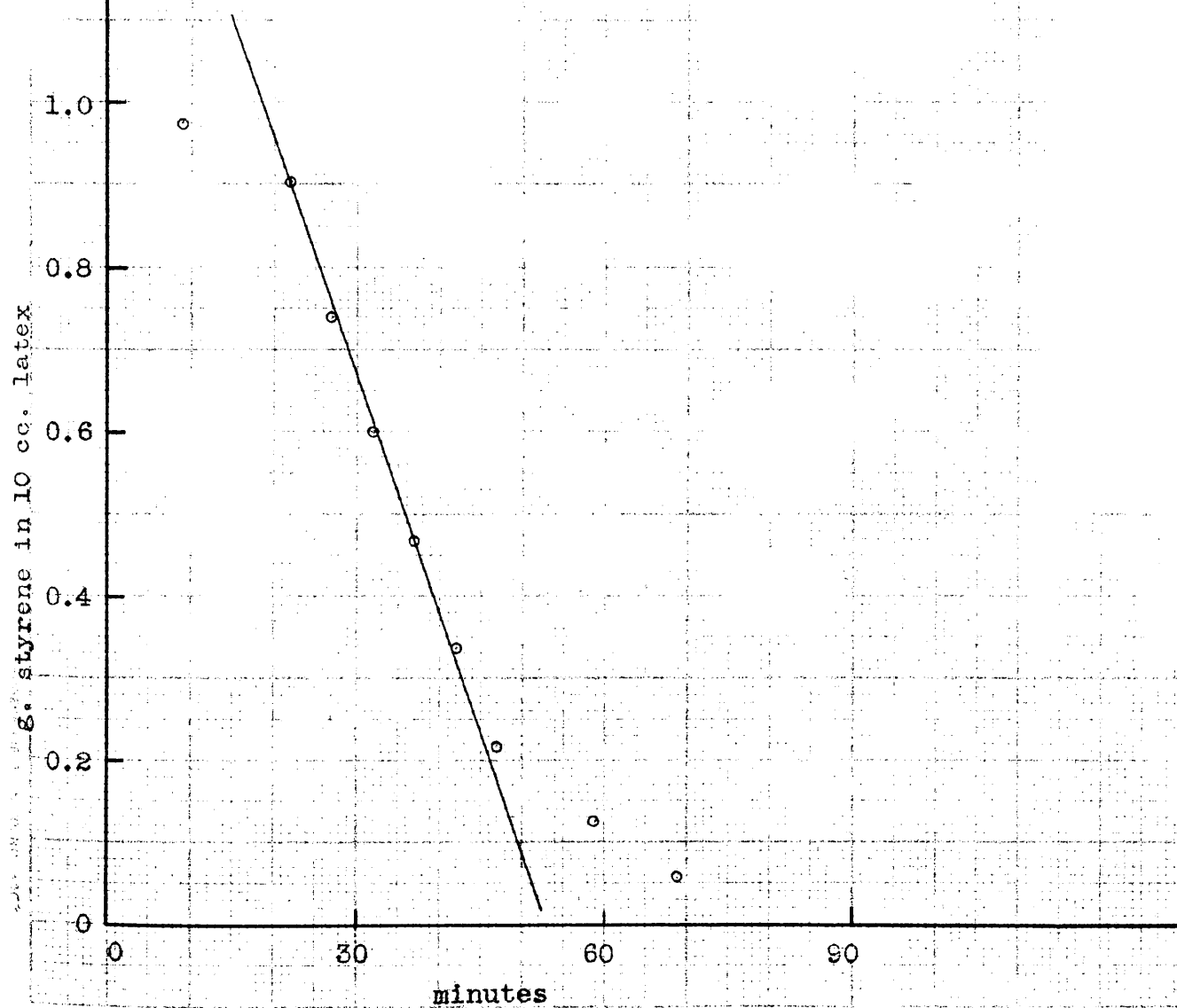
MW(C_7H_8) = 158,500

rel. viso. = 1.320

b. m. conc. = 0.00557

Polymerization 16

$$k_0 = 0.0292$$



Polymerization 17

400 cc. 0.0663 N KOH
 0.2197 g. $K_2S_2O_8$
 8.000 g. fatty acid
 50 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
9	50.0	50.0	0.9711
20	51.0	50.0	0.9424
25	51.7	49.9	0.7724
30	52.1	49.8	0.6036
35	52.1	49.7	0.4662
40	51.8	49.7	0.3388
45	51.0	49.5	0.2588
54	50.3	50.0	0.1712
64	50.1	50.0	0.1242

Rate: $k_0 = 0.0294$

$MW(C_7H_8) = 219,700$

rel. visc. = 1.468

b. m. conc. = 0.00555

Polymerization 17

$$k_0 = 0.0284$$

g. styrene in 10 cc. latex

1.0

0.8

0.6

0.4

0.2

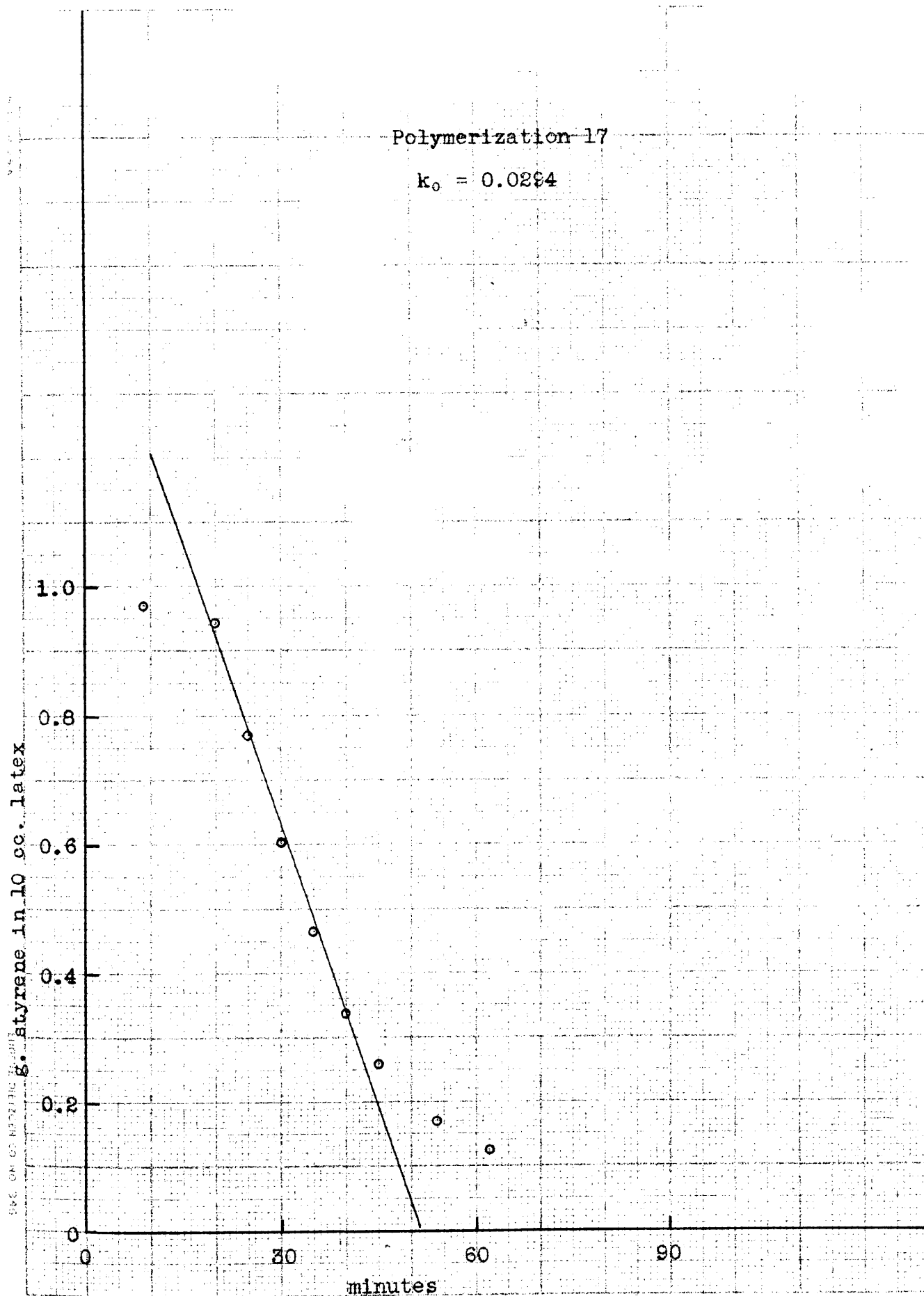
0

30

60

90

minutes



Fatty acid through which oxygen was passed for four hours at 120° and which was shown to have a high active oxygen content gave results (polymerization 18) similar to the control (polymerization 19). Thus air oxidation of the fatty acid during storage was not considered to be of importance.

Polymerization 18

400 cc. 0.0665 N NaOH0.2197 g. $K_2S_2O_8$

8.000 g. fatty acid

 O_2 passed through four hours at $120^\circ C$,
active oxygen content 848 parts per million

50 cc. styrene, Monsanto special, distilled

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
5	50.0	50.0	0.9776
37.5	50.6	50.0	0.9625
42	51.4	50.0	0.8175
47	51.6	49.9	0.7083
52	51.5	49.8	0.5950
57	51.3	49.7	0.5010
62	51.0	49.4	0.4183
67	50.6	49.3	0.3497
72	50.0	49.1	0.3062
85	50.2	49.1	0.1521

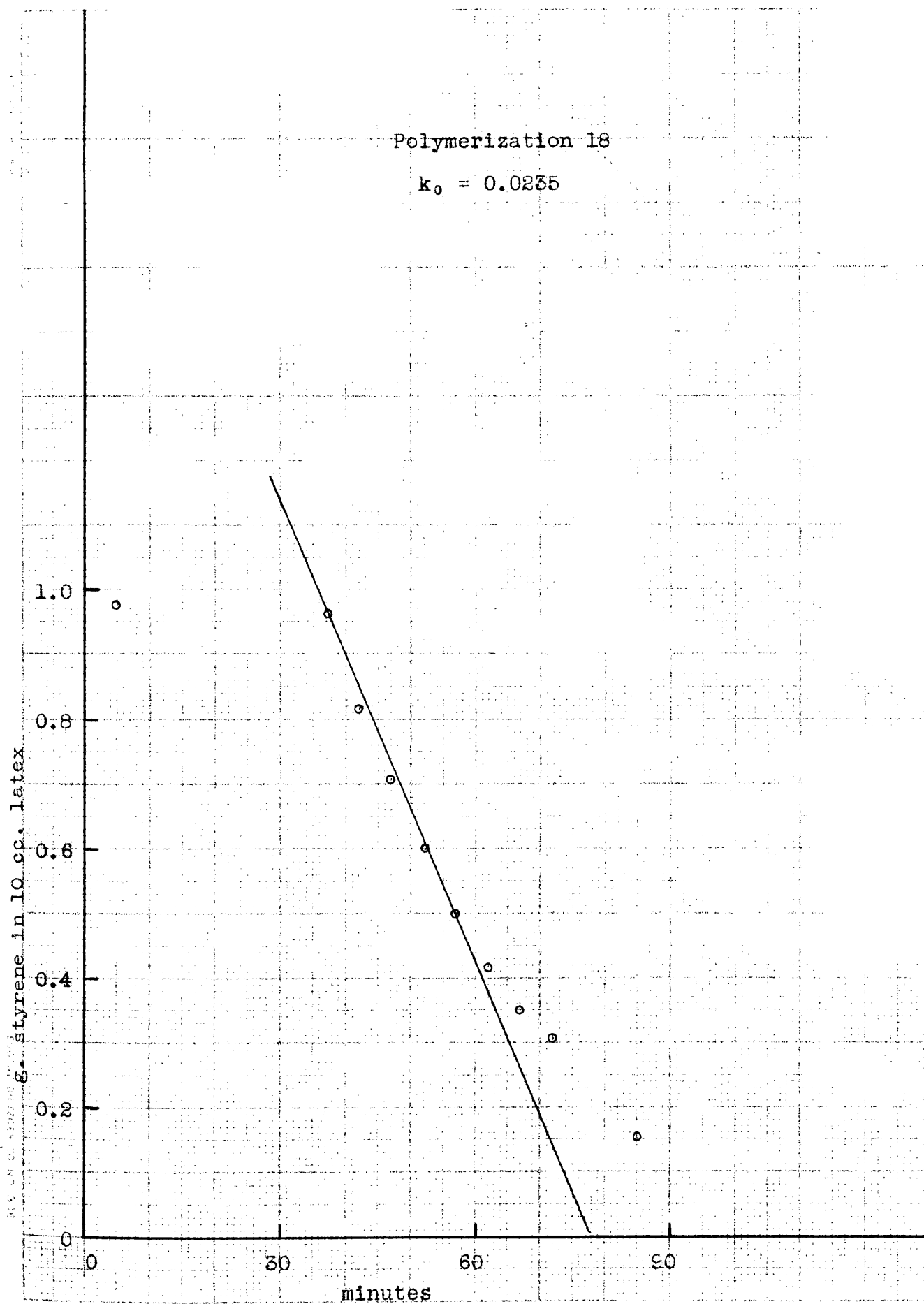
Rate: $k_0 = 0.0235$ $MW(C_7H_8) = 223.700$

rel. visc. = 1.480

b. m. conc. = 0.00555

Polymerization 18

$$k_0 = 0.0235$$



Polymerization 19

400 cc. 0.0665 N NaOH0.2197 g. $K_2S_2O_8$

8.000 g. fatty acid

active oxygen content 3.27

parts per million

50 cc. styrene, Monsanto special, distilled

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
11	50.0	50.0	0.9778
31	50.5	50.0	0.9277
36.2	51.0	49.8	0.7964
41	51.4	49.7	0.6868
46	51.5	49.6	0.5397
51	51.3	49.5	0.4125
56	51.0	49.3	0.3399
61	50.0	49.2	0.2853
78	50.0	49.0	0.1671

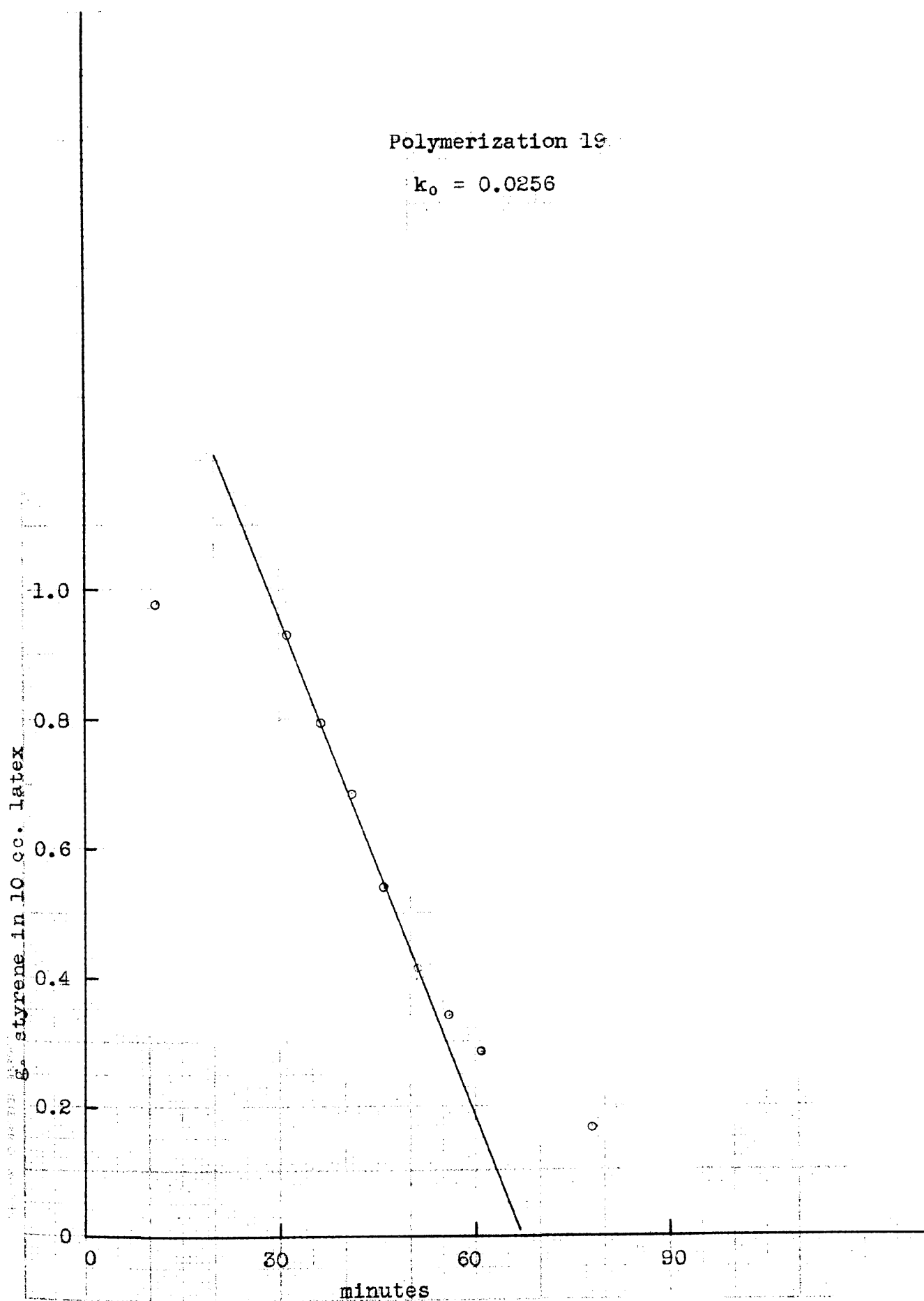
Rate: $k_0 = 0.0256$ $MW(C_7H_8) = 246,700$

rel. visc. = 1.450

b. m. conc. = 0.00559

Polymerization 19

$$k_0 = 0.0256$$



Potassium dehydroabietate was tested as an emulsifier in polymerization 20. The rate of polymerization was slower and the molecular weight of the polymer produced less than in similar runs where fatty acid soap was the emulsifier, polymerizations 32 and 33.

Polymerization 20

400 cc. 0.0665 N KOH
 10 cc. $K_2S_2O_8$ solution = 0.3295 g.
 8.000 g. Dehydroabiatic acid*
 bromine number 1, 2; 0.0267 mole
 50 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
6	50.0	50.0	0.9374
13	50.1	50.0	0.9119
21	50.6	49.8	0.8096
31	50.7	49.8	0.6996
41	50.7	49.8	0.5786
51	50.7	49.8	0.4630
61	50.5	49.8	0.3537
71	50.3	49.8	0.2539
81	50.2	50.0	0.1678
91	50.0	50.0	0.1297

Rate: $k_0 = 0.0115$

$MW(C_7H_8) = 168,600$

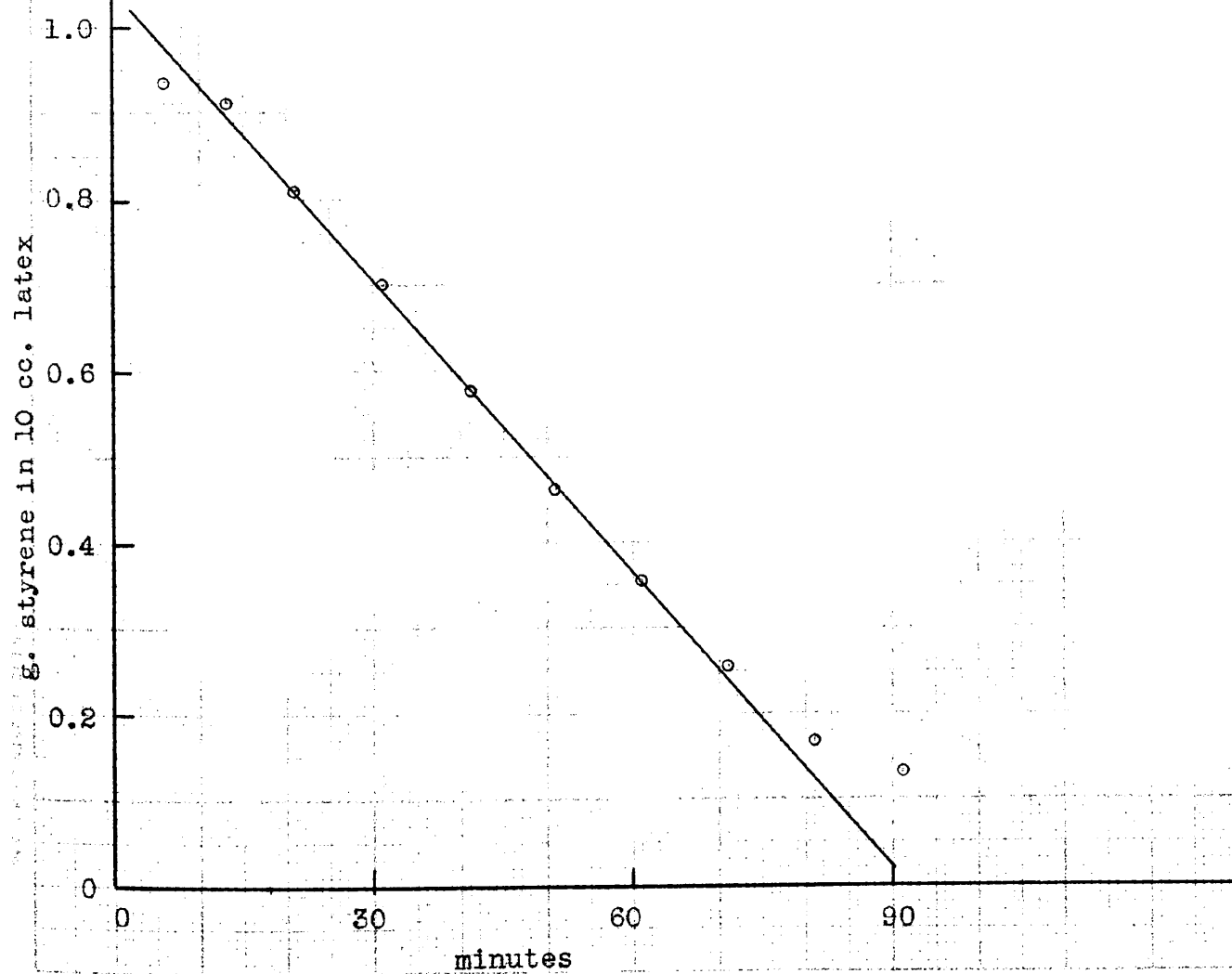
rel. visc. = 1.343

b. m. conc. = 0.00555

* sample kindly furnished by Hercules Powder Company

Polymerization 20

$$k_0 = 0.0115$$



The addition of 0.5 per cent (based on the weight of styrene) of dodecyl mercaptan to polymerization 21 was found to decrease decidedly the molecular weight of the polymer formed and decrease slightly the rate of polymerization, compare with polymerizations 32 and 34. The induction period found in the control runs, was shortened in the presence of mercaptan.

Polymerization 21

400 cc. 0.0665 N KOH
 10 cc. $K_2S_2O_8$ solution = 0.3295 g.
 8.000 g. fatty acid
 50 cc. research styrene
 0.02358 g. 96 per cent dodecyl mercaptan
 (0.5 per cent weight monomer)

Time. (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
3	50.8	50.0	0.9044
9	51.8	49.9	0.7472
14	52.4	49.8	0.5786
19	52.5	49.8	0.4167
24	52.1	49.7	0.2765
29	51.5	49.5	0.1817
39	50.0	50.0	0.1185

Rate: $k_0 = 0.0310$

$MW(C_7H_8) = 15,400$

rel. visc. = 1.115

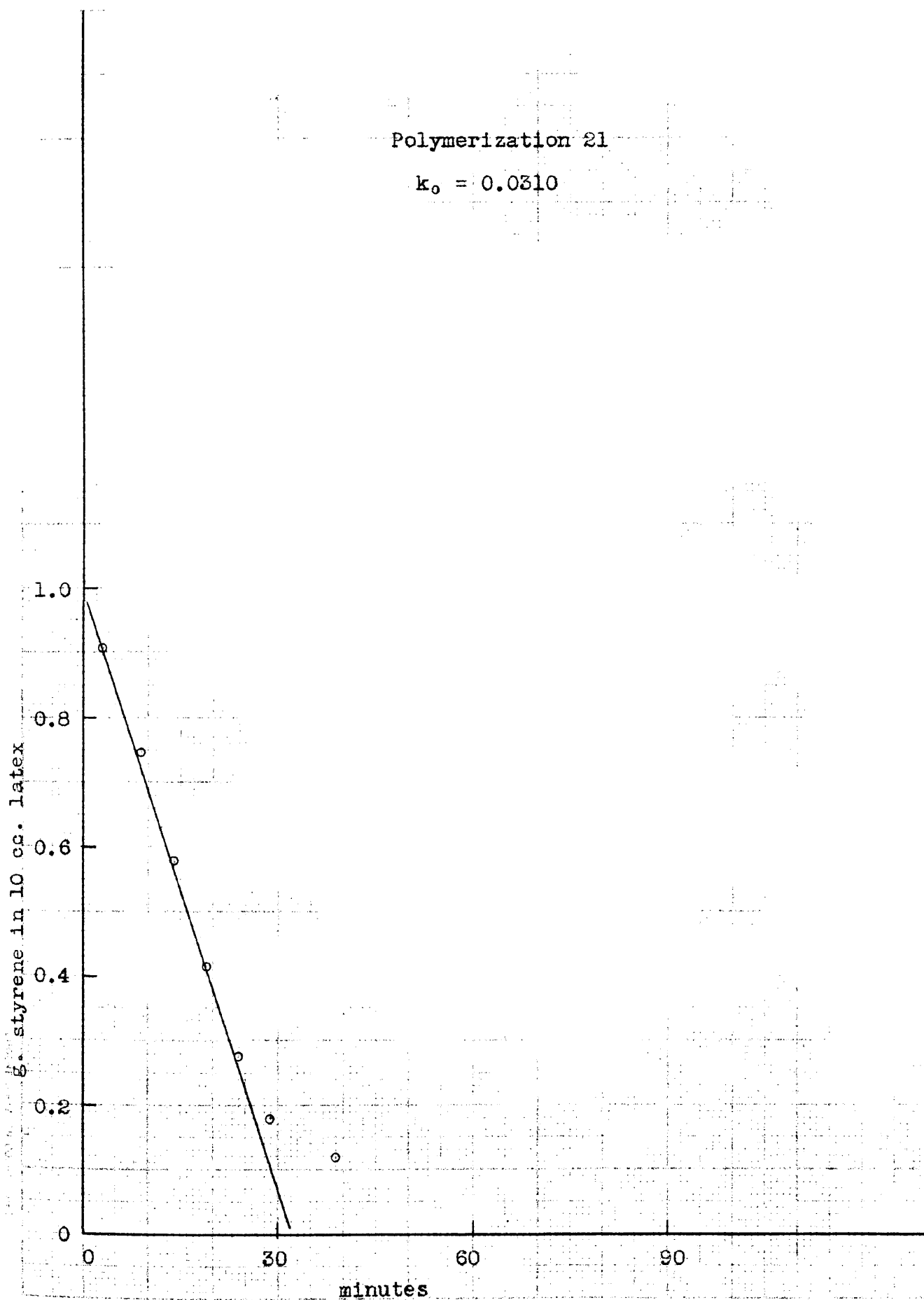
b. m. conc. = 0.0224

Anal. polymer. Calcd. for $(C_8H_8)_{148}S$: C, 92.06; H, 7.73; S, 0.21

Found : C, 92.09; H, 8.09; S, 0.018

Polymerization 21

$$k_0 = 0.0310$$



Polymerizations 22-38 were run using the same reagents under comparable conditions in order to study the effect of change of styrene and potassium persulfate concentration on the rate of polymerization and molecular weight of the polymers produced. Polymerizations 5 and 10 were carried out under these same conditions and the results obtained may be added to this series. The results of these polymerizations, 5, 10 and 22-38, are summarized in Tables I and II.

Polymerization 22

400 cc. 0.0665 N KOH
 10 cc. $K_2S_2O_8$ solution = 0.1098 g.
 8.000 g. fatty acid
 50 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
5	50.0	50.0	0.9465
20	50.1	50.0	0.9424
25	50.7	49.8	0.8737
30	51.0	49.6	0.7850
35	51.2	49.5	0.6746
40	51.3	49.3	0.5797
45	51.1	49.1	0.4669
50	50.8	49.0	0.3855
60	50.3	49.7	0.2931
70	50.0	49.8	0.1983
80	50.0	50.0	0.1504

Rate: $k_0 = 0.0193$

$MW(C_7H_8) = 314,000$

rel. visc. = 1.552

b. m. conc. = 0.00444

Polymerization 22

$$k_0 = 0.0193$$

g. styrene in 10 cc. latex

1.0

0.8

0.6

0.4

0.2

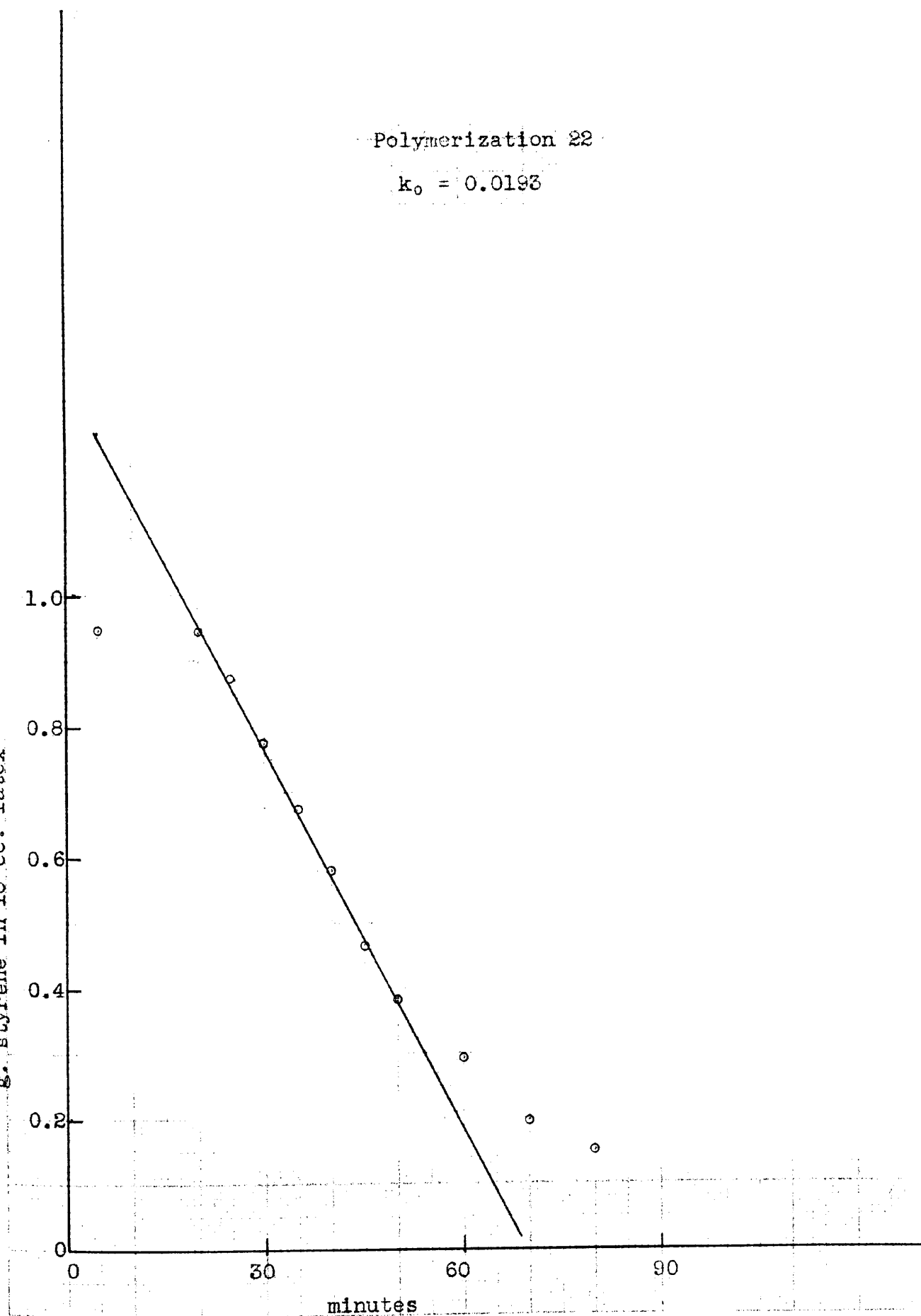
0

30

60

90

minutes



Polymerization 23

400 cc. 0.0665 M KOH
 10 cc. $\text{K}_2\text{S}_2\text{O}_8$ solution = 0.1098 g
 8.000 g. fatty acid
 50 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
7	50.0	50.0	0.9494
12	50.0	50.0	0.9538
79	50.1	50.0	0.9436
84	50.5	49.9	0.9188
88	50.8	49.8	0.8250
93	51.0	49.7	0.7443
98	51.0	49.6	0.6563
103	51.0	49.4	0.5707
108	50.8	49.2	0.4863
117	50.2	49.3	0.3791
127	50.0	49.5	0.2988
137	50.0	50.0	0.2189

Rate: $k_0 = 0.0171$

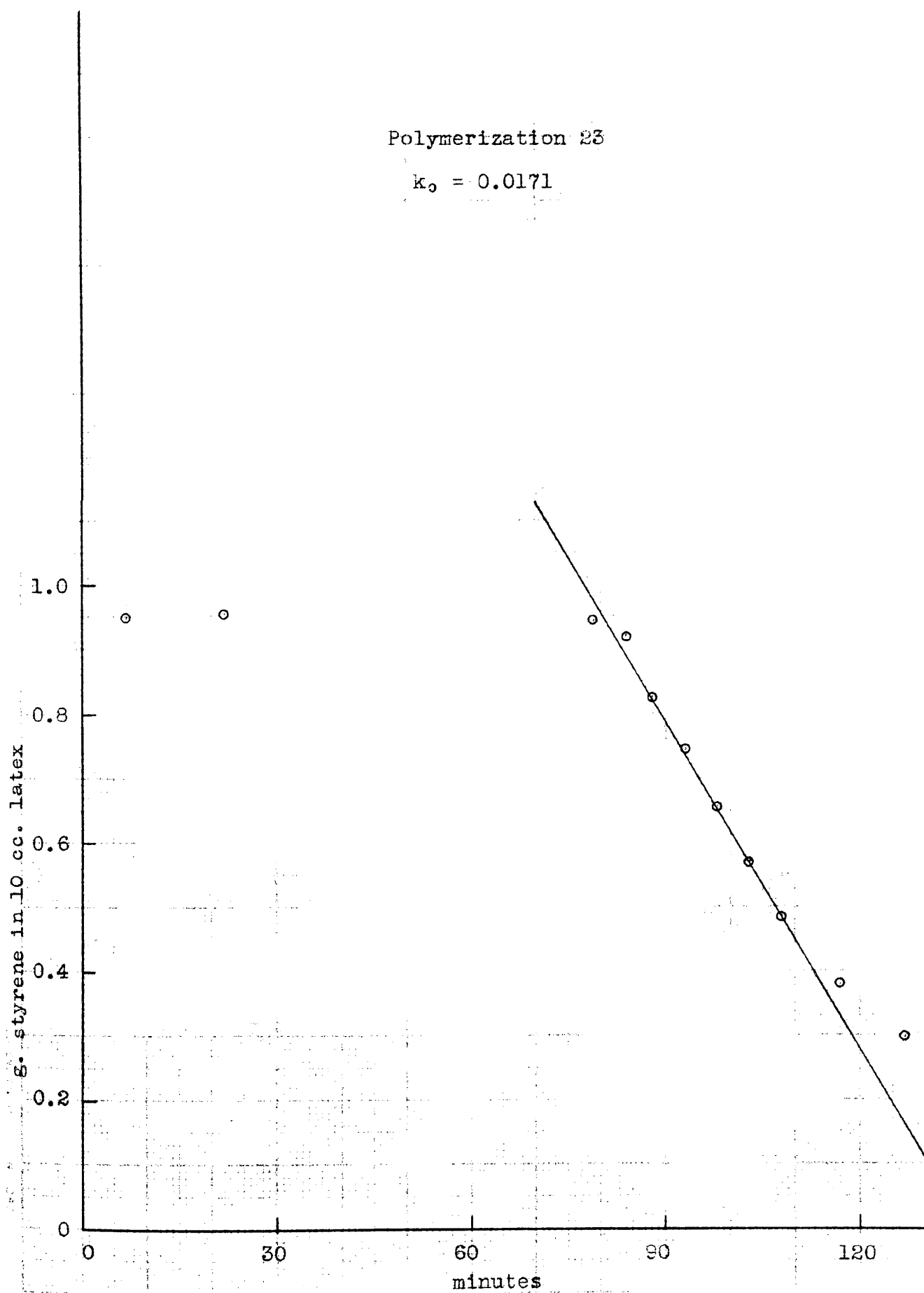
$\text{MW}(\text{C}_7\text{H}_8) = 352,000$

rel. visc. = 1.645

b. m. conc. = 0.00448

Polymerization 23

$$k_0 = 0.0171$$



Polymerization 24

400 cc. 0.0665 N KOH
 10 cc. $K_2S_2O_8$ solution = 0.1098 g.
 8.000 g. fatty acid
 50 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
8	50.0	50.0	1.0041
74	50.5	50.0	0.9078
78	51.0	50.0	0.8273
83	51.3	50.0	0.7411
88	51.4	49.9	0.6513
93	51.4	49.9	0.5534
98	51.4	49.8	0.4527
108	50.8	49.7	0.3062
118	50.0	49.5	0.2164
128	50.0	49.9	0.1679
138	50.0	50.0	0.1355

Rate: $k_0 = 0.0190$

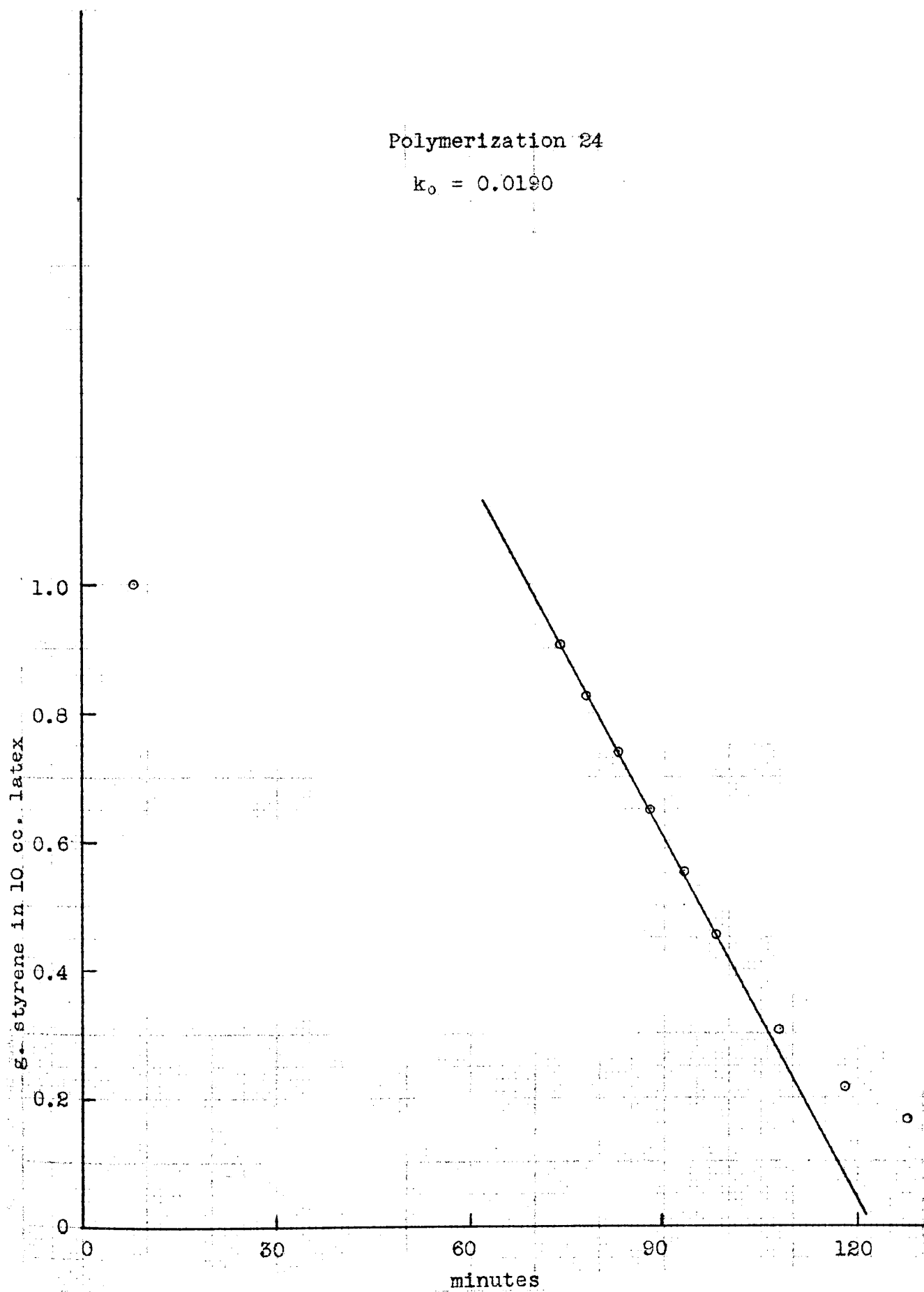
MW(C_7H_8) = 290,500

rel. visc. = 1.505

b. m. conc. = 0.00444

Polymerization 24

$$k_0 = 0.0190$$



Polymerization 25

400 cc. 0.0665 N KOH
 10 cc. $K_2S_2O_8$ solution = 0.1098 g.
 8.000 g. fatty acid
 75 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
10	50.0	50.0	1.3485
25	50.4	49.9	1.3086
30	50.9	49.7	1.2238
35	51.0	49.4	1.1431
40	50.9	49.2	1.0538
45	50.9	49.0	0.9629
50	50.7	49.0	0.8724
60	50.4	49.1	0.7004
70	51.0	49.3	0.5115
80	50.4	49.1	0.3633
90	50.0	49.3	0.2444
100	50.0	50.0	0.1843

Rate: $k_0 = 0.0175$

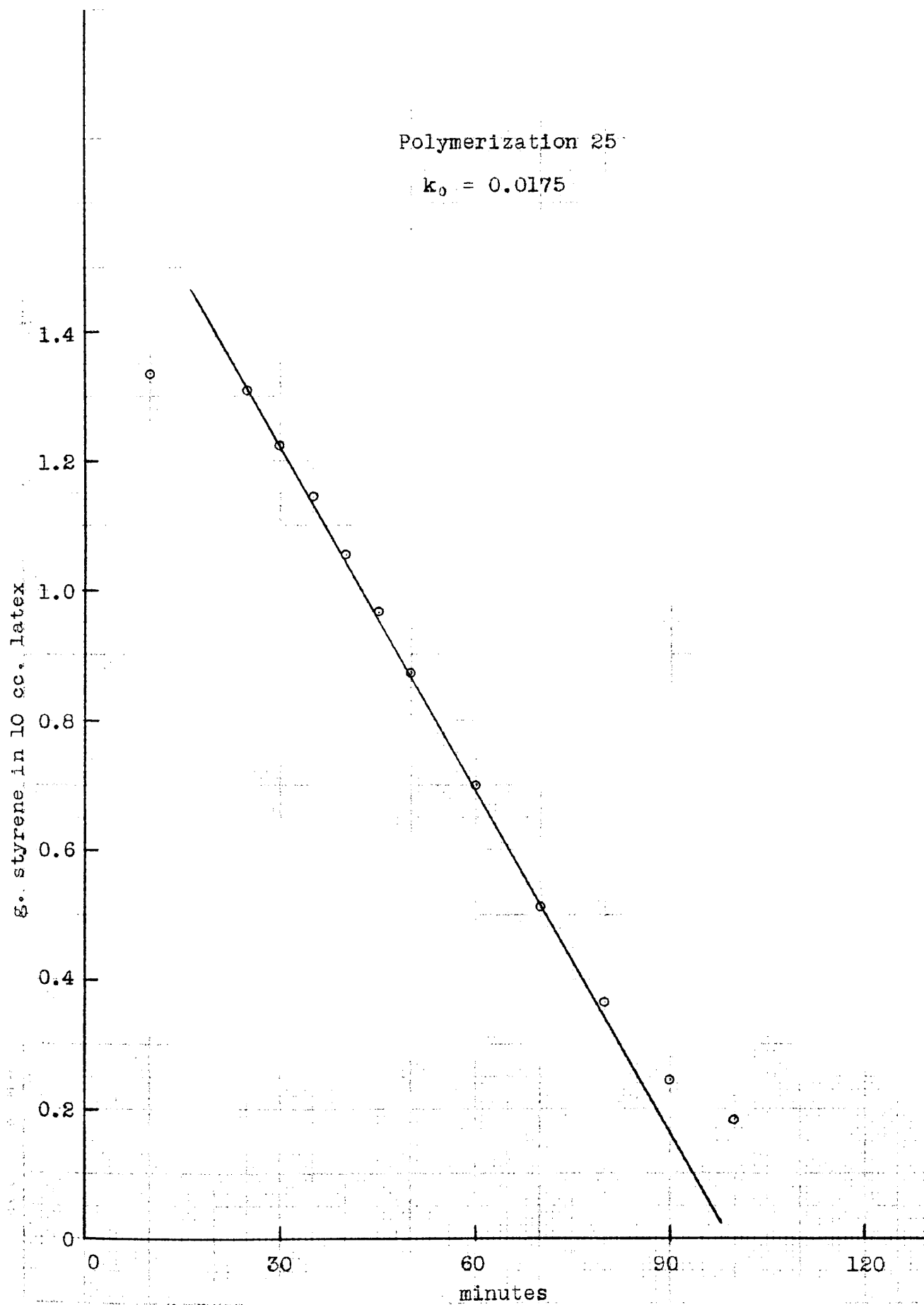
MW(C_7H_8) = 301,000

rel. visc. = 1.525

b. m. conc. = 0.00444

Polymerization 25

$$k_0 = 0.0175$$



Polymerization 26

400 cc. 0.0665 N KOH
 10 cc. $K_2S_2O_8$ solution = 0.1098 g.
 8.000 g. fatty acid
 75 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
8	50.0	50.0	1.3461
29	50.2	50.0	1.3308
34	50.7	49.9	1.2718
39	50.8	49.8	1.2090
44	50.9	49.7	1.1301
49	51.0	49.5	1.0470
54	51.0	49.3	0.9610
59	51.0	49.2	0.8501
69	51.0	49.0	0.6560
79	50.7	49.2	0.4745
89	50.3	49.3	0.3552
99	50.2	49.9	0.2543

Rate: $k_0 = 0.0186$

MW(C_7H_8) = 332,000

rel. visc. = 1.592

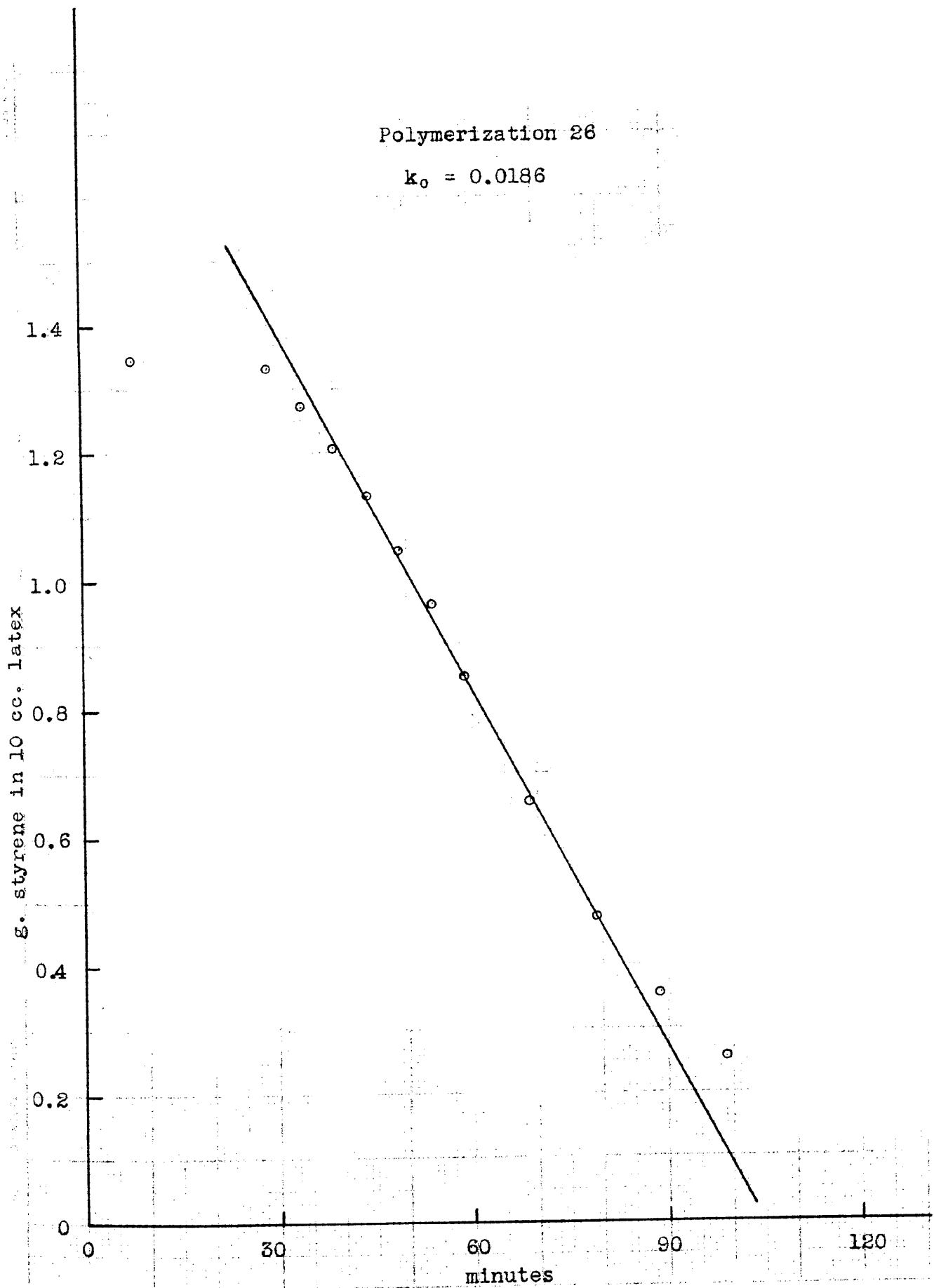
b. m. conc. = 0.00444

Anal. Calcd. for $(C_8H_8)_x$: C, 92.25; H, 7.75.

Found : C, 92.46; H, 7.78.

Polymerization 26

$$k_0 = 0.0186$$



Polymerization 27

400 cc. 0.0665 N KOH
 10 cc. $K_2S_2O_8$ solution = 0.1098 g.
 8.000 g. fatty acid
 100 cc. research styrene

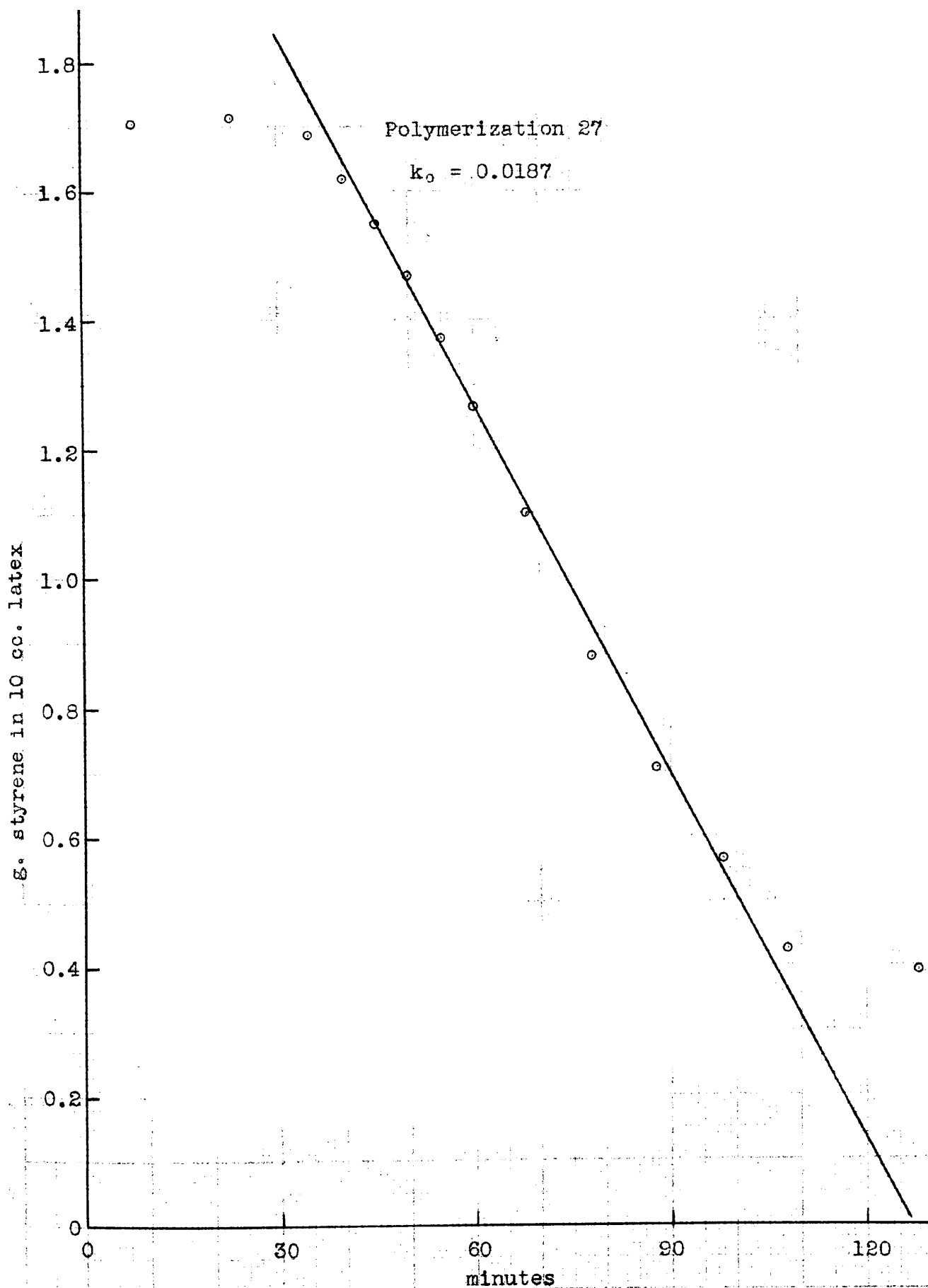
Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
8	50.0	50.0	1.7037
23	50.0	50.0	1.7123
35	50.3	50.0	1.6877
40	50.9	49.9	1.6186
45	51.0	49.7	1.5495
50	51.0	49.6	1.4686
55	51.1	49.5	1.3709
60	51.2	49.4	1.2637
68	51.2	49.1	1.0957
78	51.0	49.1	0.8790
88	50.7	49.2	0.7073
98	50.4	49.2	0.5660
108	50.3	49.7	0.4260
128	50.1	49.5	0.3930

Rate: $k_0 = 0.01875$

MW(C_7H_8) = 375,000

rel. visc. = 1.691

b. m. conc. = 0.00444



Polymerization 28

400 cc. 0.0667 $\underline{N}$ KOH
 10 cc. $K_2S_2O_8$ solution = 0.2197 g.
 8.000 g. fatty acid
 75 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex	log. styrene conc.
10	50.0	50.0	1.3551	0.13947
16	50.3	50.0	1.3261	0.12257
20	51.2	49.9	1.2441	0.09485
25	51.9	49.8	1.1012	0.04183
30	52.2	49.7	0.9435	-0.02526
35	52.5	49.6	0.7328	-0.13501
40	52.2	49.5	0.6302	-0.20052
45	51.8	49.4	0.5167	-0.28676
50	51.2	49.2	0.4133	-0.38373
55	50.7	49.1	0.3427	-0.46509
60	50.0	49.0	0.2880	-0.54061
70	50.0	50.0	0.2216	-0.65443

Rate: $k_0 = 0.0302$

$k_1 = 0.0161$

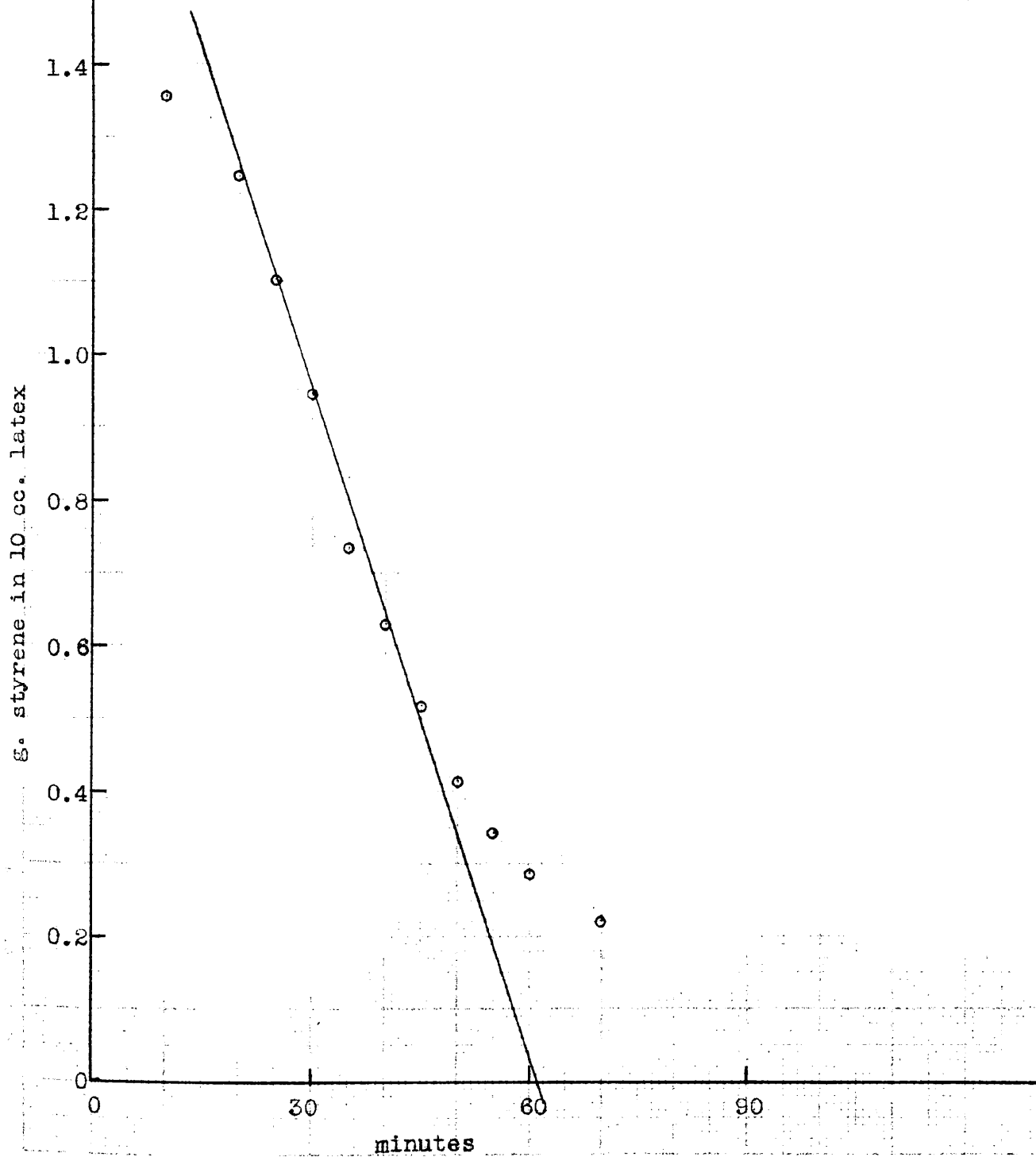
$MW(C_7H_8) = 321,000$

rel. visc. = 1.756

b. m. conc. = 0.00555

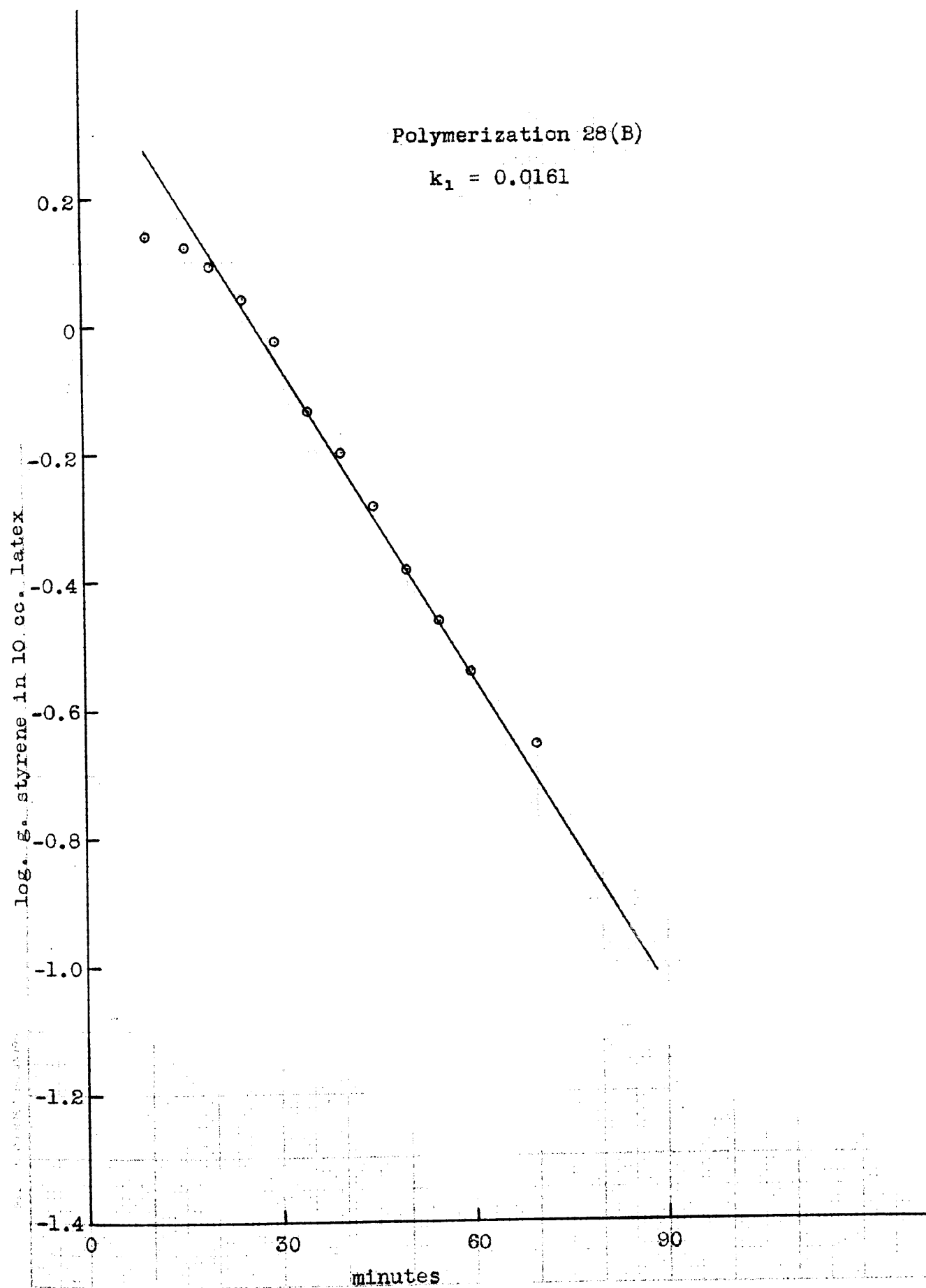
Polymerization 23

$$k_0 = 0.0302$$



Polymerization 28(B)

$$k_1 = 0.0161$$



Polymerization 29

400 cc. 0.0667 N KOH
 10 cc. $K_2S_2O_8$ solution = 0.2197 g.
 8.000 g. fatty acid
 75 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex	log. styrene conc.
5	50.0	50.0	1.3427	0.12808
20	50.0	50.0	1.3427	0.12808
25	50.9	50.0	1.2569	0.09934
30	51.3	49.8	1.1653	0.06633
35	51.8	49.7	1.0294	0.00817
40	52.1	49.7	0.8766	-0.05720
45	52.2	49.6	0.7346	-0.13395
50	52.0	49.5	0.5566	-0.25446
55	51.5	49.4	0.4636	-0.33386
60	50.9	49.3	0.3894	-0.40960
70	50.0	49.3	0.2724	-0.56479
80	50.0	50.0	0.2075	-0.68298
90	50.0	50.0	0.1749	-0.75721

Rate: $k_0 = 0.0298$

$k_1 = 0.0166$

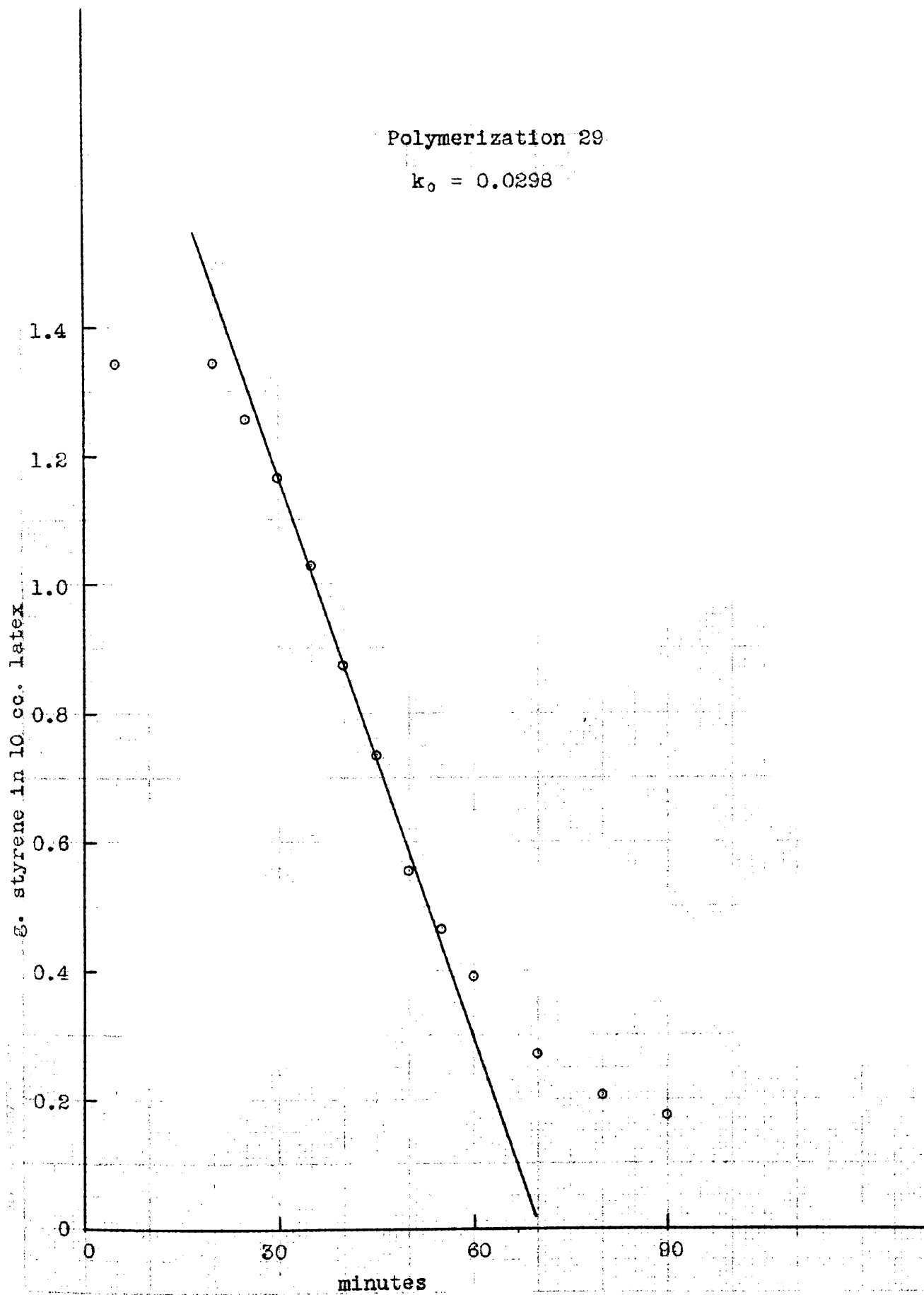
$MW(C_7H_8) = 299,300$

rel. visc. = 1.521

b. m. conc. = 0.00444

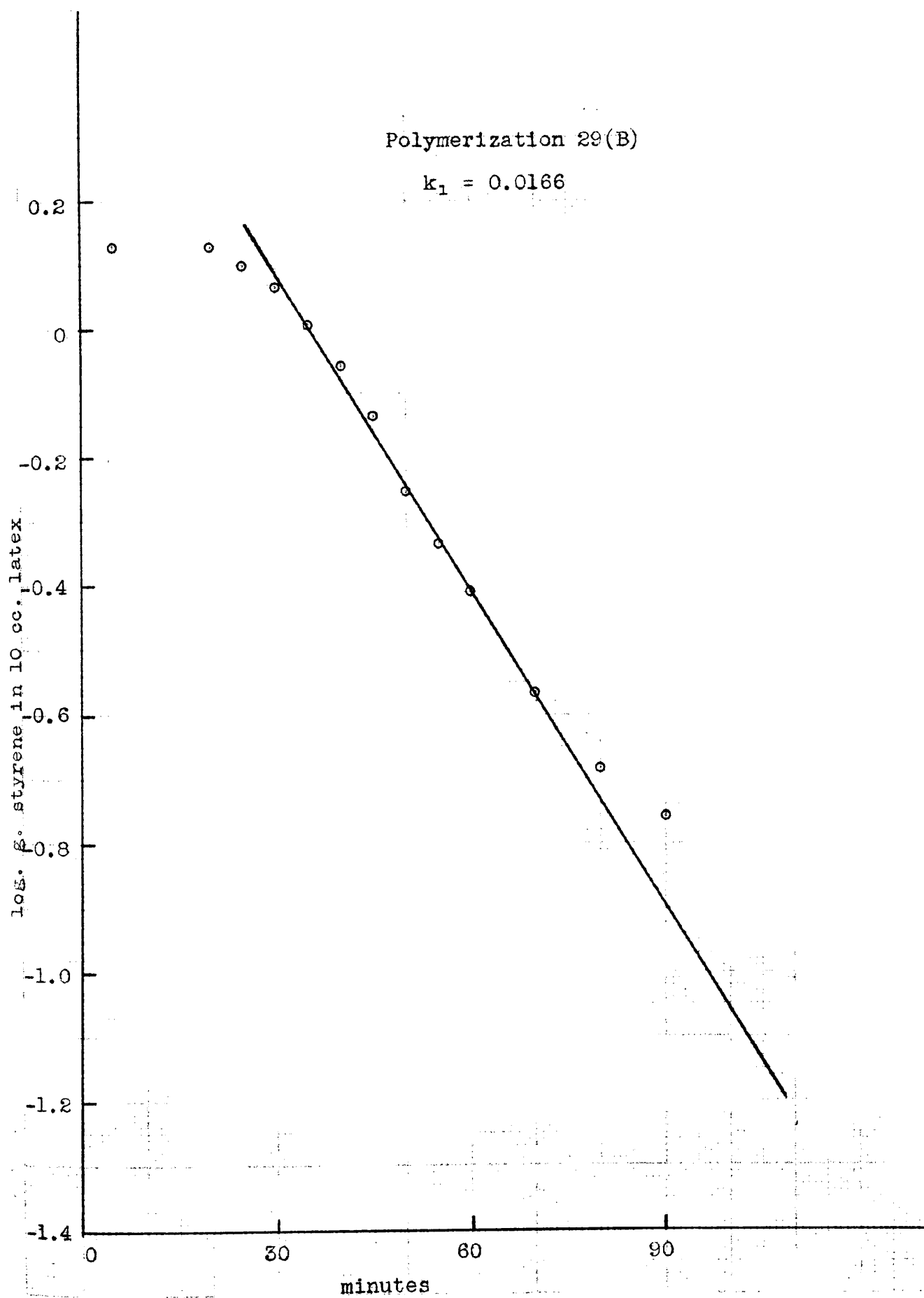
Polymerization 29

$$k_0 = 0.0298$$



Polymerization 29(B)

$$k_1 = 0.0166$$



Polymerization 30

400 cc. 0.0667 N KOH
 10 cc. $K_2S_2O_8$ solution = 0.2197 g.
 8.000 g. fatty acid
 100 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex	log. styrene conc.
5	50.0	50.0	1.7271	0.23731
20	50.0	50.0	1.7216	0.23593
25	50.5	50.0	1.6664	0.22178
30	51.0	49.8	1.5872	0.20063
35	51.4	49.8	1.4837	0.17134
40	51.8	49.7	1.3370	0.12613
45	52.1	49.6	1.1855	0.07390
50	52.3	49.6	1.0272	0.01165
55	52.1	49.5	0.8761	-0.05745
60	51.9	49.4	0.7482	-0.12598
65	51.5	49.3	0.6411	-0.19307
75	50.6	49.1	0.4867	-0.31274
85	50.0	49.6	0.3879	-0.41128

Rate: $k_0 = 0.0294$

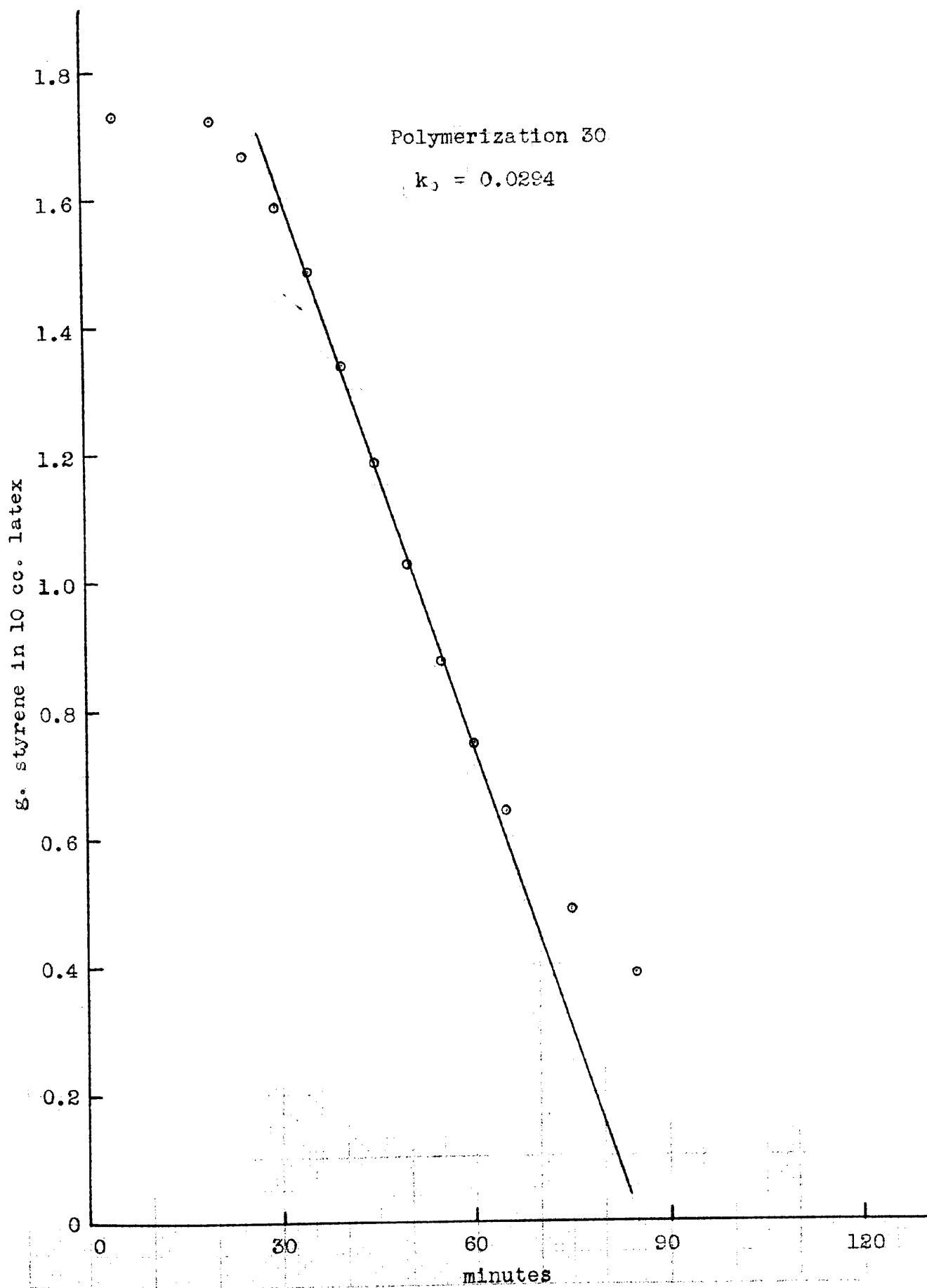
$k_1 = 0.0127$

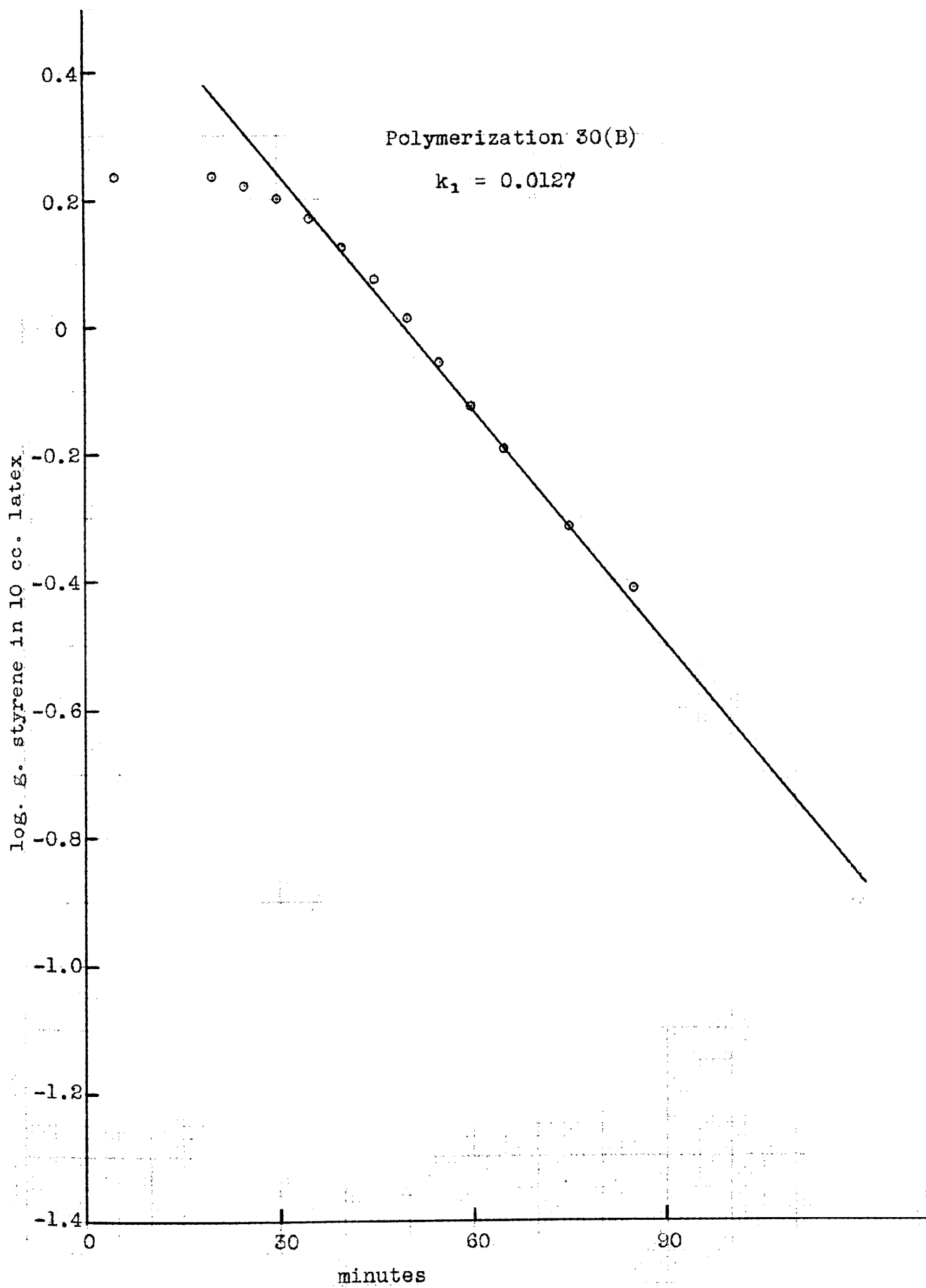
$MW(C_7H_8) = 299,300$

rel. visc. = 1.519

b. m. conc. = 0.00444

Anal. Calcd. for $(C_8H_8)_x$: C, 92.25; H, 7.75.
 Found : C, 91.74; H, 7.97.





Polymerization 31

400 cc. 0.0667 N KOH
 10 cc. $K_2S_2O_8$ solution = 0.2197 g.
 8.000 g. fatty acid
 100 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex	log. styrene conc.
9	50.0	50.0	1.7276	0.23744
18	50.2	50.0	1.6990	0.23019
24	51.5	49.9	1.5838	0.19970
29	52.0	49.9	1.4506	0.16153
34	52.3	49.8	1.2883	0.11002
39	52.6	49.8	1.1400	0.05690
44	52.7	49.8	0.9117	-0.04015
49	52.4	49.8	0.7936	-0.10040
54	52.0	49.7	0.6238	-0.20495
59	51.8	49.6	0.5656	-0.24749
64	51.4	49.6	0.4716	-0.32643
69	51.0	49.5	0.4527	-0.34419
79	50.1	49.2	0.3476	-0.45892
89	50.0	49.9	0.2660	-0.57512

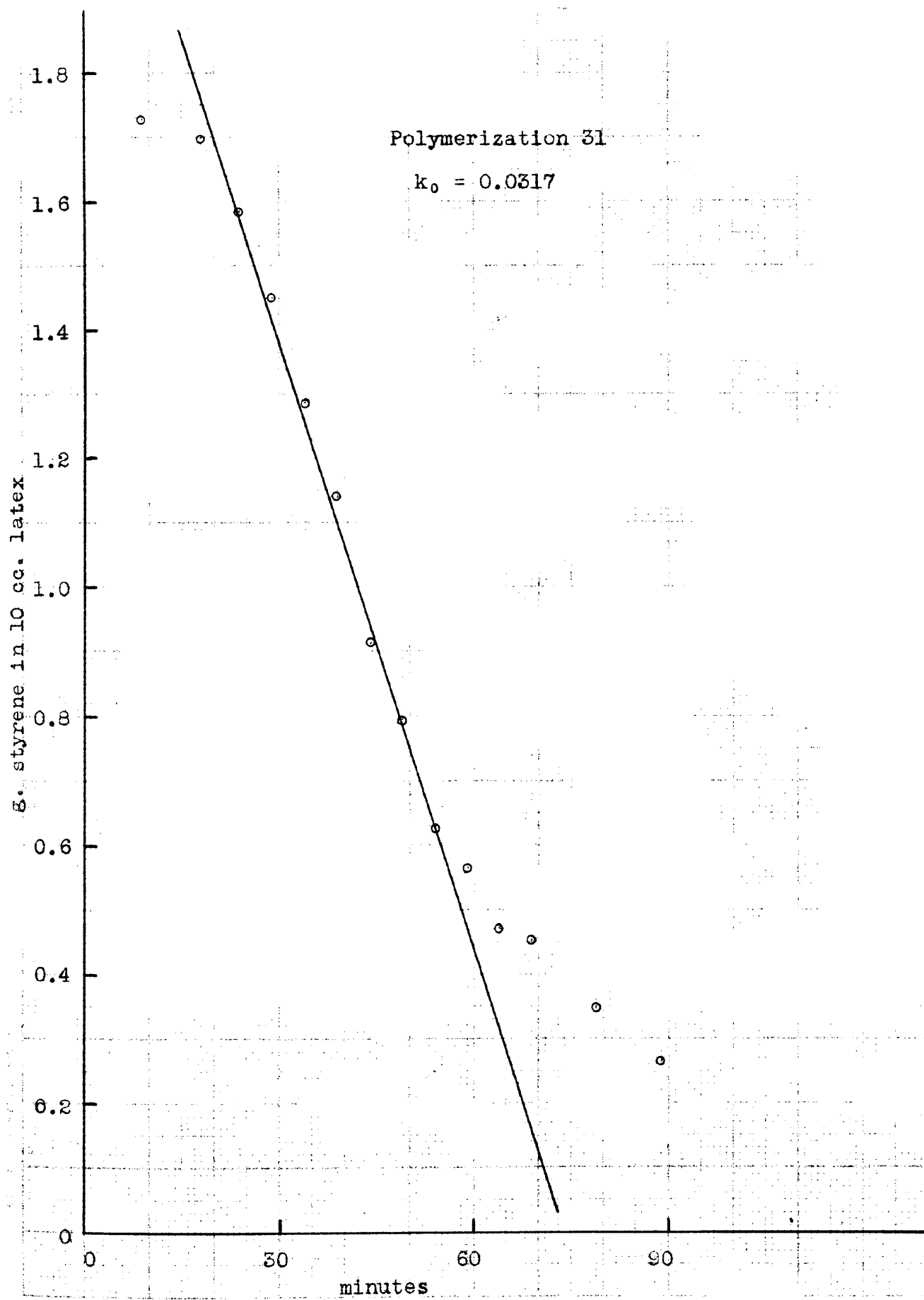
Rate: $k_0 = 0.0317$

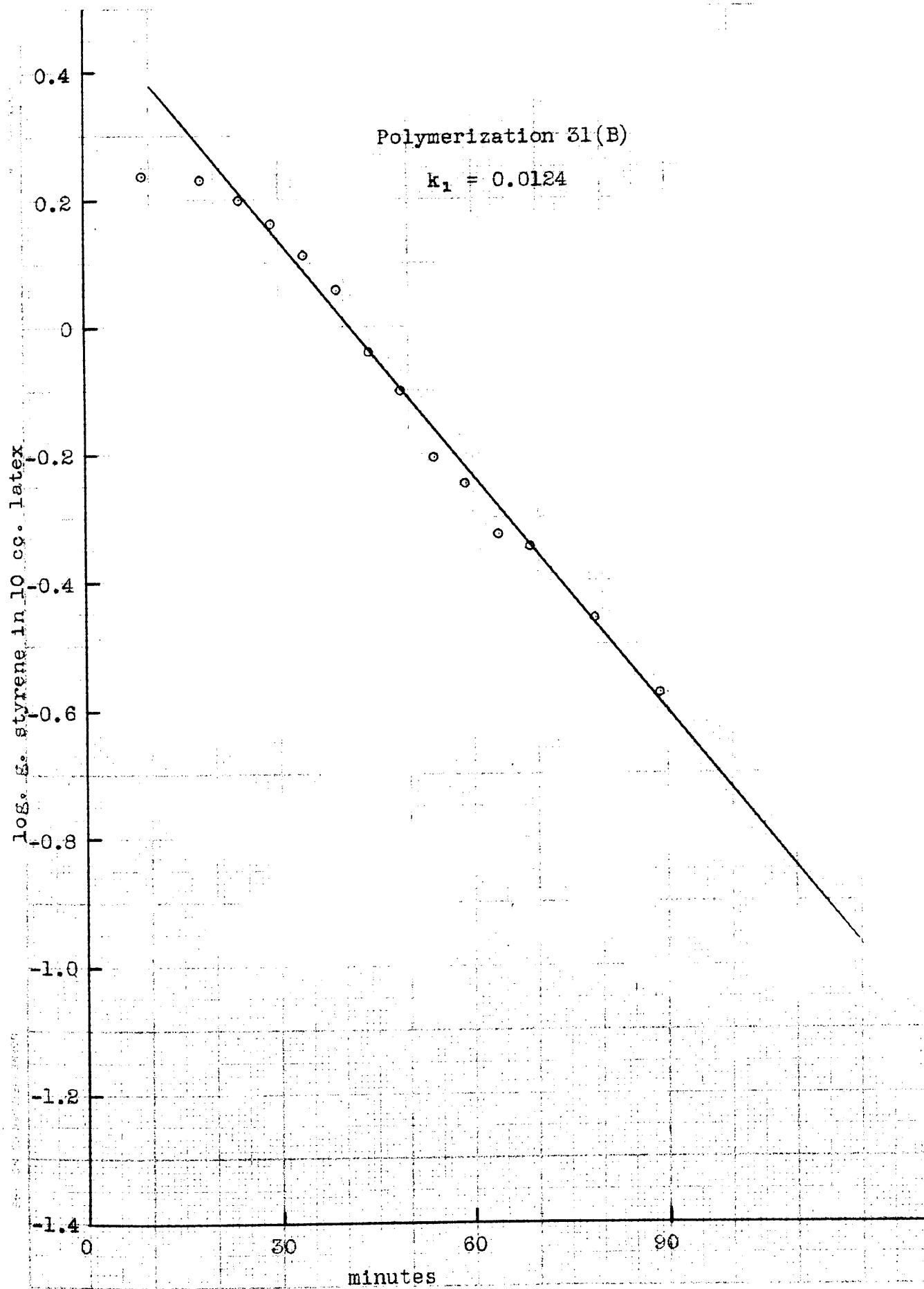
$k_1 = 0.0124$

$MW(C_7H_8) = 305,200$

rel. visc. = 1.707

b. m. conc. = 0.00555





Polymerization 32

400 cc. 0.0665 N KOH
 10 cc. $K_2S_2O_8$ solution = 0.3295 g.
 8.000 g. fatty acid
 50 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
5	50.0	50.0	0.9398
10	51.1	49.9	0.8596
15	52.2	49.8	0.6778
20	52.9	49.8	0.4810
25	52.8	49.7	0.3086
30	52.0	49.5	0.1927
40	50.3	49.8	0.1114
47	50.0	50.0	0.0911

Rate: $k_o = 0.0366$

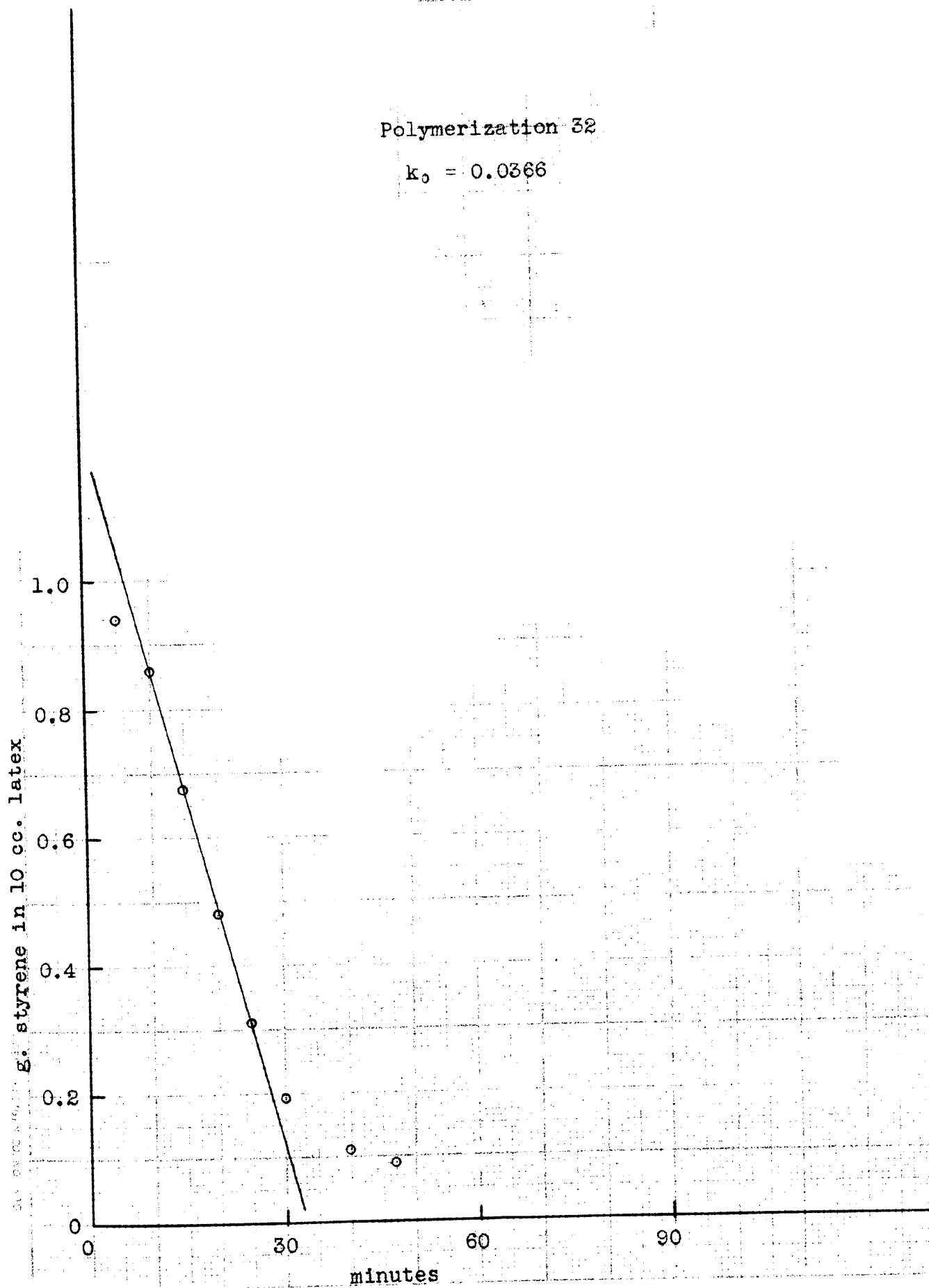
MW(C_7H_8) = 279,500

rel. visc. = 1.479

b. m. conc. = 0.00444

Polymerization 32

$$k_0 = 0.0366$$



Polymerization 33

400 cc. 0.0665 N KOH
 10 cc. $K_2S_2O_8$ solution = 0.3295 g.
 8.000 g. fatty acid
 50 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
5	50.0	50.0	0.9394
10	50.9	49.9	0.8754
15	52.0	49.8	0.7038
20	52.7	49.7	0.5109
25	52.7	49.6	0.3439
30	51.9	49.5	0.2169
35	51.0	49.3	0.1551
45	50.0	50.0	0.1086

Rate: $k_0 = 0.0357$

$MW(C_7H_8) = 250,500$

rel. viso. = 1.420

b. m. conc. = 0.00444

Anal. polymer. Calcd. for $(C_8H_8)_x$: C, 92.25; H, 7.75.

Found : C, 92.03; H, 7.85

Polymerization 33

$$k_0 = 0.0357$$

g. styrene in 10 cc. latex

1.0

0.8

0.6

0.4

0.2

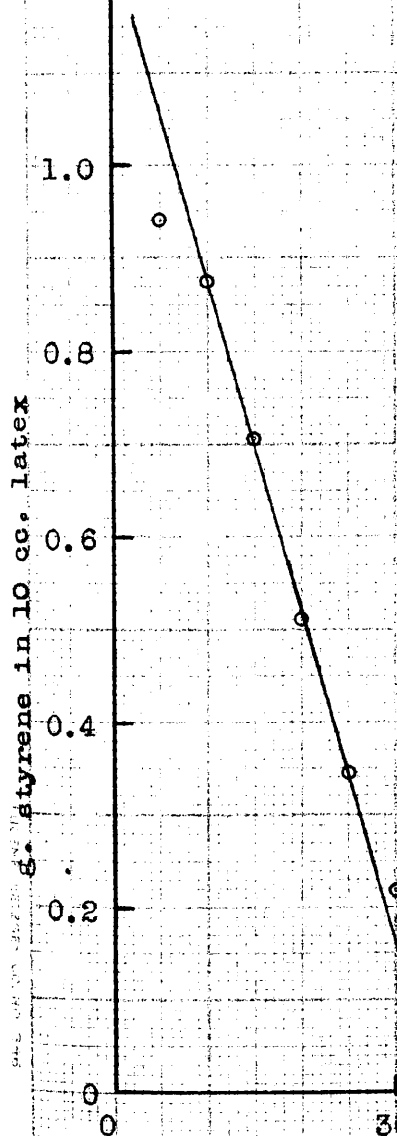
0

minutes

30

60

90



Polymerization 34

400 cc. 0.0665 $\underline{N}$ KOH
 10 cc. $K_2S_2O_8$ solution = 0.4394 g.
 8.000 g. fatty acid
 50 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
6	50.2	50.0	0.9055
11	52.0	49.8	0.7150
16	53.0	49.7	0.4938
21	53.0	49.5	0.2929
26	51.9	49.3	0.1829
37	49.9	49.3	0.1075
46	50.0	50.0	0.0883

Rate: $k_0 = 0.0410$

$MW(C_7H_8) = 269,900$

rel. visc. = 1.458

b. m. conc. = 0.00444

Polymerization 34

$$k_0 = 0.0410$$

g. styrene in 10 cc. latex

1.0

0.8

0.6

0.4

0.2

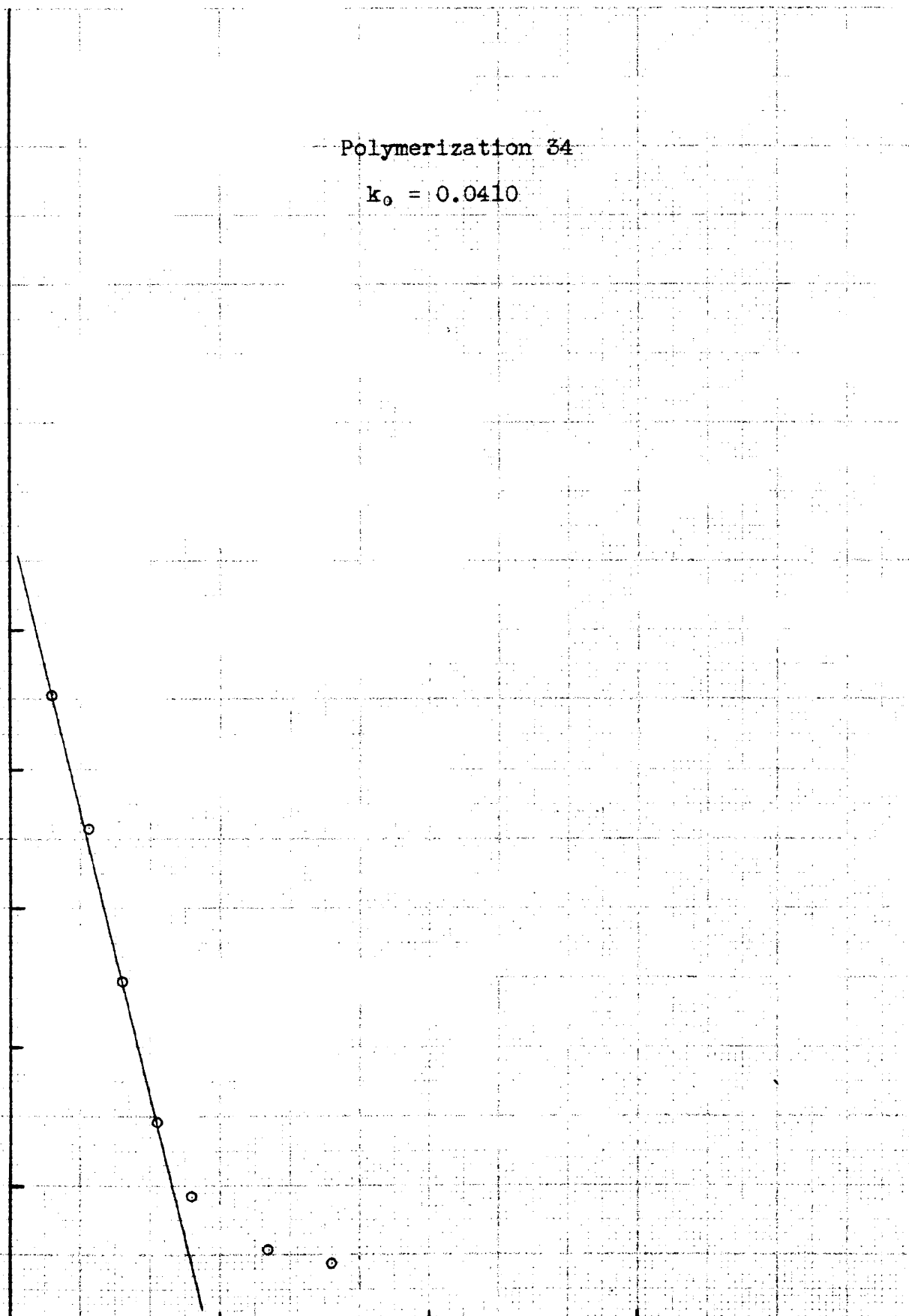
0

30

60

90

minutes



Polymerization 35

400 cc. 0.0665 N KOH
 10 cc. $K_2S_2O_8$ solution = 0.4394 g.
 8.000 g. fatty acid
 50 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
3	50.0	50.0	0.9418
8	51.0	49.9	0.8556
13	52.7	49.8	0.6254
18	53.2	49.7	0.4075
23	52.8	49.7	0.2435
28	51.6	49.4	0.1607
38	50.0	50.0	0.1122

Rate: $k_0 = 0.0403$

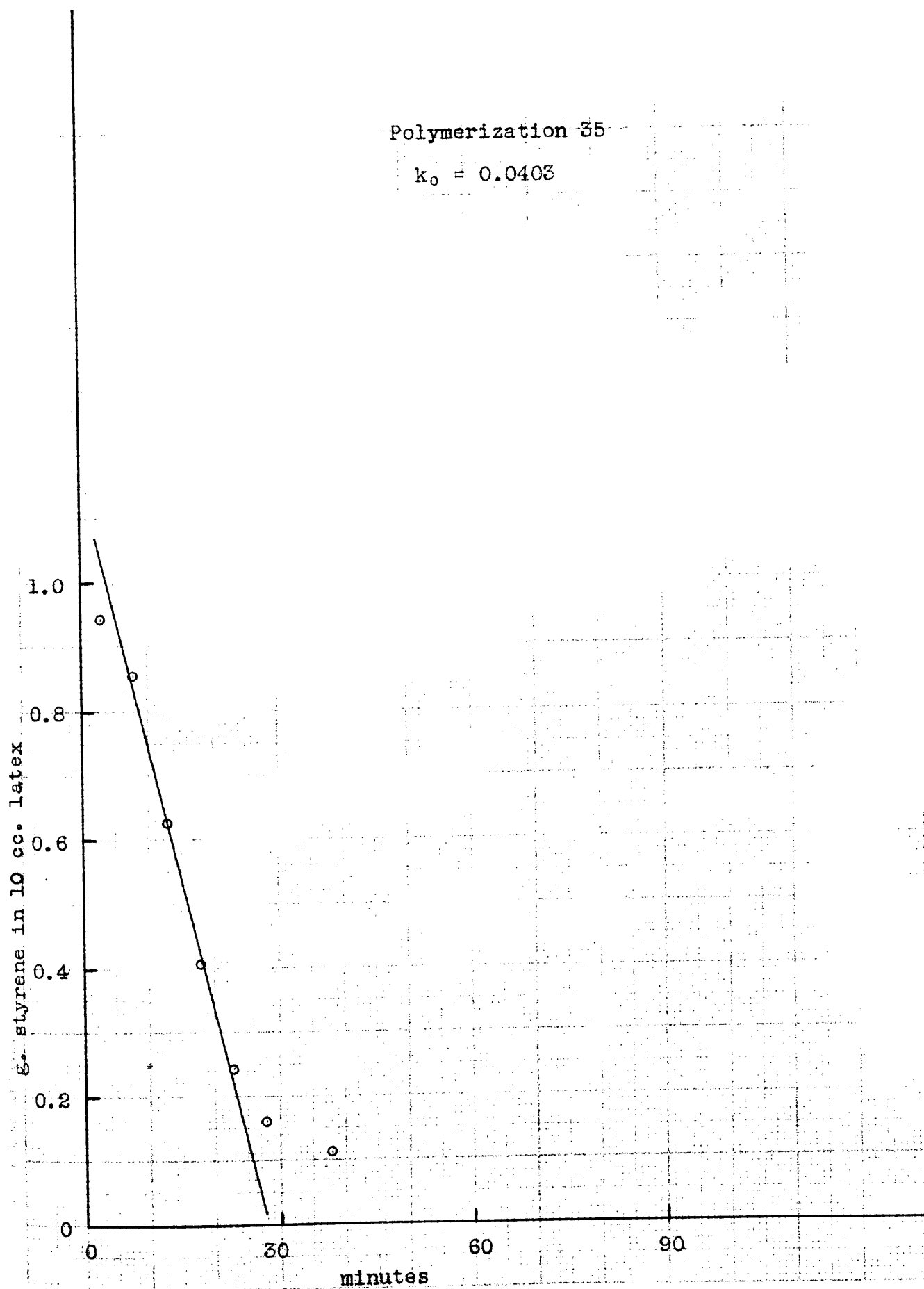
MW(C_7H_8) = 238,400

rel. visc. = 1.394

b. m. conc. = 0.00444

Polymerization 35

$$k_0 = 0.0403$$



Polymerization 36

400 cc. 0.0665 N KOH
 10 cc. $K_2S_2O_8$ solution = 0.4394 g.
 8.000 g. fatty acid
 75 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
3	50.0	50.0	1.3453
23	50.7	50.0	1.2985
28	51.9	49.9	1.1388
33	52.9	49.8	0.9354
38	53.1	49.8	0.7209
43	53.0	49.8	0.5514
48	52.3	49.8	0.4012
58	51.2	49.4	0.1833
68	50.0	50.0	0.1361

Rate: $k_0 = 0.0397$

$MW(C_7H_8) = 226,800$

rel. visc. = 1.377

b. m. conc. 0.00444

Polymerization 36

$$k_0 = 0.0397$$

g. styrene in 10 cc. latex

1.4

1.2

1.0

0.8

0.6

0.4

0.2

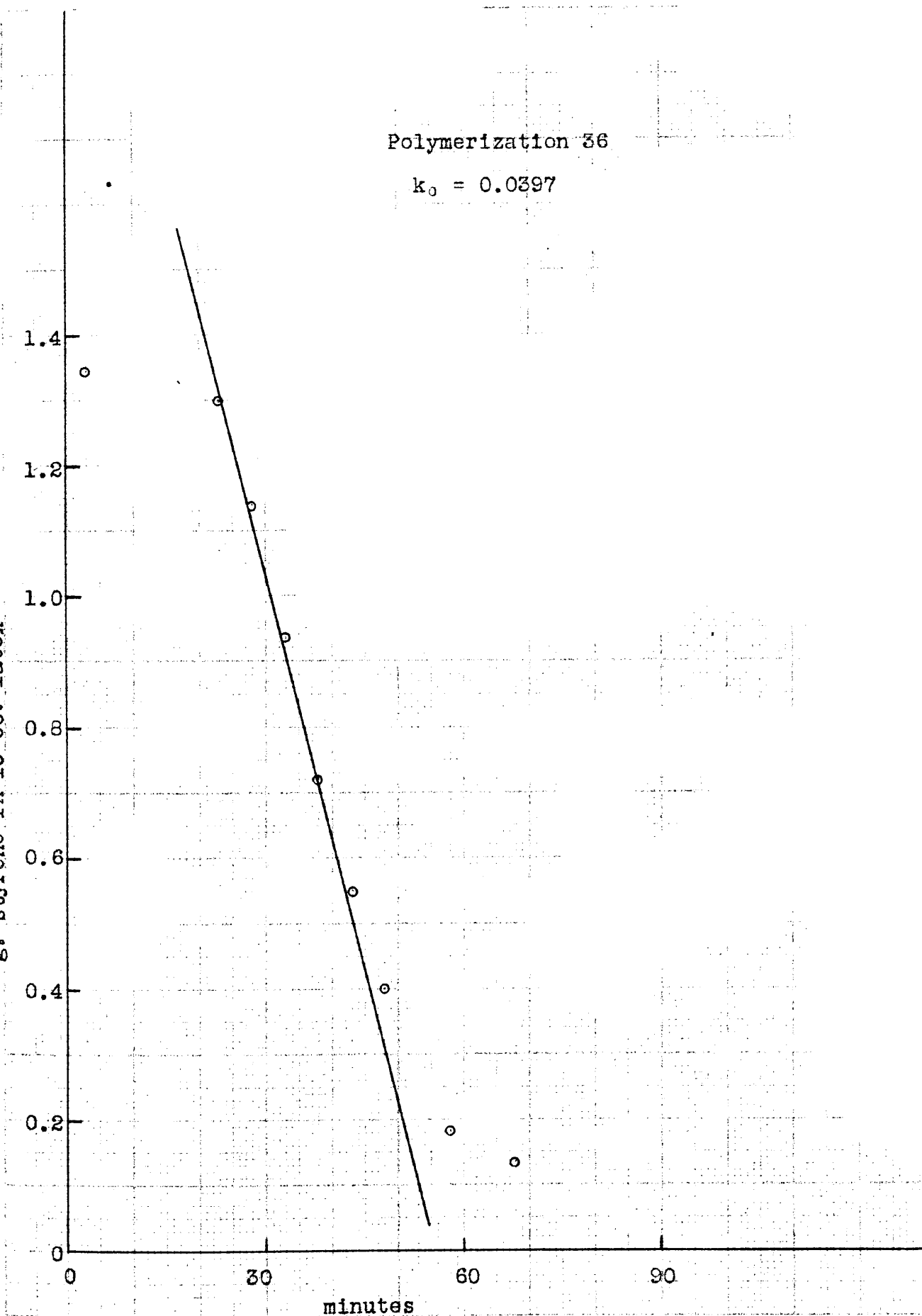
0

30

60

90

minutes



Polymerization 37

400 cc. 0.0665 N KOH
 10 cc. $K_2S_2O_8$ solution = 0.4394 g.
 8.000 g. fatty acid
 100 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
2	50.0	50.0	1.7019
11	50.3	50.0	1.6785
15	51.6	49.9	1.5740
20	52.6	49.8	1.3774
25	53.1	49.8	1.1660
30	53.4	49.7	0.9577
35	53.2	49.7	0.7517
40	52.9	49.6	0.5883
48	52.0	49.5	0.3838
60	50.2	50.0	0.1977

Rate: $k_0 = 0.0404$

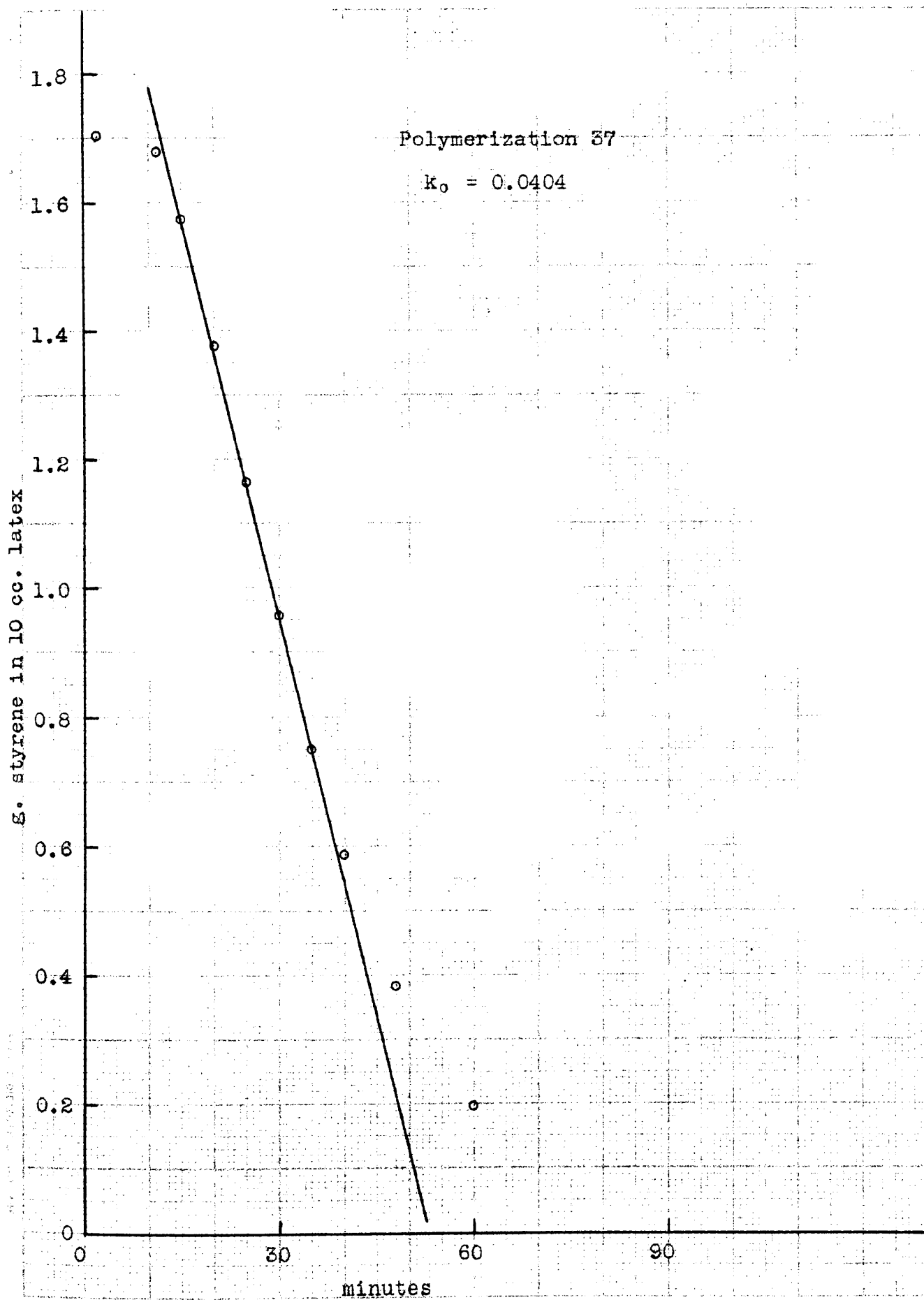
MW(C_7H_8) = 258,100

rel. visc. = 1.435

b. m. conc. = 0.00444

Anal. Calcd. for $(C_8H_8)_x$: C, 92.25; H, 7.75.

Found : C, 92.38; H, 7.93.



Polymerization 38*

400 cc. 0.0665 N KOH
 4.3940 g. $K_2S_2O_8$
 8.000 g. fatty acid
 50 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
0	51.5	50.0	--
1	52.5	50.0	0.5945
2	53.5	50.0	0.5168
3	54.5	50.0	0.3110
4	55.1	50.1	0.2725
5	55.8	50.1	0.2315
7	55.8	50.2	0.1356

* latex samples taken in 10-cc. volumetric flasks. These were made to volume and transferred after the polymerization was finished.

Rate: $k_0 = 0.365$

MW(C_7H_8) = 196,200

rel. visc. = 1.510

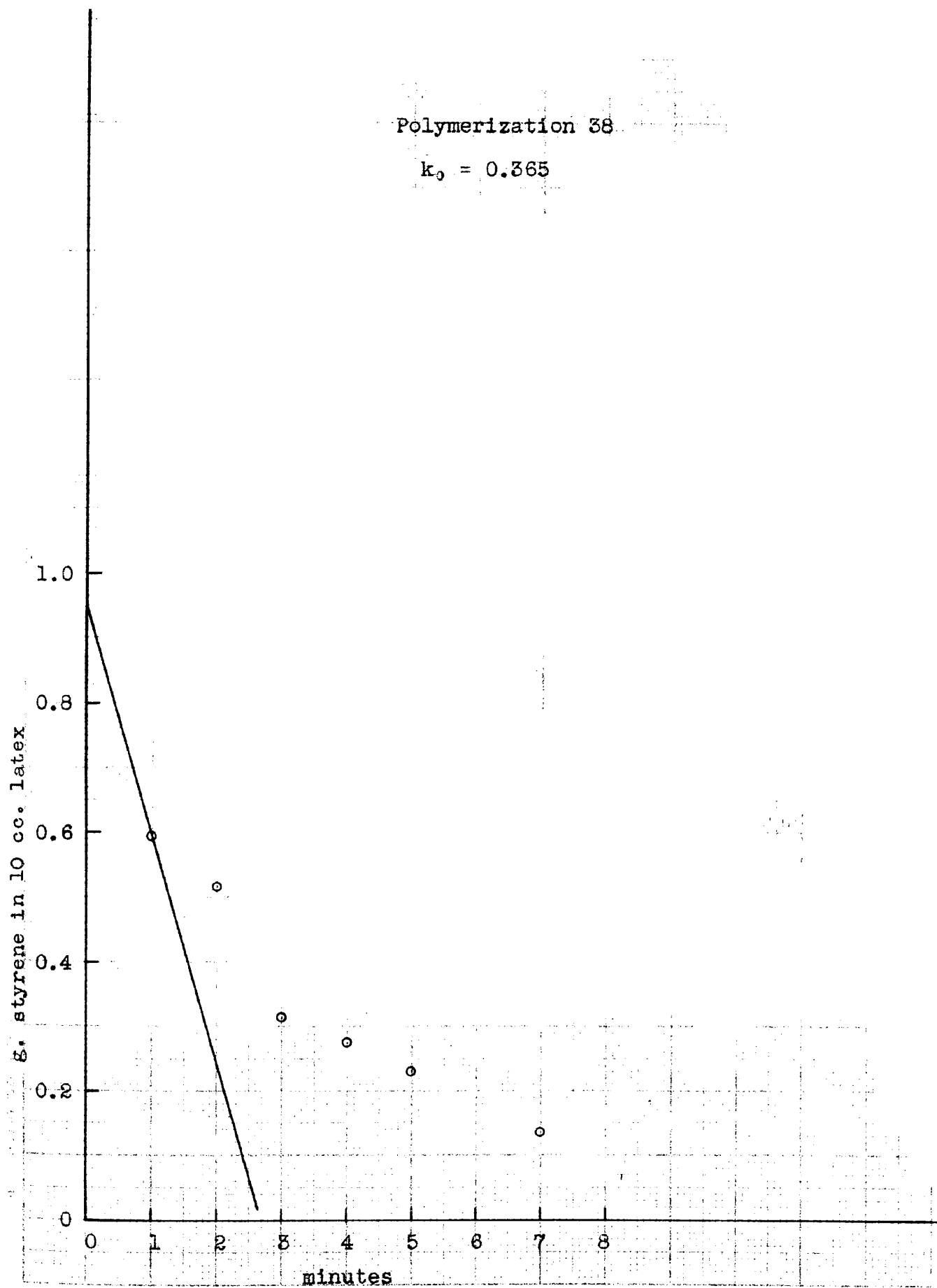
b. m. conc. = 0.00666

Anal. polymer. Calcd. for $(C_8H_8)_x$: C, 92.25; H, 7.75.

Found : C, 92.16; H, 8.08.

Polymerization 38

$$k_p = 0.365$$



Polymerizations 39-41 were run at 60° C under the same conditions as polymerizations 22-38. The effect of the increase in temperature and the effect of variation of catalyst concentration at this temperature on the rate of polymerization and the molecular weight of the polymer formed were studied. The results of these runs are summarized in Table III.

Polymerization 39

400 cc. 0.0665 N KOH
 10 cc. $K_2S_2O_8$ solution = 0.2197 g.
 8.000 g. fatty acid
 50 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
6	60.7	60.0	0.8689
10	63.2	59.8	0.6055
14	64.3	59.8	0.3420
18	63.3	59.7	0.1879
22	62.0	59.4	0.1270
26	60.7	59.1	0.1010
32	60.0	60.0	0.0794

Rate: $k_0 = 0.0667$

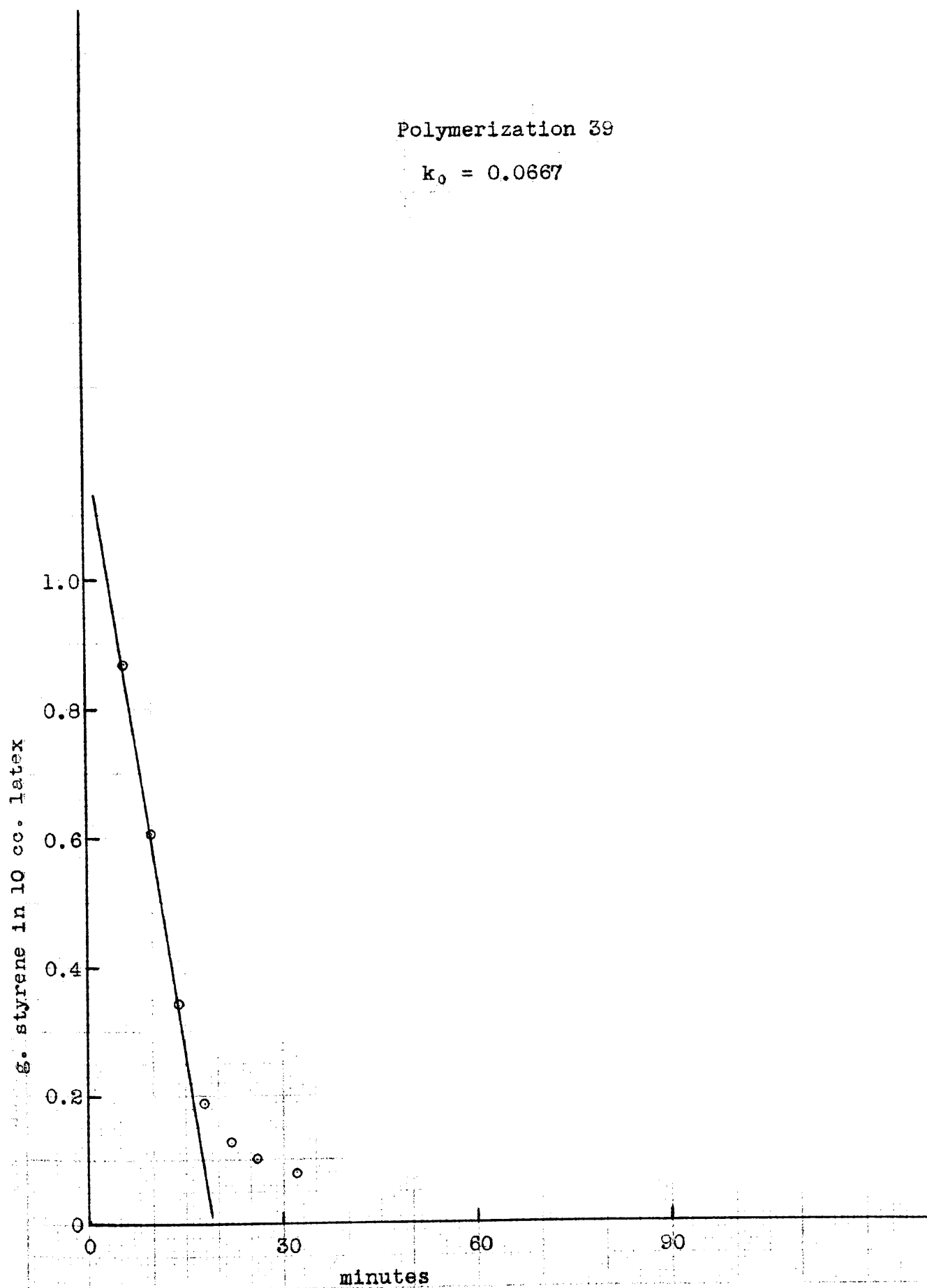
$MW(C_7H_8) = 219,300$

rel. visc. = 1.362

b. m. conc. = 0.00446

Polymerization 39

$$k_0 = 0.0667$$



Polymerization 40

400 cc. 0.0665 N KOH
 10 cc. $K_2S_2O_8$ solution = 0.1098 g.
 8.000 g. fatty acid
 50 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
2	59.9	60.0	0.9366
8	60.8	60.0	0.8730
12	62.8	59.9	0.6637
17	63.7	59.8	0.3888
22	62.8	59.5	0.2058
27	61.2	59.3	0.1292
32	60.2	60.0	0.0974
37	60.0	60.0	0.0899

Rate: $k_0 = 0.0547$

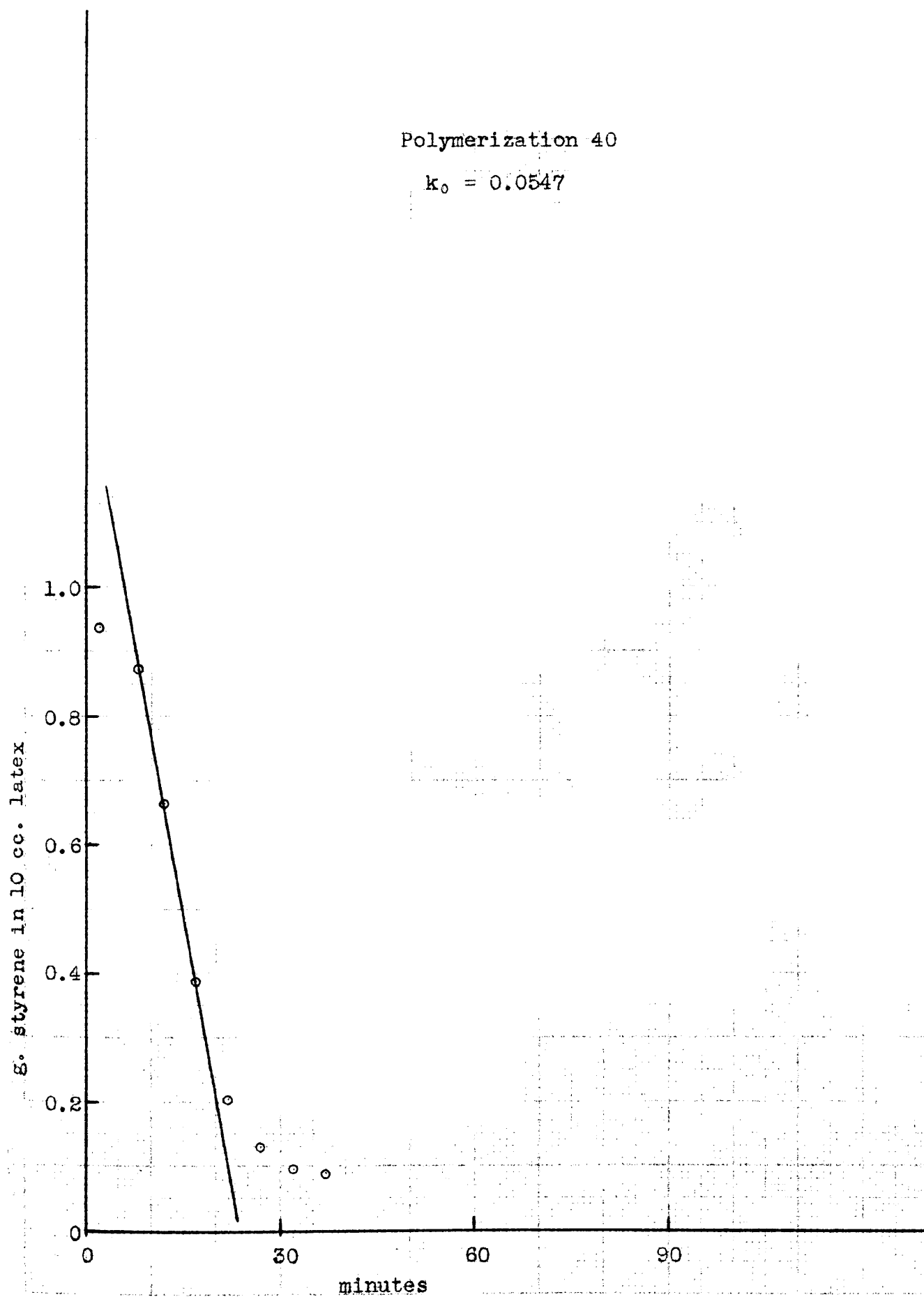
MW(C_7H_8) = 256,700

rel. visc. = 1.433

b. m. conc. = 0.00444

Polymerization 40

$$k_0 = 0.0547$$



Polymerization 41

400 cc. 0.0665 N KOH
 10 cc. $K_2S_2O_8$ solution = 0.0549 g.
 8.000 g. fatty acid
 50 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
3	60.0	60.0	0.9386
10	60.2	60.0	0.9048
14	61.7	59.7	0.7642
18	62.3	59.4	0.6012
23	62.6	59.2	0.3994
28	61.7	59.0	0.2549
33	60.8	59.0	0.1681
45	60.0	60.0	0.0927

Rate: $k_0 = 0.0357$

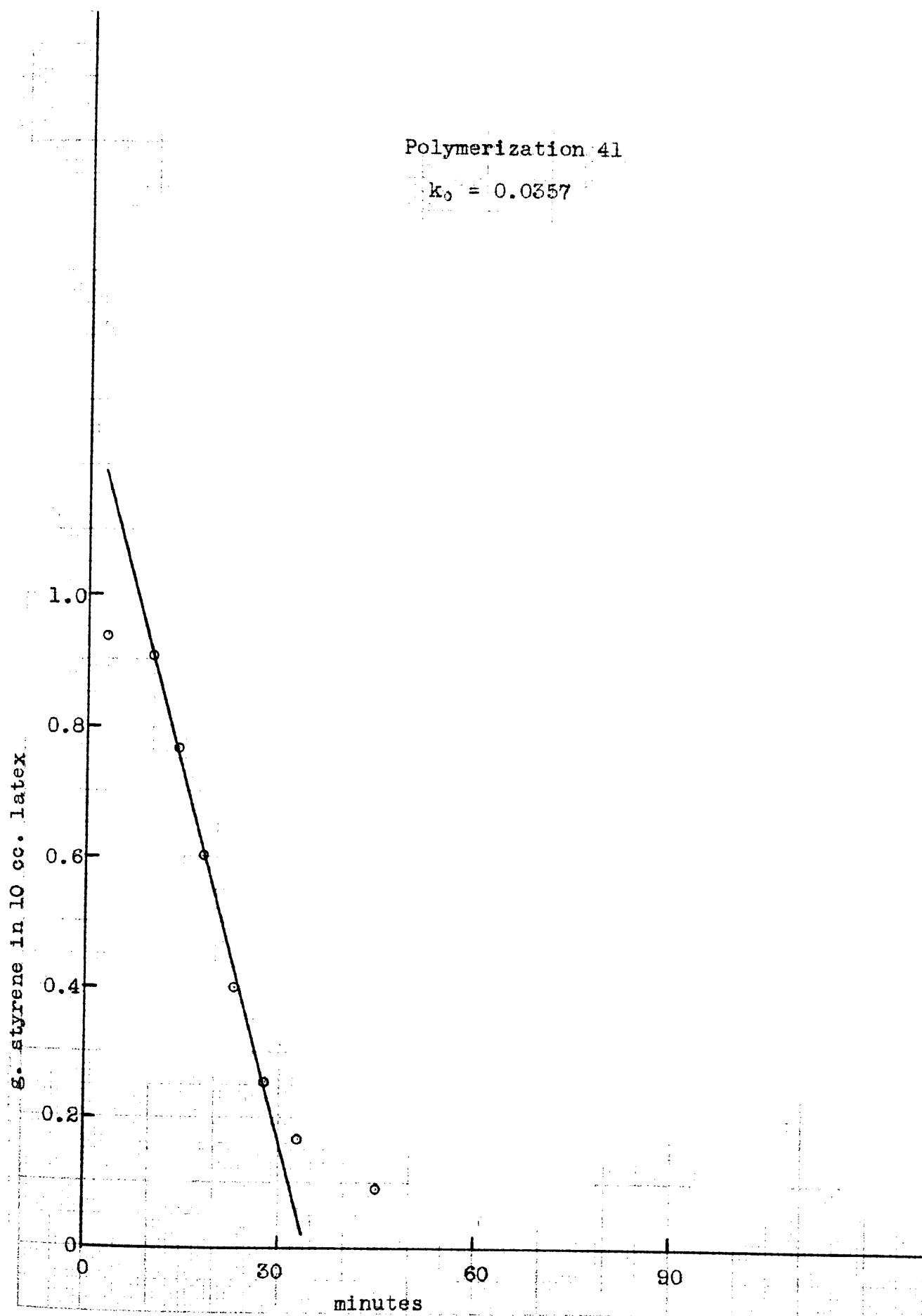
MW(C_7H_8) = 271,300

rel. visc. = 1.462

b. m. conc. = 0.00444

Polymerization 41

$$k_0 = 0.0357$$



Polymerizations 42-46 were carried out at 40° under conditions comparable to polymerizations 22-41. The results of these runs at various catalyst concentrations are summarized in Table IV.

Polymerization 42

400 cc. 0.0665 N KOH
 10 cc. $K_2S_2O_8$ solution = 0.2197 g.
 8.000 g. fatty acid
 50 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
3	40.0	40.0	0.9443
48	40.0	40.0	0.9546
58	40.2	40.0	0.9188
65	40.5	40.0	0.8705
73	40.7	39.9	0.7980
80	40.7	39.9	0.7394
88	40.8	39.8	0.6530
95	40.8	39.7	0.5640
103	40.7	39.7	0.4713
113	40.5	39.7	0.3612
130	40.1	40.0	0.2238

Rate: $k_0 = 0.0115$

MW(C_7H_8) = 325,300

rel. viso. = 1.577

b. m. conc. = 0.00444

Polymerization 42

$$k_0 = 0.0115$$

g. styrene in 10 cc. latex

1.0
0.8
0.6
0.4
0.2
0

minutes

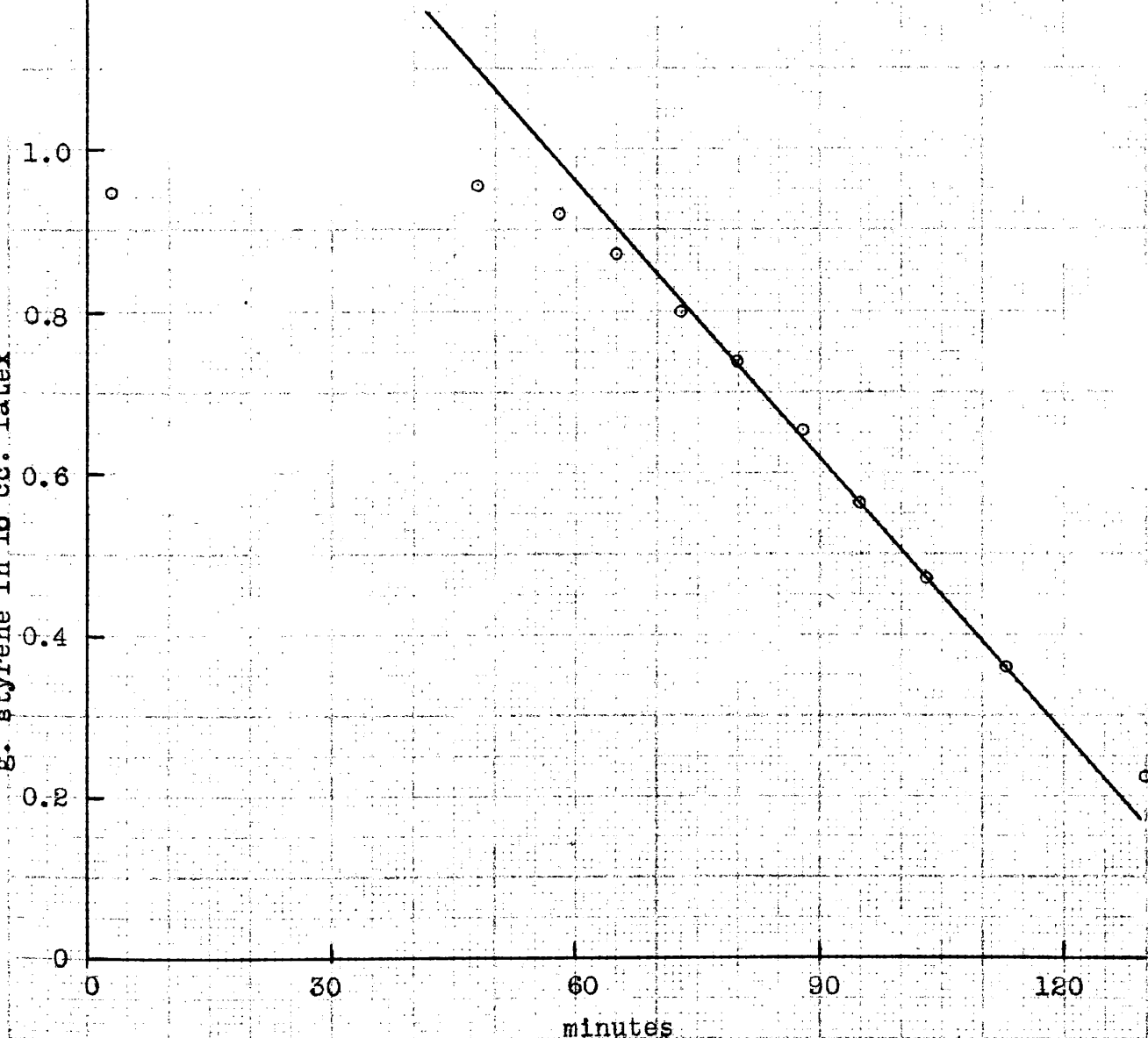
0

30

60

90

120



Polymerization 43

400 cc. 0.0665 N KOH
 10 cc. $K_2S_2O_8$ solution = 0.4394 g.
 8.000 g. fatty acid
 50 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
5	40.0	40.0	0.9444
35	40.2	40.0	0.9300
42	40.7	40.0	0.8562
57	40.9	39.9	0.6935
65	41.0	39.8	0.5888
72	41.0	39.8	0.4882
80	40.9	39.8	0.3845
90	40.6	39.7	0.2750
100	40.1	39.5	0.1990
110	40.0	40.0	0.1574

Rate: $k_0 = 0.0135$

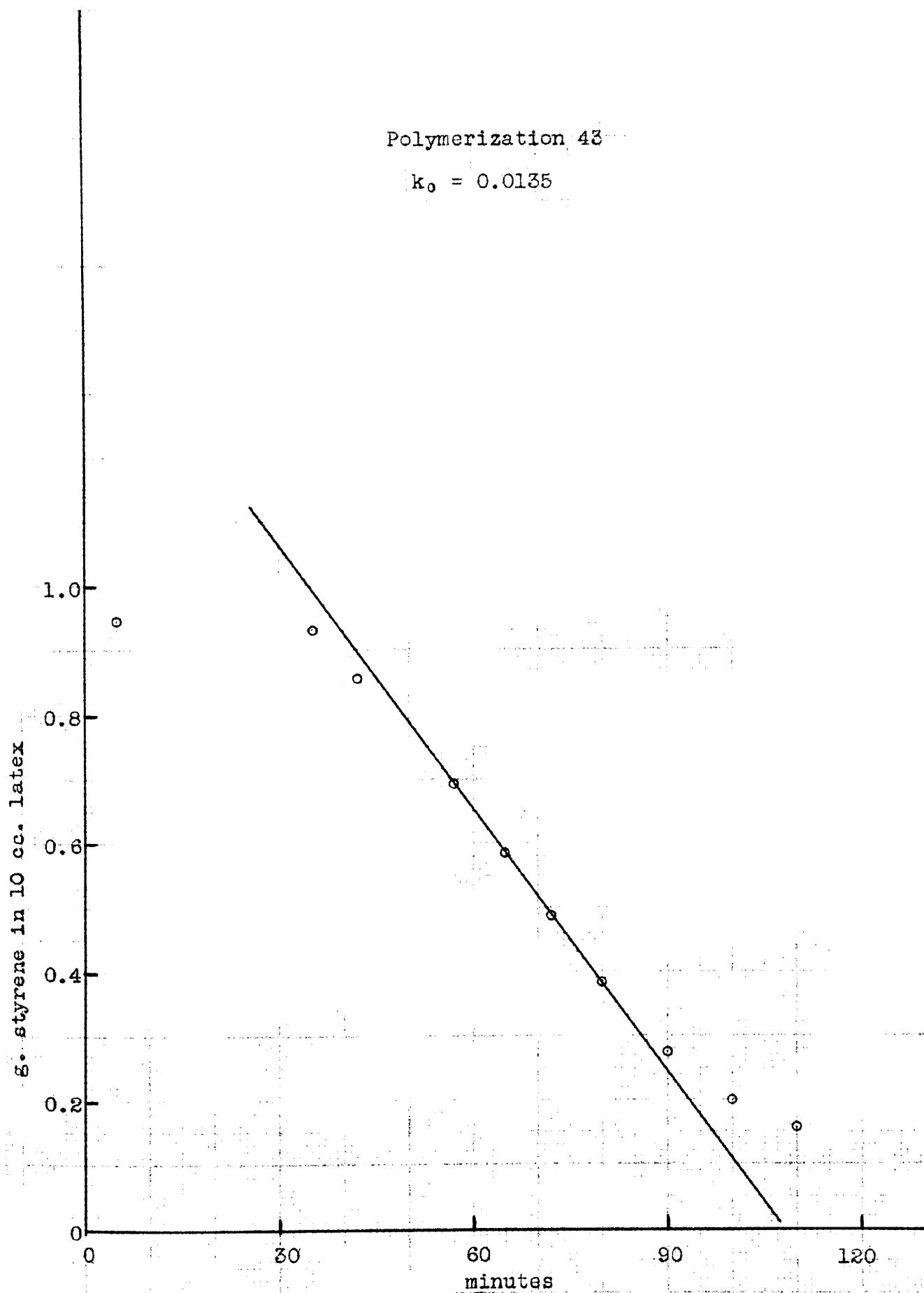
MW(C_7H_8) = 292,700

rel. visc. = 1.507

b. m. conc. = 0.00444

Polymerization 43

$$k_0 = 0.0135$$



Polymerization 44

400 cc. 0.0665 N KOH
 10 cc. $K_2S_2O_8$ solution = 0.4394 g.
 8.000 g. fatty acid
 50 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
8	40.0	40.0	0.9472
26	40.1	40.0	0.9290
33	40.8	40.0	0.8546
41	41.0	39.9	0.7609
48	41.0	39.8	0.6609
56	40.9	39.8	0.5564
63	40.8	39.7	0.4734
73	40.4	39.5	0.3656
88	40.2	40.0	0.2346

Rate: $k_0 = 0.0127$

MW(C_7H_8) = 279,400

rel. visc. = 1.479

b. m. conc. = 0.00444

Polymerization 44

$$k_0 = 0.0127$$

g. styrene in 10 cc. latex

1.0

0.8

0.6

0.4

0.2

0

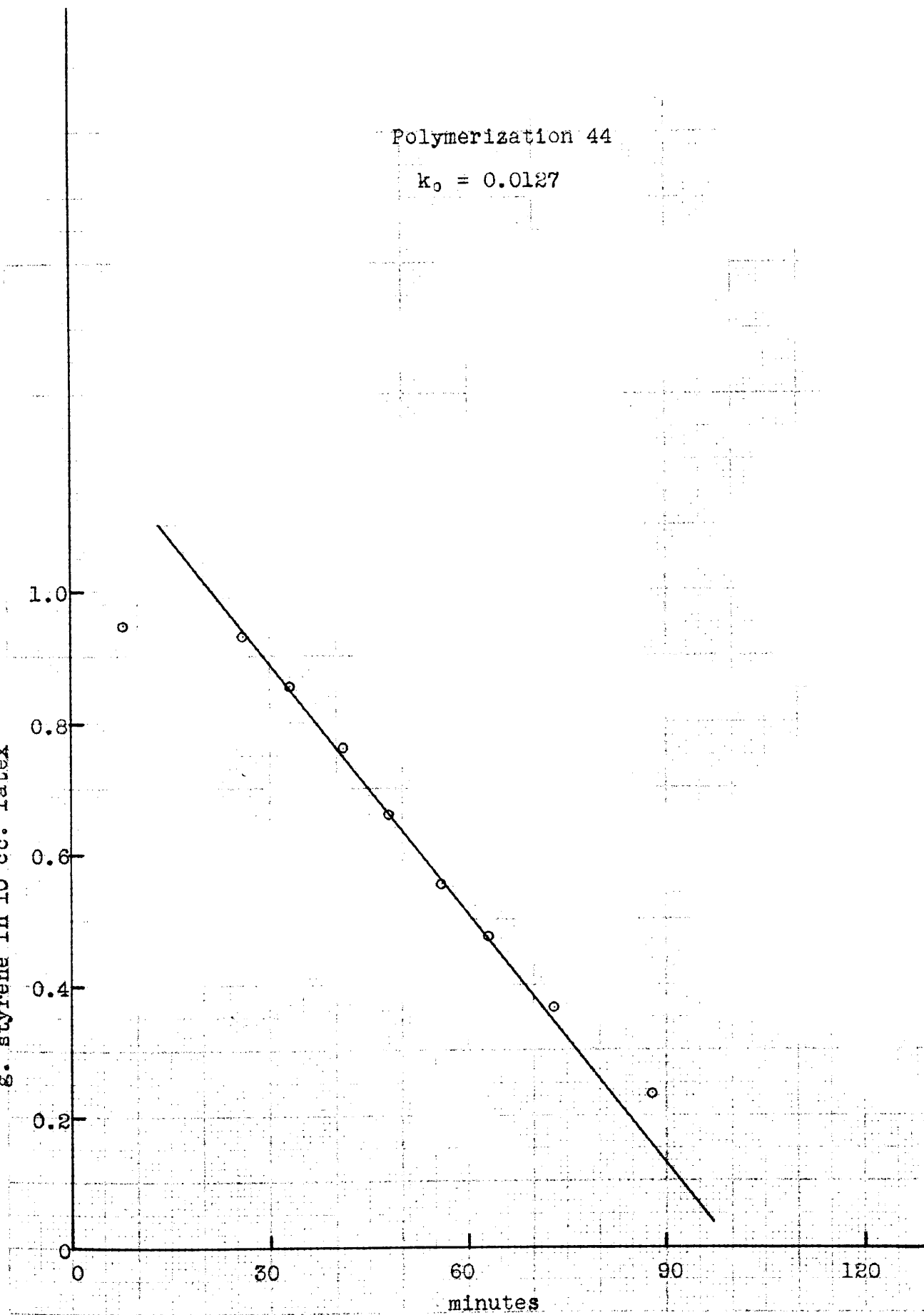
30

60

90

120

minutes



Polymerization 45

400 cc. 0.0665 N KOH
 15 cc. $K_2S_2O_8$ solution = 0.6591 g.
 8.000 g. fatty acid
 50 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
11	40.0	40.0	0.9256
16	40.5	39.9	0.8740
23	41.0	39.8	0.7538
28	41.3	39.7	0.6622
33	41.5	39.7	0.5607
38	41.5	39.6	0.4463
43	41.3	39.6	0.3484
51	40.9	39.4	0.2301
59	40.0	39.3	0.1678
66	40.0	40.0	0.1437

Rate: $k_0 = 0.0207$

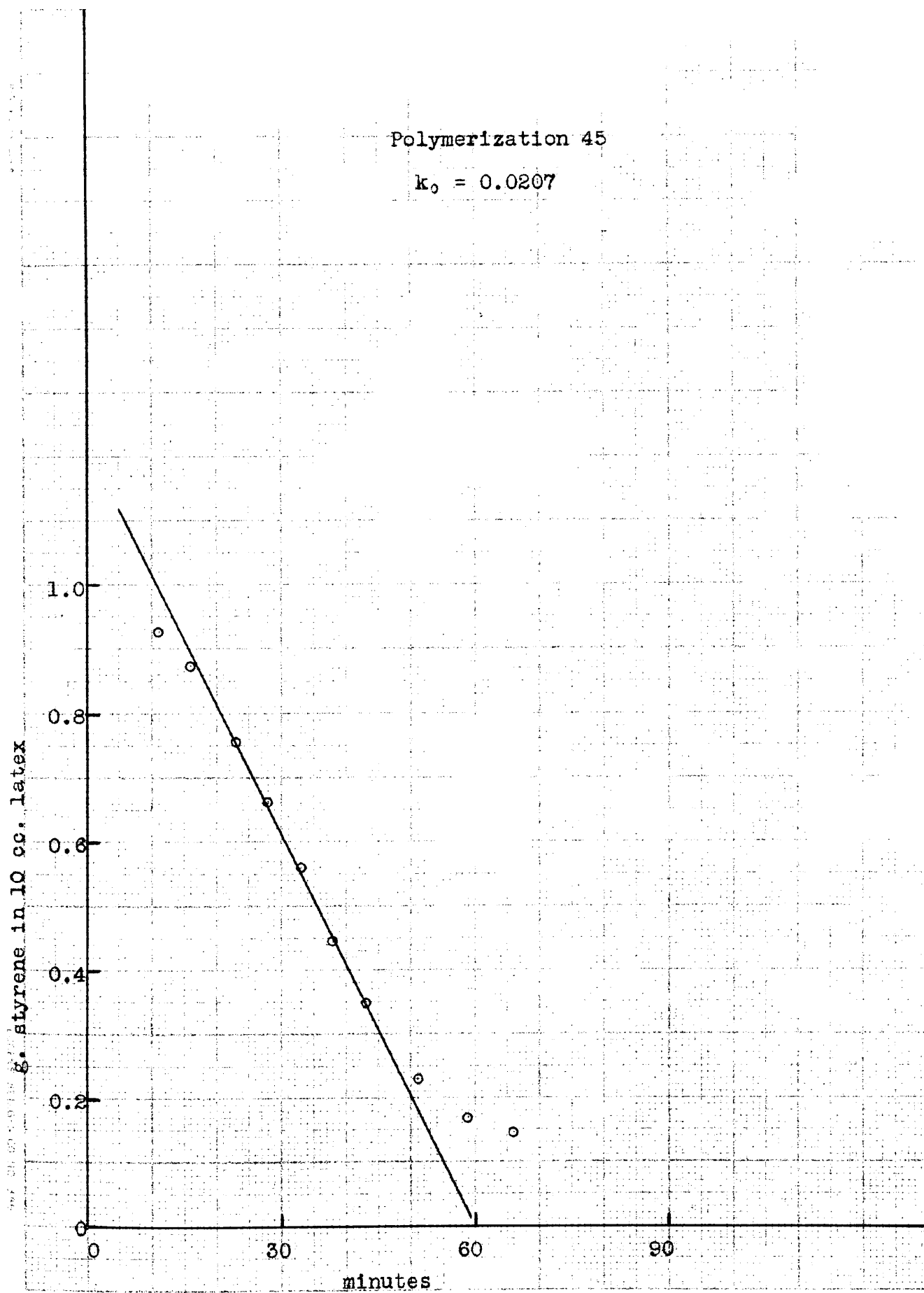
MW(C_7H_8) = 306,600

rel. viso. = 1.552

b. m. conc. = 0.00455

Polymerization 45

$$k_0 = 0.0207$$



Polymerization 46

400 cc. 0.0665 N KOH
 0.8788 g. $K_2S_2O_8$
 8.000 g. fatty acid
 50 cc. research styrene

Time (min.)	Reaction Temp.	Bath Temp.	g. Styrene in 10 cc. latex
7	40.0	40.0	0.9483
12	40.3	40.0	0.9273
17	41.0	40.0	0.8413
22	41.5	39.9	0.7413
27	41.9	39.9	0.6253
32	42.0	40.0	0.5143
37	42.0	40.0	0.4040
44	41.4	40.0	0.2851
54	40.9	40.0	0.1892
64	40.1	39.9	0.1481

Rate: $k_0 = 0.0226$

Polymerization 46

$$k_0 = 0.0226$$

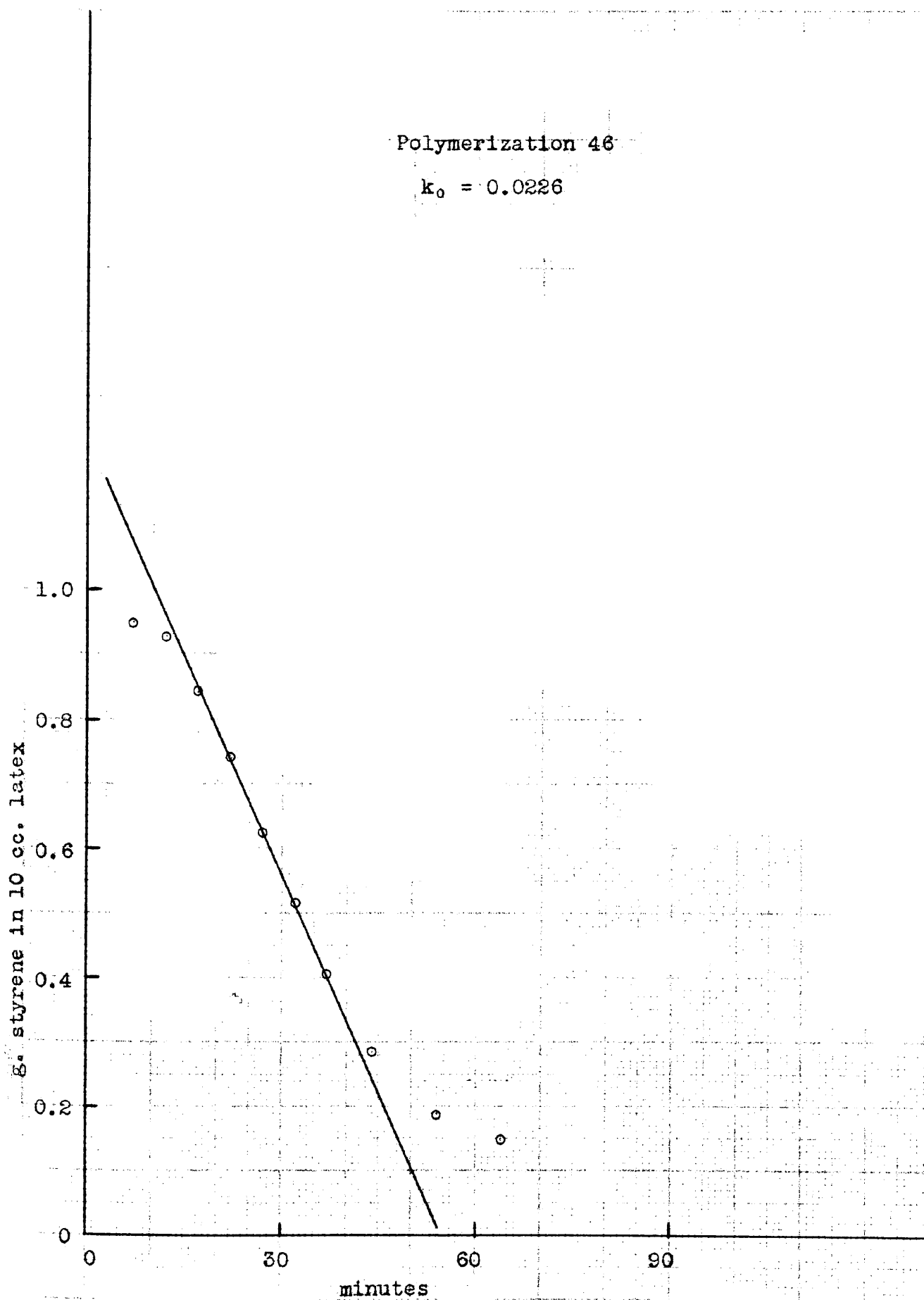


Table I summarizes the results of polymerizations 5, 10 and 22-38. These polymerizations were carried out at 50° with comparable reagents and under similar conditions. Thus the results of these polymerizations are applicable to a study of the effect of the concentration of styrene and potassium persulfate on the zero-order rate constant and the molecular weight of the polymers produced.

The zero-order rate constants have been corrected for the temperature increase observed during the reaction. The temperature coefficient, 0.0030 g. styrene/10 cc. latex/minute/degree, was determined from the increase in the rate constant of polymerizations run at the same catalyst concentration at 50° and 60° divided by the difference between the maximum temperatures observed in these reactions. It will be noted that these corrections bring the observed results in closer agreement and make the comparison of the rate constants at different catalyst concentrations more applicable.

Table I

50°

Polymer- ization	Weight Catalyst	Ratio Styrene	Max. Temp.	k_0		MW
				found	corrected	
22	0.1098	1:8	51.3	0.0193	0.0154	314,000
23		1:8	51.0	0.0171	0.0141	352,000
24		1:8	51.4	0.0190	0.0148	290,500
25		1:6	51.0	0.0175	0.0145	301,000
26		1:6	51.0	0.0184	0.0154	332,000
27		1:4	51.2	0.0187	<u>0.0151</u>	375,000
				average	0.0147	
5	0.2197	1:8	52.0	0.0293	0.0233	290,700
10		1:8	52.5	0.0294	0.0219	269,500
28		1:6	52.5	0.0302	0.0227	321,000
29		1:6	52.2	0.0298	0.0232	299,300
30		1:4	52.3	0.0293	0.0224	299,300
31		1:4	52.7	0.0317	<u>0.0236</u>	305,200
				average	0.0229	
32	0.3295	1:8	52.9	0.0366	0.0279	279,500
33		1:8	52.7	0.0357	<u>0.0276</u>	250,500
				average	0.0277	
34	0.4394	1:8	53.0	0.0410	0.0320	269,900
35		1:8	53.2	0.0403	0.0307	238,400
36		1:6	53.1	0.0397	0.0304	226,800
37		1:4	53.4	0.0404	<u>0.0302</u>	258,100
				average	0.0308	
38	4.3940	1:8	55.8	0.365	---	196,200

Table II compares the zero- and first-order rate constants found in polymerizations 5, 10 and 28-31 with the styrene concentration used. It is noted that the zero-order rate constant remains constant as the styrene concentration is varied which is expected if the reaction is zero order. The first-order rate "constants", however, vary in inverse proportion to the initial styrene concentration.

Table II

50°

Polymer- ization	Styrene Ratio	Rate	
		k_0	k_1
5	1:8	0.0293	0.0260
10	1:8	0.0294	0.0269
28	1:6	0.0302	0.0161
29	1:6	0.0298	0.0166
30	1:4	0.0293	0.0127
31	1:4	0.0317	0.0124

Table III summarizes the results of polymerizations 39, 40, and 41 run at 60° and at different catalyst concentrations. The zero-order rate constants have been corrected for the increase in temperature above 60° observed for the reactions. The same temperature coefficient discussed in the explanation to Table I was used in this correction.

Table III

Polymer- ization	Weight Catalyst	Ratio Styrene	Max. Temp.	k_0		MW
				Found	corrected	
39	0.2197	1:8	64.3	0.0667	0.0538	219,300
40	0.1098	1:8	63.7	0.0547	0.0436	256,700
41	0.0549	1:8	62.6	0.0357	0.0279	271,300

Table IV summarizes the results of polymerizations 42-46 run at 40° at various catalyst concentrations. The zero-order rate constants of these polymerizations were corrected by the temperature coefficient, 0.0019 g. styrene/10 cc. latex/minute/degree, derived in the same manner as the coefficient discussed in the explanation to Table I from the differences between the rate constants found at 40° and 50°.

Table IV

Polymer- ization	Weight Catalyst	Ratio Styrene	Max. Temp.	k_0		MW
				found	corrected	
42	0.2197	1:8	40.8	0.0115	0.0100	235,300
43	0.4394	1:8	41.0	0.0135	0.0116	292,700
44	0.4394	1:8	41.0	0.0127	0.0108	379,400
45	0.6591	1:8	41.5	0.0207	0.0168	306,600
46	0.8788	1:8	42.0	0.0226	0.0188	---

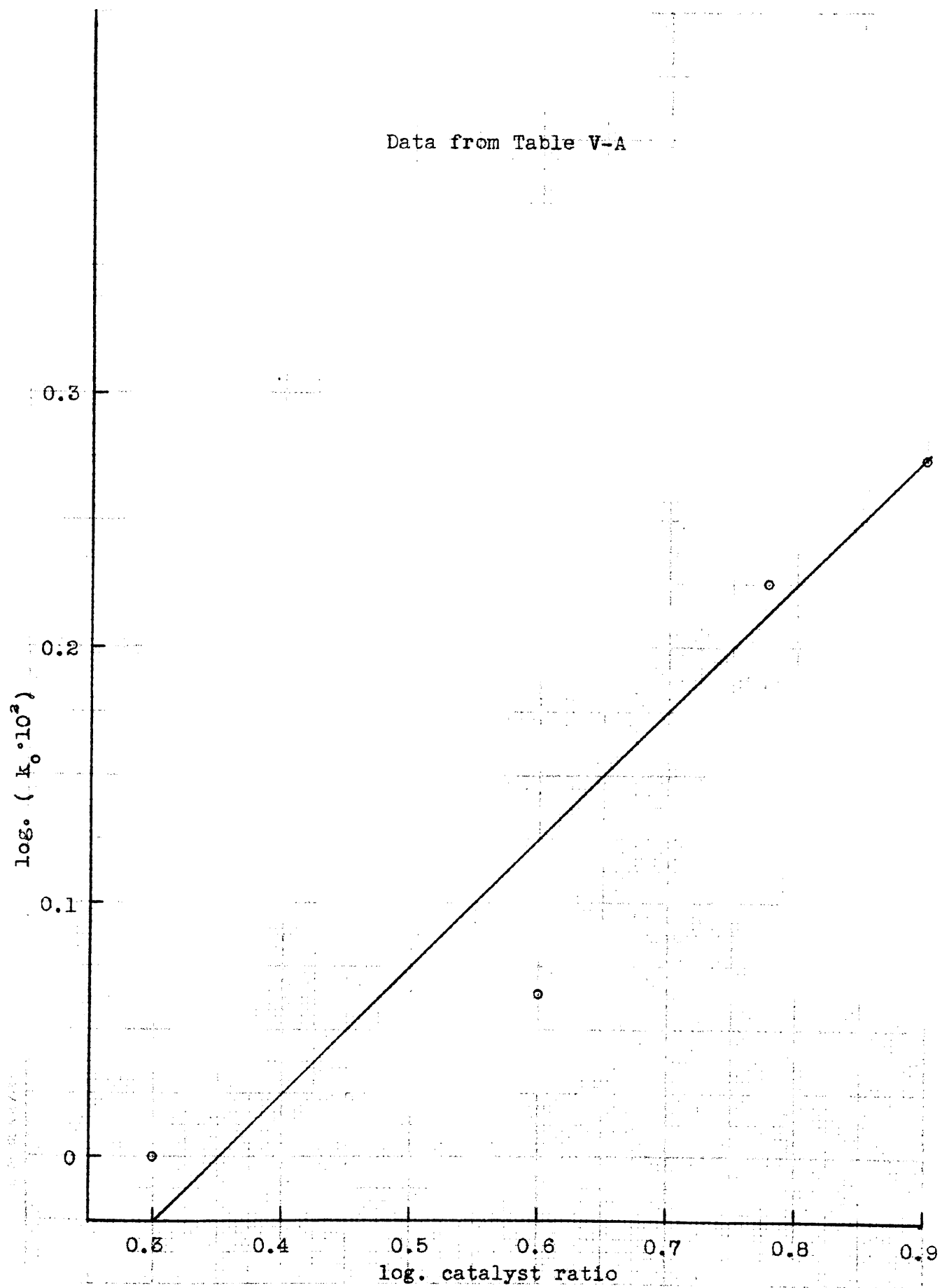
Table V summarizes the data obtained in various runs and series of runs on the relationship between the value of the zero-order rate constant for the emulsion polymerization of styrene and the catalyst concentration used. The rate constants have been corrected to the temperature at which the polymerization started.

The data from the three sections of Table V are plotted in the three graphs which follow it. It is observed from these plots of the logarithm of the catalyst ratio and the logarithm of the rate constant, that a straight line of one-half slope best fits the data. This corresponds to a linear relationship of the rate constant and the square root of the catalyst concentration.

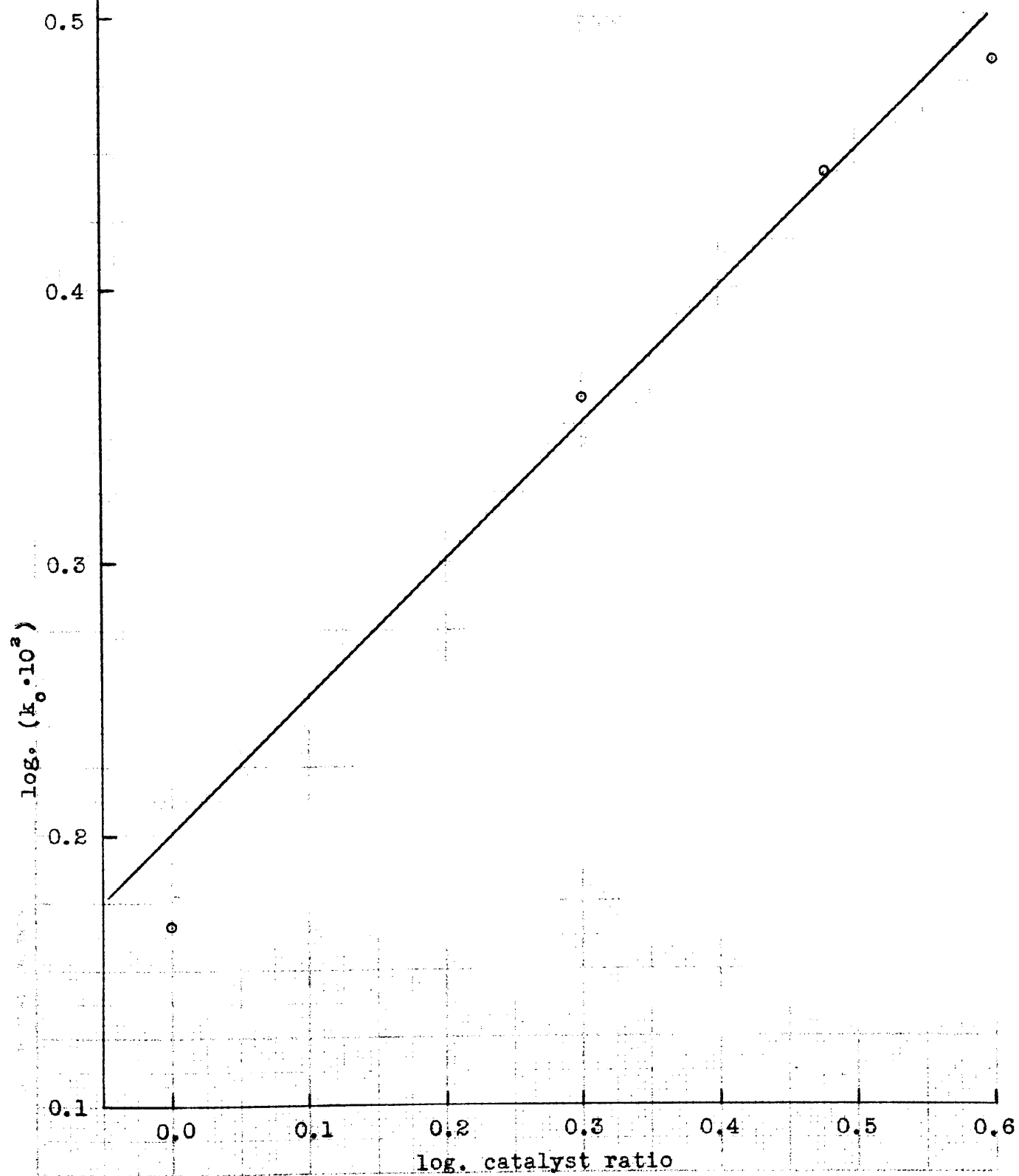
Table V

Polymer- ization	Catalyst Ratio	log. Ratio	k_o corrected $\times 10^2$	log. ($k_o \times 10^2$)
A 40°				
42	2	0.301	1.00	0.000
43	4	0.602	1.16	0.064
44	4	0.602	1.08	0.033
45	6	0.778	1.68	0.225
46	8	0.903	1.88	0.274
B 50°				
22-27	1	0.000	1.47	0.167
5, 10, 28-31	2	0.301	2.29	0.360
32,33	3	0.477	2.77	0.442
34-37	4	0.602	3.04	0.483
C 60°				
39	0.5	-0.301	2.79	0.446
40	1	0.000	4.36	0.640
41	2	0.301	5.38	0.731

Data from Table V-A



Data from Table V-B



Data from Table V-C

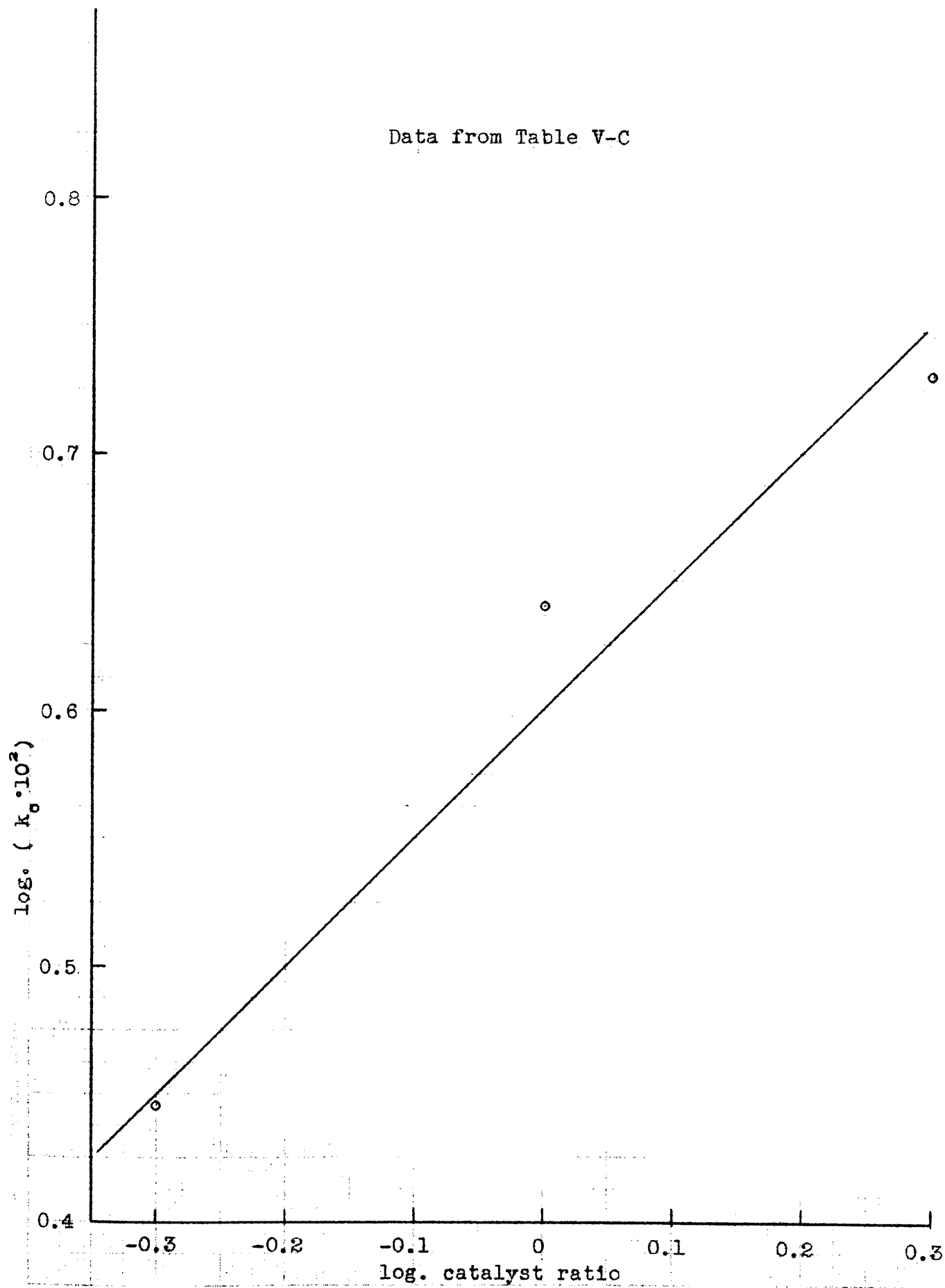


Table VI summarizes the data relating the rate of polymerization and temperature. The value K was calculated from the equation

$$K = k_0 \times 1000 / \text{Catalyst Ratio}$$

This equation was derived from the relationship found to exist between the rate constant and the square root of the catalyst concentration as shown in Table V and corresponding graphs. These values of K are essentially constant for a definite temperature, regardless of the catalyst concentration used.

The natural logarithm of the average values of K found at 40°, 50° and 60° were plotted against the inverse of the absolute temperature in the graph of Table VI. This relationship was found to be linear as predicted by the equation

$$\ln k = \text{const} \frac{-E}{RT}$$

The activation energy, E, was estimated from the slope of the straight line drawn through the points of Graph VI and was found to be 18,900 ± 2000 calories per mole.

Table VI

Polymer- ization	Temp.	Catalyst Ratio Ratio		k_o corrected $\times 10^3$	K	ln K	1000/T
42	40°	2	1.41	10.0	7.09		
43		4	2	11.6	5.80		
44		4	2	10.8	5.40		
45		6	2.45	16.8	6.87		
46		8	2.83	18.8	<u>6.64</u>		
				average	6.36	1.850	3.195
22-27	50°	1	1	14.7	14.7		
5, 10, 28-31		2	1.41	22.9	16.2		
32, 33		3	1.73	27.9	16.0		
34-37		4	2	30.4	<u>15.2</u>		
				average	15.5	2.741	3.096
39	60°	0.5	0.707	27.9	39.5		
40		1	1	43.6	43.6		
41		2	1.41	53.8	<u>38.2</u>		
				average	40.4	3.699	3.003

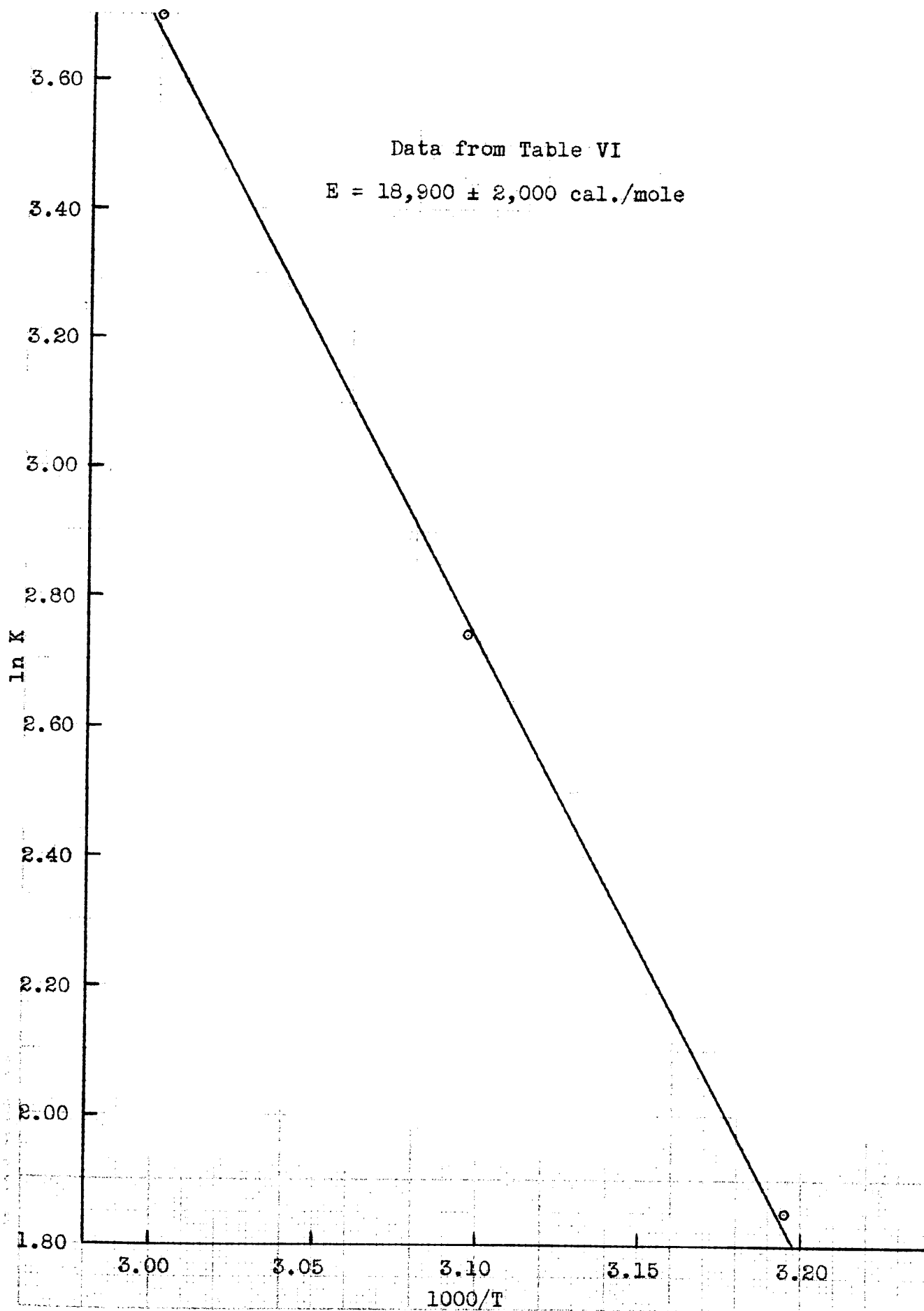


Table VII
Evaluation of Toluene Constant for
Molecular Weight Determination

MW Chloroform	Toluene solution		Constant Toluene Solution $\times 10^{-4}$
	conc. polymer base molal	log. relative viscosity	
185,200	0.00557	0.144	0.716
201,600	0.00564	0.153	0.742
237,400	0.00559	0.179	0.739
283,000	0.00562	0.222	0.717
203,300	0.00555	0.152	0.743
		average	0.731

V. SUMMARY

A method which gives satisfactory results for studying the rate of polymerization of styrene in emulsion has been developed. The rate of reaction was found to be independent of the styrene concentration and dependent on the square root of the catalyst concentration. The concentration of the catalyst was shown to remain constant during the polymerization.

The disappearance of monomer from the latex to form polystyrene was more rapid than in solution polymerization and was shown to follow a zero-order reaction rate. It is believed that the polymerization reaction is not different from the first-order reaction, based on monomer concentration, of solution polymerization, but is limited by the solution of the styrene in the water phase, where the polymerization takes place.

Similarity between emulsion and solution polymerization was evidenced by (1) approximately the same average-molecular-weight polymer formed throughout the polymerization, (2) the dependence of the rate of reaction on the square root of the catalyst concentration, and (3) an energy of activation approximately the same as for solution polymerization of styrene.

The energy of activation for the over-all reaction of the emulsion polymerization of styrene was determined graphically from the values of the rate constant at three different temperatures and was found to be $18,900 \pm 2000$ calories per mole.

Polymerization of styrene emulsified by potassium dehydroacetate gave a lower molecular-weight polymer and a slower rate of reaction than emulsification by soaps of high-molecular-weight fatty acids.

VI. BIBLIOGRAPHY

1. Bonastre, Journal de pharmacie, 17, 341 (1831).
2. Simon, E., Ann., 31, 287 (1839).
3. Breitenbach, J. W., Oester. Chem. Ztg., 11, 232 (1939).
4. Melville, H. W., Trans. Inst. Rubber Ind., 15, 209 (1939).
5. Schulz, G. V. and Husemann, E., Z. physik Chem., B39, 246 (1938).
6. Williams, G., J. Chem. Soc., 775 (1940).
7. Zeigler, K. and Jakob, L., Ann., 511, 45 (1934).
8. Schulz, G. V. and Wittig, G., Naturwissenschaften, 27, 377, 659 (1939).
9. Risi, J. and Gauvin, D., Can. J. Research, B14, 225 (1936).
10. Whitby, G. S., Trans. Faraday Soc., 32, 315 (1936).
11. Staudinger, H., ibid., 32, 97 (1936).
12. Price, C. C. and Kell, R. W., J. Am. Chem. Soc., 62, 3499 (1940).
13. Kamenskaya, S. and Medvedev, S., Acta. Physiochim, U. R. S. S., 13, 565 (1940).
14. Price, C. C. and Kell, R. W., 101st Meeting of American Chemical Society, St. Louis, Mo., April, 1941.
15. Hunter, W. H. and Yohe, R. V., J. Am. Chem. Soc., 55, 1248 (1933).
16. Whitmore, F. C., Ind. Eng. Chem., 26, 94 (1934).
17. Jorde, W., Monatsh., 70, 193 (1937).
Jorde, W. and Dostal, H., Z. physik. Chem., A179, 23 (1937).
18. Thompson, H. E. and Burk, R. E., J. Am. Chem. Soc., 57, 711 (1935).
19. Stanley, H. M., Chemistry and Industry, 58, 1080 (1939).
20. Mark, H. and Raff, R., "High Polymeric Reactions", Interscience Publishers, Inc., New York, 1941, p. 341.
21. Price, C. C., J. Am. Chem. Soc., 58, 1834 (1936).
22. Chalmers, W., ibid., 56, 912 (1934).
23. Staudinger, H. and Kohlschutter, W., Ber., B64, 2091 (1932).

24. Houtz, R. C. and Adkins, H., J. Am. Chem. Soc., 55, 1609 (1933).
25. Signer, R. and Weiler, G., Helv. Chim. Acta, 15, 649 (1932).
26. Staudinger, H. and Steinhofer, A., Ann., 517, 35 (1935).
27. Flory, P. J., J. Am. Chem. Soc., 59, 241 (1937).
28. Norrish, R. G. W. and Brookman, E. F., Proc. Royl. Soc., A171, 147 (1940).
29. Midgley, T., Henne, A. L., and Leicester, H. M., J. Am. Chem. Soc., 58, 1961 (1936).
30. Koizumi, M. and Titani, T., Bull. Chem. Soc., Japan, 13, 304 (1938).
31. Dostal, H. and Raff, R., Z. physik. Chem., B32, 417 (1936).
32. Suess, H., Pilch, K. and Husemann, E., ibid., A179, 371 (1937).
33. Melville, W. H., Ann. Reports, 36, 67 (1939).
34. Schulz, G. V. and Husemann, E., Z. physik. Chem. B34, 187 (1936).
35. F. Bayer and Company, German Pat. 254,672,255,129 (1912);
British Patent 14556 (1912); French Patent 419,316 (1913).
36. Mark, H. and Raff, R., loc. cit., p. 81.
37. Fikentscher, H., Angew Chem., 51, 433 (1938).
38. Fryling, C. F. and Harrington, E. W., Ind. Eng. Chem., 36, 114 (1944).
39. McBain, J. W. and Soldate, A. M., J. Am. Chem. Soc., 64, 1556 (1942).
40. Harkins, W. D., Private communication through the Office of Rubber Reserve, December, 1943.
41. Harkins, W. D., Corrin, M. L. and Stearns, R. S. Private communication through the Office of Rubber Reserve, June, 1944.
42. Harkins, W. D., Private communication through the Office of Rubber Reserve, March, 1943.
43. Harkins, W. D., Corrin, M. L. and Stearns, R. S. Private communication through the Office of Rubber Reserve, March, 1944.
44. McBain, J. W. Private communication through the Office of Rubber Reserve, November, 1943.
45. Reynolds, W. P., Private communication through the Office of Rubber Reserve, July, 1943.

46. McBain, J. W., Private communication through the Office of Rubber Reserve, February, 1943.
47. Kharash, M. S. and Westheimer, F. H., Private communication through the Office of Rubber Reserve, July, 1943.
48. Snyder, H. R. and Wall, F. T., Private communication, June, 1943.
49. Snyder, Wall, Stewart, Allen, Banes, Dearborn and Sands, Private communication, April, 1944.
50. Ewart, R. H., and Roe, C. P., Private communication through the Office of Rubber Reserve, March, 1944.
51. Potter, W. J., Borders, A. M. and Osterhof, H. J., Private communication through the Office of Rubber Reserve, June, 1943.
52. Kharash, M. S., and Westheimer, F. H., Private communication through the Office of Rubber Reserve, December, 1943.
53. Kolthoff, I. M. and Dale, W. J., Private communication through the Office of Rubber Reserve, May, 1944.
54. Corrin, M., Private communication through the Office of Rubber Reserve, January, 1944.
55. Fichter, Fr. and Lapin, H., *Helv. Chim. Acta.*, 12, 993 (1929).
Fichter, Fr. and Panizzon, L. P., *ibid.*, 15, 986 (1932).
Fichter, Fr. and Suederhauf, H. E., *ibid.*, 16, 338 (1933).
56. Green, L. and Masson, O., *J. Chem. Soc.*, 97, 2083 (1910).
57. Staudinger, H. and Husemann, E., *Ber.*, 68, 1691 (1935).
58. Yamamoto, S. and Kawata, S. *J. Soc. Chem. Ind., Japan*, 43, suppl. binding, 350 (1940).
59. Uhrig, K and Levin, H., *Ind. Eng. Chem. (Anal. Ed.)*, 13, 90 (1941).
60. Kolthoff, I. M. and Guss, L. S., Private communication through the Office of Rubber Reserve, February, 1944.
61. Kemp, A. R. and Peters, H., *Ind. Eng. Chem.*, 34, 1097 (1942).
62. Staudinger, H., "Die Hochmolekularen Organischen Verbindungen", J. Springer, Berlin, 1932, p. 209.
63. Alfrey, T., Bartovics, A. and Mark, H., *J. Am. Chem. Soc.*, 65, 2319 (1943).
64. Staudinger, H. and Frost, W., *Ber.*, 68, 2351 (1935).

65. Johnson, J. R. and McEwen, W. L., J. Am. Chem. Soc., 48, 469 (1926).
66. McBain, J. W. and Dean, R. B. Private communication through the Office of Rubber Reserve, March, 1944.
67. Mark, H. and Raff, R., loc. cit., p. 214.

68. Schulz, G. V., Z. physik. Chem., B34, 187 (1936); B36, 184 (1937).
69. von Braun, H. and Moldanke, K., Ber., 154, 618 (1921).
70. Fieser, L. F., "Experiments In Organic Chemistry", D. C. Heath and Company, New York, second edition, 1941, p. 395.
71. Fieser, L. F., ibid., p. 364.

VITA

The writer was born in Chandler, Oklahoma on December 12, 1919. He attended the public schools of that city through the tenth grade. The last two years of high school were completed at Kemper Military School, where he graduated in June, 1937. From September, 1937 to June, 1942 he attended Vanderbilt University and was granted the Bachelor of Arts degree in June, 1941 and the Master of Science degree in June, 1942. In September, 1942 he entered the Graduate School of the University of Illinois. He served as assistant in Chemistry from February, 1943 to June, 1943. From June, 1943 to October, 1944 he held a University Fellowship.

ProQuest Number: 29404091

INFORMATION TO ALL USERS

The quality and completeness of this reproduction is dependent on the quality and completeness of the copy made available to ProQuest.



Distributed by ProQuest LLC (2022).

Copyright of the Dissertation is held by the Author unless otherwise noted.

This work may be used in accordance with the terms of the Creative Commons license or other rights statement, as indicated in the copyright statement or in the metadata associated with this work. Unless otherwise specified in the copyright statement or the metadata, all rights are reserved by the copyright holder.

This work is protected against unauthorized copying under Title 17,
United States Code and other applicable copyright laws.

Microform Edition where available © ProQuest LLC. No reproduction or digitization of the Microform Edition is authorized without permission of ProQuest LLC.

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 - 1346 USA