SOME STUDIES OF THE EMULSION POLYMERIZATION OF STYRENE USING POTASSIUM PERSULFATE AS A CATALYST AND SODIUM BISULFITE AS A PROMOTER

Thesis for the Degree of M. S.
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Thomas Millard Loring
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This is to certify that the

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SOME STUDIES OF EMULSION POLYMERIZATION OF STYRENE USING POTASSIUM PERSULFATE AS A CATALYST AND SODIUM BISULFITE AS A PROMOTER

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Ralph L Guile
Major professor

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SOME STUDIES OF THE EMULSION POLYMERIZATION OF STYRENE USING POTASSIUM PERSULFATE AS A CATALYST AND SODIUM BISULFITE AS A PROMOTER

By

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INTRODUCTION

Research in emulsion polymerization in this laboratory began in the year 1946 with preliminary work by Morgan.[1] In 1947 Yang,[2] using potassium persulfate as a catalyst for styrene polymerization, observed a minimum limit of catalyst concentration for obtaining high molecular weight polymer. Early in 1948 Hallenbeck[3] found an effect of stirring on the polymerization rate of styrene catalyzed by hydrogen peroxide. Later in this same year, Mihina[4] presented his thesis work on alcohols as deactivation agents for the emulsion polymerization of styrene.

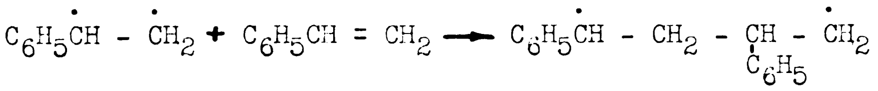
This paper reports the results of the first attempt within this laboratory to closely examine the effect of one redox system on polymerization. The redox system employed was that of meta sodium bisulfite with potassium persulfate.

HISTORICAL

Polymerization of olefinic molecules such as styrene has long been recognized as a chain reaction. The first mechanism for chain initiation was proposed by Staudinger[5] who suggested that the double bond in the monomer molecule could be opened by thermal activation to form a diradical.

$$C_6H_5CH = CH_2 \rightarrow C_6H_5\dot{C}H - \dot{C}H_2$$

The diradical was then believed to react with monomer molecules without loss of free radical activity.

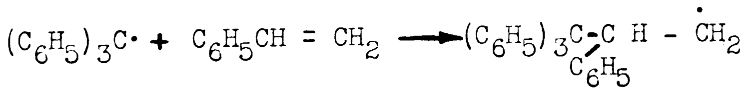


$$C_6H_5\dot{C}H - \dot{C}H_2 + C_6H_5CH = CH_2 \rightarrow C_6H_5\dot{C}H - CH_2 - \underset{C_6H_5}{CH} - \dot{C}H_2$$

More recently this diradical state has been assumed by Melville[6] to be the chain initiator for the photo-activated polymerization of vinyl acetate.

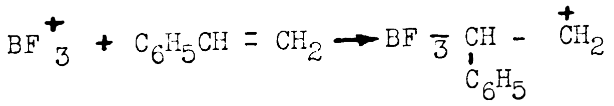
Another type of chain initiation is that of catalytic activation of monomer. The compounds successful as initiators may be classified into two catagories:

1) Compounds which produce free radical fragments and induce polymerization by activation of the double bond.



$$(C_6H_5)_3C\cdot + C_6H_5CH = CH_2 \rightarrow (C_6H_5)_3C-\underset{C_6H_5}{C}H - \dot{C}H_2$$

2) Reagents which produce an ionic state in the monomer molecule.



$$B\overset{+}{F}_3 + C_6H_5CH = CH_2 \rightarrow BF_3\underset{C_6H_5}{CH} - \overset{+}{C}H_2$$

Confirmation that these radicals and ions actually initiate polymerization has been in the fact that they occur as end fragments in many different polymers.[7,8] Free radical initiation will be the only type referred to throughout this paper as the catalyst used in this work is of a type that has been considered to give free radicals.

The propagation process by a free radical mechanism is expressed by the following equations:

$$M\cdot + M \longrightarrow M_2\cdot$$

$$M_2\cdot + M \longrightarrow M_3\cdot$$

$$M_n\cdot + M \longrightarrow M^{\cdot}_{(n+1)}$$

Termination may occur by the following methods:

1) Addition of the initiator radical at the active end of a chain.

2) Reaction of the free radical end of one chain with a similar end of another molecule.

3) Transfer of activation to another molecule.

4) Termination by impurities.

Extensive kinetic studies have shown that the usual termination reaction in the absence of a chain transfer agent is bimolecular, and probably similar to type 2.

$$(C_6H_5)_3C(M)^{\cdot}_n + \cdot(M)_mC(C_6H_5)_3 \longrightarrow (C_6H_5)_3\,C(M)_{mn}\;C(C_6H_5)_3$$

All of these mechanisms for initiating, propagating and terminating the polymerization reaction were proposed when the only polymerization known was in bulk and solution. The overall velocity constant for bulk or solution polymerization has been found most satisfactorily expressed in the form of a second order reaction equation. For example, the rate of benzoyl peroxide catalyzed styrene polymerization in toluene solution[9] is expressed as follows:

$$\frac{-dM}{dt} = k_o\,B^{1/2}\,M^{3/2}$$

$\frac{-dM}{dt}$ = rate of disappearance of monomer

B = concentration of catalyst

M = concentration of monomer

k_o = overall rate constant

The use of other monomers indicated that the rate of polymerization always varied with the square root of the catalyst concentration and some root of the monomer concentration; the exact root of monomer concentration varied with the monomer.

Emulsion polymerization was first studied in connection with synthetic rubber. It was found that a monomer could be polymerized in an emulsion system to produce a latex from which the polymer could be coagulated. Instead of the usual rubbery product, a powdery product was produced on coagulation. The emulsion consisted of an aqueous phase, monomer, emulsifying agent and a water soluble catalyst.

In an extensive review of emulsion polymerizations, Hohenstein and Mark[10] described some simple experiments in which monomer vapor was permitted to come in contact with an aqueous solution of an initiator (persulfate). These experiments clearly indicated that polymerization was initiated in the aqueous phase. Further evidence supporting the belief that emulsion polymerization is initiated in the aqueous phase was contributed by Fryling,[11] whose work showed that the monomer was solubilized by soap to give micelles in the aqueous phase before polymer formation. Harkins[12,13] postulated that polymerization began in the aqueous phase and that beyond 20%, polymerization occurred in the polymer-monomer particles. The kinetics and mechanisms of emulsion polymerization have been studied by many different workers[14,15,16] and the general conclusions reached are as follows:

1) Monomer is solubilized into soap micelles.

2) Activation occurs by the same methods as in bulk polymerization, i.e. catalytic salts or heat.

3) The reaction is fed in these micelles by more solubilized monomer.

4) As these micelles enlarge they become polymer particles and

because monomer is soluble in polymer, the reaction continues in these latex particles.

In the case of the emulsion polymerization of styrene, the reaction is characterized by a well defined induction period after which the rate becomes a linear function with time. The apparent inhibiting agent present which must be overcome is oxygen.[17] It has been shown that if oxygen contamination is eliminated and the reagents are very pure, the induction period approaches zero.[18] A possible explanation of the inhibiting role of oxygen was offered by Kolthoff,[19] who stated that oxygen reacts with activated monomer to form peroxides and with activated polymer to form polyperoxides.

Although the mechanism of persulfate polymerization is still unsolved, it has been shown that the concentration of persulfate decreases very slightly during the course of polymerization.[20,22] Kolthoff[20,21] has shown that the rate of polymerization is proportional to the square root of the catalyst concentration. This relationship is in agreement with bulk or solution polymerization by catalytic activation.

Extensive investigations have shown that:

1) After the induction period the rate of reaction is independent of the concentration of emulsified styrene.

2) The activation energy is approximately the same as that necessary for polymerization in solution.

3) The average molecular weight is constant during polymerization. These facts indicate that the reaction proceeds by a free radical mechanism which is similar to the mechanism of polymerization in solution. The zero order dependence on monomer concentration may be explained by the fact that the loci of reaction is continually being replenished with monomer at a rate fast enough to maintain the natural propagation rate.

Other possible methods of termination in emulsion polymerization in addition to those already listed for bulk and solution polymerization include local exhaustion of monomer and dissipation of activation energy.[23,24]

In the year 1946 several English workers[25,26,27] described a new method of activating the polymerization reaction. Morgan[27] termed the mechanism "reduction activation polymerization". The outstanding feature of this redox type activation was the increased rate of polymerization. This increased rate permitted polymerization at much lower temperatures than were possible by conventional methods. Evans and his coworkers[26,28,29] have conducted a thorough examination of the effect of a redox system in polymerization. They measured the polymerization rate of several vinyl monomers using hydrogen peroxide and ferrous ions. In the absence of the monomer, the peroxide decomposed according to the Haber-Weiss mechanism[30] with the evolution of oxygen.

$$H_2O_2 + Fe^{++} \rightarrow HO^- + HO\cdot + Fe^{+++}$$

$$HO\cdot + Fe^{++} \rightarrow HO^- + Fe^{+++}$$

$$HO\cdot + H_2O_2 \rightarrow H_2O + HO_2\cdot$$

$$HO_2\cdot + H_2O_2 \rightarrow HO\cdot + H_2O + O_2$$

In the presence of monomer the oxygen production was negligible because of the reaction of the hydroxyl radical with monomer to produce the propagating chain.

$$HO\cdot + C_6H_5\,CH = CH_2 \rightarrow \underset{\displaystyle C_6H_5}{HOCH} - \dot{C}H_2$$

Baxendale and Evans[26,28,29] showed in their work that the rate of production of ferric ion in presence or absence of monomer was the same. Their experimental data also indicated that the termination was as follows:

$$HO(M)_n^{\cdot} + \cdot(M)_mOH \rightarrow HO(M)_{mn}OH$$

rather than:

$$HO(M)_n^{\cdot} + \cdot OH \rightarrow HO(M)_nOH$$

Bacon[25] and Morgan[27] found in the persulfate catalyzed emulsion polymerization of acrylonitrile and styrene, that many reducing agents hasten the polymerization similar to the action of the ferrous ion with hydrogen peroxide. Baun[31] proposed, by analogy to the above system, the following reactions for the persulfate and thiosulfate catalysis:

$$S_2O_8^{=} + S_2O_3^{=} \rightarrow SO_4^{=} + SO_4^{\overline{\cdot}} + S_2O_3^{\overline{\cdot}}$$

$$SO_4^{\overline{\cdot}} + H_2O \rightarrow HSO_4^{-} + HO\cdot$$

$$HO\cdot + M \rightarrow HOM\cdot$$

$$SO_4^{\overline{\cdot}} + M \rightarrow {}^{-}O_4S\ M\cdot$$

$$S_2O_3^{\overline{\cdot}} + M \rightarrow {}^{-}O_3S_2\ M\cdot$$

Morgan[27] also pointed out the fact that addition of cupric ion in the persulfate-thiosulfate system increased the rate of the catalysis.

The molecular weights of polymers are not only important in the study of mechanism of termination and rate studies, but are also significant in the industrial use of the polymers. The various methods thus far devised for determining molecular weight include methods based on the determination of certain physical properties of polymer solutions, namely, osmotic pressure,[32] viscosity,[5a] sedimation[33] (ultracentrifuge) and light scattering.[34] All of the methods listed give average molecular weight values rather than absolute values. Schulz[35] has pointed out the fact that the average molecular weight of the polymer at any stage of the reaction is fairly constant, due to a constant ratio of chain propagations to chain terminations throughout the course of polymerization. The viscosimetric method is generally used for determining molecular weight for reasons of simplicity of equipment and operation. This method will be explained in detail in the experimental part of this paper.

EXPERIMENTAL

REAGENTS:

Styrene -- The styrene used in this experimental work was obtained from the Dow Chemical Company. Before use, the styrene was vacuum distilled (20 mm.) and the fraction having an index of refraction of 1.544 was collected and used as the monomer in the following studies.

Water - - Conductance water distilled under nitrogen was used for the aqueous phase of the emulsion. The procedure for producing the impurity-free water was as follows: Fifty ml. of alkaline potassium permanganate (300 gm. potassium hydroxide, 8 gm. potassium permanganate per liter of solution) and 2000 ml. distilled water were refluxed under a nitrogen atmosphere for 30 minutes. The water was then distilled, the first 200 ml. discarded, and the receiver flushed with steam, before distillate was again collected, to insure against possible contamination by ammonia. The distilled water was then kept under a positive pressure of nitrogen until ready for use.

Potassium Persulfate -- Merck's reagent grade was dissolved in conductance water at 30°C, recrystallized at 5°C, filtered and dried at room temperature for 48 hours.

Duponol-G -- A Du Pont emulsifying agent reported as being lauryl amine sulfate. The Duponol G was stored in the liquid phase at 40°C to facilitate ease in weighing the product. A test for inorganic impurities in the emulsifying agent by decomposing a weighed amount in a silica crucible was made. No residue was present.

Sodium Bisulfite (meta) -- Merck's reagent grade.

Sodium Bisulfite -- Merck's reagent grade (95% active ingredients).

Ethanol -- USP 95% (BP 76 - 77°C).

Aluminum Chloride -- Baker and Adamson's CP ($AlCl_3 \cdot 6 H_2O$).

Nitrogen -- water pumped. The nitrogen was passed through alkaline pyrogallol solution before use. This solution was prepared according to the following recipe: Fifty gms of potassium hydroxide were added to 100 mls of water, to which were added five gms of pyrogallic acid.

Toluene -- J. T. Baker's CP and Purified.

PROCEDURE:

The technique of emulsion polymerization employed in this work was adapted from co-workers in this laboratory.[1,2,3,4] The polymerization was carried out in a four necked, one liter, round bottomed flask with standard taper ground glass joints. The flask was fitted with a mercury-sealed, swivel stirrer, nitrogen intake tube that permitted the flow of nitrogen over the emulsion, sampling tube that extended to the bottom of the flask, thermometer and a short bulb type water cooled reflux condenser. The condenser was attached to a small double water trap to permit the nitrogen to escape and prevent air from sucking back into the system.

The reaction temperature of 40°C was maintained by placing the polymerization vessel in a constant temperature water bath. Polymerization was initiated and propagated under a nitrogen atmosphere, the pressure of which was controlled by keeping the rate of nitrogen escape at one bubble per second through the water trap. Although the rate of stirring was not recorded, it was rapid and constant throughout all of the experiments in this work. Sampling of the emulsion was done periodically throughout the polymerization reaction by means of the sampling tube, previously mentioned, with the aid of an aspirator.

The emulsion consisted of a ratio of eight parts aqueous phase to one part monomer, 1% Duponol G based on the aqueous phase, and the water soluble catalyst and promoter in molarity also based on the aqueous phase as described in each experiment.

In preparing and making a run, the equipment was first assembled and flushed with nitrogen. The Duponol G and the oxygen-free conductance water were added to the flask. The solution was stirred under nitrogen while permitting the bath to come to operating temperature. The weighed amounts of catalyst and cocatalyst were then added to the system and after allowing five minutes for these to completely go into solution, the styrene was added. The initial time of the polymerization was recorded as the time of addition of the monomer, styrene. The monomer was not preheated before addition because of the activating effect of temperature and a negligible temperature drop of less than one degree observed on the addition of the styrene.

Duplicate samples of approximately 10 gms. were taken at various time intervals, the intervals depending on the rate of polymerization. One sample was used for pH determination by a Beckman pH meter, and the other sampled directly into a tared flask containing 40 gm. of chilled ethanol and .1 gm. aluminum chloride. The alcohol was measured volumetrically by means of a pipette and the density for each batch of ethanol was determined. The purpose of the ethanol and aluminum chloride was to quench the reaction and coagulate the polymer.

The weight of the sample was obtained by weight difference and the contents were centrifuged to separate the solid polymer from the liquid. The method of titrating unreacted styrene in the decanted liquid, reported by Mihina[4] and Hallenbeck[3] of this laboratory, was tried unsuccessfully. The solid polymer was washed with ethanol into an Erlenmeyer flask and allowed to stand overnight. The following day the polymer samples were filtered, washed with distilled water and finally with ethanol. They were allowed to dry for 24 hours at 40°C and weighed.

The percent solid polymer was calculated as follows:

$$\%\text{ solid polymer} = \frac{\text{polymer weight}}{\text{theoretical weight of styrene in sample}} \times 100$$

The theoretical weight of styrene in the sample was calculated by dividing the sample weight by 9 (total parts aqueous plus monomer).

The relative average molecular weight was determined on polymer samples using the Staudinger viscosity method.[5a] A weighed amount of polystyrene (approximately .1 gm.) was placed in a 100 ml. volumetric flask and toluene added to bring solution up to mark. It was necessary to keep solution at 40°C for 48 hours to permit solution of high molecular weight polymers. The time of efflux of polystyrene solutions and pure toluene at $20^\circ \pm .1^\circ\text{C}$ were determined to 0.1 second by the use of a Cannon-Fenske-Ostwald viscosity pipette. The specific viscosity was calculated from the following relationship:

$$N_{sp} = \frac{\text{time of efflux of solution at } 20^\circ\text{C}}{\text{time of efflux of solvent at } 20^\circ\text{C}} - 1 .$$

The average molecular weight was calculated by means of Staudinger's equation:

$$M = \frac{N_{sp}}{K(c)}$$

M = average molecular weight

N_{sp} = specific viscosity

C = moles of polystyrene/liter of solution
(mole of polystyrene is equivalent to weight of recurring unit)

$K = 1.8 \times 10^{-4}$

Because the value K varies slightly from polymer to polymer sample, the molecular weights are considered to be relative values only.

DATA

All experiments had the following ingredients and factors in common:

Styrene	80 grams
Water	633.6 grams
Duponol G	6.4 grams (1 percent of aqueous phase)

Nitrogen Atmosphere

Temperature 40°C

Indication is made in each experiment of the molarity (based on aqueous phase) of potassium persulfate and meta sodium bisulfite present.

EXPERIMENT #1

.001 Molar Potassium Persulfate (.1728 grams)

Sample #	Time (minutes)	Percent Solid Polymer	Average Moleculor Weight	pH
1	90	8.3	---	7.8
2	150	22.4	797,000	---
3	219	44.4	910,000	8.1
4	270	57.0	782,000	8.3
5	330	76.8	722,500	8.4
6	400	86.3	674,000	8.5
7	450	87.3	672,000	8.4
8	547	90.5	651,000	8.3
9	629	90.5	---	8.2

EXPERIMENT #2

.001 Molar Potassium Persulfate (.1728 grams)

.00014 Molar meta Sodium Bisulfite (.0167 grams)

Sample #	Time Minutes	Percent Solid Polymer	Average Molecular Weight	pH
1	20	1.7	---	7.1
2	40	14.6	543,000	7.7
3	60	26.7	842,000	7.8
4	80	41.3	834,000	7.8
5	100	53.0	817,500	7.8
6	120	58.5	827,000	7.9
7	140	67.7	734,000	7.9
8	160	75.6	664,000	7.9

EXPERIMENT #3

.001 Molar Potassium Persulfate (.1728 grams)

.00027 Molar meta Sodium Bisulfite (.0333 grams)

Sample #	Time Minutes	Percent Solid Polymer	Average Molecular Weight	pH
1	18	3.5	---	7.8
2	36	20.0	397,500	7.9
3	54	36.5	604,000	7.9
4	72	56.1	---	8.0
5	90	69.8	680,500	8.0
6	108	78.2	637,000	8.1
7	126	81.0	---	8.1
8	144	82.0	573,000	8.2

EXPERIMENT #4

.001 Molar Potassium Persulfate (.1728 grams)

.00055 Molar meta Sodium Bisulfite (.0665 grams)

Sample #	Time Minutes	Percent Solid Polymer	Average Molecular Weight	pH
1	12	1.8	---	6.5
2	24	12.4	---	6.5
3	36	33.2	652,000	6.5
4	48	49.2	716,000	6.5
5	60	62.5	639,500	6.5
6	72	75.2	632,500	6.4
7	85	83.2	637,000	6.3
8	110	90.8	598,000	6.7

EXPERIMENT #5

.001 Molar Potassium Persulfate (.1728 grams)

.0008 Molar meta Sodium Bisulfite (.0998 grams)

Sample #	Time Minutes	Percent Solid Polymer	Average Molecular Weight	pH
1	10	5.4	---	6.2
2	20	20.9	445,000	6.8
3	30	43.3	432,000	6.9
4	40	60.8	420,000	---
5	50	70.3	414,500	6.8
6	60	81.7	401,000	6.8
7	70	87.2	---	6.8
8	92	89.5	375,000	6.8

EXPERIMENT #6

.001 Molar Potassium Persulfate (.1728 grams)

.0011 Molar meta Sodium Bisulfite (.1330 grams)

Sample #	Time Minutes	Percent Solid Polymer	Average Molecular Weight	pH
1	10	1.2	---	6.3
2	31	43.2	452,000	6.4
3	40	62.0	438,000	6.5
4	50	74.5	383,500	6.5
5	60	82.8	377,000	6.6
6	70	86.0	369,000	6.5
7	81	86.3	376,000	6.6
8	90	88.5	---	6.6
9	100	88.6	---	6.6

EXPERIMENT #7

.001 Molar Potassium Persulfate (.1728 grams)

.001 Molar Sodium Acid Sulfate (.0832 grams $NaHSO_4 \cdot H_2O$)

Sample #	Time Minutes	Percent Solid Polymer	Average Molecular Weight	pH
0	00	0.0	---	3.7
1	31	0.0	---	2.6
2	119	12.1	552,000	2.6
3	181	34.9	788,000	2.4
4	240	47.3	742,000	2.4

EXPERIMENT #8

.001 M Potassium Persulfate (.1728 grams)

.0011 M Sodium Bisulfite (.0767 grams - 95% efficient)

Sample #	Time Minutes	Percent Solid Polymer	Average Molecular Weight	pH
1	10	1.4	---	7.2
2	20	20.4	---	7.2
3	30	35.8	425,000	7.3
4	40	51.6	496,500	7.4
5	50	67.3	426,000	7.3
6	60	75.8	423,000	7.3
7	70	79.3	437,500	7.2
8	90	84.3	422,500	7.2
9	101	86.4	421,000	7.2

EXPERIMENT #9

.0005 M Potassium Persulfate (.0864 grams)

.00055 M meta Sodium Bisulfite (.0665 grams)

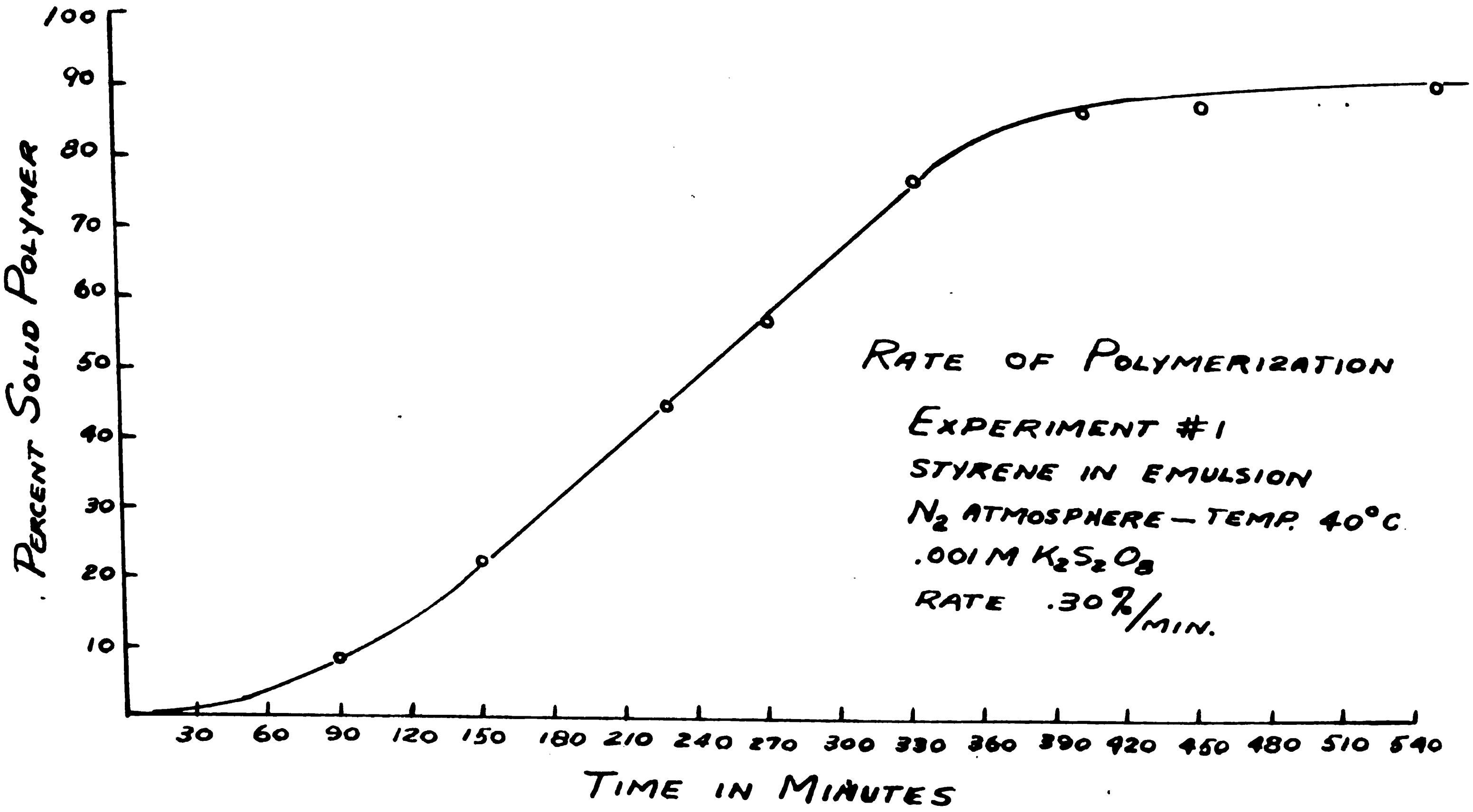
Sample #	Time Minutes	Percent Solid Polymer	Average Molecular Weight	pH
1	22	7.9	---	5.6
2	42	31.0	863,000	5.6
3	57	45.9	1,330,000	5.7
4	77	59.7	982,500	5.7
5	119	78.7	741,000	5.6
6	139	82.8	686,000	5.6
7	186	84.5	660,000	5.6

EXPERIMENT #10

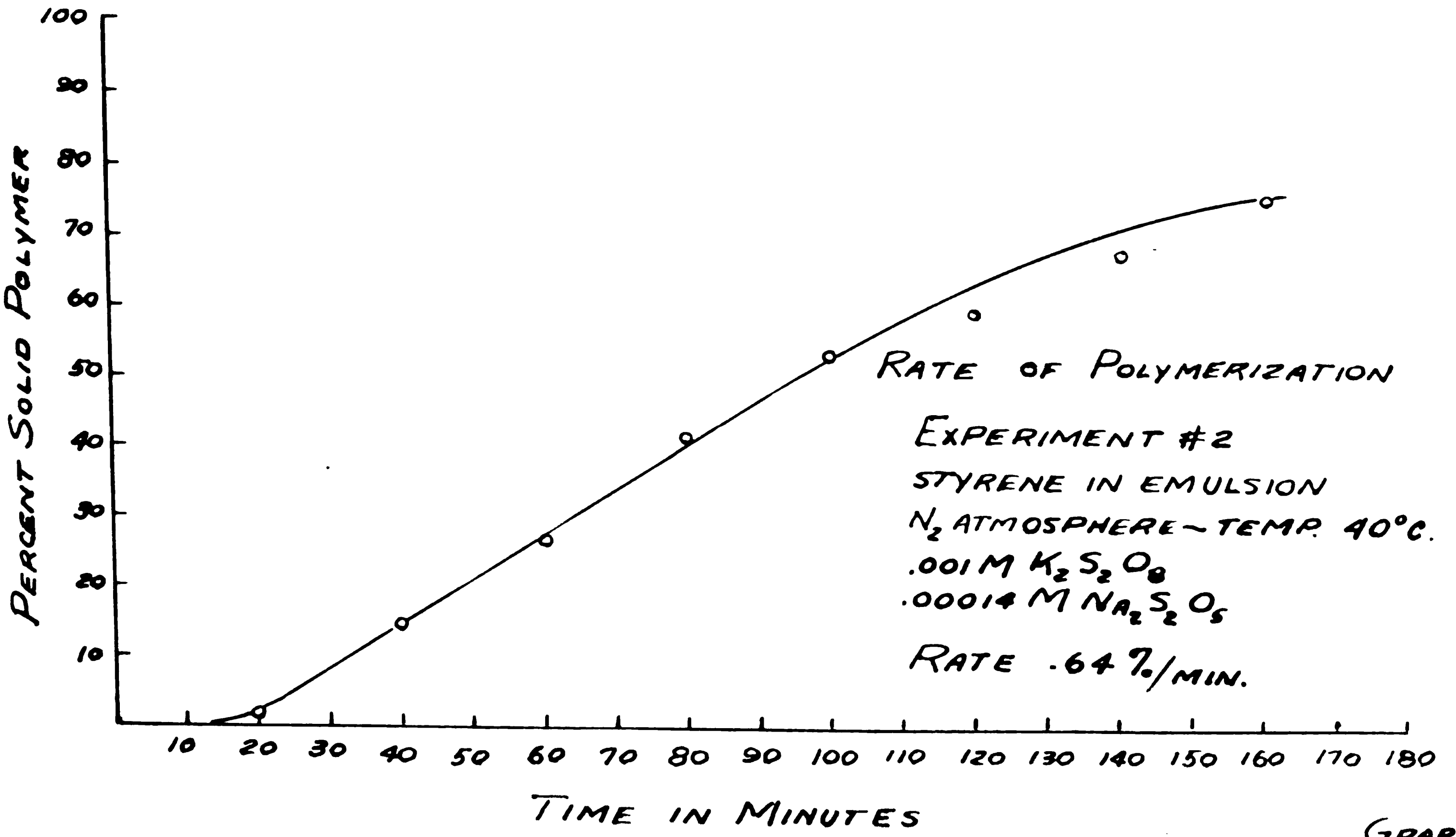
.00014 M Potassium Persulfate (.0242 grams)

.00014 meta Sodium Bisulfite (.0167 grams)

Sample #	Time Minutes	Percent Solid Polymer	Average Molecular Weight	pH
1	20	1.2	---	7.3
2	40	4.6	---	7.6
3	60	10.6	639,000	7.7
4	80	16.8	657,000	7.6
5	100	23.2	---	7.5
6	120	30.7	722,000	7.5
7	140	33.0	---	7.5
8	160	35.3	729,000	7.5
9	237	48.2	590,000	7.7


RATE OF POLYMERIZATION
EXPERIMENT #1
STYRENE IN EMULSION
N_2 ATMOSPHERE — TEMP. 40°C
.001 M $K_2S_2O_8$
RATE .30%/MIN.
PERCENT SOLID POLYMER
100
90
80
70
60
50
40
30
20
10
30
60
90
120
150
180
210
240
270
300
330
360
390
420
450
480
510
540
TIME IN MINUTES

GRAPH #1



RATE OF POLYMERIZATION

EXPERIMENT #2

STYRENE IN EMULSION

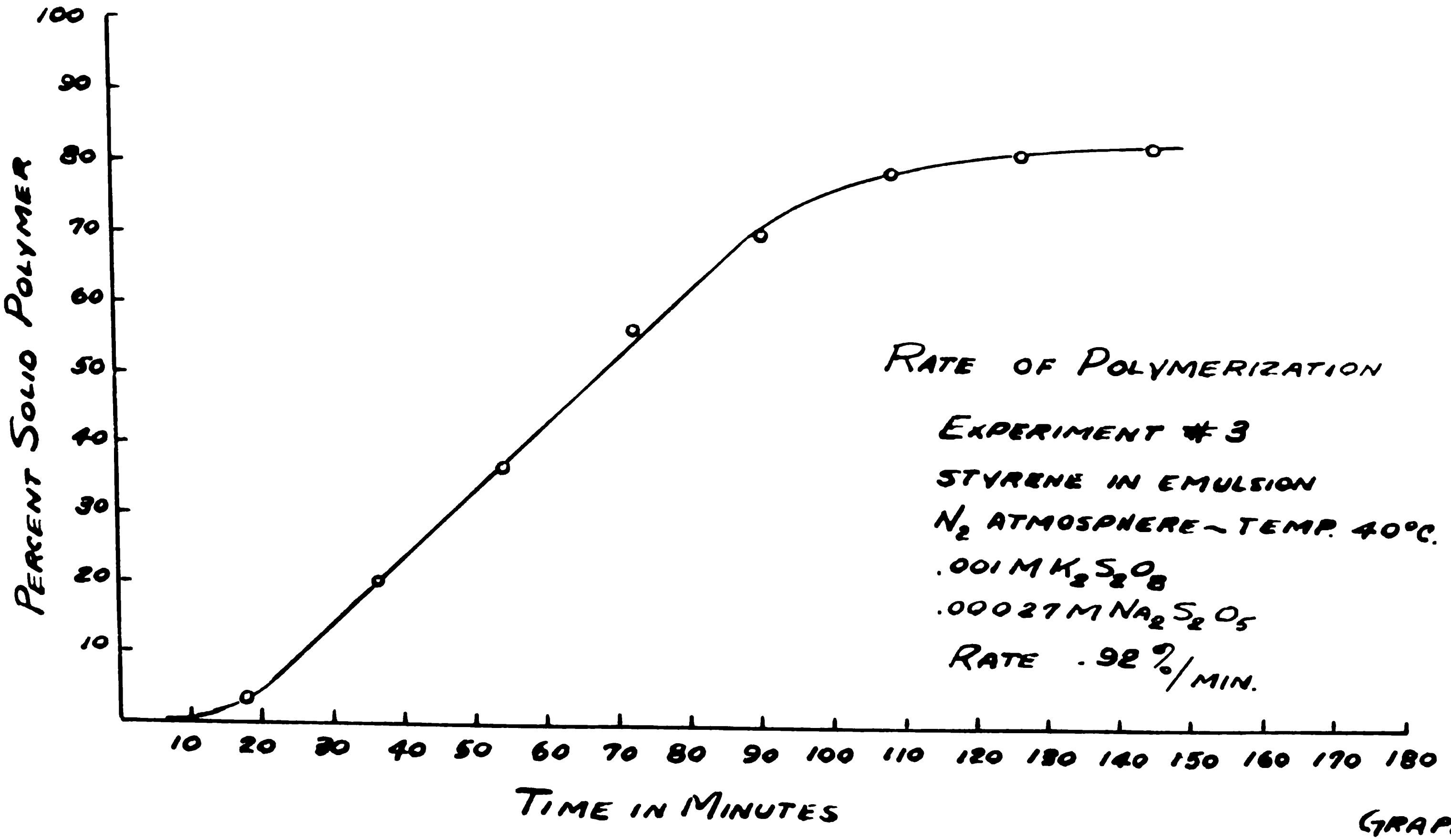
N_2 ATMOSPHERE ~ TEMP. 40°C.

.001 M $K_2S_2O_8$

.00014 M $Na_2S_2O_5$

RATE .64 %/MIN.

GRAPH #2



Rate of Polymerization

Experiment # 3

Styrene in Emulsion

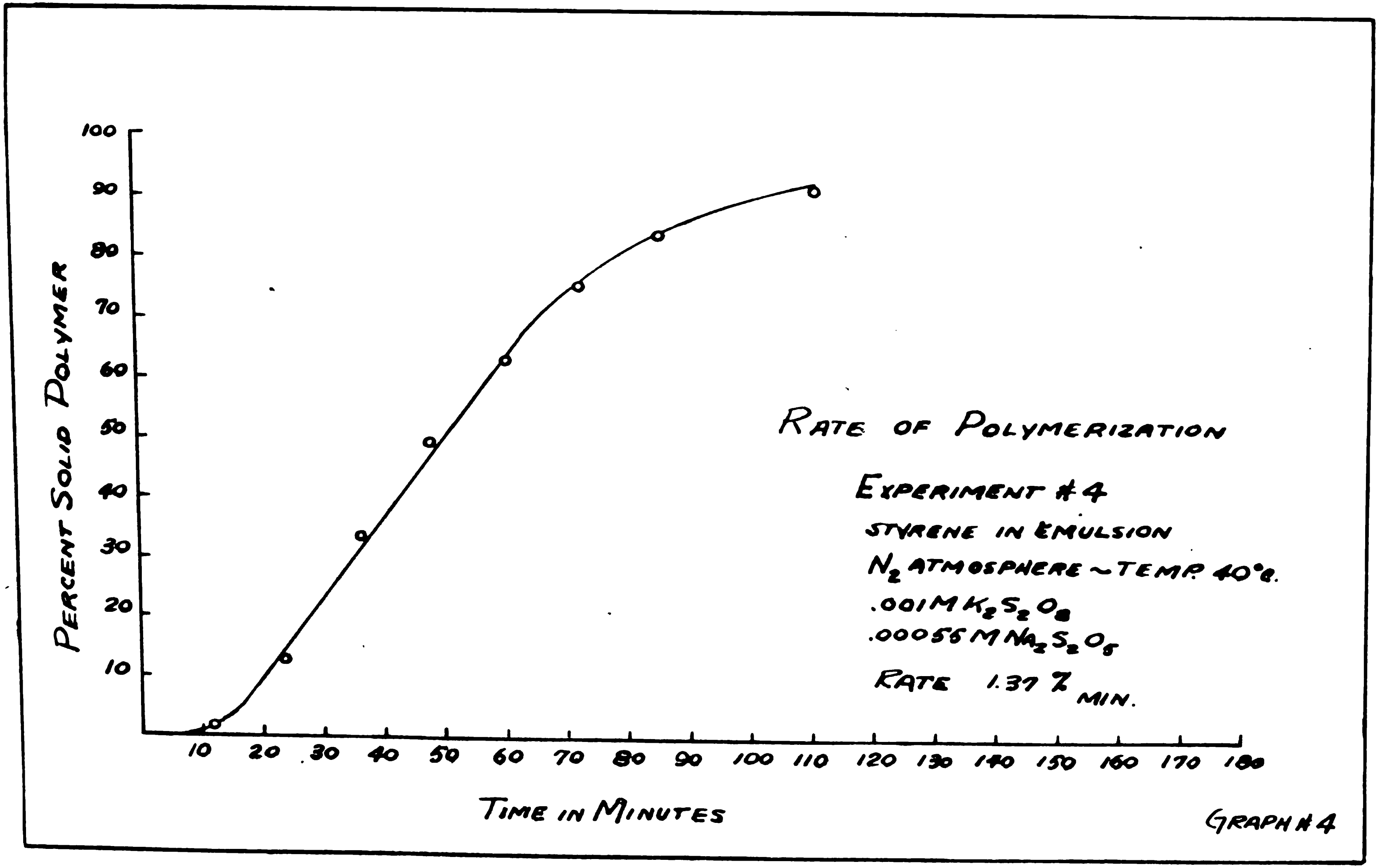
N_2 Atmosphere ~ Temp. 40°C.

.001 M $K_2S_2O_8$

.00027 M $Na_2S_2O_5$

Rate .92 %/min.

Graph # 3



RATE OF POLYMERIZATION

EXPERIMENT #4

STYRENE IN EMULSION

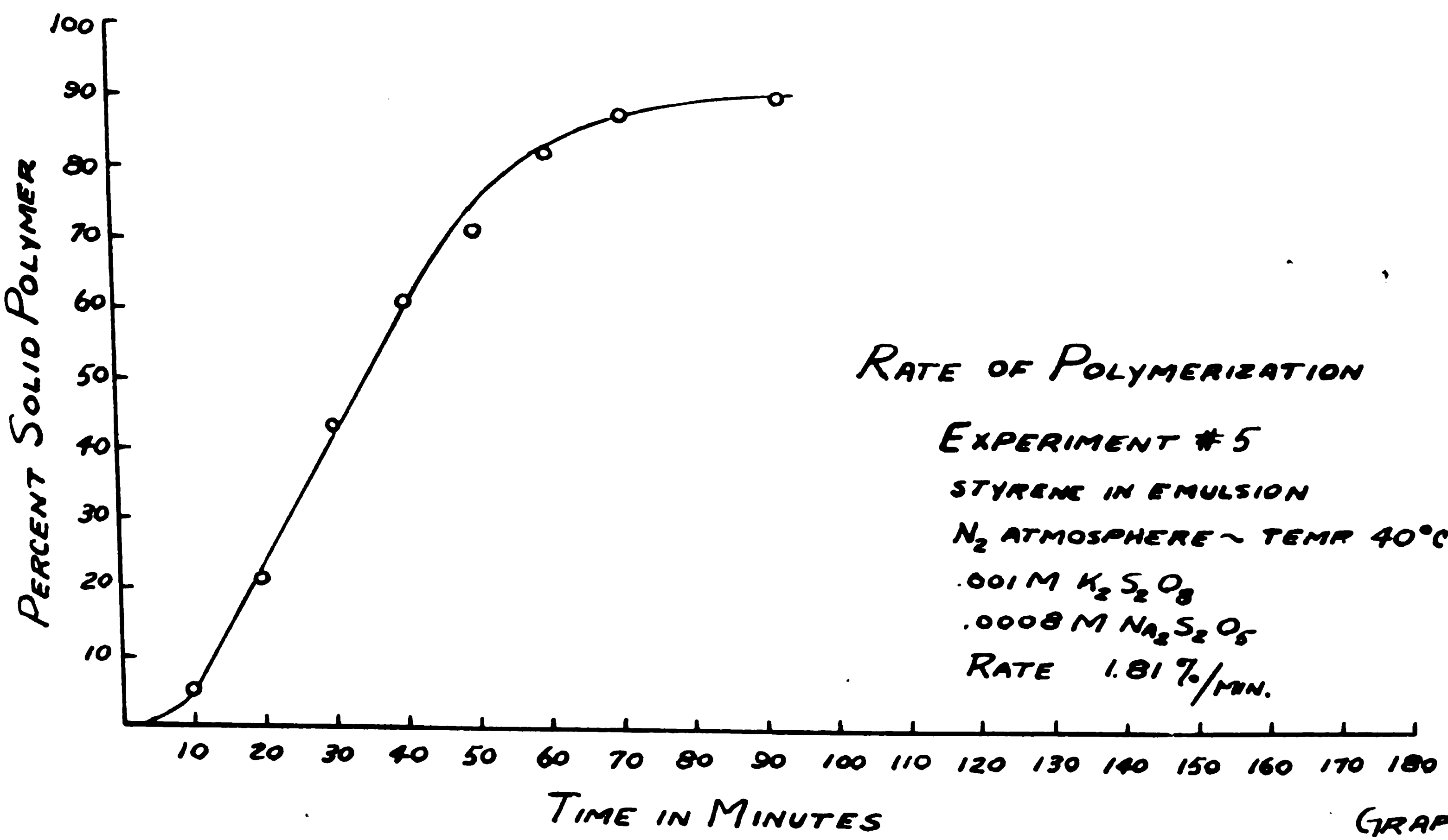
N_2 ATMOSPHERE ~ TEMP. 40°C.

.001 M $K_2S_2O_8$

.00056 M $Na_2S_2O_5$

RATE 1.37 %/MIN.

GRAPH #4



RATE OF POLYMERIZATION

EXPERIMENT # 5

STYRENE IN EMULSION

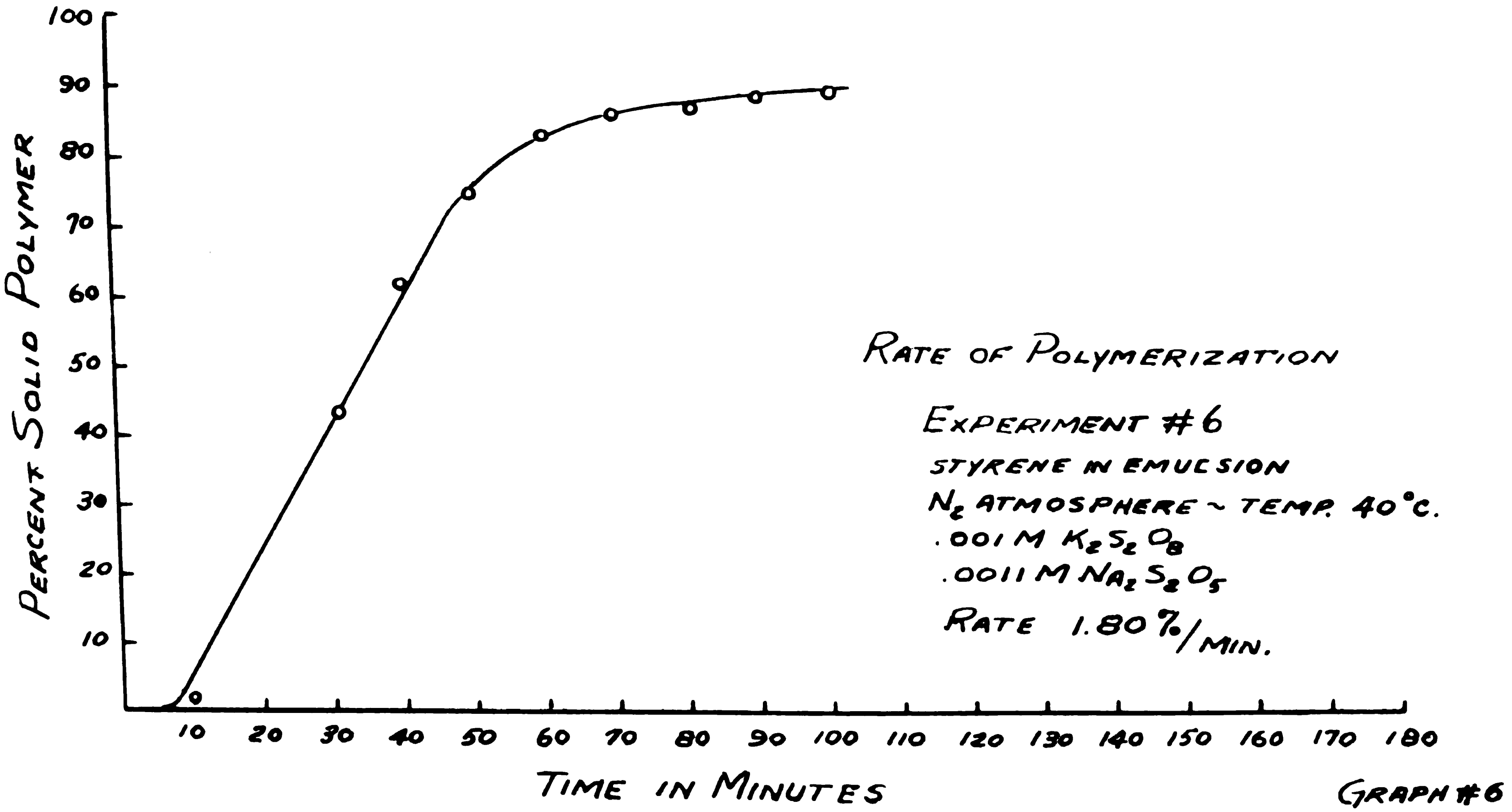
N_2 ATMOSPHERE ~ TEMP 40°C.

.001 M $K_2S_2O_8$

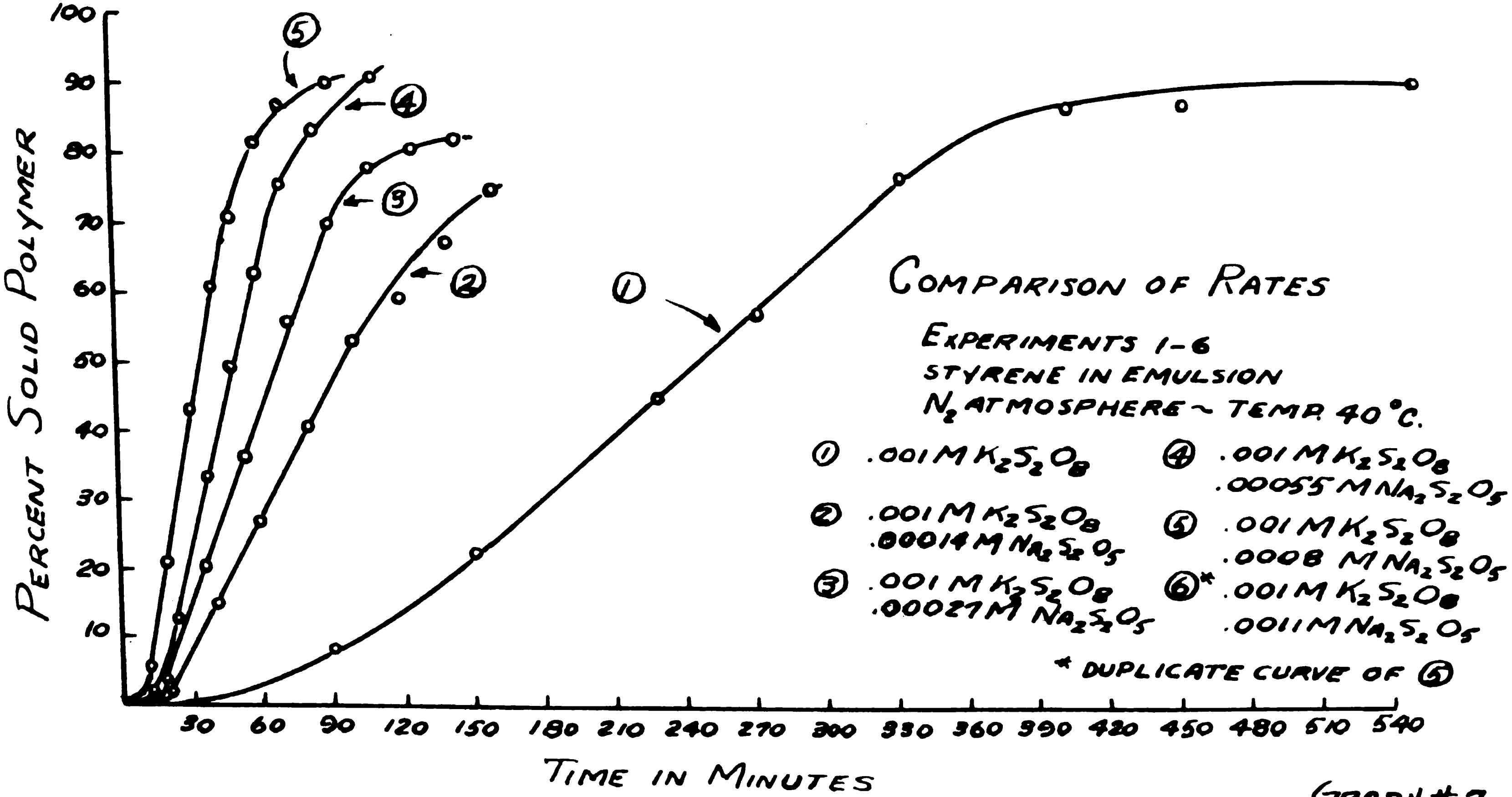
.0008 M $Na_2S_2O_5$

RATE 1.81 %/MIN.

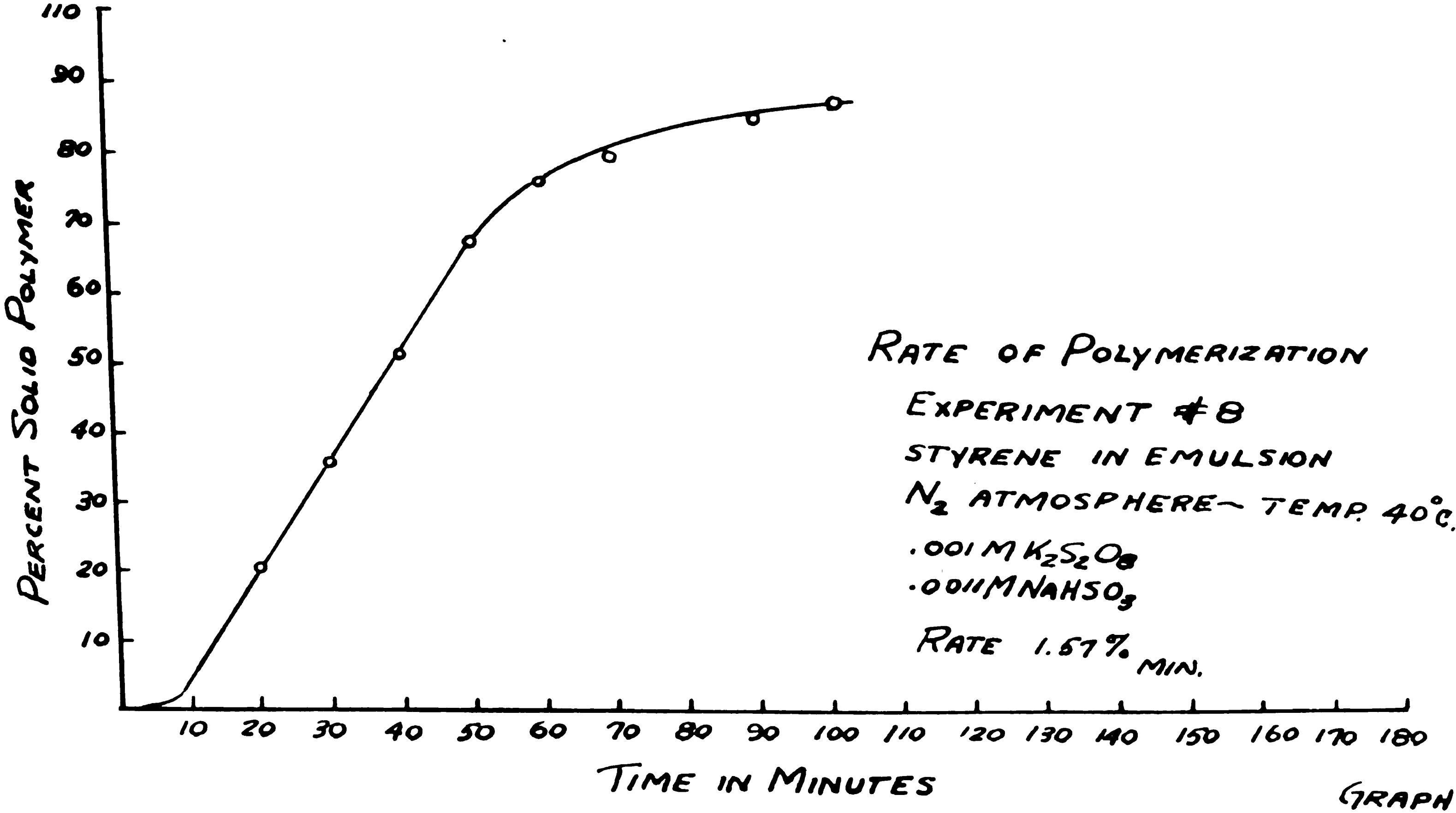
GRAPH # 5


RATE OF POLYMERIZATION
EXPERIMENT #6
STYRENE IN EMULSION
N_2 ATMOSPHERE ~ TEMP. 40 °C.
.001 M $K_2S_2O_8$
.0011 M $Na_2S_2O_5$
RATE 1.80 %/MIN.
PERCENT SOLID POLYMER
100
90
80
70
60
50
40
30
20
10
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
TIME IN MINUTES

GRAPH #6


COMPARISON OF RATES
EXPERIMENTS 1-6
STYRENE IN EMULSION
N_2 ATMOSPHERE ~ TEMP. 40 °C.
① .001 M $K_2S_2O_8$
② .001 M $K_2S_2O_8$ .00014 M $Na_2S_2O_5$
③ .001 M $K_2S_2O_8$ .00027 M $Na_2S_2O_5$
④ .001 M $K_2S_2O_8$ .00055 M $Na_2S_2O_5$
⑤ .001 M $K_2S_2O_8$ .0008 M $Na_2S_2O_5$
⑥* .001 M $K_2S_2O_8$ .0011 M $Na_2S_2O_5$
* DUPLICATE CURVE OF ⑤
PERCENT SOLID POLYMER
10
20
30
40
50
60
70
80
90
100
TIME IN MINUTES
30
60
90
120
150
180
210
240
270
300
330
360
390
420
450
480
510
540
①
②
③
④
⑤

GRAPH #7



Rate of Polymerization

Experiment #8

Styrene in Emulsion

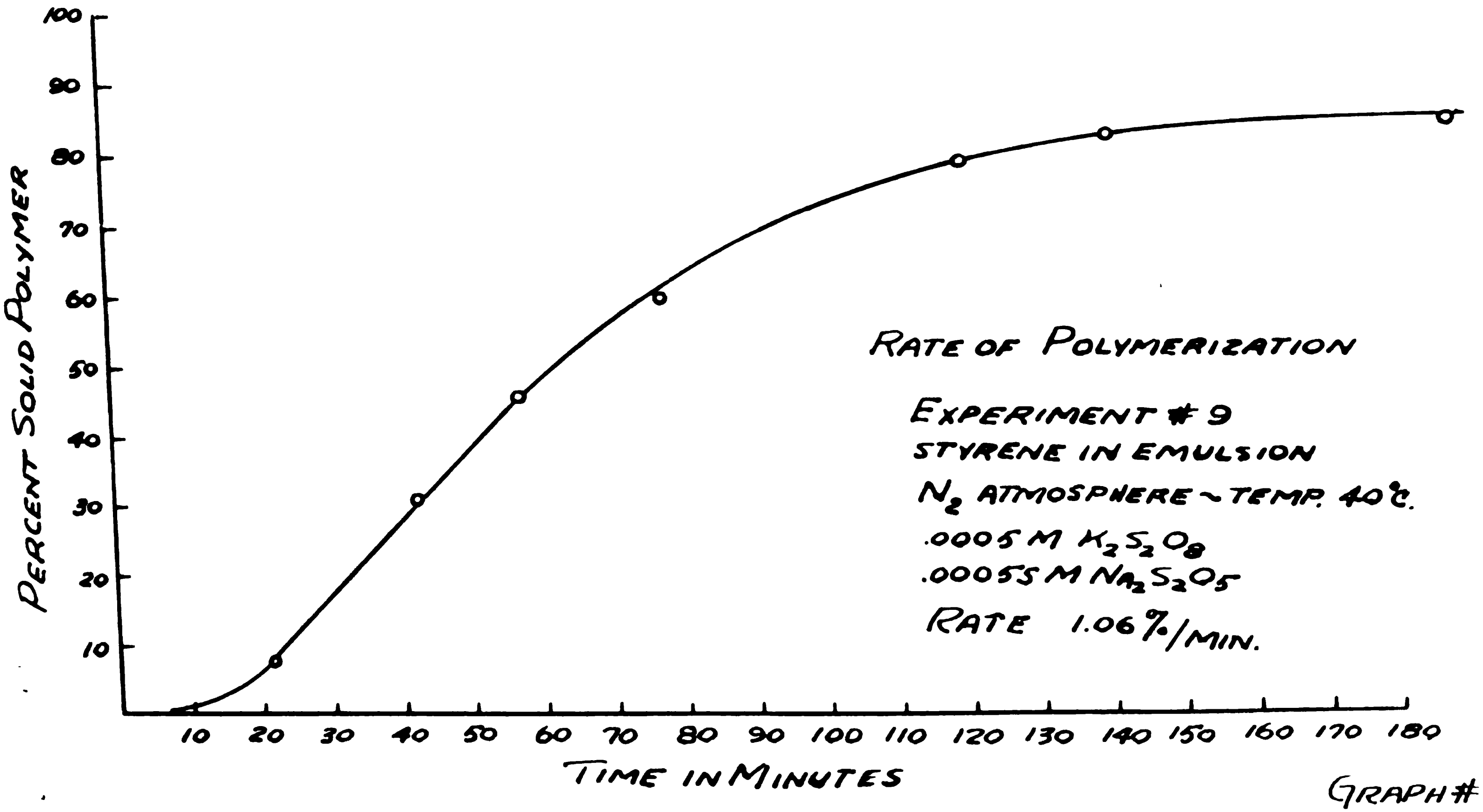
N_2 Atmosphere ~ Temp. 40°C.

.001 M $K_2S_2O_8$

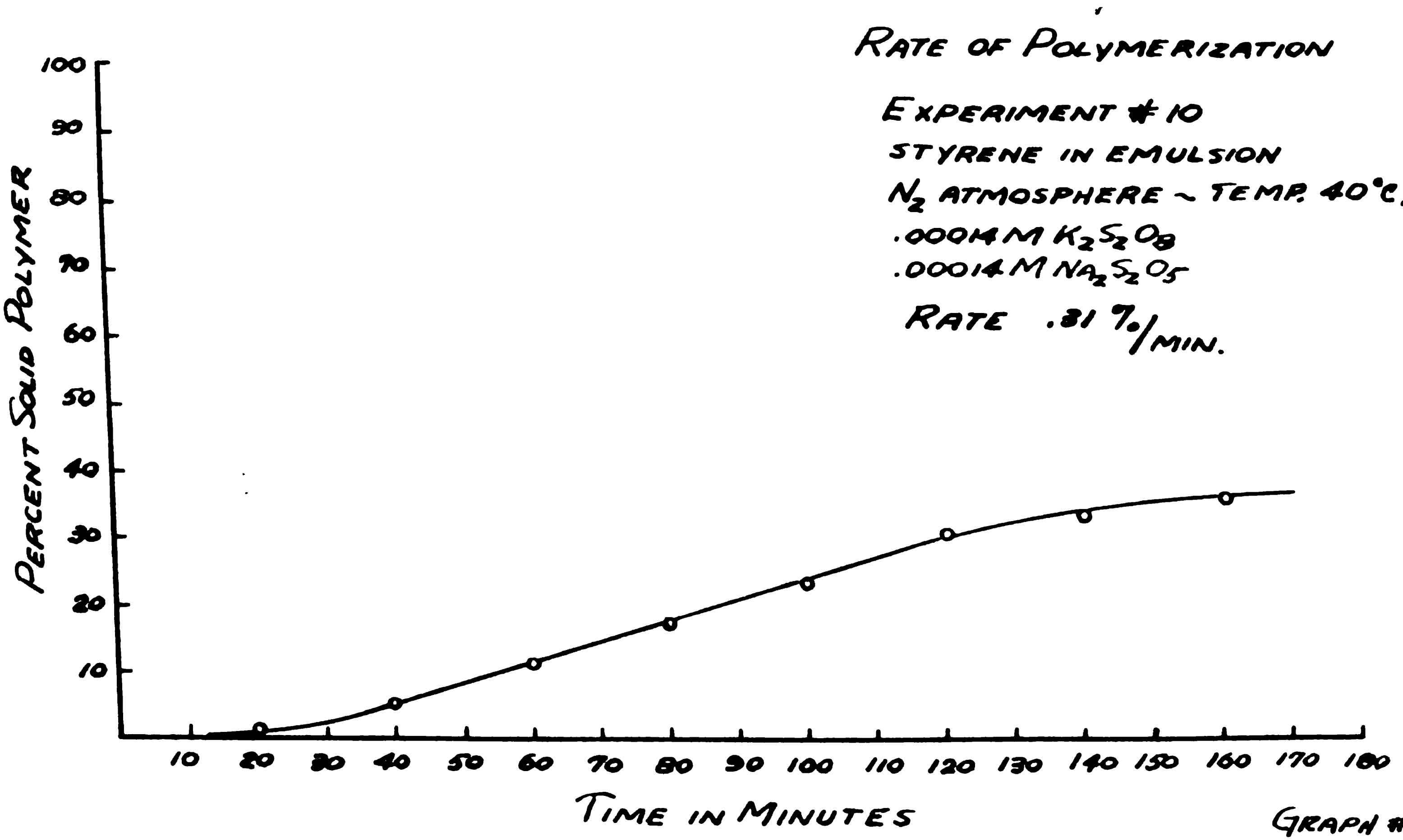
.0011 M $NaHSO_3$

Rate 1.57% min.

Graph #8


RATE OF POLYMERIZATION
EXPERIMENT # 9
STYRENE IN EMULSION
N_2 ATMOSPHERE ~ TEMP. 40°C.
.0005 M $K_2S_2O_8$
.00055 M $Na_2S_2O_5$
RATE 1.06%/MIN.
PERCENT SOLID POLYMER
100
90
80
70
60
50
40
30
20
10
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
TIME IN MINUTES

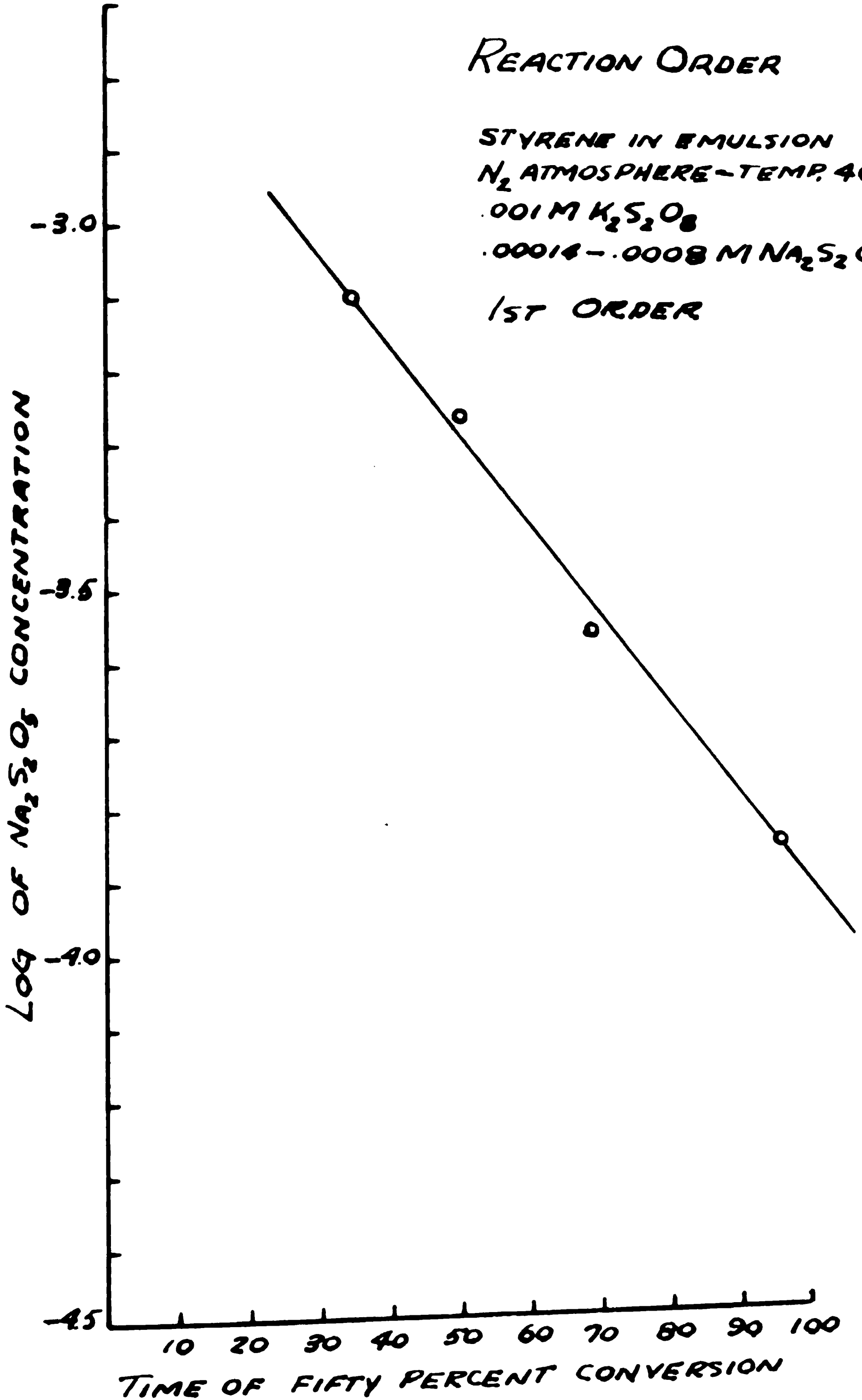
GRAPH # 9



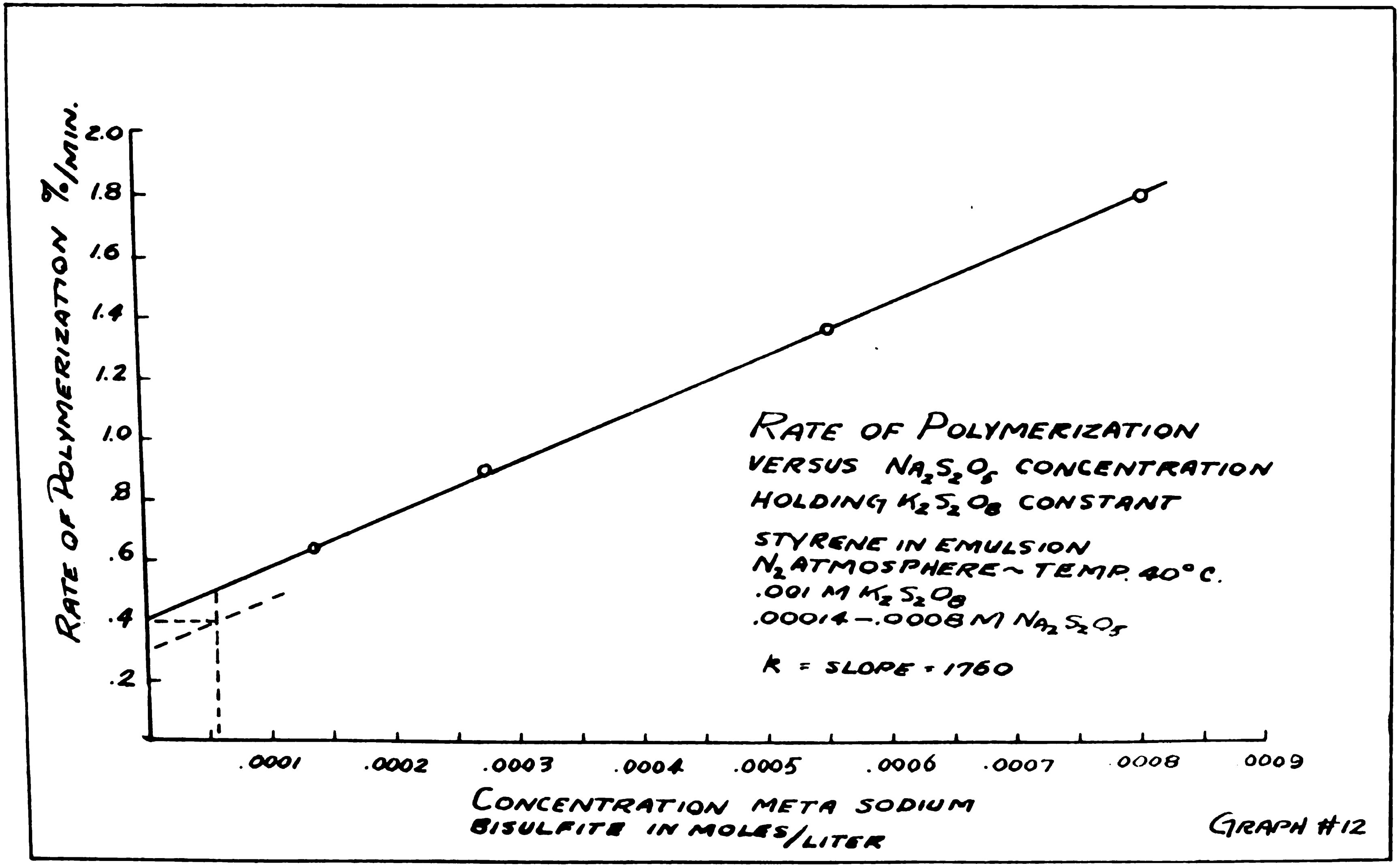
RATE OF POLYMERIZATION

EXPERIMENT # 10
STYRENE IN EMULSION
N_2 ATMOSPHERE ~ TEMP. 40°C.
.00014 M $K_2S_2O_8$
.00014 M $Na_2S_2O_5$
RATE .31 %/MIN.

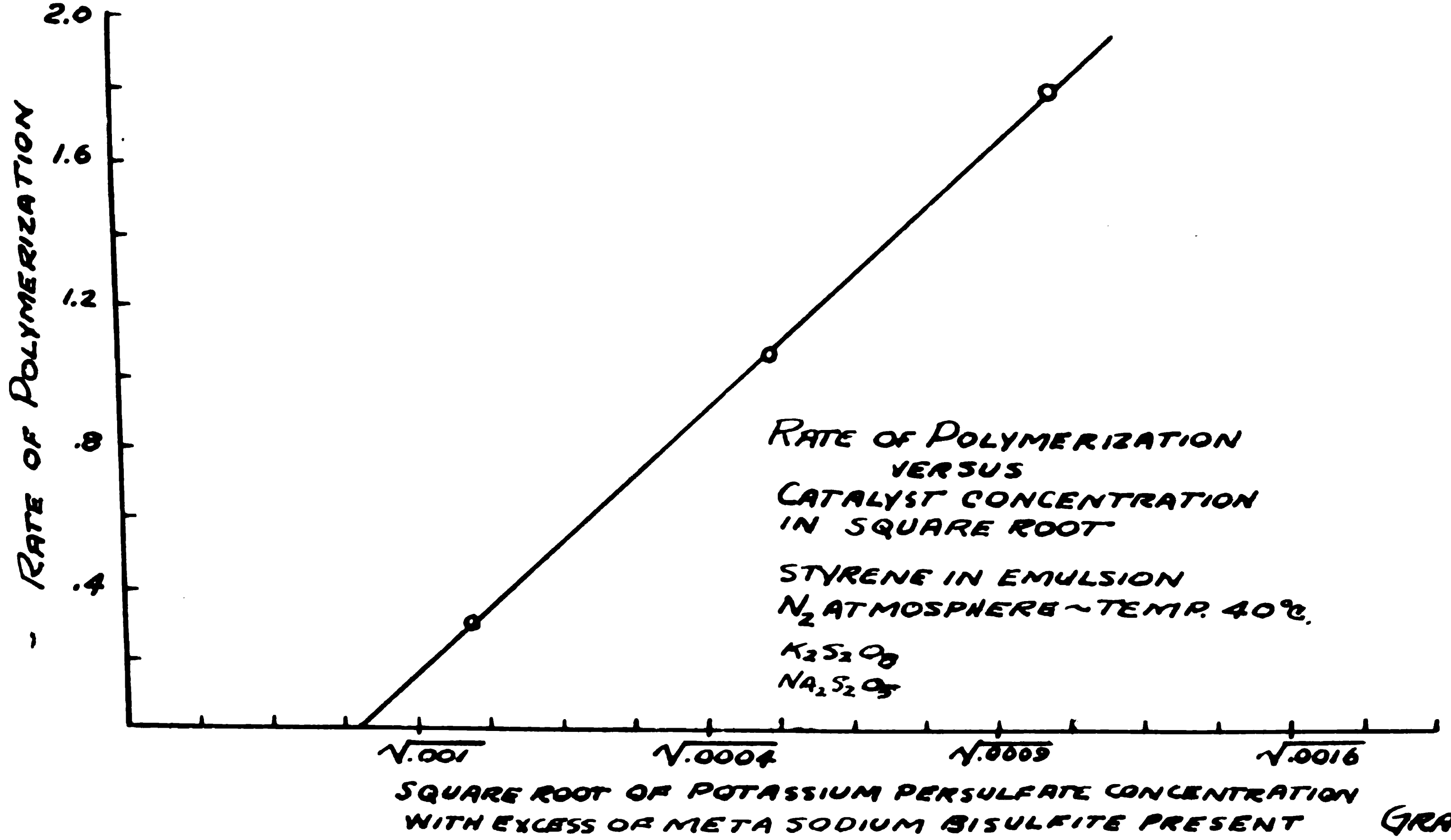
GRAPH # 10


REACTION ORDER
STYRENE IN EMULSION
N_2 ATMOSPHERE – TEMP. 40°C.
.001 M $K_2S_2O_8$
.00014 – .0008 M $Na_2S_2O_5$
1st ORDER
-3.0
-3.5
-4.0
-4.5
LOG OF $Na_2S_2O_5$ CONCENTRATION
10
20
30
40
50
60
70
80
90
100
TIME OF FIFTY PERCENT CONVERSION

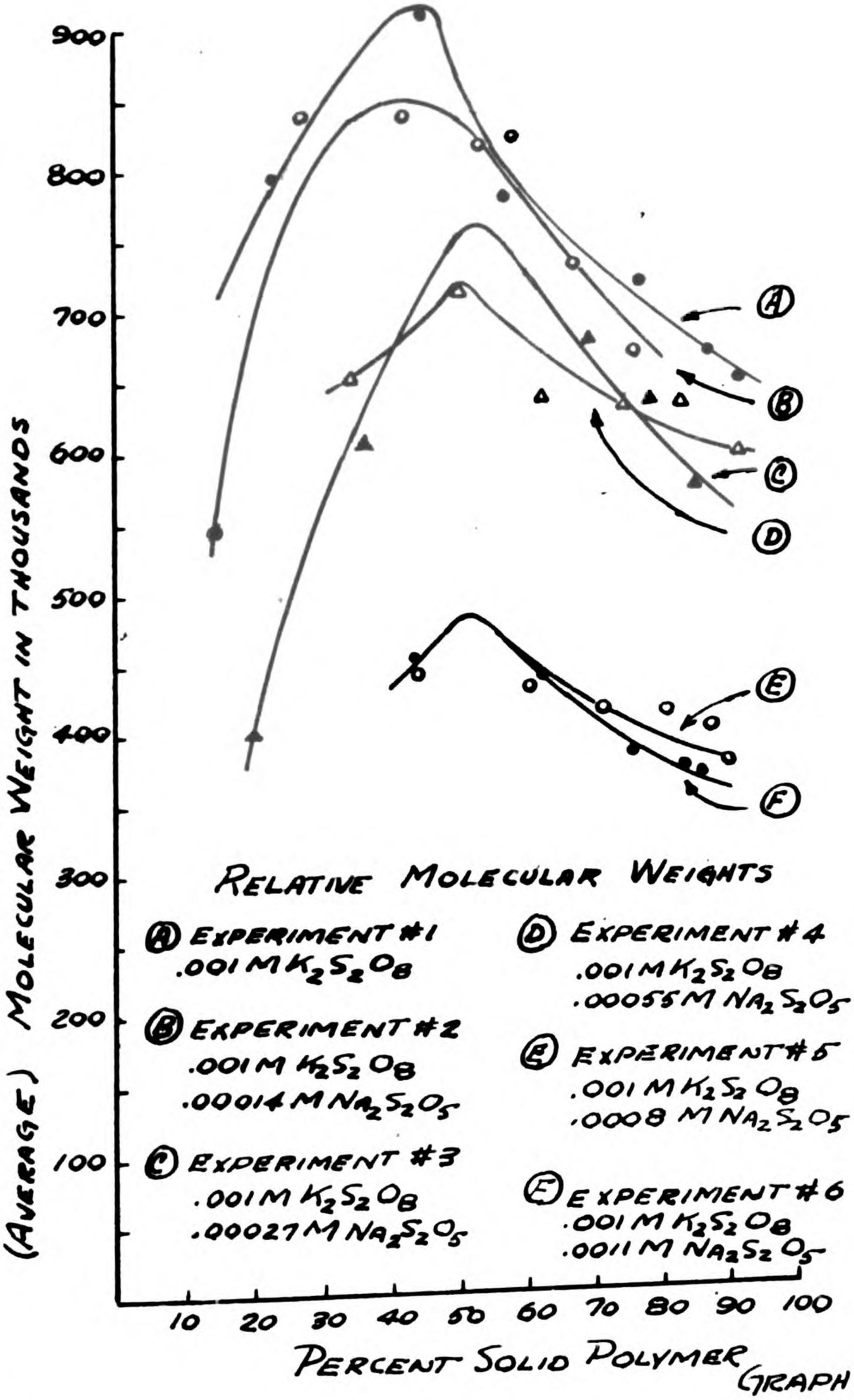
GRAPH # 11


RATE OF POLYMERIZATION
VERSUS $Na_2S_2O_5$ CONCENTRATION
HOLDING $K_2S_2O_8$ CONSTANT
STYRENE IN EMULSION
N_2 ATMOSPHERE ~ TEMP. 40° C.
.001 M $K_2S_2O_8$
.00014 -.0008 M $Na_2S_2O_5$
k = SLOPE = 1760
RATE OF POLYMERIZATION %/MIN.
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
.0001
.0002
.0003
.0004
.0005
.0006
.0007
.0008
.0009
CONCENTRATION META SODIUM
BISULFITE IN MOLES/LITER

GRAPH #12

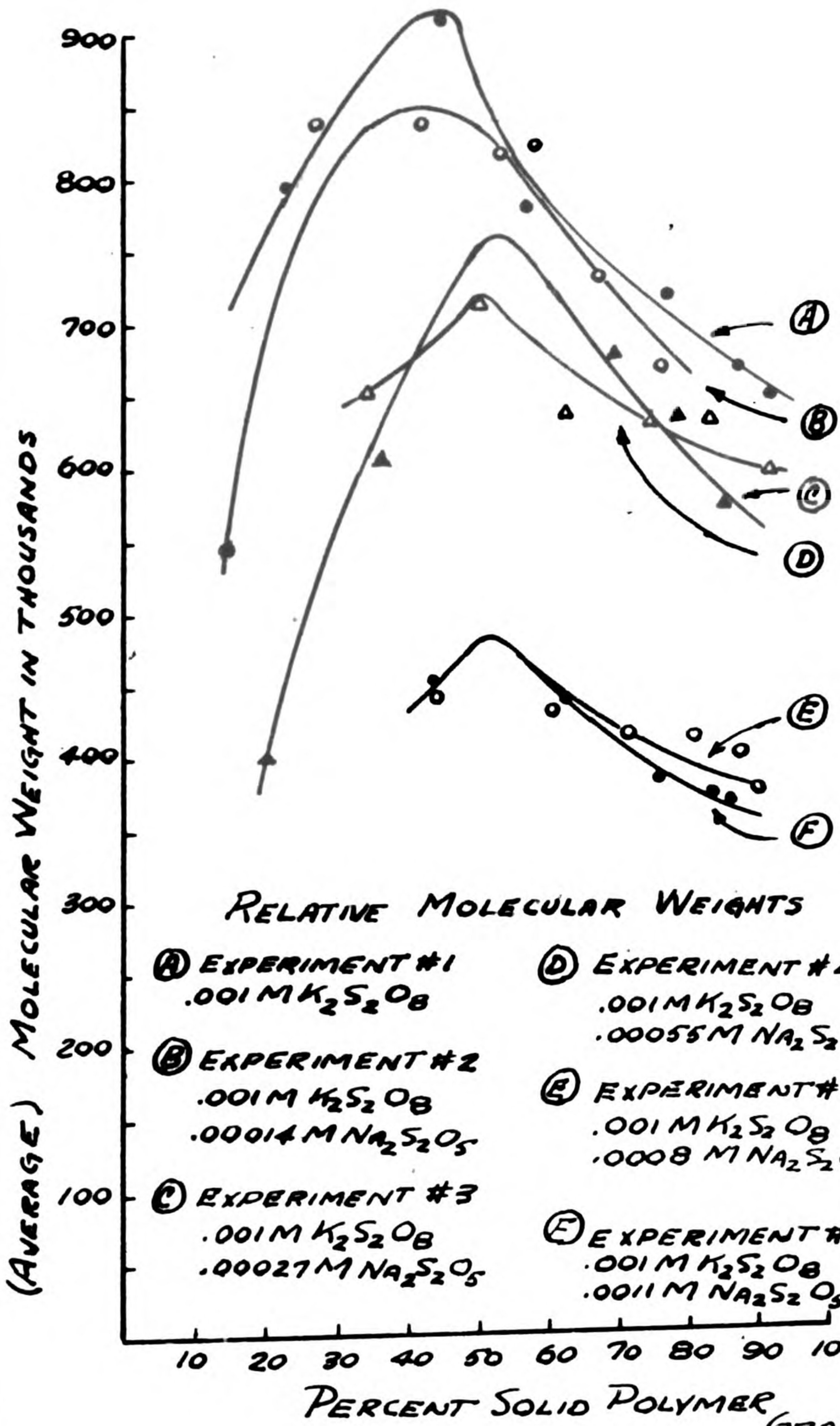

Rate of Polymerization
2.0
1.6
1.2
.8
.4
√.001
√.0004
√.0009
√.0016
Square root of potassium persulfate concentration with excess of meta sodium bisulfite present
Rate of Polymerization versus Catalyst concentration in square root
Styrene in emulsion
N_2 atmosphere ~ Temp. 40°C.
$K_2S_2O_8$
$Na_2S_2O_5$

Graph #13

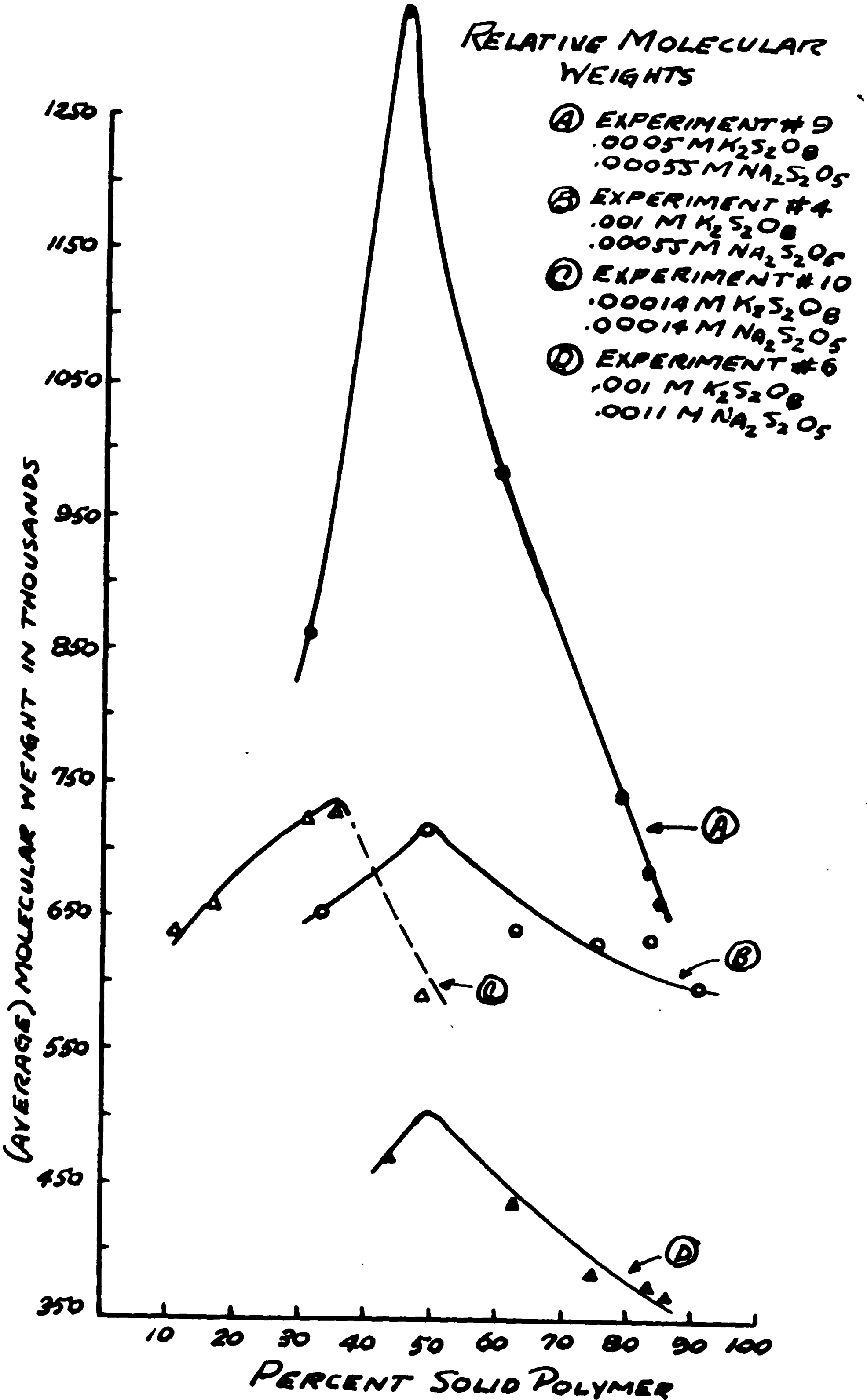


RELATIVE MOLECULAR WEIGHTS

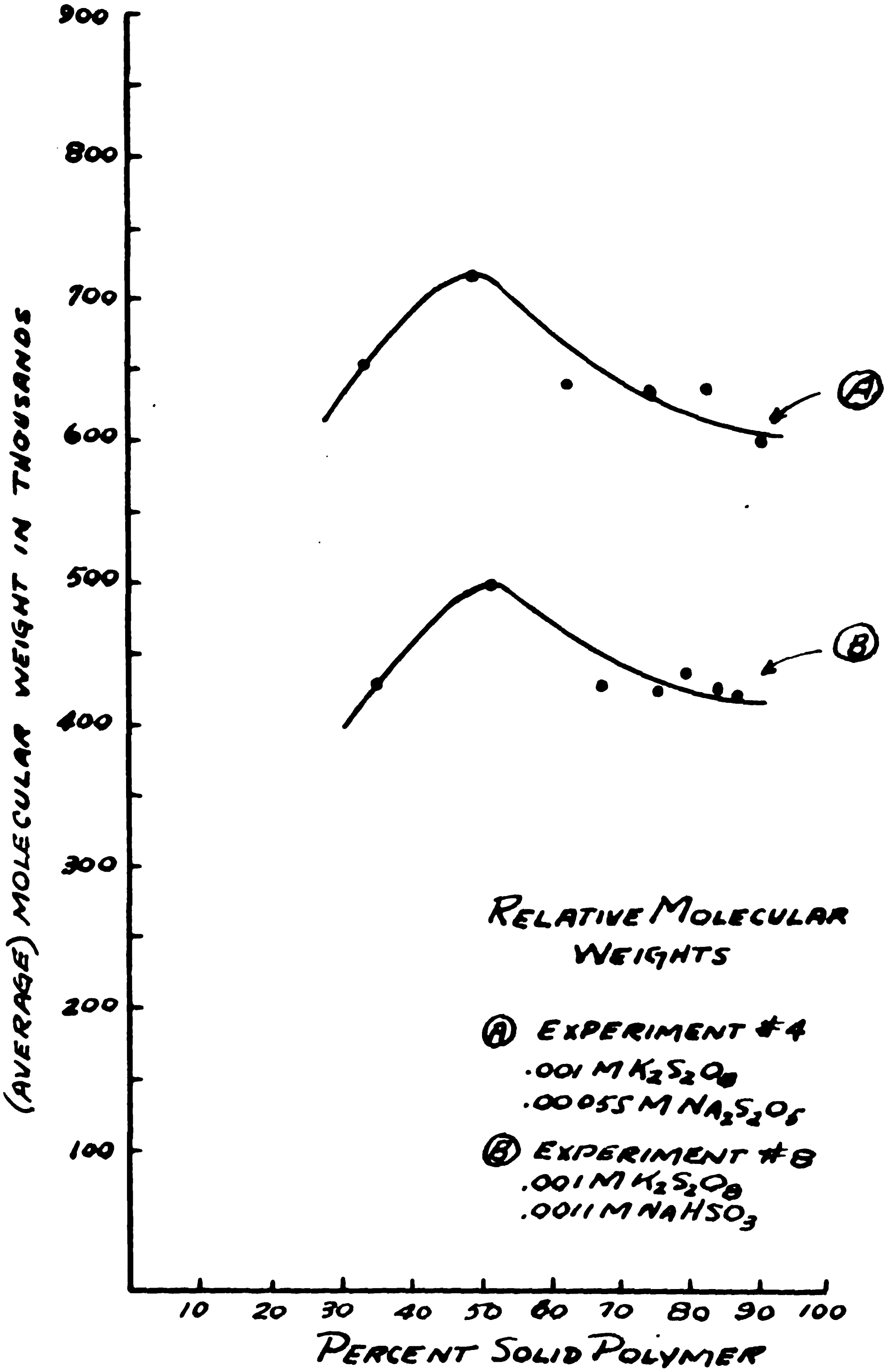
GRAPH #14


RELATIVE MOLECULAR WEIGHTS
(AVERAGE) MOLECULAR WEIGHT IN THOUSANDS
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
90
100
PERCENT SOLID POLYMER
Ⓐ
Ⓑ
Ⓒ
Ⓓ
Ⓔ
Ⓕ
Ⓐ EXPERIMENT #1
.001 M $K_2S_2O_8$
Ⓑ EXPERIMENT #2
.001 M $K_2S_2O_8$
.00014 M $Na_2S_2O_5$
Ⓒ EXPERIMENT #3
.001 M $K_2S_2O_8$
.00027 M $Na_2S_2O_5$
Ⓓ EXPERIMENT #4
.001 M $K_2S_2O_8$
.00055 M $Na_2S_2O_5$
Ⓔ EXPERIMENT #5
.001 M $K_2S_2O_8$
.0008 M $Na_2S_2O_5$
Ⓕ EXPERIMENT #6
.001 M $K_2S_2O_8$
.0011 M $Na_2S_2O_5$

GRAPH #14


RELATIVE MOLECULAR WEIGHTS
Ⓐ EXPERIMENT # 9
.0005 M $K_2S_2O_8$
.00055 M $NA_2S_2O_5$
Ⓑ EXPERIMENT # 4
.001 M $K_2S_2O_8$
.00055 M $NA_2S_2O_5$
Ⓒ EXPERIMENT # 10
.00014 M $K_2S_2O_8$
.00014 M $NA_2S_2O_5$
Ⓓ EXPERIMENT # 6
.001 M $K_2S_2O_8$
.0011 M $NA_2S_2O_5$
(AVERAGE) MOLECULAR WEIGHT IN THOUSANDS
1250
1150
1050
950
850
750
650
550
450
350
10
20
30
40
50
60
70
80
90
100
PERCENT SOLID POLYMER
Ⓐ
Ⓑ
Ⓒ
Ⓓ

GRAPH # 15


RELATIVE MOLECULAR WEIGHTS
Ⓐ EXPERIMENT #4
$.001\ M\ K_2S_2O_8$
$.00055\ M\ NA_2S_2O_5$
Ⓑ EXPERIMENT #8
$.001\ M\ K_2S_2O_8$
$.0011\ M\ NAHSO_3$
(AVERAGE) MOLECULAR WEIGHT IN THOUSANDS
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
90
100
PERCENT SOLID POLYMER
Ⓐ
Ⓑ

GRAPH #16

DISCUSSION

A series of reaction rate curves were obtained for the redox catalyzed polymerization by plotting percent solid polymer versus time of reaction for each of the experiments. (See Graphs 1-10.) The portion of the curve that is a straight line function represents the true rate of polymerization. In all cases the straight line function is preceded by a curve representing an induction period caused by inhibiting oxygen and other impurities. All polymerization rates in this work were obtained by evaluating the slopes of the straight line portion of these curves.

The polymerization rate of styrene, catalyzed by persulfate (.001 M) in the absence of bisulfite and polymerized under the conditions specified in the experimental part of this paper, was .30% per minute. (Graph #1.) Adding meta bisulfite to the above system reduced the induction period and increased the rate of polymerization. Varying the meta bisulfite concentration from .00014 M to .0008 M increased the polymerization rate from .64% per minute to 1.80% per minute. (See Graph #7.) Further increases above .0008 M meta bisulfite had no effect on the polymerization rate. (See Graph #6.)

To determine the reaction order, certain functions of meta bisulfite concentration were plotted against time of 50% polymerization, thus drawing an analogy to plotting the time of half-life of a reaction to determine reaction order.[36] The plot, log concentration meta bisulfite versus time of 50% polymerization produced a straight line indicating a first order reaction. (See Graph #11.)

The reaction being of first order, the graph of the rate of polymerization versus concentration of meta bisulfite is a straight line in accord with the equation

$$-\frac{dM}{dt} = k(c) + C$$

$-\frac{dM}{dt}$ = rate of disappearance of monomer after induction period

k = slope of line (constant)

c = concentration of meta bisulfite

C = Y intercept (variable constant)

(See Graph #12.)

From the graph the value of 1760 determined by the slope of the line is equal to k, and .4 determined by the Y intercept of the line is equal to C. The value of C should equal the rate of polymerization initiated by .001 M potassium persulfate in the absence of meta bisulfite. This value determined experimentally was .30% per minute. (See Graph #1.) The difference may be attributed to either one or both of two factors - experimental error or a minimum limit of meta bisulfite that must be necessarily present to produce a point on the line. The fact that the .001 M persulfate catalyzed polymerization reaction has been duplicated by this writer and the fact that all of the other rates when plotted against the meta bisulfite concentration (Graph #12) lie very close to the straight line, would indicate a minimum limit of the order of .000055 M meta bisulfite. However, since slight experimental variations between individual polymerizations cannot be completely eliminated, it is impossible to definitely determine an absolute minimum limit of meta bisulfite concentration based on this work.

The expression developed for this series of curves may be written as follows:

$$\left(-\frac{dM}{dt}\right)_r = 1760(C_b) + \left(-\frac{dM}{dt}\right)_p + F$$

$-\frac{dM}{dt}$ = rate of disappearance of monomer after induction period

r = redox catalyzed

p = persulfate catalyzed

C_b = concentration of meta bisulfite. C_b cannot be in excess of the molar ratio eight to ten with persulfate.

F = constant that must be added resulting from the minimum limit of bisulfite necessary for equation to hold.

A check may be made on the above expression by changing the initial persulfate concentration. Using experiment #9 as an illustration, the rate of polymerization may be calculated in the following manner:

From Kolthoff's relationship

$$\frac{(.001\ M)^{\frac{1}{2}*}}{.30\%/\text{min.}} = \frac{(.0005\ M)^{\frac{1}{2}}}{\left(\frac{-dM}{dt}\right)_p}$$

$$\left(\frac{-dM}{dt}\right)_p = .21\%/\text{min.}$$

*(See Graph #1.)

Assuming the proportion of persulfate to meta bisulfite to yield a maximum rate remains the same

$$\frac{.001\ M\ K_2S_2O_8}{.0008\ M\ Na_2S_2O_5} = \frac{.0005\ M\ K_2S_2O_8}{.X\ M\ Na_2S_2O_5}$$

$$X = .0004M\ Na_2S_2O_5$$

The difference between .0004M and .00055 M meta bisulfite is in excess and has no effect on the rate.

$$\left(\frac{-dM}{dt}\right)_r = 1760(.0004) + .21\%/\text{minute} + F$$

$$\left(\frac{-dM}{dt}\right)_r = .92\%/\text{minute} + F$$

Adding .1% as was necessary in the original set of curves, the calculated rate becomes 1.02% per minute. The rate determined experimentally for this particular reaction was 1.06% per minute. (See Graph #9.)

To observe whether or not the persulfate in presence of excess meta bisulfite catalytic system still produces a polymerization rate proportional to the square root of persulfate concentration, graph #13 was made. It would appear that the polymerization rate does follow this relationship after a minimum limit of .000064 M potassium persulfate when excess meta bisulfite is present. However, owing to the availability of only three points for the line, the writer suggests more research for confirmation.

Upon examination of the relative molecular weights of polymer obtained from the redox catalyzed polymerizations in which the persulfate concentration is held constant, it should be noted that increasing meta bisulfite concentration lowers the molecular weight. (See Graph #14.) A small excess of meta bisulfite above the concentration needed to produce a maximum rate of polymerization with a specified concentration of persulfate has no significant effect on the average molecular weight.

As would be expected, holding the meta bisulfite concentration constant and lowering the persulfate concentration, increases the molecular weight until a minimum limit of persulfate concentration is reached. (See Graph #15.) The reaction catalyzed by .00014 M persulfate with .00014 M meta bisulfite produces a lower molecular weight than that of .001 M persulfate with .00014 M meta bisulfite and .0005 M persulfate with .00055 M meta bisulfite catalyzed polymerizations.

The effect of temperature on rate of polymerization and average molecular weight of polymer can be observed by comparing this data obtained at 40°C and that obtained under the same conditions at 60°C by Yang.[2] In the .001 M persulfate catalyzed emulsion polymerization of styrene at 40°C, the rate of polymerization was .30% per minute and the average molecular weight approximately 800,000. Under the same conditions at 60°C the rate of polymerization was .82% per minute and the average molecular weight was approximately 300,000.

In the experimental procedure the writer mentioned that the method of titrating unreacted styrene reported by Mihina[4] and Hallenbeck[3] was tried unsuccessfully. The method involved mercuric acetate reacting with the double bond in styrene and liberating one mole of acetic acid per double bond. The acetic acid was then titrated with sodium hydroxide to determine the number of moles of styrene present. The difficulty in titrating the redox catalyzed polymerization reaction for unreacted styrene was that a constant blank could not be obtained for any one reaction. The redox apparently interfers with the titration.

Any attempt to explain the observed effect on polymerization of the redox system, persulfate and meta bisulfite, must be preceded by consideration of catalysis by persulfate. Yost and Russell[37] show that hydrogen peroxide can be manufactured from the breakdown of persulfate and that the intermediate product is Caro's acid (per monosulfuric acid). This breakdown may be expressed in equation form as follows:

$$S_2O_8^{=} + HOH \rightarrow SO_4^{=} + SO_5^{=} + 2H^{+}$$

$$SO_5^{=} + HOH \rightarrow SO_4^{=} + 2\ HO\cdot$$

$$HO\cdot \quad M \quad HOM\cdot$$

The $SO_5^{=}$ ion may go through an intermediate such as follows:

$$\begin{array}{l} SO_5^{=} + HOH \rightarrow SO_4^{-\cdot} + HO\cdot + HO^{-} \\ SO_4^{-\cdot} + HOH \rightarrow SO_4^{=} + HO\cdot + H^{+} \\ \hline SO_5^{=} + HOH \rightarrow SO_4^{=} + 2HO\cdot \end{array}$$

If it is felt that the breakdown through the Caro's acid intermediate is too slow, the reaction may be expressed in this manner:

$$\begin{array}{l} S_2O_8^{=} + HOH \rightarrow SO_4^{=} + SO_4^{-\cdot} + H^{+} + HO\cdot \\ SO_4^{-\cdot} + HOH \rightarrow SO_4^{=} + HO\cdot + H^{+} \\ \hline S_2O_8^{=} + 2HOH \rightarrow 2SO_4^{=} + 2H^{+} + 2HO\cdot \end{array}$$

$$HO\cdot + M \rightarrow HOM\cdot$$

or

$$S_2O_8^{=} \rightarrow 2SO_4^{\bar{\cdot}}$$

$$SO_4^{\bar{\cdot}} + HOH \rightarrow SO_4^{=} + H^{+} + HO\cdot$$

$$HO\cdot + M \rightarrow HOM\cdot$$

In any case the initiation is assumed to be primarily by the hydroxyl free radical and the remainder by the negative sulfate radicals liberated in the above equations.

Having outlined the possible breakdown of persulfate, consideration is now in order of the active ions or molecules in the persulfate-meta bisulfite redox system. Bisulfite is acid and a possibility existed that the observed increase in rate of polymerization was due to a pH effect. This possibility was ruled out by experiment #7 (persulfate-sodium bisulfate as catalyst and pseudo promoter), since the rate of polymerization by experimental determination was neither increased nor decreased from the rate of neutral persulfate initiated polymerization. Bacon[25] has shown in his work that sodium sulfite and persulfate together will not increase the polymerization rate in acrylonitrile over persulfate initiated polymerization unless the concentration of sodium sulfite is low enough to permit an acid medium to exist. Bacon's and my work indicate that the active reducing agent is either the bisulfite ions, pyrosulfite ions or sulfurous acid molecules. To test the possibility of pyrosulfite ions being the active ingredient, a run was made using persulfate and sodium bisulfite to provide the initiator, the concentrations of which were equivalent to those in experiment #4. The rate of the persulfate-bisulfite catalyzed polymerization was 1.57% per minute. The rate in the case of persulfate-meta bisulfite catalysis was 1.37% per minute. It should also be noted that the induction period was noticeably longer and molecular weight was slightly higher (See

Graph #16) for the persulfate-meta bisulfite system. These facts further indicate that the bisulfite ions or sulfurous acid molecules were the active reducing particles in the redox as both bisulfite and pyrosulfite ions are available from meta bisulfite. The pyrosulfite ions are available from bisulfite in only an extremely acid medium. The small difference in rate, the noticeable difference in induction period, and the increased molecular weight may be attributed to the hydrolysis rate of the pyrosulfite ions to bisulfite ions or sulfurous acid molecules.

The writer favors sulfurous acid molecules as being the active reducing agent because an increasing pH value is noted in most cases of the persulfate-meta bisulfite redox catalysis. The decreased acidity is probably caused by the hydrolysis of the sodium bisulfite to sulfurous acid and sodium hydroxide.

From the conclusions drawn thus far, the writer postulates the following possible mechanisms:

1) $S_2O_8^{=} + HOH \rightarrow SO_5^{=} + SO_4^{=} + 2H^{+}$

$$SO_5^{=} + H_2SO_3 \rightarrow S_2O_6^{=} + 2HO\cdot$$

$$HO\cdot + M \rightarrow HOM\cdot$$

The intermediate steps for the reaction between $SO_5^{=}$ and sulfurous acid are probably

$$\begin{array}{llll} SO_5^{=} + H_2SO_3 & \rightarrow & SO_4^{\overline{\cdot}} + HO\cdot + HSO_3^{-} \\ SO_4^{\overline{\cdot}} + H_2SO_3 & \rightarrow & S_2O_6^{=} + HO\cdot + H^{+} \\ \hline SO_5^{=} \quad H_2SO_3 & & S_2O_6^{=} \quad 2HO\cdot \end{array}$$

2) $S_2O_8^{=} \rightarrow 2SO_4^{\overline{\cdot}}$

$$SO_4^{\overline{\cdot}} + H_2SO_3 \rightarrow S_2O_6^{=} + HO\cdot + H^{+}$$

$$HO\cdot + M \rightarrow HOM\cdot$$

Mechanisms 1 and 2 would require one and two moles of sulfurous acid respectively to react with one mole of persulfate. Actually three-quarters of a mole of meta bisulfite, capable in theory of producing one and one-half moles of sulfurous acid, was required to produce the fastest rate of polymerization with one mole of persulfate catalyst. The fact that some of the pyrosulfite ions may not completely dissociate to bisulfite ions and the bisulfite ions do not completely associate into sulfurous acid molecules would indicate that mechanism 1 is the probable reaction. On the other hand, it is impossible to tell how many $SO_4^{-}\cdot$ radicals initiate polymerization by reaction with monomer directly. Therefore it is a matter of individual preference at to which mechanism is the more logical. The important fact is that the persulfate and meta bisulfite redox system yields dithionate $S_2O_6^{=}$ ions and hydroxyl radicals,[38] the latter of which initiates polymerization.

Bacon[25] also found that thiosulfate-persulfate catalyzed polymerization took place in only an acid medium and accompanied by an increasing pH value. This may be accounted for by the fact that thiosulfate is quite readily decomposed in a dilute acid medium to the bisulfite ion.[37a]

$$S_2O_3^{=} + H^{+} \rightarrow HSO_3^{-} + S$$

Another reducing agent used by Bacon in his redox catalysis with persulfate was hyposulfite. Yost and Russell[37b] show that hyposulfite is quite readily hydrolyzed to bisulfite ions.

$$2S_2O_4^{=} + HOH \rightarrow 2HSO_3^{-} + S_2O_3^{=}$$

$$S_2O_3^{=} + H^{+} \rightarrow HSO_3^{-} + S$$

The writer has presented these last two examples to bring more bearing on the fact that the probable active reducing particle is the sulfurous acid molecule. Potassium persulfate, possibly through the

Caro's acid intermediate, reacts much faster with sulfurous acid to produce hydroxyl free radicals than it will hydrolyze with water to produce them. These hydroxyl free radicals in turn initiate the polymerization reaction; however, it should be understood that some of the initiation can be attributed to the $SO_4^{\overline{\cdot}}$ radical attacking the monomer.

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37a) Yost, D.M., and Russell, H., ibid, p. 389.

37b) Yost, D.M., and Russell, H., ibid, p. 354.

38) Ephriam, F., "Inorganic Chemistry", Nordeman Publishing Co., Inc., New York, 1948, p. 570.

SUMMARY

1) The polymerization rate of styrene in emulsion catalyzed by potassium persulfate is sharply increased by the addition of meta sodium bisulfite.

2) The molar ratio of meta sodium bisulfite to potassium persulfate that produces the maximum rate of polymerization was found to be eight to ten.

3) A theoretical expression was derived for the polymerization rate of styrene in emulsion, catalyzed by the potassium persulfate-meta sodium bisulfite redox system, under the conditions specified in the experimental part of this paper.

$$\left(\frac{-dM}{dt}\right)_r = 1760(C_b) + \left(\frac{-dM}{dt}\right)_p + F$$

4) The rate of the emulsion polymerization of styrene catalyzed by potassium persulfate in presence of excess meta sodium bisulfite, is proportional to the square root of the persulfate concentration. There appears to be a minimum limit of persulfate concentration for this expression to hold.

5) The average molecular weight of the polystyrene formed decreases with increasing rate of polymerization if the persulfate concentration is held constant in the meta sodium bisulfite-potassium persulfate redox catalyzed polymerization of styrene.

6) Probably mechanisms for the redox, persulfate-meta bisulfite, initiation of polymerization have been cited.