EMULSION POLYMERIZATION OF STYRENE: ALCOHOLS AS DEACTIVATION AGENTS

Thesis for the Degree of M. S.
MICHIGAN STATE COLLEGE
Joseph Stephen Mihina
1948

This is to certify that the

thesis entitled

"Emulsion Polymerization of Styrene: Alcohols as Deactivation Agents"

presented by

Joseph S. Mihina

has been accepted towards fulfillment
of the requirements for

M.S. degree in Chemistry

Ralph L. Guile
Major professor

Date May 27, 1948

M-795

EMULSION POLYMERIZATION OF STYRENE:
ALCOHOLS AS DEACTIVATION AGENTS

By

JOSEPH STEPHEN MIHINA

A THESIS

Submitted to the School of Graduate Studies of Michigan
State College of Agriculture and Applied Science
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry

1948

ACKNOWLEDGMENT

The writer wishes to express his appreciation to Doctor Ralph L. Guile, for his counsel and guidance.

****
******
****
**
*

INTRODUCTION

Polymerization proceeding in a homogenous phase, such as in bulk or solution, is not as complicated as that in heterogeneous phase as examplified by suspension or emulsion polymerization.

There are many factors which can complicate an emulsion polymerization, such as the type of monomer, character of the aqueous phase, emulsifier, type and purity of initiator, atmosphere, presence or absence of inhibitors, rate of stirring, temperature of reaction and many others which are dependent on the particular system studied. However, it is possible to make a study of the effect of varying a single factor in a system by keeping all other factors constant or reasonably so during the course of the reaction.

The systems studied in this paper are those of the emulsion polymerization of styrene where the atmosphere is varied using nitrogen, carbon dioxide, and a mixture of nitrogen and oxygen. The other variable factor was the composition of the aqueous phase which was varied by the addition of water soluble alcohols, such as methanol, ethanol, isopropanol and t-butanol.

HISTORICAL

Styrene, orginally obtained from natural sources, was observed to polymerize in the presence of light and heat by Simon[1]. This was the first observation of what later became known as "bulk" polymerization.

Berthelot[2] synthesized styrene from acetylene and benzene and found that it polymerized on standing.

Until recently, the major work in polymerizing styrene was carried out in bulk or in solution of styrene in carbon tetrachloride[10] and various hydrocarbons[11]. In these homogeneous phase reactions the polymerization was catalyzed by heat[3], light[4], salts, such as stannic chloride[5] or zinc chloride[6], alkali metals[7], ozone[8], and organic peroxides[9].

Early work on polymerization theory led Staudinger[12] to suggest that the process occurred in three steps; chain initiation, chain propagation, and chain termination. Shortly thereafter Whitby[3] suggested that polymerization was the stepwise addition of monomer to double bond, however, further studies of the mechanism and kinetics of polymerization led to the concept of the formation of active centers from which long polymer chains were formed[13]. A further modification of the latter theory is that of chain transfer in which growing chains transfer activation energy on collision, causing branching, and thereby termination of their own growth.

The molecular weight of the polymer at different stages of the reaction is significant for mechanism and rate studies. Many methods have been used to determine these molecular weights, the most important being osmotic[14], viscoscimetric[15], ultracentrifugal[16], and light scattering[17] all of which give values that are average molecular weights rather than absolute values. The viscoscimetric method for reasons of simplicity of equipment and operation is generally used for such molecular weight determinations. Staudinger[15a] developed an expression for molecular weight based on viscoscity which has generally been used in reporting average molecular weights.

The average molecular weight of the polymer at any stage of the reaction is fairly constant, a fact that has been explained by Schulz[18] as being due to a constant ratio of chain propagations to chain terminations throughout the course of polymerization.

Heterogeneous polymerization with particular reference to emulsion polymerization, was first studied in connection with synthetic rubber. It was observed that a monomer could be polymerized in an emulsion system to give a latex from which the polymer could be coagulated. Styrene latex prepared by the emulsion technique on coagulation gave a powder and not a rubber-like product[19]. Mark and co-workers[20] further developed the technique of emulsion polymerization and a theory of mechanism.

The emulsion system consists of aqueous phase, monomer, emulsifying agent, and initiator. It is preferred to use some sort of initiator due to the fact that polymerization takes place in a much shorter length of time, but in the cases of polymerization by light or heat it is omitted.

Hohenstein[20b] showed in an experiment that when styrene was placed in one container and water with initiator placed in another container, all under a single bell jar, polymerization occurred in the water. The explanation was advanced that styrene vapor diffused through the atmosphere and dissolved into the water whereupon polymerization took place. Further evidence that emulsion polymerization proceeds in the aqueous phase was given by Fryling[22] who showed that the monomer was solubilized by soap to give micelles in the aqueous phase prior to any polymer formation. This micellular theory was also used by Harkins[23] and Montroll[24], who further postulated that polymerization began in the aqueous phase and that, beyond approximately 20%, polymerization occurred in the polymer-monomer (latex) particles.

The kinetics and mechanism have been studied by many workers[25,24,15b,13a,c] and in general the theories state that the monomer is first solubilized and activated by reaction with salts, light, or heat. Thereafter the activated monomer reacts in any of a number of ways among which are; reaction with unactivated monomer leading to the formation of long chains, reaction with an impurity or solvent causing deactivation, and disproportionation resulting in deactivation.

Emulsion polymerizations generally have an induction period; this is the interval during which the activated monomers are reacting with inhibiting components until the latter are substantially neutralized, whereupon chain propagation becomes the predominant reaction. The inhibiting agent most commonly encountered is oxygen[26] but it has been shown that with proper care as to oxygen contamination and purity of the reagents used in polymerization, the induction period should approach zero[27]. Breitenboch[21] polymerized styrene using a nitrogen atmosphere to prevent oxygen inhibition.

The mechanisms proposed for chain termination reactions in emulsion polymerization include local exhaustion of monomer, disproportionation, reaction with solvent, and dissipation of activation energy[25c,d].

It has been found that activation energies for emulsion polymerizations are generally less than those for bulk polymerization[28,20a].

Although it is possible to use heat or light to initiate an emulsion polymerization, it is advantageous to use a water soluble per-salt or peroxide since the polymerization starts in the aqueous phase. Among the best salts are the salts of per-acids, such as potassium persulfate and sodium perborate[29], the former being more commonly used. Although the mechanism of persulfate activation has not been solved, it has been demonstrated that the concentration of persulfate decreases very slightly during the course of polymerization[30]. Price[25b] and Kolthoff[27,30a] have shown through a series of experiments that the rate of polymerization of styrene is dependent on the square root of the persulfate concentration. Yang[31] carried out polymerizations on a system similar to that used by the above authors, and his results showed the same relationship between persulfate concentration and rate of polymerization.

The inhibiting effect of oxygen, which has been mentioned previously, has received a great deal of attention. It has been reported that the inhibiting effect results from the reaction of oxygen with activated monomer to form peroxides[26,31] and polyperoxides in which the oxygen is actually a part of the polymer[32].

EXPERIMENTAL

Reagents:

Styrene -- The styrene obtained from Dow Chemical Company was vacuum distilled, and that fraction distilling at 41-43°C @ 14-16mm, or 55-58° C @ 30-33 mm, $n^{20} = 1.5444$, was used. The styrene was used immediately after distillation, or if not used the same day, it was stored in a refrigerator under nitrogen. It was not considered good practice to use styrene that was more than one day old even when kept in a refrigerator since low molecular weight polymers form and contaminate the monomer. A test made on styrene which had been stored in a refrigerator for approximately three months showed the presence of alcohol insoluble polymer.

Potassium Persulfate -- This salt was Merck's reagent grade which was recrystallized before being used in any reaction. It was noted that if the salt was taken directly from the bottle and dissolved, the pH reading of the solution was 3 while the recrystallized material when dissolved gave a pH reading of 7.0 ± 0.5. The lowered pH was believed to be due to the decomposition of the persulfate while in storage. An experiment conducted to determine the decomposition of potassium persulfate in solution showed that the pH decreased from 7 to 3 indicating that the persulfate as obtained from the stockroom was not pure enough to be used in polymerization reactions. The procedure for purification of the salt was to make a saturated solution of the salt in water at 25° C and then cooling it in an ice bath for one hour with intermittent stirring to prevent caking. The crystals were filtered, washed with cold water, and dried at room temperature.

Duponol-G — This was an emulsifying agent manufactured by duPont and described as "an organic alcohol amine sulfate", the particular alcohol being lauryl. The reagent was used without purification.

Water — The distilled water used was refluxed at least four hours with nitrogen bubbling through it to remove the dissolved oxygen. It was then distilled under nitrogen and kept under nitrogen until ready for use.

Methanol — Anhydrous Merck reagent grade was used (BP 64-65°C), after treating it in the above manner in order to eliminate or minimize the amount of dissolved oxygen.

Ethanol, USP 95% (BP76-77°C); *Isopropanol*, Eastman Kodax (BP 81½-82½°C); *t-Butanol*, Eastman Kodax (BP 81-82°C). These alcohols were also treated as described above.

Aluminum Chloride - Baker and Adamson reagent grade $AlCl_3.3H_2O$

Mercuric Acetate - J. T. Baker, C. P.

Carbon Tetrachloride - J. T. Baker, C. P.

Sodium Chloride - Baker and Adamson reagent grade.

The apparatus used for the polymerization reactions was adapted from that used by Price[25f] and previous workers in this laboratory[31,33]. It consisted of a four-necked flask with standard-taper ground glass joints and was fitted with a mercury-sealed stirrer, reflux condenser, thermometer, a tube for introducing gas into the system, and a tube that extended below the surface of the reaction for the purpose of sampling.

All reactions were conducted under a nitrogen atmosphere, except as designated, and at a constant temperature maintained by a water bath controlled to 60°C ± 0.2°. The nitrogen was passed through two gas absorption bottles containing alkaline pyrogallol to remove traces of oxygen.

The general formula for the emulsion system based on the aqueous phase before addition of monomer was:

1% emulsifier
one part monomer to nine parts aqueous phase
potassium persulfate to make 0.0017M.

When the aqueous phase consisted of water and alcohol, both the weight of the aqueous phase and the ratio of monomer to aqueous phase were maintained constant. The particular concentration of potassium persulfate used was chosen from Yang's[31] work since the resulting rate of reaction was convenient for sampling.

The emulsion was prepared by first weighing the emulsifying agent in the four-necked flask. The equipment was then assembled and flushed with nitrogen. A weighed amount of oxygen-free water was added to the flask followed by stirring in the constant temperature bath until the temperature reached 60°C. The potassium persulfate was added and, as soon as it dissolved, a weighed amount of styrene preheated to 60°C was introduced. The time of addition of the styrene was noted and recorded as zero time. The stirring in all experiments was at the same speed using the same stirrer.

The composition of a typical emulsion was: aqueous phase, 678.0 gm.; Duponol-G, 6.78 gm.; potassium persulfate, 0.3116 gm.; and styrene, 75.3 gm.

The technique of sampling was to aspirate duplicate samples from the emulsion at various intervals of time. One sample was used in the determination of the pH of the system by a Beckmann pH meter, and the other caught in a tared flask containing a precooled (-10°C), weighed amount of ethanol and 0.1 gm. aluminum chloride.

The purpose of the alcohol and the aluminum chloride was to quench the reaction and coagulate the polymer. The chilling of the ethanol to a very low temperature assists in quenching by the rapid reduction of the temperature. The weight of the sample removed was determined by weight difference. The liquid was separated as soon as possible from polymer by centrifugation and analyzed by a method indicated below. The polymer was transferred to a flask and washed with ethanol several times by decantation generally allowing ten minutes to an hour to elapse between decantations depending upon the amount and rate of settling of the polymer. It was then washed with water and finally ethanol in the above manner to complete the removal of emulsifier, water soluble material, monomer, and other alcohol soluble material. The polymer was filtered, partially air dried, oven-dried for 24 hours at 75°C and weighed. The percent theoretical yield of solid polymer is determined by:

$$\%\ \text{Theoretical Yield of Solid Polymer} = \frac{\text{Wt. of Polymer in sample} \times \dfrac{\text{Initial Wt. of Emulsion}}{\text{Weight of sample}}}{\text{Weight of Styrene used}} \times 100$$

In addition, the percent of styrene which polymerized during the course of the reaction was determined by a titration method which depended on the reaction of mercuric acetate with a double bond to liberate one molecule of acetic acid per double bond. The procedure followed in this determination was to remove a 15 ml. sample from the supernatent liquid obtained from centrifugation, to which was added 4 gm. of mercuric acetate followed by 20 ml. of absolute methanol. At this point the solution was agitated in order to dissolve the salts as rapidly as possible, and 20 ml. of a saturated solution of sodium chloride were added. The solution was allowed to stand at least five minutes before adding 20 ml. of carbon tetrachloride. The acetic acid liberated in the reaction was titrated with standard sodium hydroxide using phenolphthalein indicator. The amount of double bond, calculated as styrene, was obtained from the number of milliequivalents of standard sodium hydroxide used.

In order to evaluate the accuracy of the titration method an emulsion system was prepared from styrene, water, and emulsifying agent, omitting potassium persulfate. A sample was removed and the amount of styrene present in the sample was obtained by titration and compared with the weight calculated to be present in the sample. Samples were also taken at various time intervals to see whether the results obtained were reproducible.

A further evaluation of the titration scheme was made by preparing a system in which freshly distilled styrene was weighed directly into a flask and an emulsion made to correspond to a 1-9 ratio of styrene to water and a 1% concentration of emulsifying agent. The weight of styrene obtained by the titration procedure was compared to that weighed into the flask.

Another check was obtained by weighing monomeric styrene directly into a flask and then comparing this weight with that obtained from the titration method. A blank was run in all cases.

In order to determine the stability of the potassium persulfate in solution a system was prepared consisting of 600.0 gm. of water, 6.0 gm. of Duponol-G, and 0.264 gm.(0.0017M) potassium persulfate. The solution was maintained at 60°C and samples removed for pH determinations at various intervals of time.

For the determination of the average molecular weight of the polymers, a 0.01M solution of polystyrene in toluene was prepared. A sample of polystyrene weighing 0.0141 gm. was placed in a 100 ml. volumetric flask and covered with approximately 50 ml. of toluene. The flask was then allowed to stand overnight at 40°C in order to dissolve the high molecular weight polystyrene, after which toluene was added to make 100 ml. at 20°C.

A Cannon-Fenske-Ostwald viscoscity pipette, K-100, was used to determine the time of efflux of pure styrene and the polystyrene solutions. The time was recorded by a timer to 0.1 seconds while keeping the pipette in a constant temperature bath maintained at 20°C ± 0.1. The specific viscoscity was determined from the following expression:

$$\eta_{sp} = \frac{\text{Time of efflux of solution at } 20^{\circ}\text{C}}{\text{Time of efflux of solvent at } 20^{\circ}\text{C}} - 1$$

Using Staudinger's[15a] equation the average molecular weight was determined:

$$M = \frac{\eta_{sp}}{(K)\ (C)}$$

M = average molecular weight

η_{sp} = specific viscoscity

C = mols per liter of polystyrene in toluene

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

EXPERIMENTS & DATA

Temperature 60° C± 0.2°

(Weight of Water	678.0 gms
(Styrene	75.3 gms
(Duponol G	6.78 gms
(Potassium persulfate	0.3116 gms (0.0017 M) based on the aqueous phase

Experiment #1 Nitrogen Atmosphere

Time (Mins)	% Solid Polymer	% Reacted Styrene	pH	Average Molecular Wt.
14.8	0.7	—	6.4	
25.2	0.9	15.0	6.4	
34.8	21.1	26.5	—	417,000
42.6	—	49.6	7.0	—
49.6	53.9	69.1	7.0	494,000
57.6	67.4	74.2	7.0	466,000
66.0	74.7	85.2	7.5	461,000
78.9	82.7	91.8	—	439,000
100.0	94.9	—	8.3	455,000

Experiment #2 Carbon Dioxide Atmosphere

Time (Mins)	% Solid Polymer	% Reacted Styrene	pH	Average Molecular Wt.
3.0	0	19.7	4.9	
20.0	5.4	22.2	4.6	
25.0	10.7	26.1	4.9	268,000
30.3	18.5	35.4	4.8	340,000
35.1	26.2	44.3	4.9	393,000
40.4	31.9	—	4.6	403,000
47.0	51.4	67.9	4.3	517,000
52.6	57.2	77.9	4.2	448,000
59.0	66.7	81.4	4.2	430,000
73.2	76.9	91.7	4.2	417,000
80.8	79.1	96.6	4.1	397,000

Experiment #3 95% Nitrogen & 5% Oxygen Atmosphere

Time (Mins)	% Solid Polymer	% Reacted Styrene	pH	Average Molecular Wt.
21.6	0.2		6.6	
34.0	1.7		7.1	
50.4	4.4		6.9	
66.3	---		6.4	
84.9	3.0		7.1	
101.4	5.6		6.7	
136.8	7.9		6.4	33,000
181.8	15.6		---	46,000
240.0	34.2		6.2	150,000
299.6	62.8		5.2	111,000
317.1	74.7		4.6	122,000
430.0	77.7		3.9	122,000

In the following experiments the percentage of alcohol in the aqueous phase is by weight of anhydrous alcohol.

Experiment #4 5% Methanol

Time (Mins)	% Solid Polymer	% Reacted Styrene	pH	Average Molecular Wt.
3.3	0	13.5	7.2	
10.8	0.4	12.9	7.5	
25.0	2.6	15.0	7.3	
40.2	12.0	28.4	6.8	264,000
48.8	21.6	48.7	7.2	321,000
56.2	38.9	51.2	7.2	327,000
62.6	45.8	58.1	7.4	326,000
69.8	56.3	68.4	7.4	328,000
74.0	---	75.2	7.6	332,000
90.0	77.0	86.5	7.8	321,000

Experiment #5 10% Methanol

Time (Mins)	% Solid Polymer	% Reacted Styrene	pH	Average Molecular Wt.
3.2	0	18.5	7.2	
13.4	1.6	19.4	7.5	
24.5	5.9	21.4	7.5	192,000
39.9	22.4	39.5	7.6	316,000
49.3	36.7	52.5	7.6	360,000
58.6	49.7	64.2	7.8	405,000
66.7	60.6	73.5	7.5	386,000
73.4	68.3	79.6	7.7	383,000
79.8	73.6	85.0	7.7	380,000
86.3	——	90.1	7.8	401,000
92.3	84.3	92.6	8.0	391,000

Experiment #6 15% Methanol

Time (Mins)	% Solid Polymer	% Reacted Styrene	pH	Average Molecular Wt.
3.2	0	——	7.3	
16.3	2.7	13.2	7.5	
30.9	12.5	——	7.4	254,000
36.3	15.6	35.0	7.1	237,000
43.0	26.0	43.5	7.2	273,000
48.9	——	52.0	7.2	326,000
55.4	42.5	59.3	7.3	338,000
61.8	50.5	67.6	7.4	317,000
71.8	60.9	76.5	7.3	344,000
82.0	71.6	84.8	7.4	313,000

Experiment #7 20% Methanol

Time (Mins)	% Solid Polymer	% Reacted Styrene	pH	Average Molecular Wt.
3.0	0	10.9	7.4	
15.0	2.3	16.7	7.1	
30.0	13.9	29.6	7.4	241,000
36.0	18.0	37.4	7.2	282,000
42.0	28.7	44.1	7.3	297,000
48.0	32.9	50.9	7.3	297,000
55.5	42.9	59.2	7.4	303,000
63.0	52.0	66.0	7.3	300,000
71.3	56.2	69.7	7.5	314,000
80.2	64.5	77.8	7.5	306,000
90.0	——	83.1	7.5	307,000

Experiment #8 30% Methanol

Time (Mins)	% Solid Polymer	% Reacted Styrene	pH	Average Molecular Wt.
3.2	0	23.0	7.6	
20.2	1.9	26.2	7.8	
30.0	4.4	25.1	7.7	
40.2	7.3	27.7	7.4	134,000
50.1	9.5	31.9	7.3	118,000
60.0	12.7	35.4	7.3	107,000
70.2	17.7	40.2	7.1	148,000
85.0	22.3	45.7	7.2	122,000
101.2	23.7	49.8	7.1	144,000
115.0	29.5	54.9	7.3	125,000
140.0	36.6	61.3	7.3	126,000
170.9	46.2	67.3	7.3	121,000

Experiment #9 5% Ethanol

Time (Mins)	% Solid Polymer	% Reacted Styrene	pH	Average Molecular Wt.
3.1	0	—	7.1	
10.6	0.8	12.7	7.0	
20.1	1.0	13.9	7.2	
33.7	—	18.5	7.1	233,000
49.8	29.8	45.2	7.2	352,000
63.6	47.6	63.3	7.3	393,000
74.4	62.5	78.6	7.4	387,000
85.8	72.2	86.1	7.4	388,000
95.1	80.8	92.1	7.5	382,000
117.3	85.7	96.6	—	371,000

Experiment #10 10% Ethanol

Time (Mins)	% Solid Polymer	% Reacted Styrene	pH	Average Molecular Wt.
4.1	0		6.6	
28.2	5.0		6.5	188,000
42.7	18.4		6.7	288,000
50.8	30.9		6.6	350,000
59.1	39.3		6.5	333,000
68.1	49.7		6.4	350,000
77.4	61.0		6.5	328,000
86.5	68.1		6.6	361,000
101.1	80.1		6.7	344,000

Experiment #11 10% Ethanol

Time (Mins)	% Solid Polymer	% Reacted Styrene	pH	Average Molecular Wt.
0.0	0		6.7	
36.0	0		6.5	
49.7	13.0		6.7	205,000
62.7	25.3		6.6	320,000
78.3	42.3		6.7	406,000
95.5	60.7		6.7	417,000
111.2	79.6		6.9	375,000
157.0	87.3		6.9	293,000

Experiment #12 15% Ethanol

Time (Mins)	% Solid Polymer	% Reacted Styrene	pH	Average Molecular Wt.
3.1	0	12.8	6.8	
30.5	4.5	18.3	6.9	155,000
40.2	11.0	21.4	6.7	217,000
50.6	21.3	29.9	6.6	244,000
61.1	28.5	41.9	7.0	262,000
71.7	37.8	51.2	7.1	266,000
81.9	48.5	59.9	7.0	275,000
92.5	58.6	70.2	—	263,000
106.5	65.4	74.0	7.7	288,000
123.0	76.9	88.1	7.7	275,000

Experiment #13 20% Ethanol

Time (Mins)	% Solid Polymer	% Reacted Styrene	pH	Average Molecular Wt.
1.9	0	13.6	7.1	
10.0	0.9	12.5	7.1	
30.3	1.7	16.8	7.1	
45.6	7.3	20.8	7.0	
60.1	8.3	27.0	7.2	74,000
75.2	11.7	30.4	7.0	81,000
95.9	14.7	30.0	7.0	105,000
115.6	19.7	39.8	6.9	100,000
136.3	—	40.8	7.1	92,000
155.0	32.4	44.3	7.1	101,000
175.1	37.6	47.8	7.2	103,000
203.3	42.8	54.6	7.2	107,000
266.6	60.4	69.8	7.1	113,000

Experiment #14 20% Ethanol

Time (Mins)	% Solid Polymer	% Reacted Styrene	pH	Average Molecular Wt.
5.2	0	14.5	7.5	
9.3	0	16.3	7.7	
31.3	1.7	20.1	7.4	
43.4	5.2	26.3	7.8	
57.6	6.9	27.0	7.5	
71.8	9.3	28.3	7.4	
85.0	11.6	32.5	7.4	70,000
100.6	14.0	33.0	7.4	70,000
117.0	15.6	34.4	7.5	76,000
133.5	18.8	34.2	7.4	75,000
154.2	25.1	37.2	7.4	93,000
170.7	31.0	43.6	7.6	85,000
190.1	30.0	46.5	7.3	85,000
211.1	31.1	46.7	7.2	85,000
253.6	39.3	56.6	7.0	79,000

Experiment #15 5% Isopropanel

Time (Mins)	% Solid Polymer	% Reacted Styrene	pH	Average Molecular Wt.
4.1	0		7.3	
20.7	0.7		7.4	
28.5	0.9		7.3	
40.0	1.7		7.3	
53.3	4.8		7.4	
67.2	6.3		7.4	
75.4	11.3		7.3	103,000
83.3	19.0		7.2	146,000
99.7	29.9		7.3	204,000
112.7	50.3		7.3	280,000
127.3	59.8		7.4	334,000

Experiment #16 10% Isopropanol

Time (Mins)	% Solid Polymer	% Reacted Styrene	pH	Average Molecular Wt.
3.2	0		7.6	
20.0	1.9		7.5	
30.0	1.2		7.7	
40.1	2.5		7.7	
55.1	3.1		7.5	
70.0	2.5		7.5	
93.0	4.1		7.4	
145.4	4.6		7.6	41,000
205.0	7.1		7.3	40,000
304.2	9.3		7.5	43,000
495.8	28.2		6.8	47,000

Experiment #17 5% Tertiary Butanol

Time (Mins)	% Solid Polymer	% Reacted Styrene	pH	Average Molecular Wt.
4.4	0	----	7.3	
15.0	1.2	19.8	7.3	
30.0	3.6	20.5	7.4	
36.0	8.7	23.0	7.4	180,000
44.3	13.5	30.8	7.4	233,000
53.3	25.1	42.9	7.5	313,000
63.3	34.9	57.1	7.5	347,000
73.3	52.6	70.4	7.5	362,000
86.6	70.5	81.7	7.6	376,000
93.3	----	85.2	7.7	355,000
103.8	75.0	90.8	7.7	353,000

Experiment #18 10% Tertiary Butanol

Time (Mins)	% Solid Polymer	% Reacted Styrene	pH	Average Molecular Wt.
3.2	0	19.9	7.4	
15.0	0.8	18.6	7.5	
26.6	2.1	----	7.5	
40.0	3.2	22.6	7.4	
65.0	5.1	26.4	7.0	42,000
83.0	4.1	28.1	7.0	47,000
110.0	4.7	30.2	7.0	40,000
159.0	9.7	36.0	7.1	43,000
196.0	9.6	37.8	7.2	50,000
235.0	16.2	43.2	7.3	40,000
280.0	20.4	47.0	7.2	51,000
340.0	23.6	50.0	7.2	54,000

Experiment #19 Comparison in an emulsion system with no potassium persulfate of the calculated weight of styrene vs the observed weight obtained by titration of the double bond.

Sample #	Minutes	Calculated Weight (gms)	Observed Weight(gms)	pH	% Styrene Present
1a	3.2	1.40	1.20	6.9	85.7
1b		1.40	1.21		86.4
2a	15.0	1.10	0.90	7.0	81.8
2b		1.10	0.89		80.9
3a	90.0	1.90	1.67	7.1	87.9
3b		1.90	1.66		87.4
4	121.5	1.62	1.48	6.9	91.4
5	231.3	1.78	1.45	6.8	81.5

Experiment #20 This is a duplication of the above experiment using a new emulsion sample.

Sample #	Minutes	Calculated Weight (gms)	Observed Weight(gms)	pH	% Styrene Present
1	9.0	2.07	1.92	7.0	92.8
2	26.5	2.45	2.25	7.0	91.8
3	40.6	1.32	1.09	6.9	82.6

Experiment #21 This experiment is a variation of the above. Instead of determining the weight of styrene in an aliquot portion of a large sample, two samples were made up by weighing out styrene, water and Duponol-G in the proper ratio and then using the whole sample to determine the weight of styrene by titration.

Sample #	Wt. Styrene Added (gms)	Wt. Calculated From Titration	% Styrene
1	1.11	1.08	97.4
2	1.11	1.08	97.4

Experiment #22 To determine the effect of water and emulsifying agent on the determination of weight of styrene by the titration method, two samples were made omitting the water and emulsifying agent. Pure monomeric styrene was weighed out and then applying the procedure for determining the amount of styrene by titration, the weight of styrene was found and compared.

Sample #	Wt. Styrene Added (gms)	Wt. Calculated From Titration	% Styrene
1	1.08	1.02	94.4
2	0.83	0.78	94.0

Experiment #23 Decomposition of potassium persulfate vs time followed by pH. System was standard, i.e., except for styrene.

Time (Mins.)	pH
0	8.52
25	8.32
57	8.00
85	7.60
161	5.31
178	4.72
362	3.28

Experiment #24 Nitrogen Atmosphere

Time (Mins)	% Solid Polymer	% Styrene Reacted	pH	Average Molecular Wt.
3.0	0	----	7.2	
11.3	0.7	----	7.5	
22.2	2.9	16.7	7.5	
35.1	16.6	35.0	7.6	339,000
42.2	----	47.0	7.6	407,000
49.4	43.8	60.6	7.7	397,000
56.5	54.4	71.8	7.8	397,000
63.8	68.3	79.3	7.8	424,000
71.0	76.6	86.0	7.8	386,000
91.0	80.0	94.8	7.9	377,000

Experiment #25 Nitrogen Atmosphere

Time (Mins)	% Solid Polymer	% Styrene Reacted	pH	Average Molecular Wt.
3.0	0	----	6.9	
12.6	0.6	5.7	7.2	
22.2	2.5	8.1	7.4	
28.9	9.4	16.4	7.2	149,000
35.2	16.9	23.2	7.2	257,000
42.6	29.7	34.5	7.4	311,000
49.8	41.8	52.6	7.7	353,000
56.5	----	64.2	7.7	416,000
64.4	55.7	77.1	7.8	402,000
72.4	76.7	83.8	7.9	403,000
91.0	84.1	96.4	7.9	362,000

Data from P. T. Yang's polymerization of styrene in a water, Duponol-G, and potassium persulfate system[31]. The concentration of potassium persulfate was 0.0017M.

Time (Mins)	% Solid Polymer	% Styrene Reacted	pH	Average Molecular Wt.
0	0		6.9	
60	0.62		6.8	
90	25.1		6.3	336,000
100	39.4		7.1	374,000
110	54.1		7.4	376,000
125	70.0		7.6	378,000
150	87.6		6.8	353,000
225	91.1		7.5	310,000

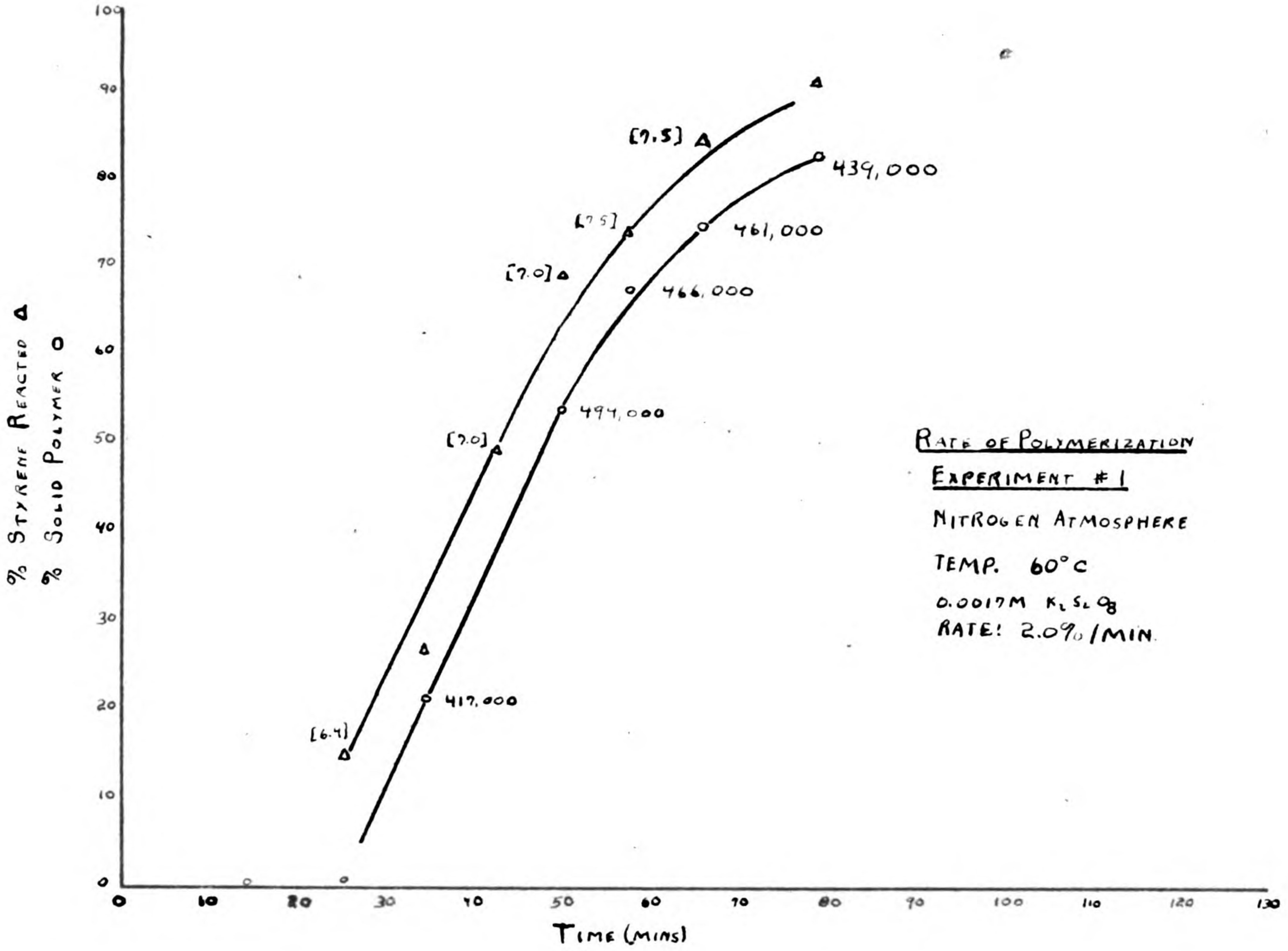
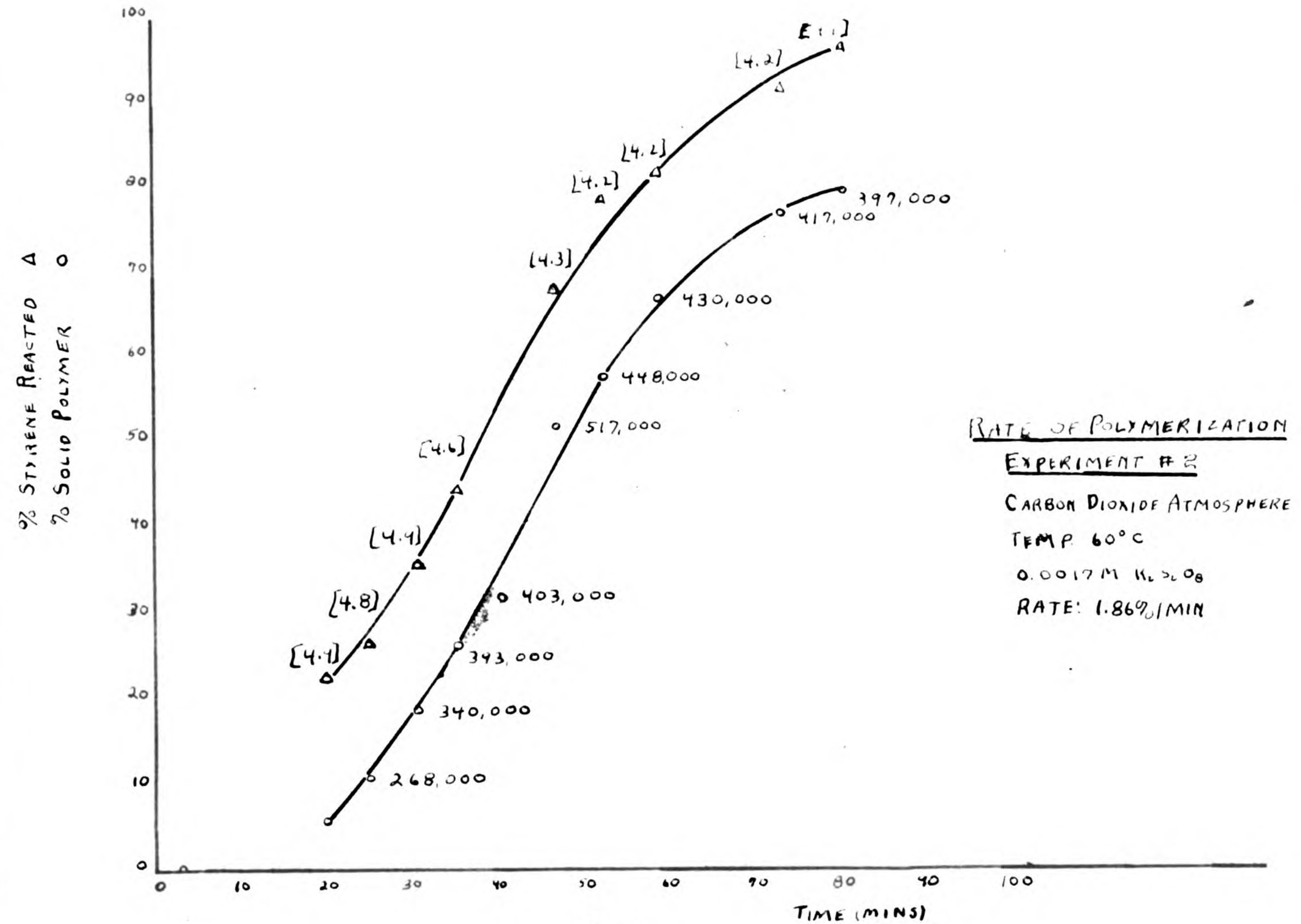

% Styrene Reacted Δ
% Solid Polymer o
0
10
20
30
40
50
60
70
80
90
100
0
10
20
30
40
50
60
70
80
90
100
110
120
130
Time (mins)
[6.4]
[7.0]
[7.0]
[7.5]
[7.5]
417,000
494,000
466,000
461,000
439,000
Rate of Polymerization
Experiment #1
Nitrogen Atmosphere
Temp. 60°C
0.0017M $K_2S_2O_8$
Rate: 2.0%/min

Fig. 1



RATE OF POLYMERIZATION

EXPERIMENT #2

CARBON DIOXIDE ATMOSPHERE

TEMP. 60°C

0.0017 M $K_2S_2O_8$

RATE: 1.86%/MIN

FIG. 2

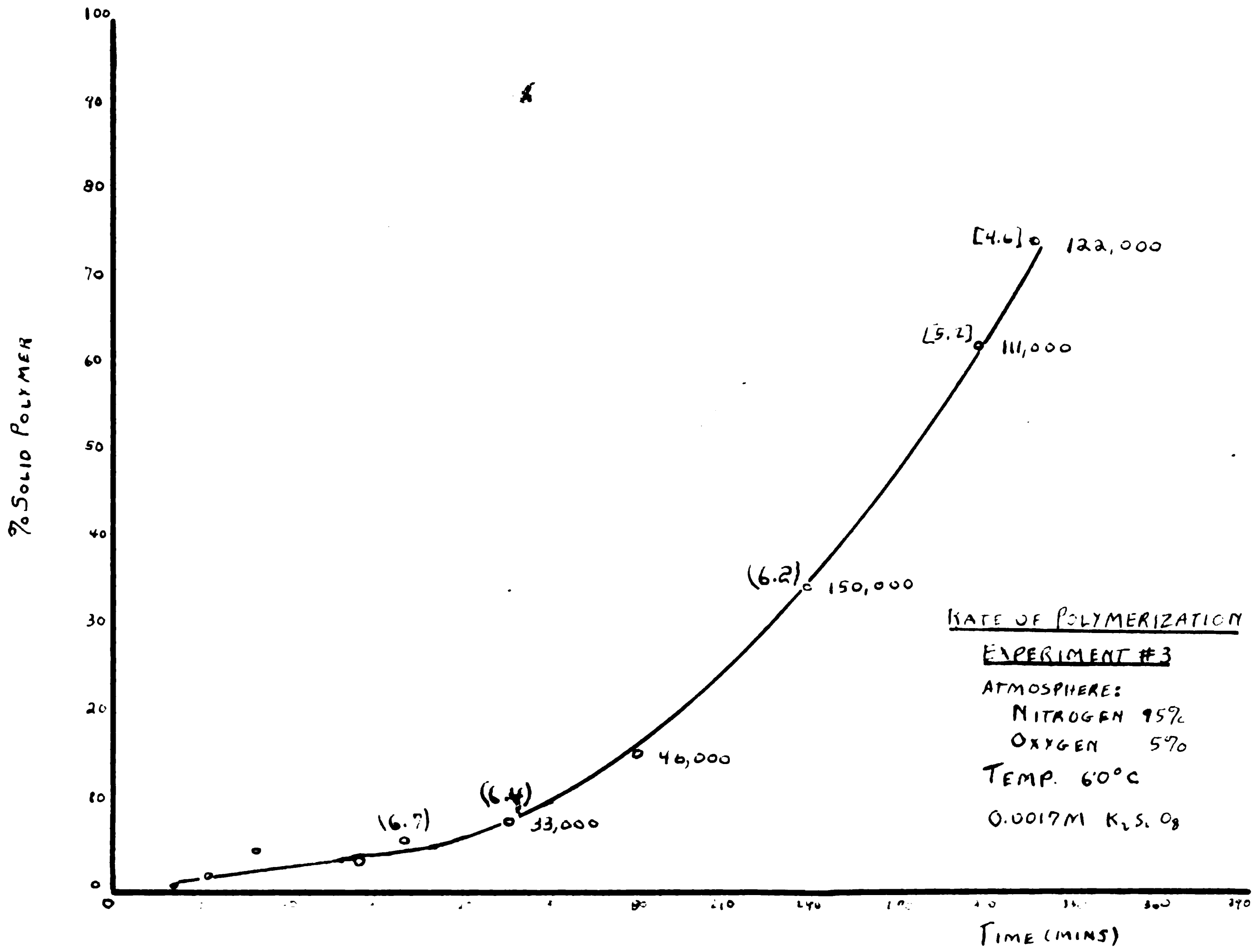

RATE OF POLYMERIZATION
EXPERIMENT #3
ATMOSPHERE:
NITROGEN 95%
OXYGEN 5%
TEMP. 60°C
0.0017M K2S2O8
% SOLID POLYMER
100
90
80
70
60
50
40
30
20
10
0
0
180
210
240
270
300
330
360
390
TIME (MINS)
[4.6] 122,000
[5.2] 111,000
(6.2) 150,000
46,000
(6.4) 33,000
(6.7)

Fig. 3

RATE OF POLYMERIZATION VS ATMOSPHERE

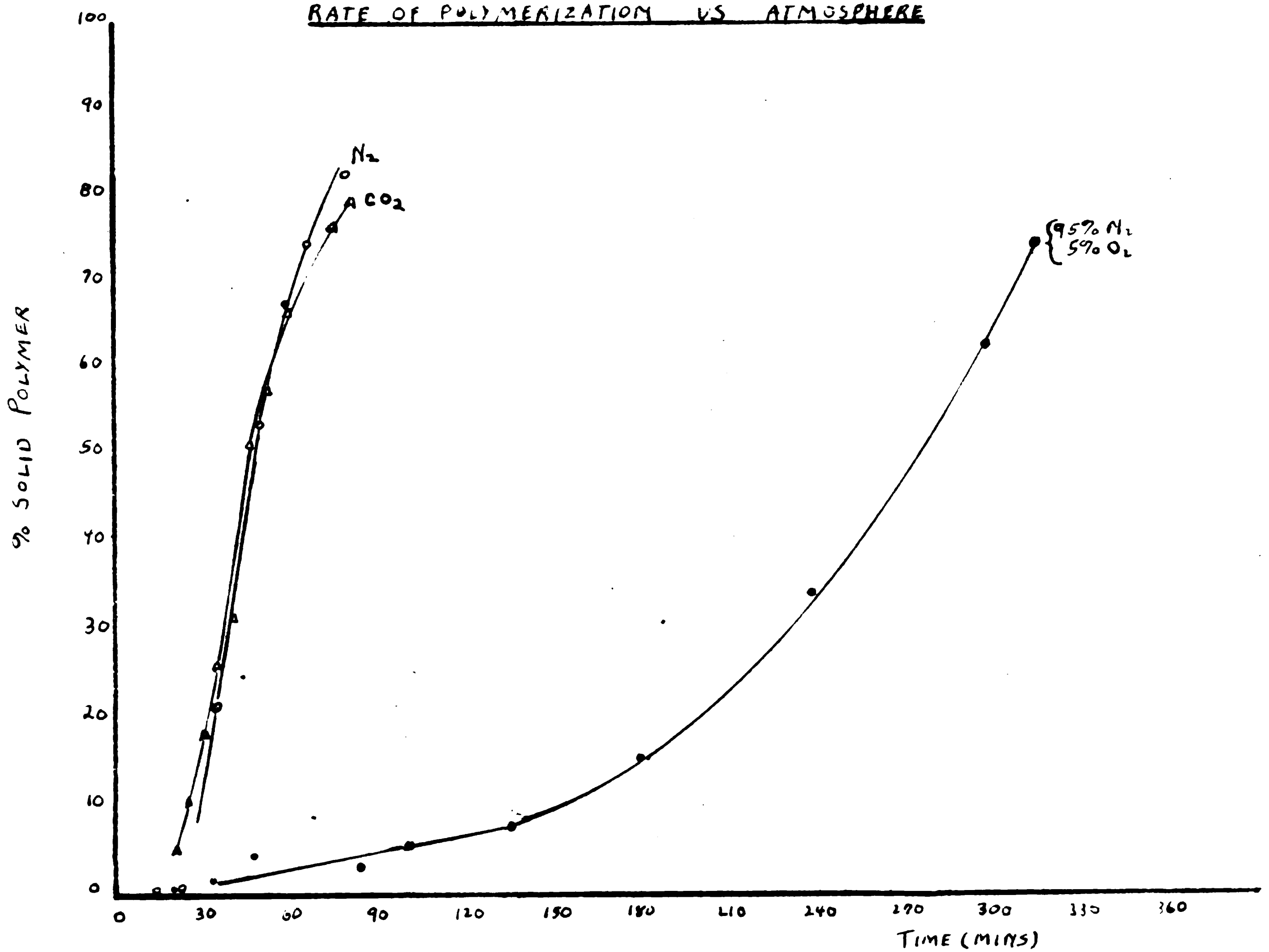
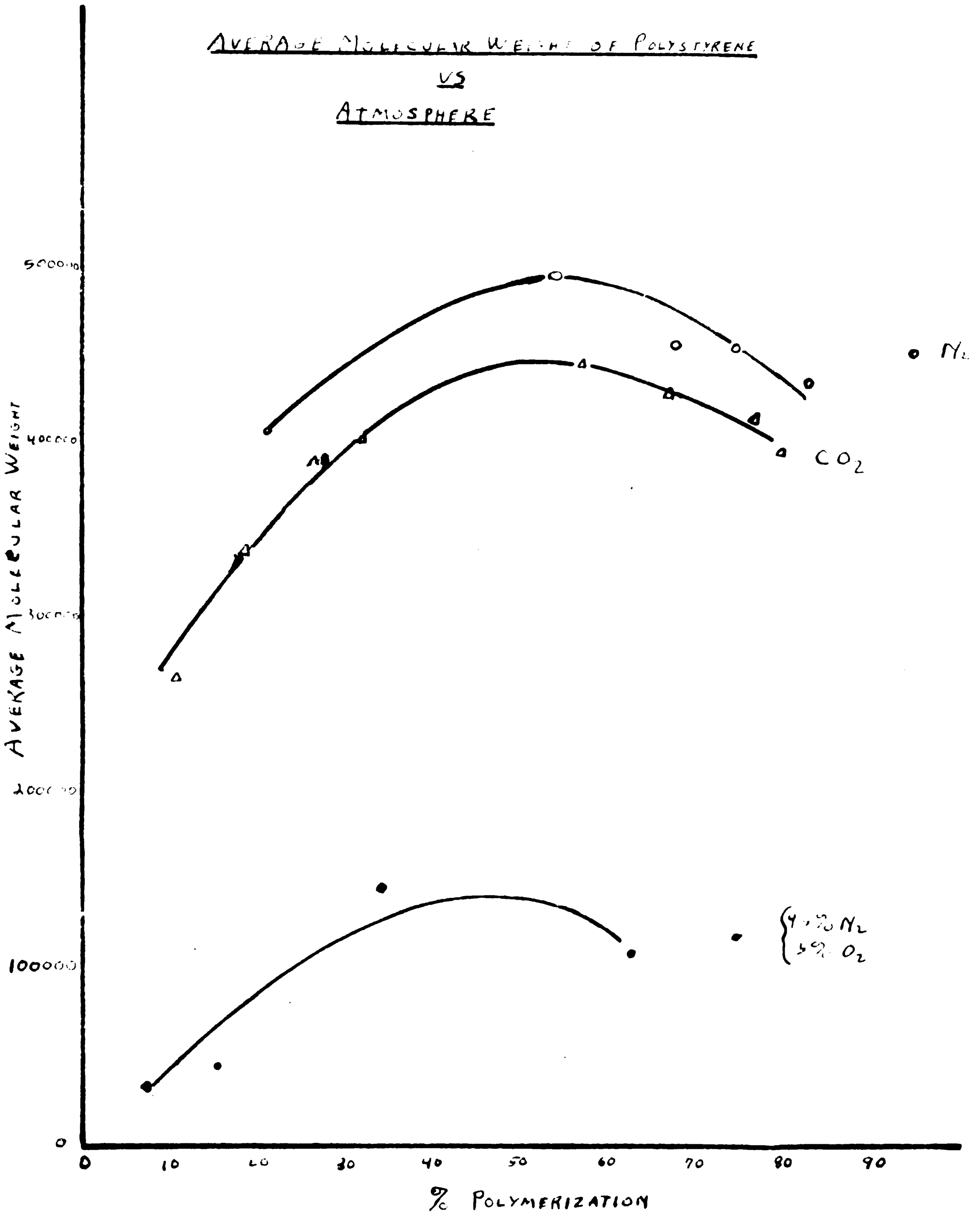


FIG 4



Average Molecular Weight of Polystyrene
vs
Atmosphere
Average Molecular Weight
500000
400000
300000
200000
100000
0
0
10
20
30
40
50
60
70
80
90
% Polymerization
N2
CO2
95% N2
5% O2

Fig 5

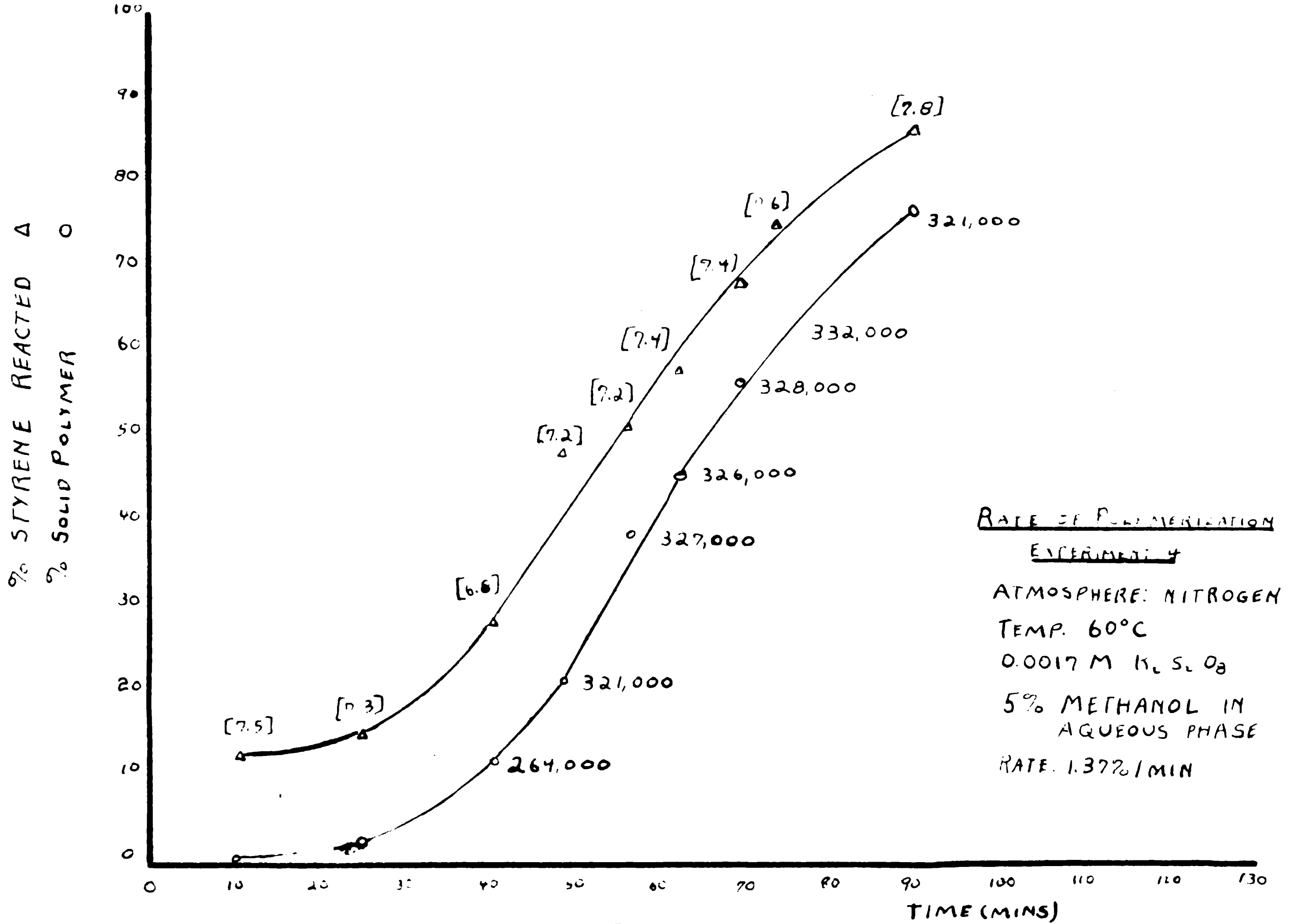

% STYRENE REACTED △
% SOLID POLYMER ○
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
TIME (MINS)
[7.5]
[7.3]
[6.6]
[7.2]
[7.2]
[7.4]
[7.4]
[7.6]
[7.8]
264,000
321,000
327,000
326,000
328,000
332,000
321,000
RATE OF POLYMERIZATION
EXPERIMENT 4
ATMOSPHERE: NITROGEN
TEMP. 60°C
0.0017 M $K_2S_2O_8$
5% METHANOL IN AQUEOUS PHASE
RATE 1.37%/MIN

FIG 6

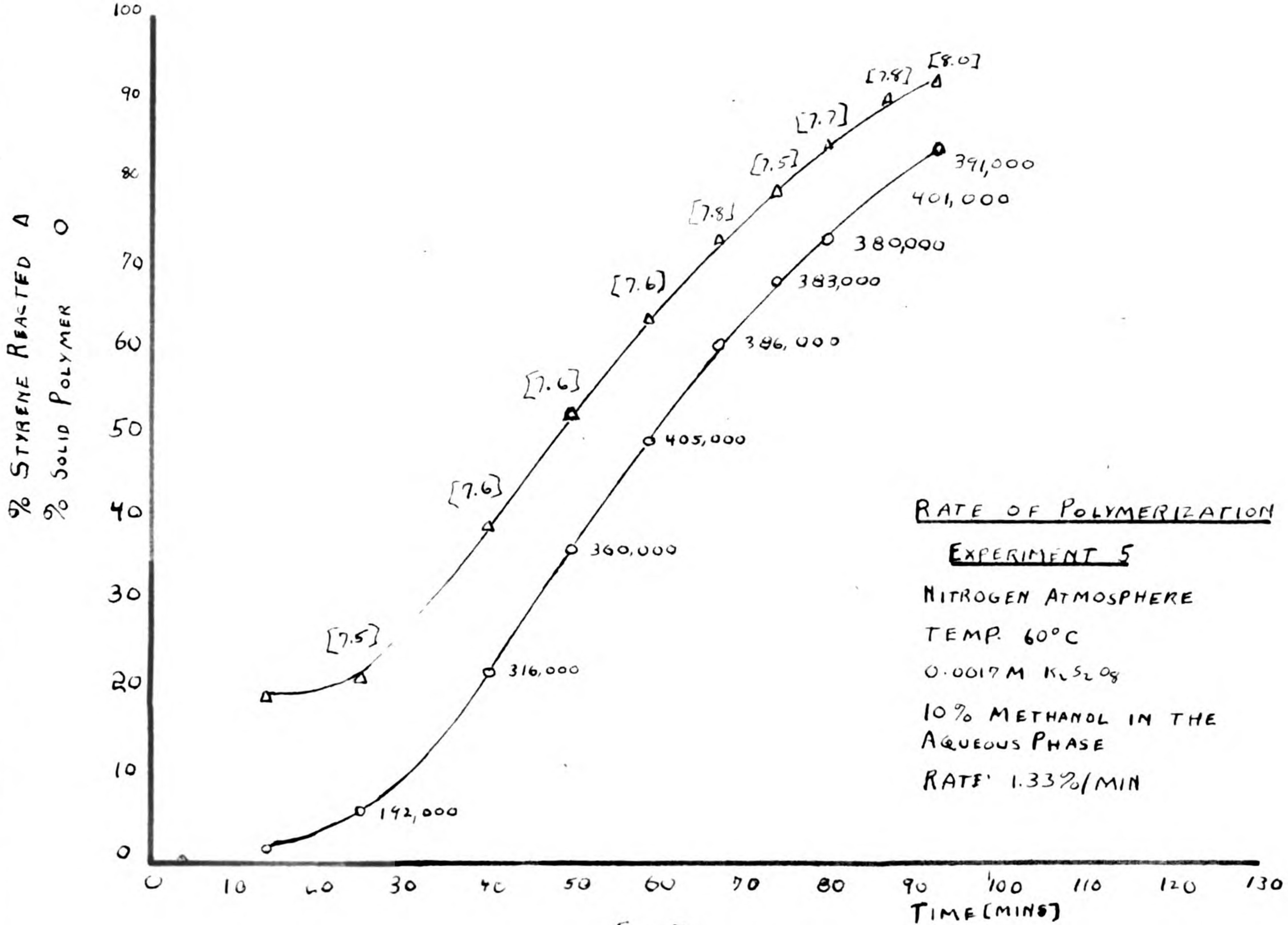
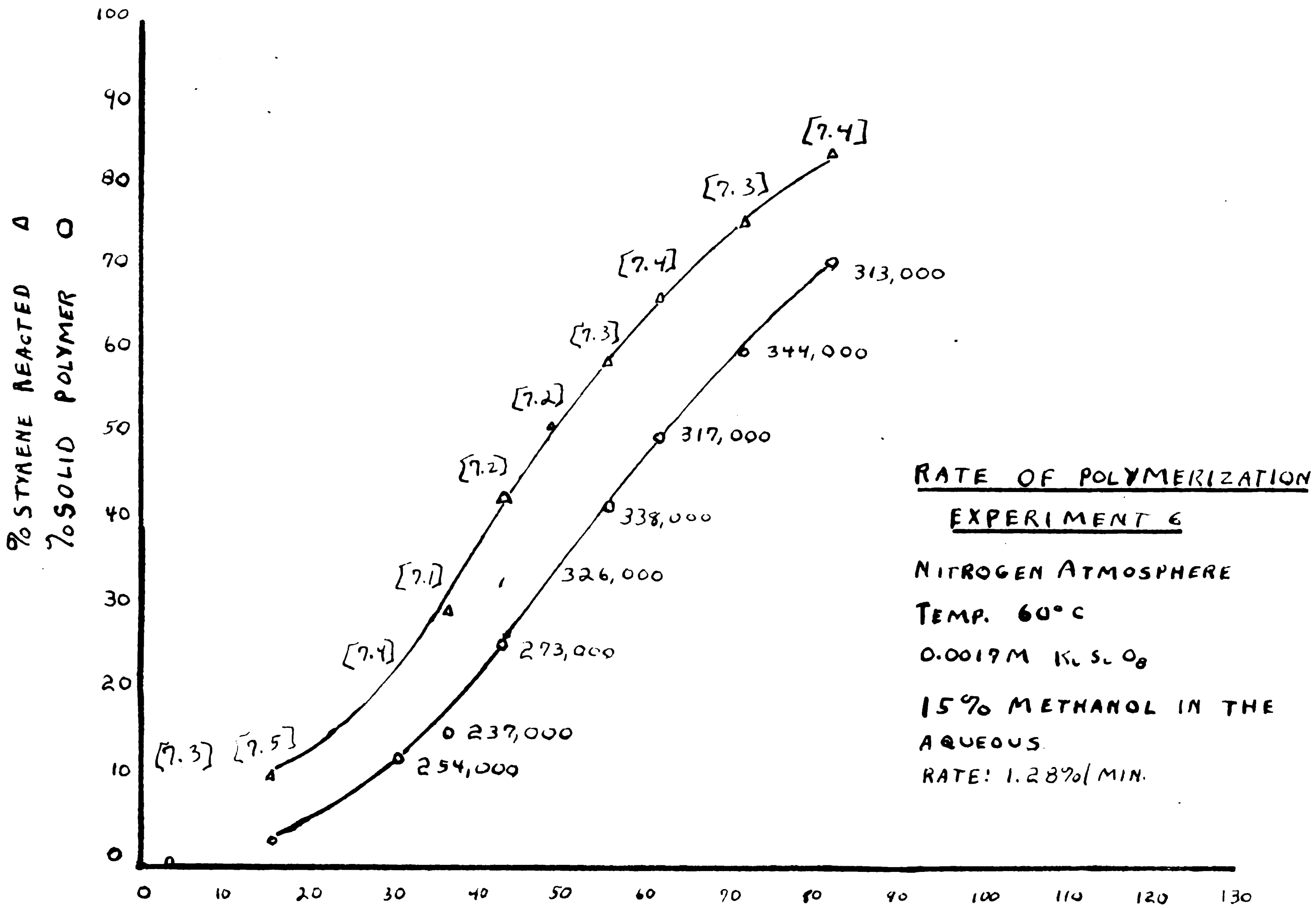

% Styrene Reacted △
% Solid Polymer ○
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
Time (mins)
[7.5]
[7.6]
[7.6]
[7.6]
[7.8]
[7.5]
[7.7]
[7.8]
[8.0]
142,000
316,000
360,000
405,000
386,000
383,000
380,000
401,000
391,000
Rate of Polymerization
Experiment 5
Nitrogen Atmosphere
Temp. 60°C
0.0017 M K₂S₂O₈
10% Methanol in the Aqueous Phase
Rate: 1.33%/min

Fig 7



RATE OF POLYMERIZATION

EXPERIMENT 6

NITROGEN ATMOSPHERE

TEMP. 60° C

0.0017M $K_2S_2O_8$

15% METHANOL IN THE AQUEOUS

RATE: 1.28%/MIN.

FIG 8

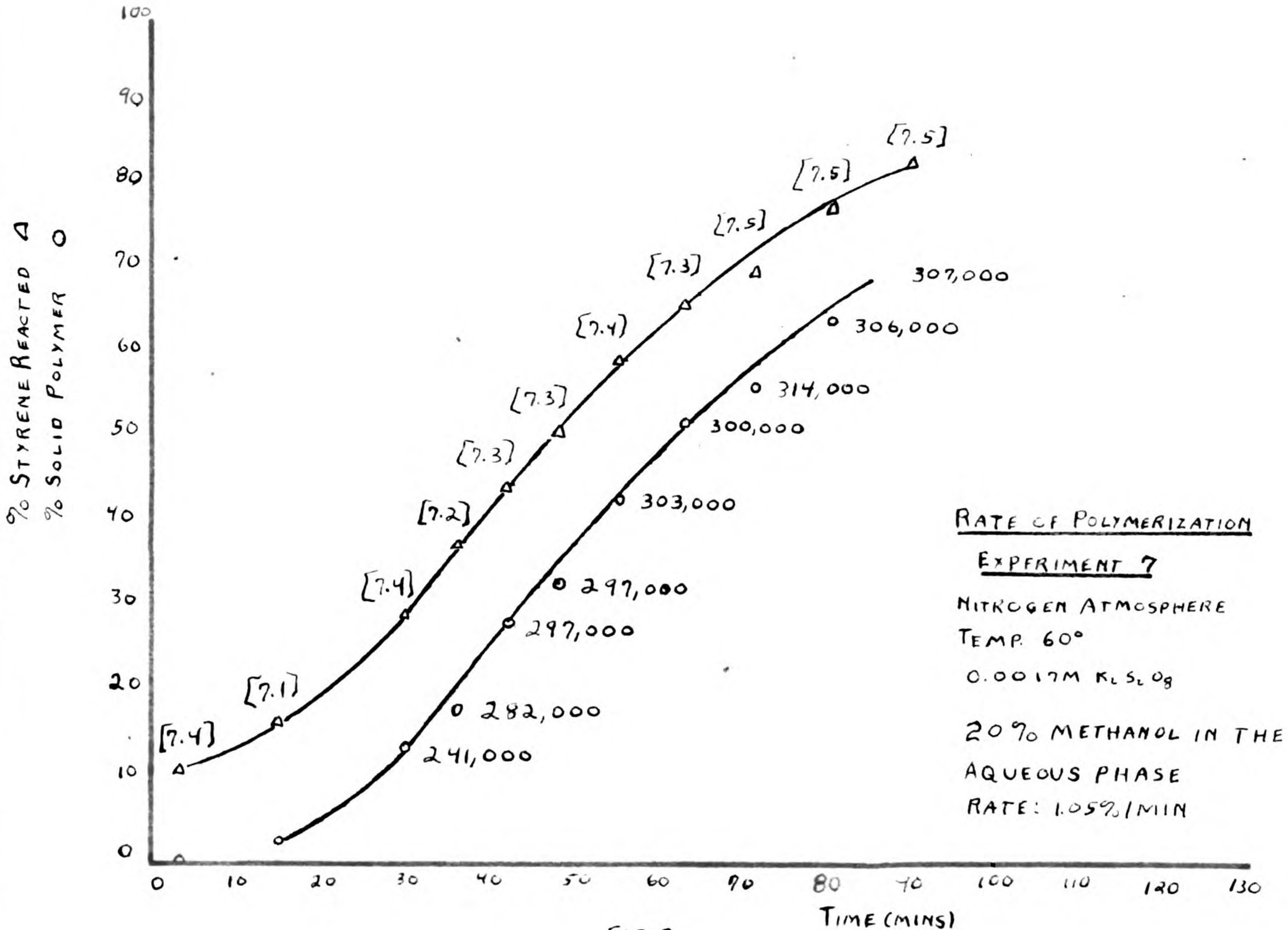

% Styrene Reacted Δ
% Solid Polymer O
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
Time (mins)
[7.4]
[7.1]
[7.4]
[7.2]
[7.3]
[7.3]
[7.4]
[7.3]
[7.5]
[7.5]
[7.5]
241,000
282,000
297,000
297,000
303,000
300,000
314,000
306,000
307,000
Rate of Polymerization
Experiment 7
Nitrogen Atmosphere
Temp. 60°
0.0017M $K_2S_2O_8$
20% Methanol in the Aqueous Phase
Rate: 1.05%/min

Fig 9

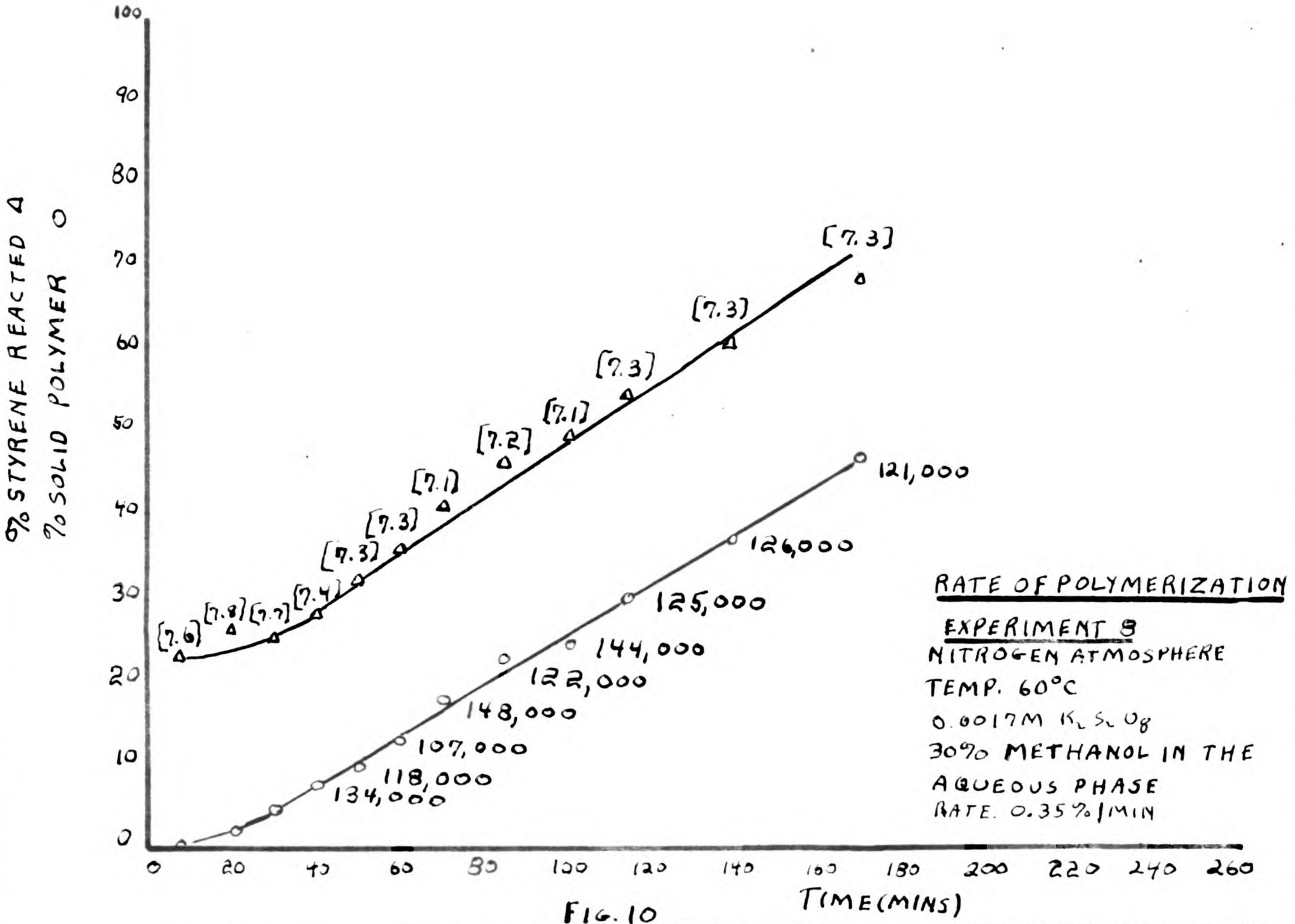

% STYRENE REACTED △
% SOLID POLYMER ○
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
160
180
200
220
240
260
TIME (MINS)
[7.6]
[7.8]
[7.7]
[7.4]
[7.3]
[7.3]
[7.1]
[7.2]
[7.1]
[7.3]
[7.3]
[7.3]
134,000
118,000
107,000
148,000
122,000
144,000
125,000
126,000
121,000
RATE OF POLYMERIZATION
EXPERIMENT 8
NITROGEN ATMOSPHERE
TEMP. 60°C
0.0017M K2 S2 O8
30% METHANOL IN THE
AQUEOUS PHASE
RATE 0.35%/MIN

FIG. 10

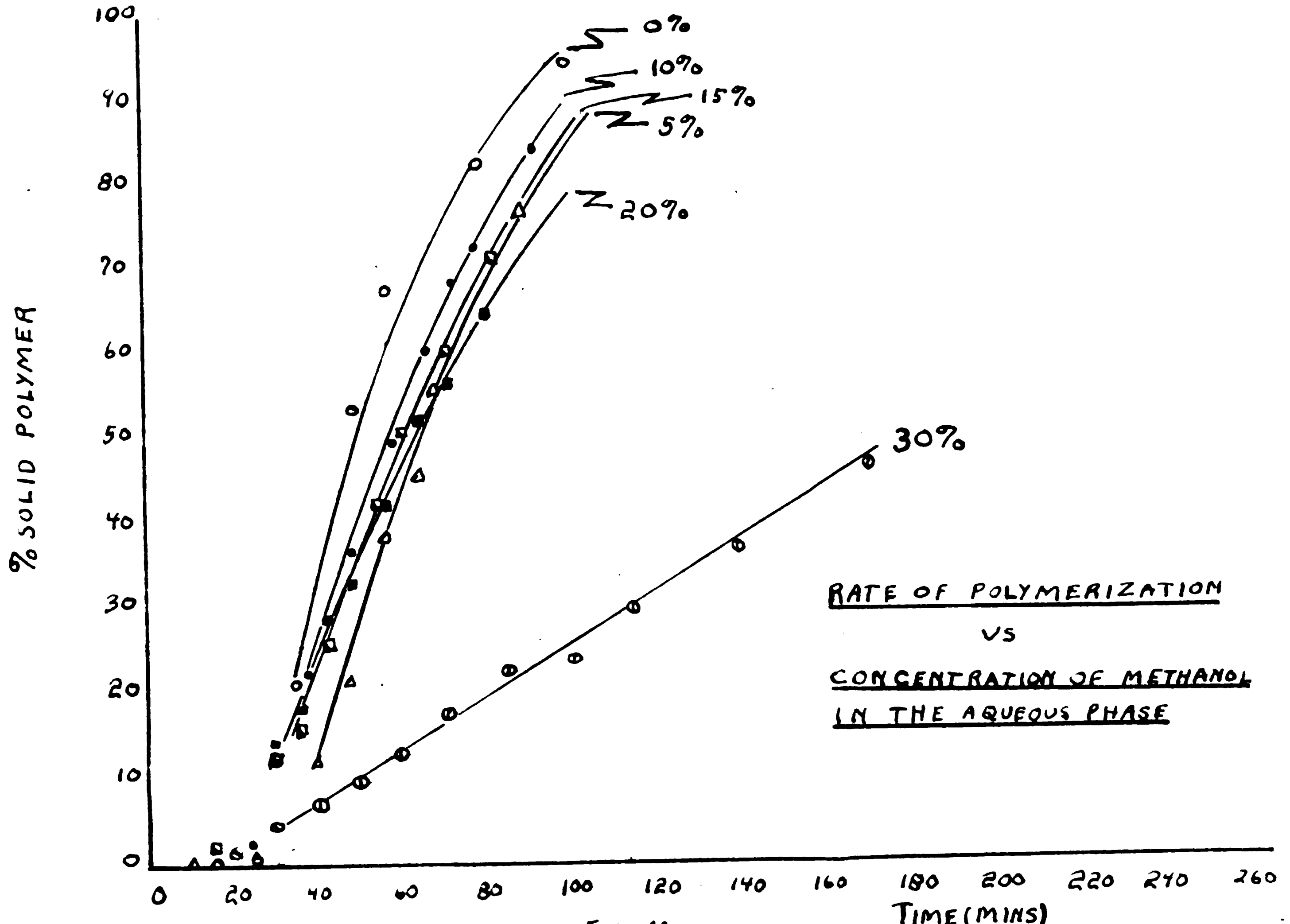

RATE OF POLYMERIZATION VS CONCENTRATION OF METHANOL IN THE AQUEOUS PHASE

FIG. 11

VARIATION OF AVERAGE MOLECULAR WEIGHT OF STYRENE WITH VARIOUS CONCENTRATIONS OF METHANOL IN THE AQUEOUS PHASE.

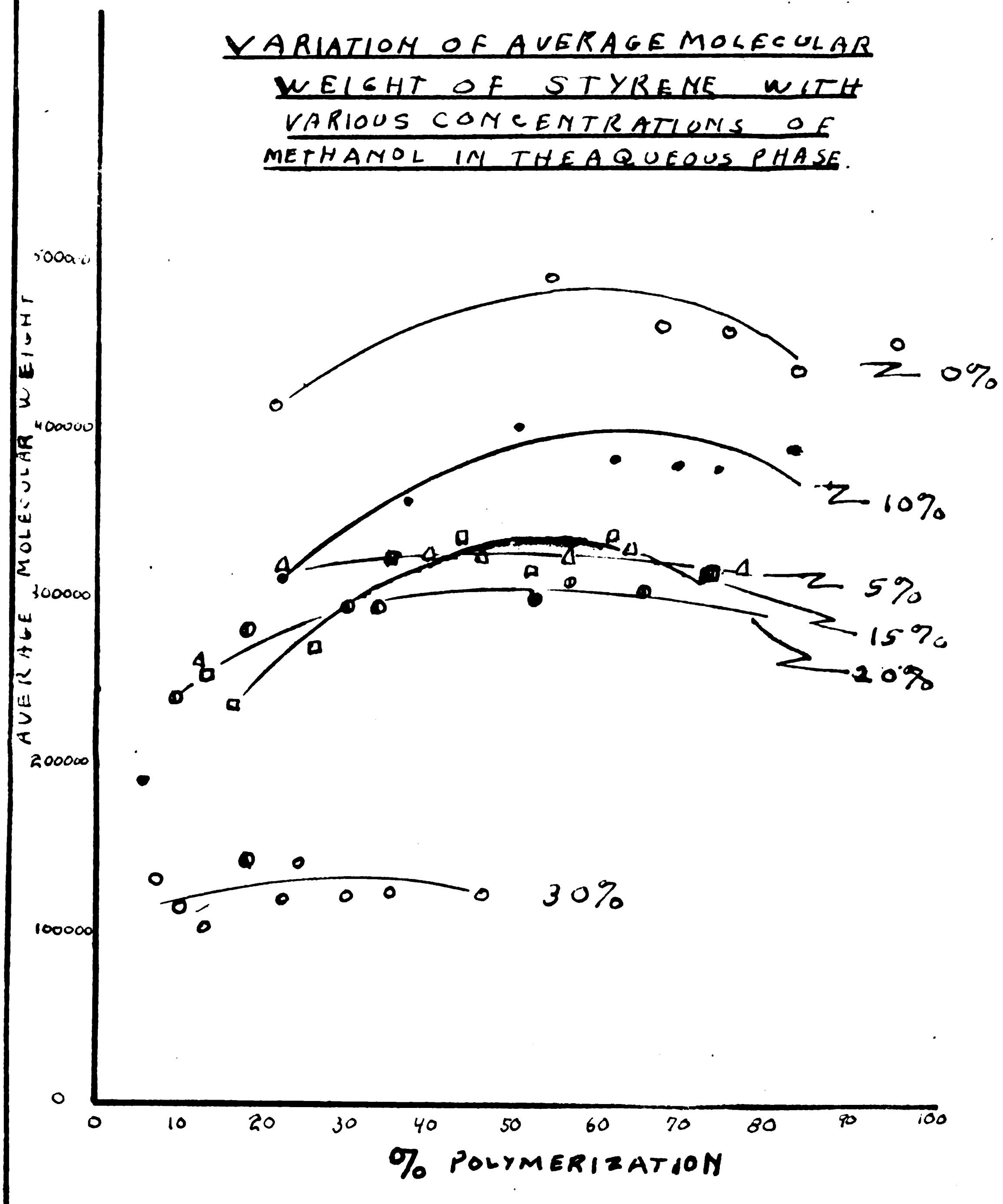


FIG. 12

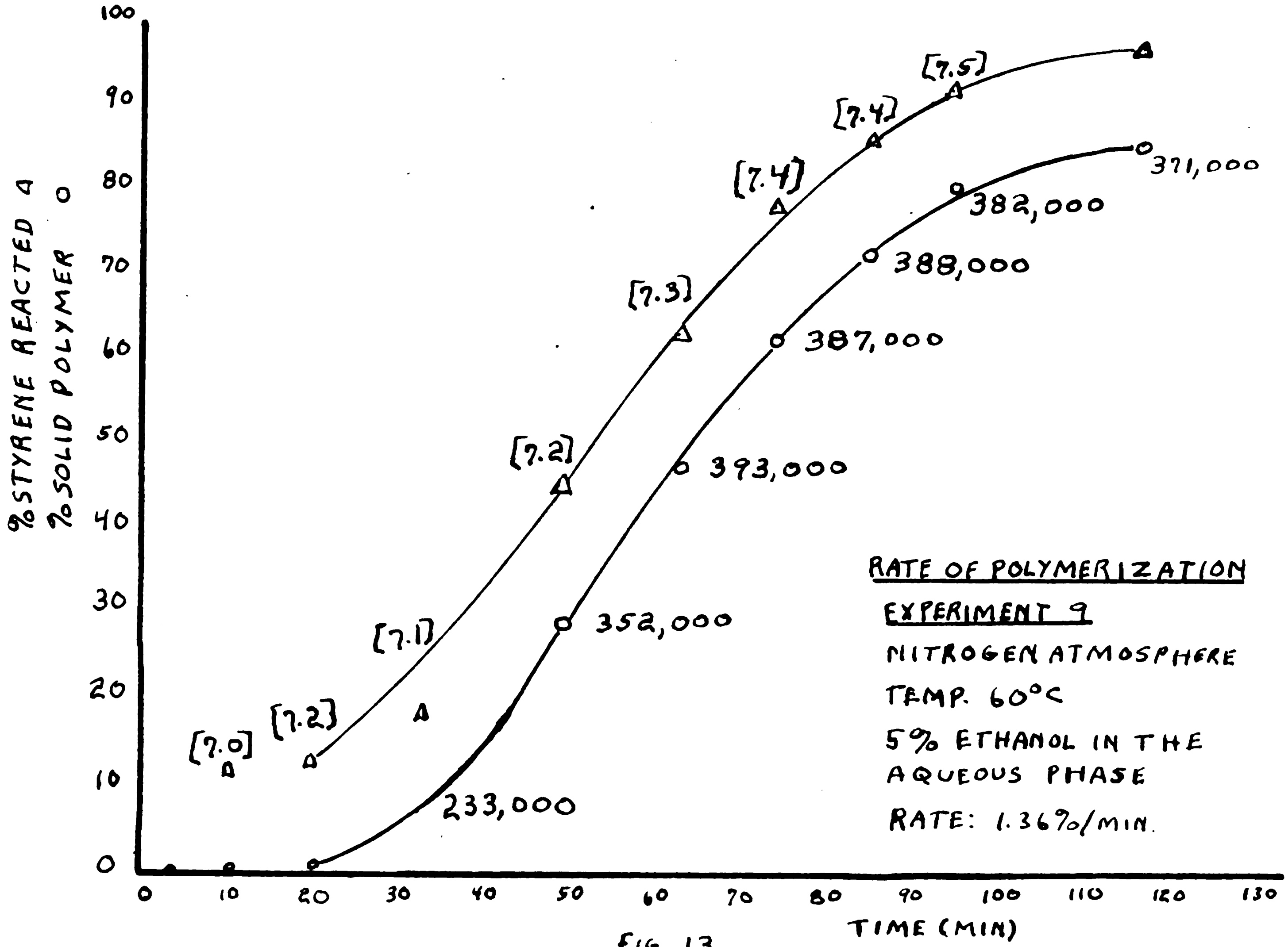

%STYRENE REACTED △
%SOLID POLYMER ○
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
TIME (MIN)
[7.0]
[7.2]
[7.1]
[7.2]
[7.3]
[7.4]
[7.4]
[7.5]
233,000
352,000
393,000
387,000
388,000
382,000
371,000
RATE OF POLYMERIZATION
EXPERIMENT 9
NITROGEN ATMOSPHERE
TEMP. 60°C
5% ETHANOL IN THE
AQUEOUS PHASE
RATE: 1.36%/MIN.

FIG. 13

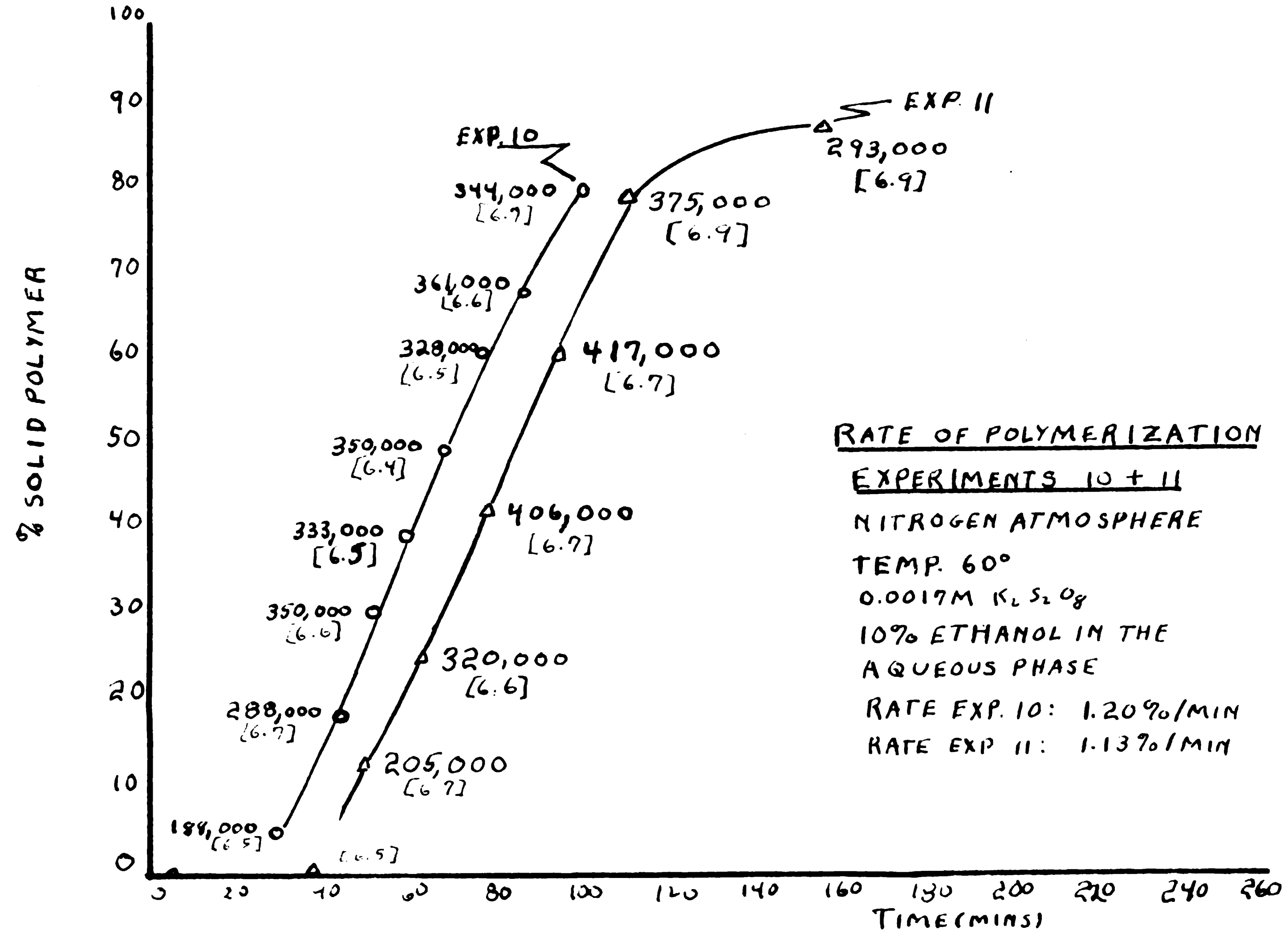
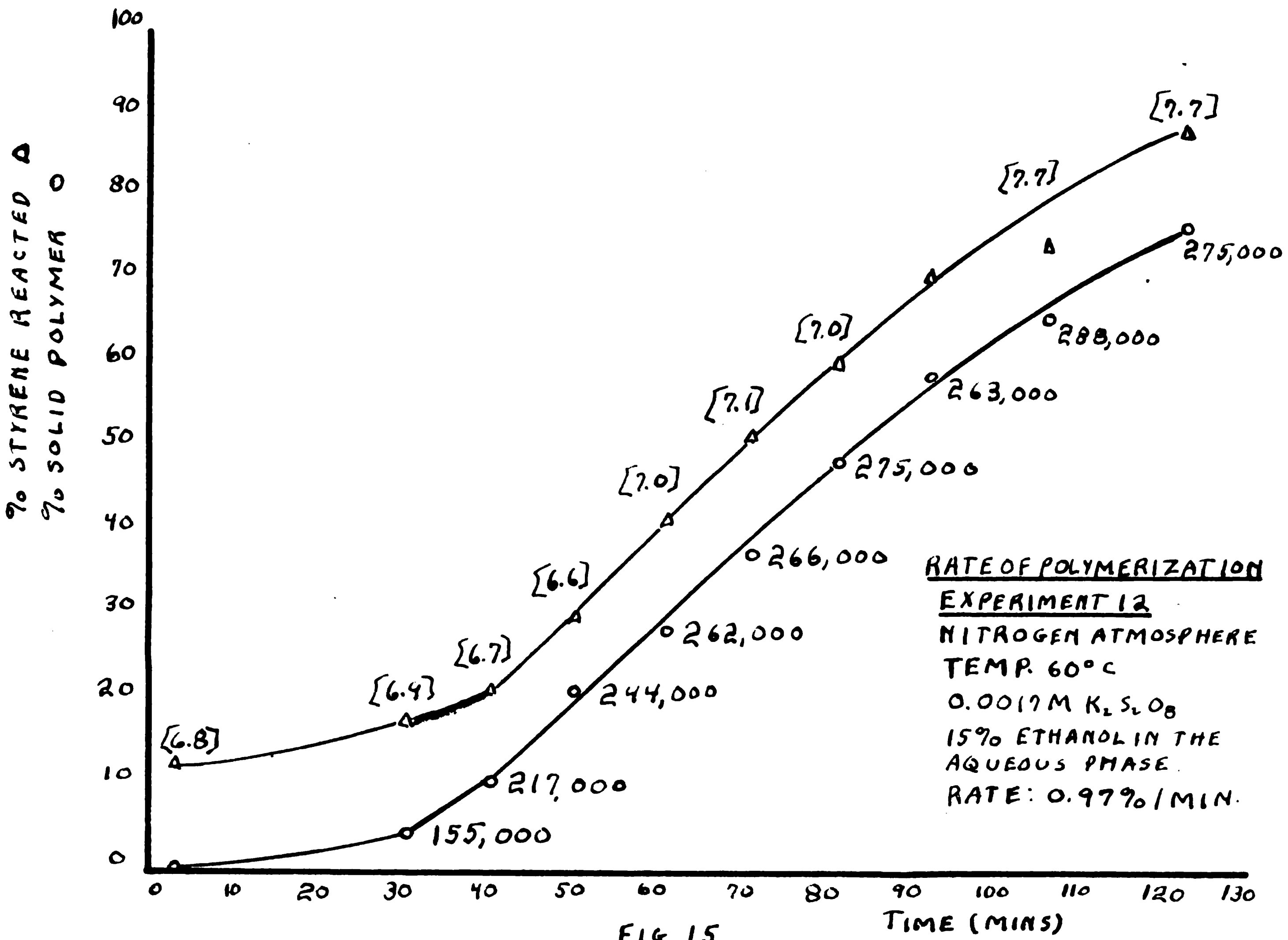

RATE OF POLYMERIZATION
EXPERIMENTS 10 + 11
NITROGEN ATMOSPHERE
TEMP. 60°
0.0017M $K_2S_2O_8$
10% ETHANOL IN THE AQUEOUS PHASE
RATE EXP. 10: 1.20%/MIN
RATE EXP 11: 1.13%/MIN
EXP. 10
EXP. 11
344,000 [6.7]
364,000 [6.6]
328,000 [6.5]
350,000 [6.4]
333,000 [6.5]
350,000 [6.6]
288,000 [6.7]
184,000 [6.5]
293,000 [6.9]
375,000 [6.9]
417,000 [6.7]
406,000 [6.7]
320,000 [6.6]
205,000 [6.7]
[6.5]
% SOLID POLYMER
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200
220
240
260
TIME (MINS)

FIG. 14



% STYRENE REACTED Δ
% SOLID POLYMER O
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
TIME (MINS)
[6.8]
[6.4]
[6.7]
[6.6]
[7.0]
[7.1]
[7.0]
[7.7]
[7.7]
155,000
217,000
244,000
262,000
266,000
275,000
263,000
288,000
275,000
RATE OF POLYMERIZATION
EXPERIMENT 12
NITROGEN ATMOSPHERE
TEMP. 60°C
0.0017M $K_2S_2O_8$
15% ETHANOL IN THE AQUEOUS PHASE
RATE: 0.97%/MIN.

FIG 15

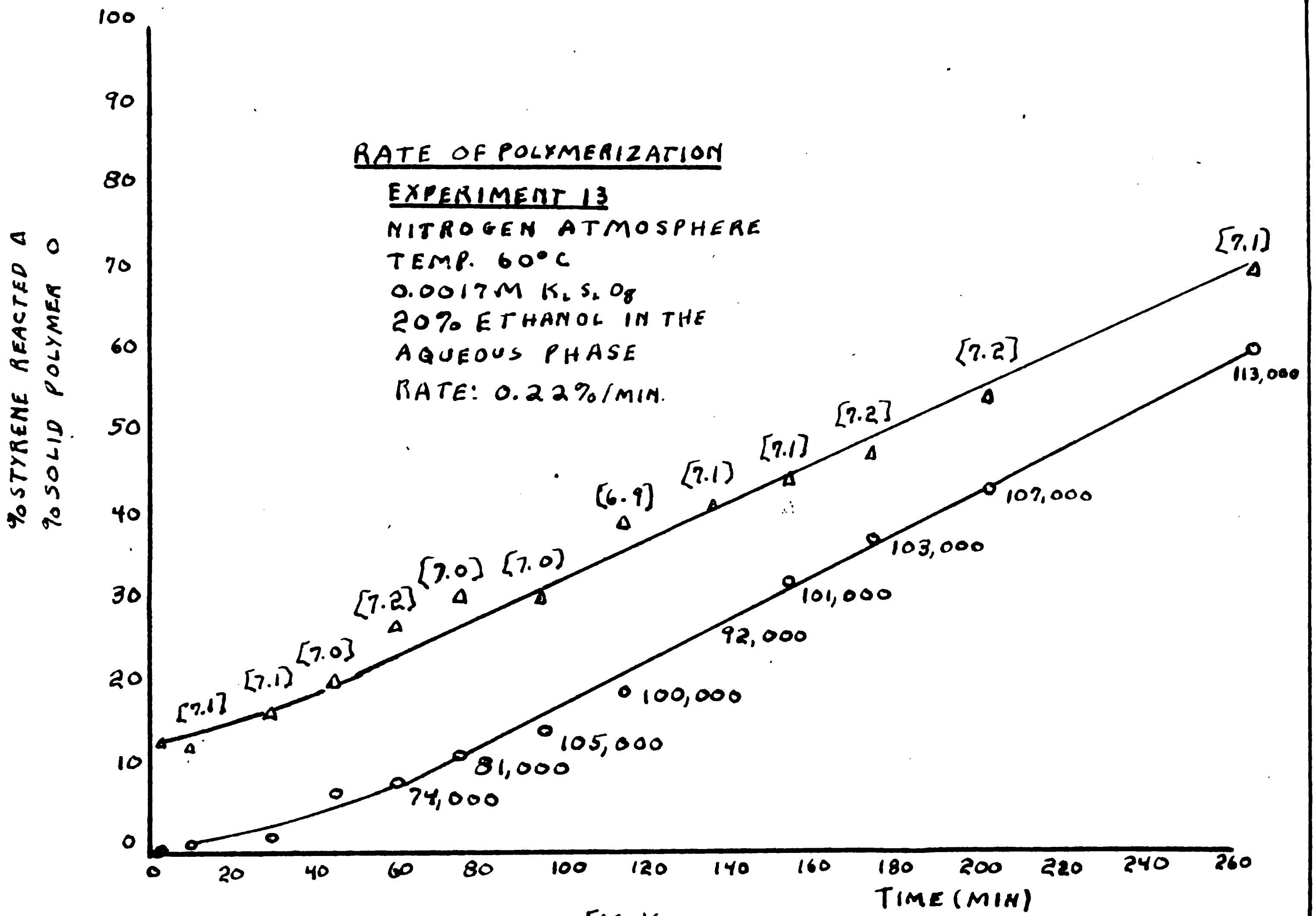

RATE OF POLYMERIZATION
EXPERIMENT 13
NITROGEN ATMOSPHERE
TEMP. 60°C
0.0017M $K_2S_2O_8$
20% ETHANOL IN THE
AQUEOUS PHASE
RATE: 0.22%/MIN.
% STYRENE REACTED Δ
% SOLID POLYMER O
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
160
180
200
220
240
260
TIME (MIN)
[7.1]
[7.1]
[7.0]
[7.2]
[7.0]
[7.0]
[6.9]
[7.1]
[7.1]
[7.2]
[7.2]
[7.1]
74,000
81,000
105,000
100,000
92,000
101,000
103,000
107,000
113,000

FIG 16

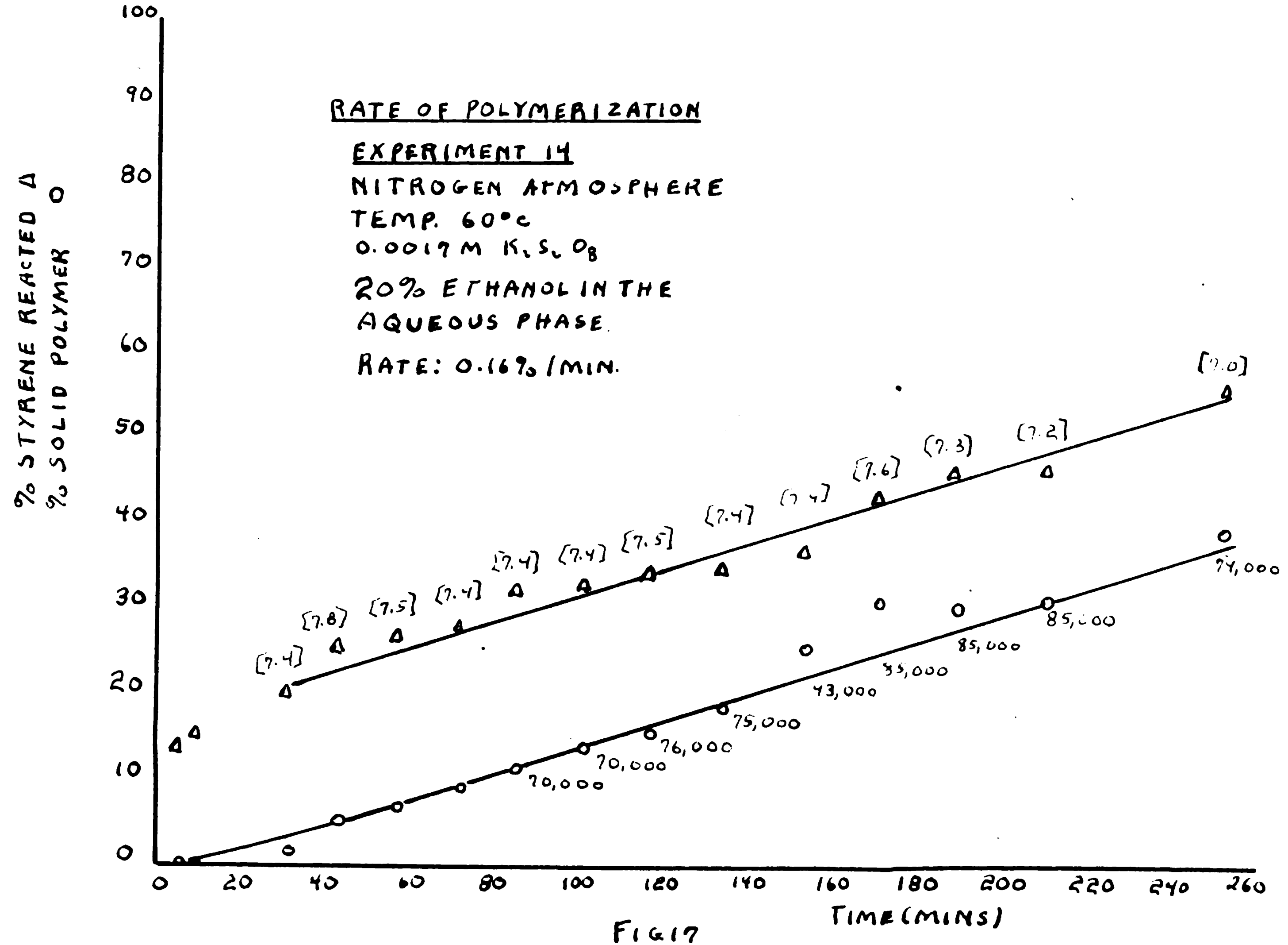
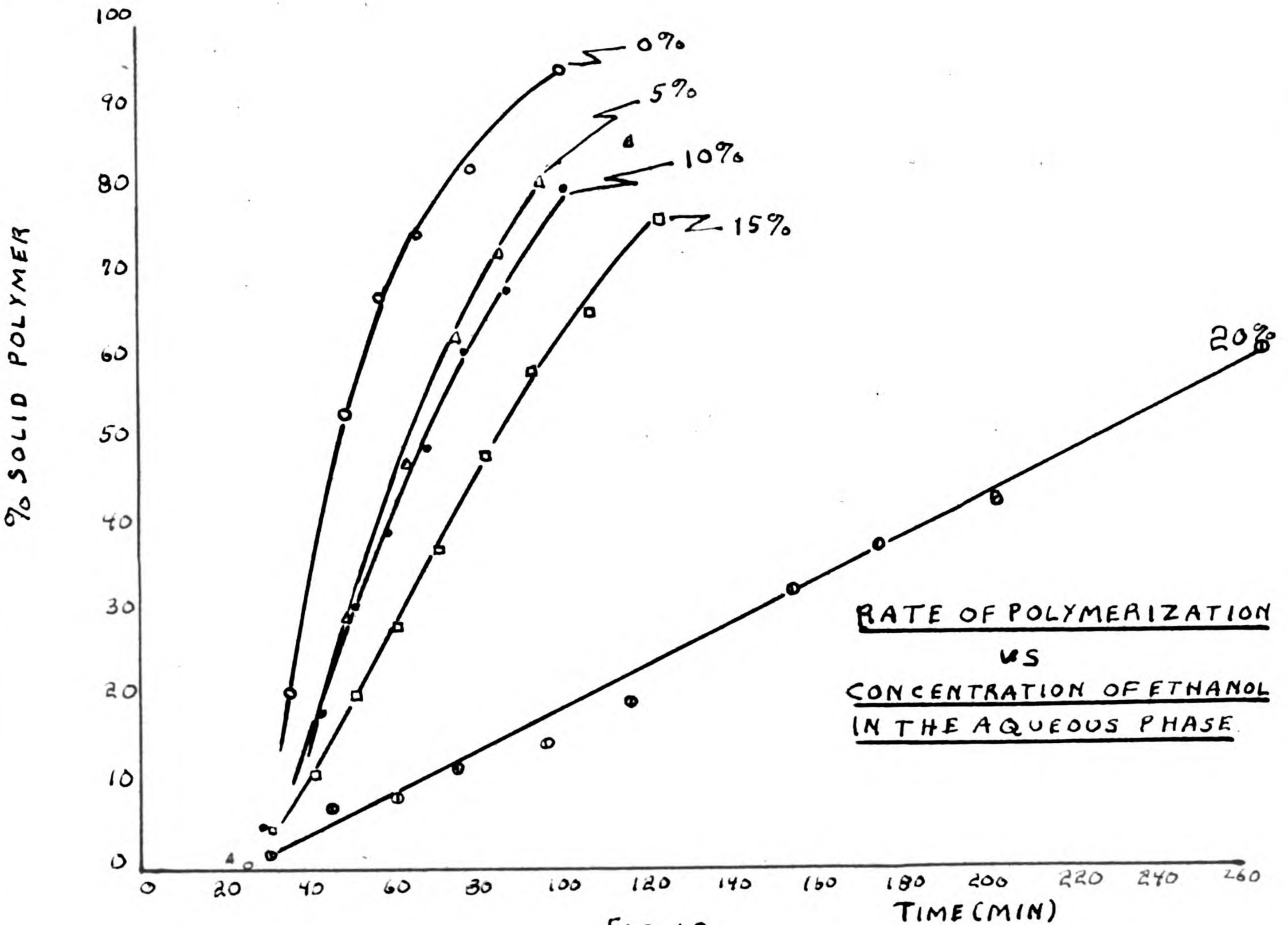

RATE OF POLYMERIZATION
EXPERIMENT 14
NITROGEN ATMOSPHERE
TEMP. 60°C
0.0017M $K_2S_2O_8$
20% ETHANOL IN THE AQUEOUS PHASE
RATE: 0.16%/MIN.
% STYRENE REACTED Δ
% SOLID POLYMER O
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
160
180
200
220
240
260
TIME (MINS)
[7.4]
[7.8]
[7.5]
[7.4]
[7.4]
[7.4]
[7.5]
[7.4]
[7.4]
[7.6]
[7.3]
[7.2]
[7.0]
70,000
70,000
76,000
75,000
43,000
35,000
85,000
85,000
74,000

FIG 17



RATE OF POLYMERIZATION
VS
CONCENTRATION OF ETHANOL
IN THE AQUEOUS PHASE

FIG 18

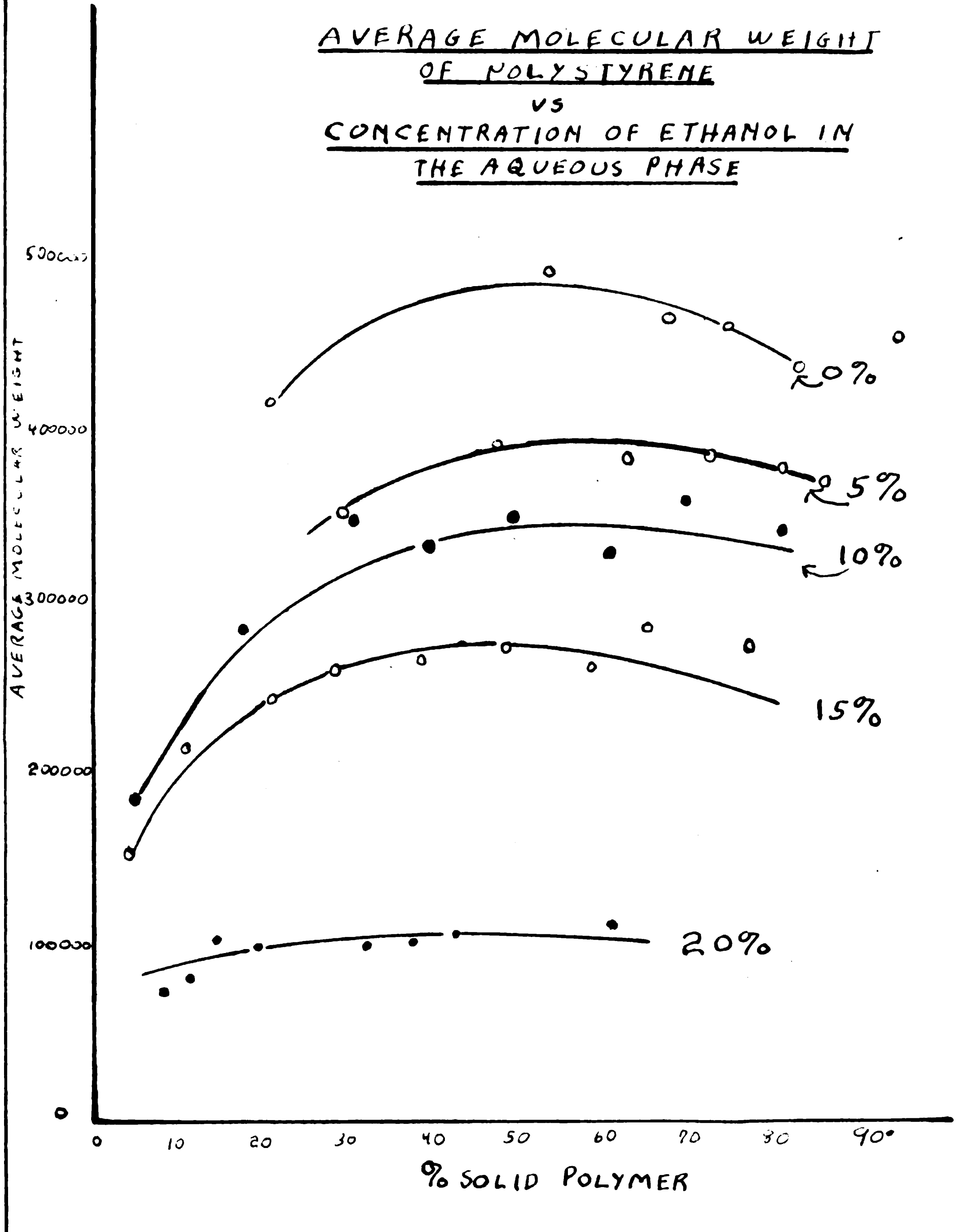

AVERAGE MOLECULAR WEIGHT OF POLYSTYRENE VS CONCENTRATION OF ETHANOL IN THE AQUEOUS PHASE

FIG 19

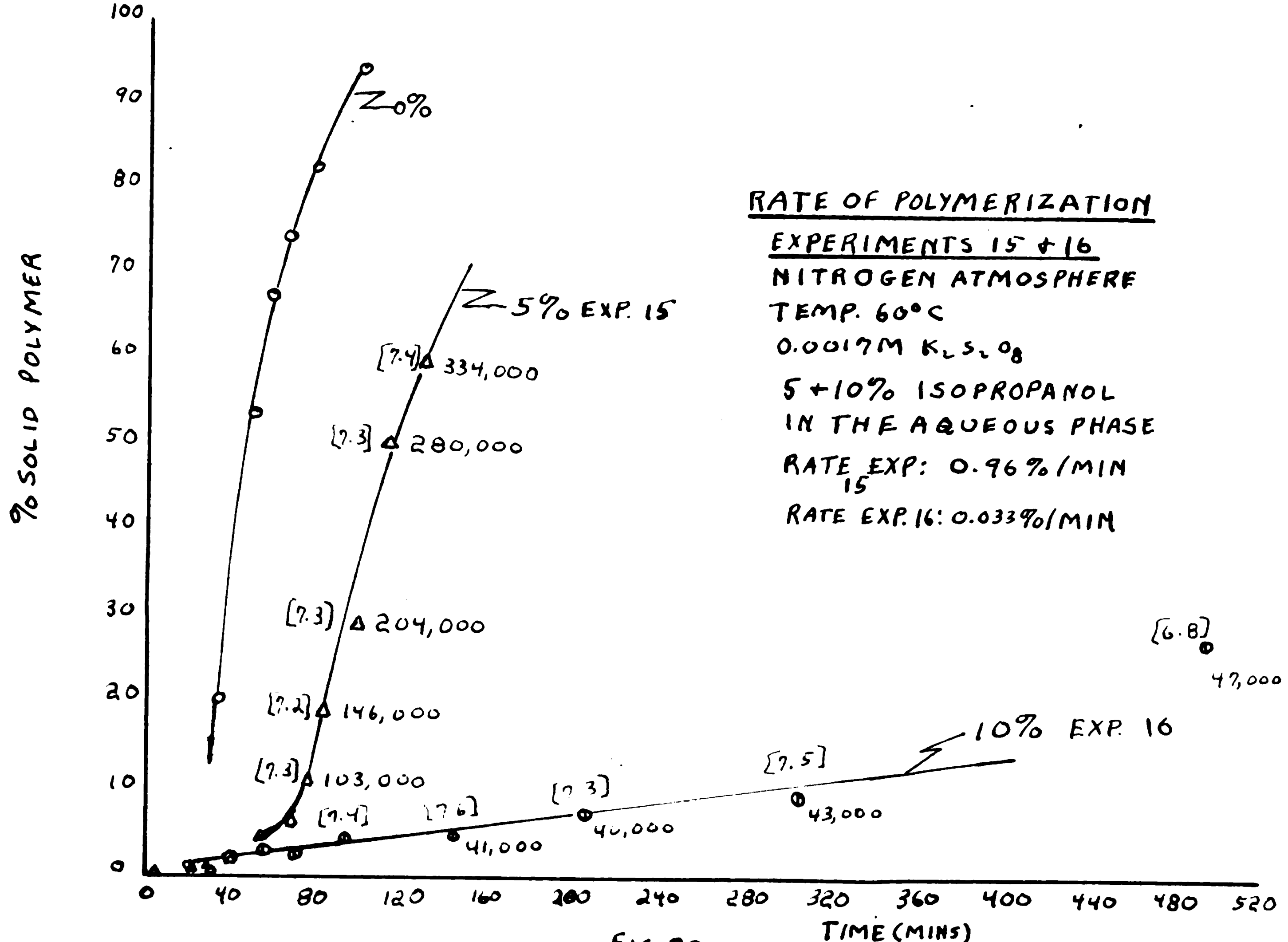
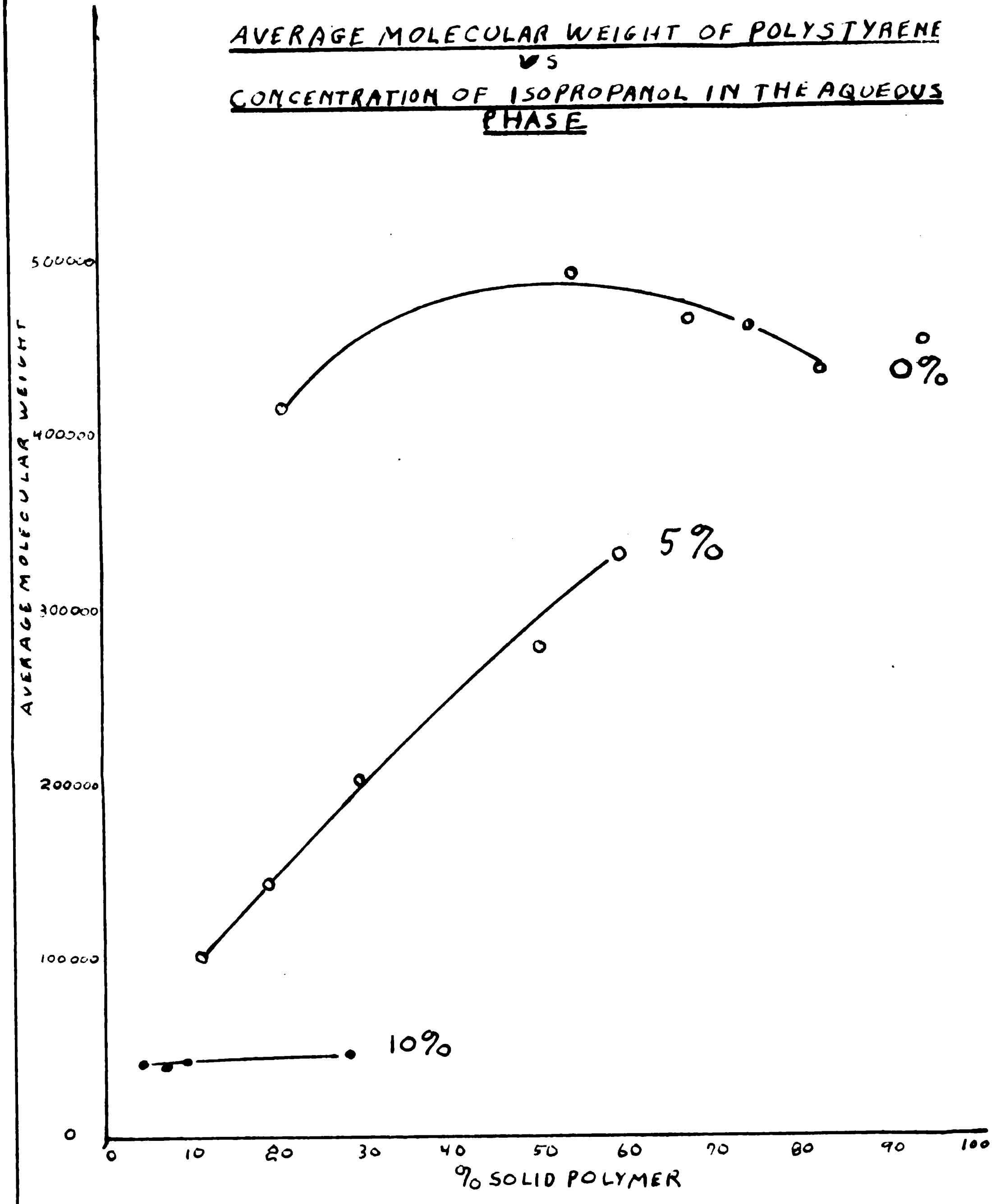

RATE OF POLYMERIZATION
EXPERIMENTS 15 + 16
NITROGEN ATMOSPHERE
TEMP. 60°C
0.0017M $K_2S_2O_8$
5 + 10% ISOPROPANOL
IN THE AQUEOUS PHASE
RATE EXP$_{15}$: 0.96%/MIN
RATE EXP. 16: 0.033%/MIN
% SOLID POLYMER
100
90
80
70
60
50
40
30
20
10
0
0
40
80
120
160
200
240
280
320
360
400
440
480
520
TIME (MINS)
0%
5% EXP. 15
10% EXP. 16
[7.4] 334,000
[7.3] 280,000
[7.3] 204,000
[7.2] 146,000
[7.3] 103,000
[7.4]
[7.6] 41,000
[7.3] 40,000
[7.5] 43,000
[6.8] 47,000

FIG 20



AVERAGE MOLECULAR WEIGHT OF POLYSTYRENE VS CONCENTRATION OF ISOPROPANOL IN THE AQUEOUS PHASE

FIG. 21

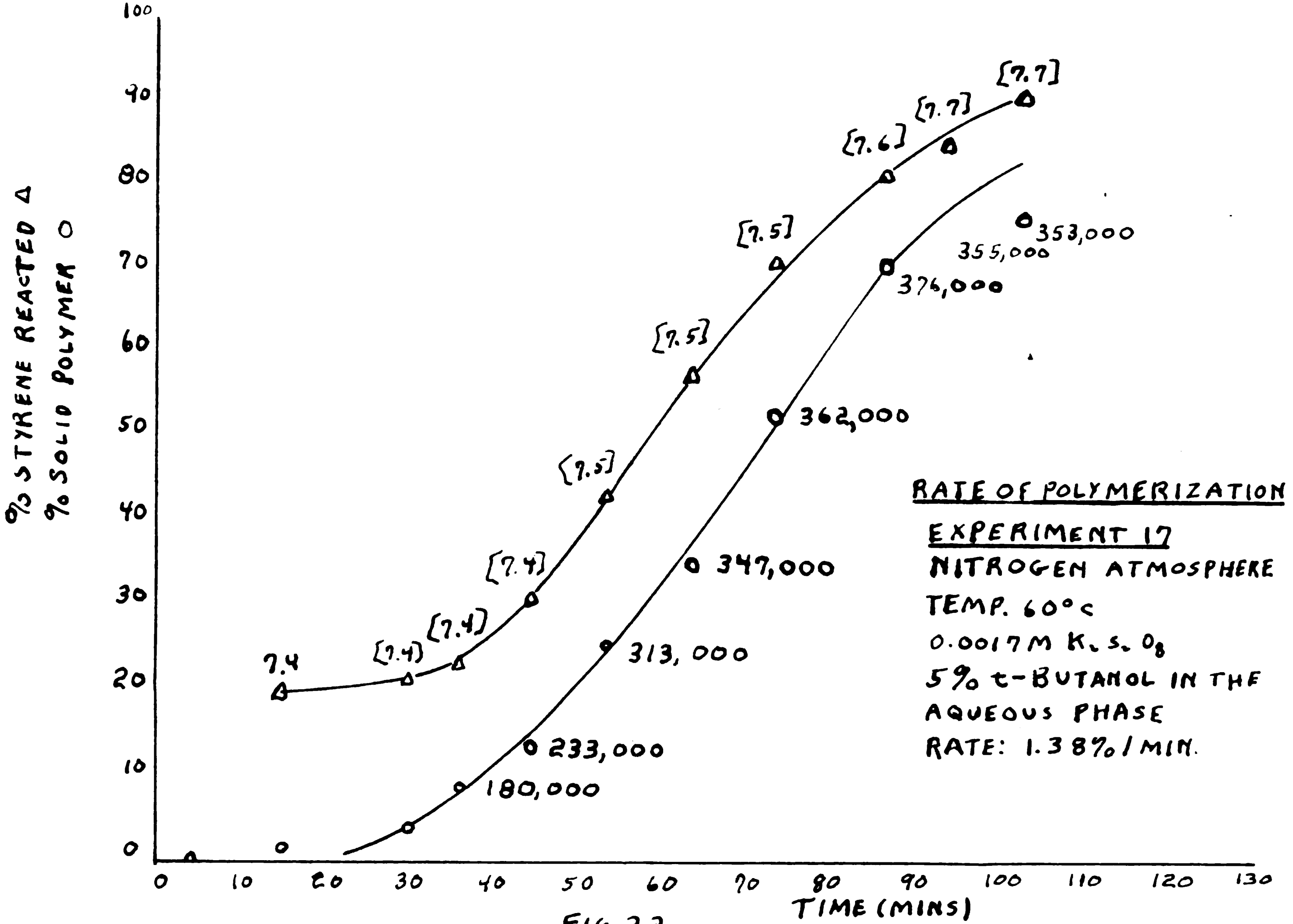

% STYRENE REACTED △
% SOLID POLYMER ○
0
10
20
30
40
50
60
70
80
90
100
0
10
20
30
40
50
60
70
80
90
100
110
120
130
TIME (MINS)
7.4
[7.4]
[7.4]
[7.4]
[7.5]
[7.5]
[7.5]
[7.6]
[7.7]
[7.7]
180,000
233,000
313, 000
347,000
362,000
376,000
355,000
353,000
RATE OF POLYMERIZATION
EXPERIMENT 17
NITROGEN ATMOSPHERE
TEMP. 60°c
0.0017M K₂S₂O₈
5% t-BUTANOL IN THE
AQUEOUS PHASE
RATE: 1.38%/MIN.

FIG. 22

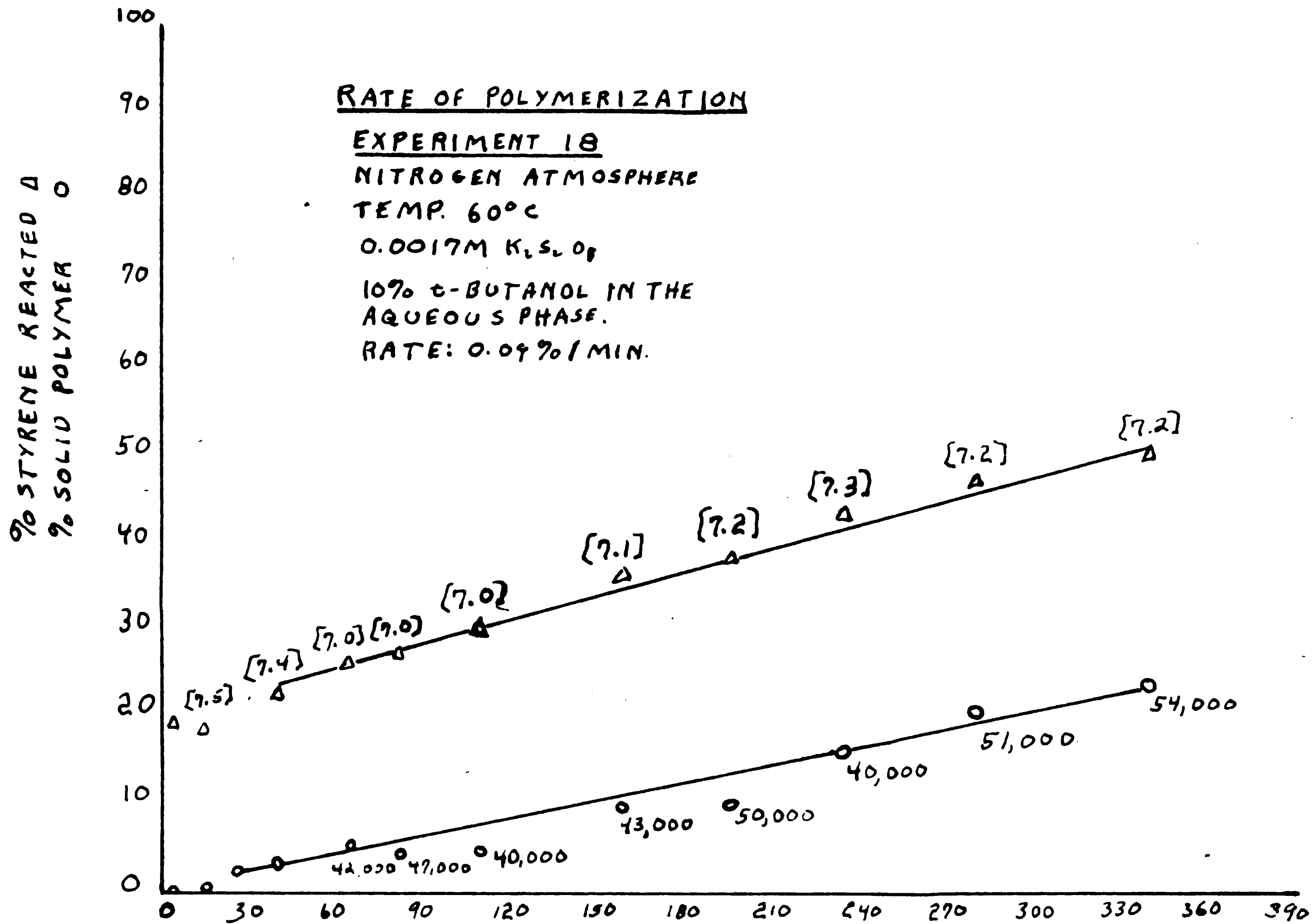

RATE OF POLYMERIZATION
EXPERIMENT 18
NITROGEN ATMOSPHERE
TEMP. 60°C
0.0017M $K_2S_2O_8$
10% t-BUTANOL IN THE AQUEOUS PHASE.
RATE: 0.09%/MIN.
% STYRENE REACTED △
% SOLID POLYMER O
0
10
20
30
40
50
60
70
80
90
100
0
30
60
90
120
150
180
210
240
270
300
330
360
390
TIME (MINS)
[7.5]
[7.4]
[7.0]
[7.0]
[7.0]
[7.1]
[7.2]
[7.3]
[7.2]
[7.2]
42,000
47,000
40,000
43,000
50,000
40,000
51,000
54,000

FIG. 23

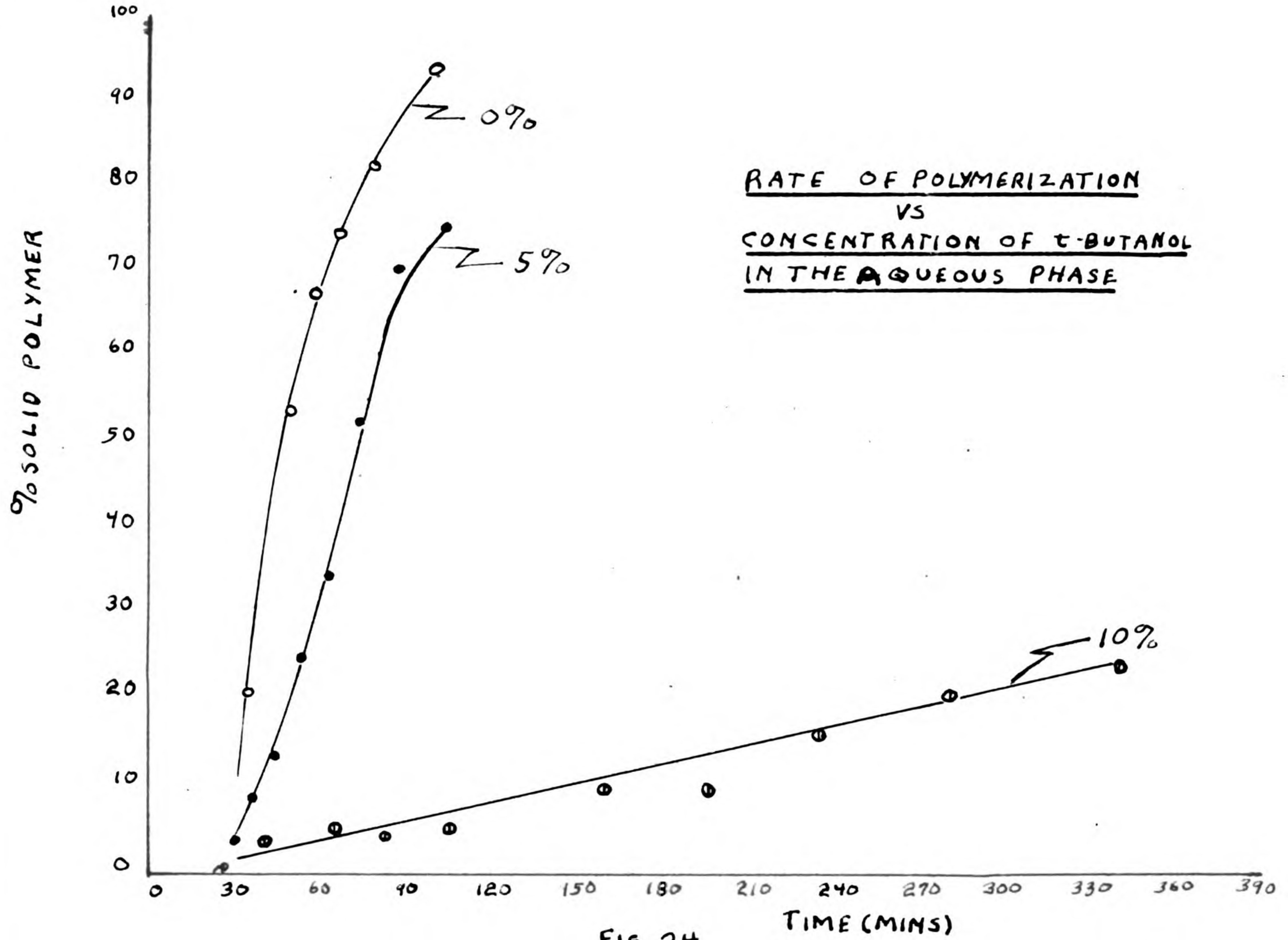
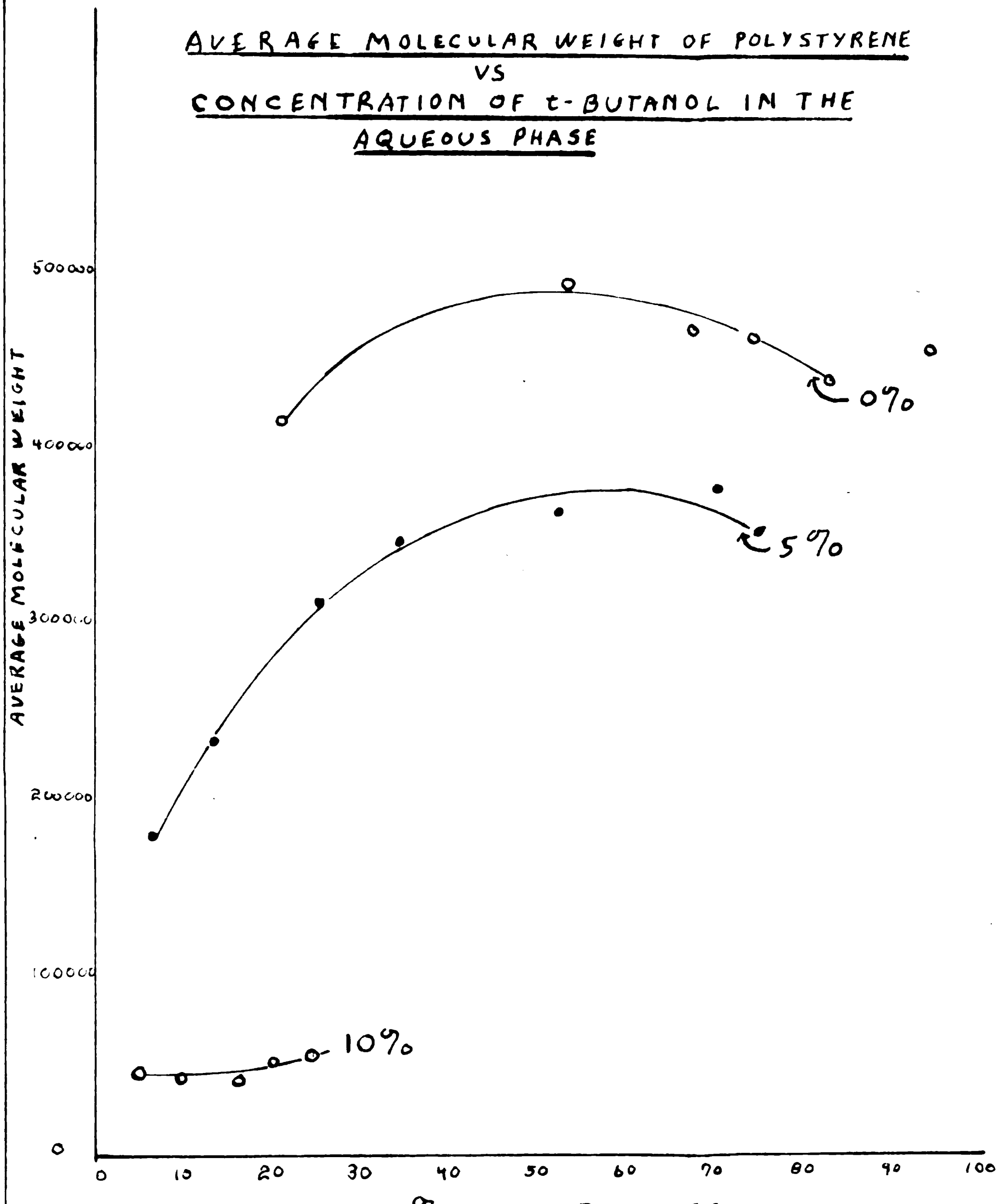
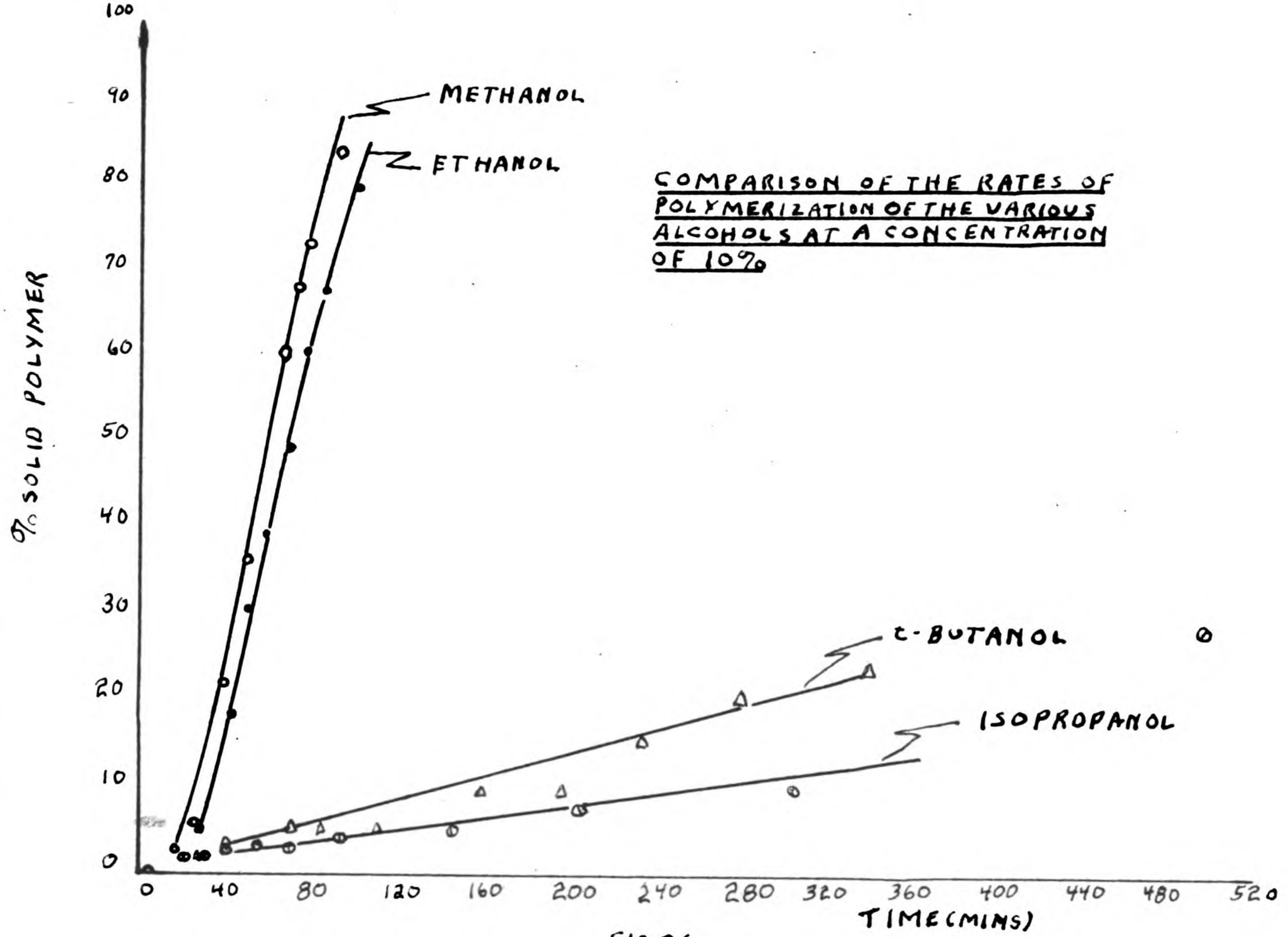

RATE OF POLYMERIZATION
VS
CONCENTRATION OF t-BUTANOL
IN THE AQUEOUS PHASE
% SOLID POLYMER
0
10
20
30
40
50
60
70
80
90
100
TIME (MINS)
0
30
60
90
120
150
180
210
240
270
300
330
360
390
0%
5%
10%

FIG. 24



AVERAGE MOLECULAR WEIGHT OF POLYSTYRENE
VS
CONCENTRATION OF t-BUTANOL IN THE
AQUEOUS PHASE

FIG. 25



COMPARISON OF THE RATES OF POLYMERIZATION OF THE VARIOUS ALCOHOLS AT A CONCENTRATION OF 10%

FIG 26

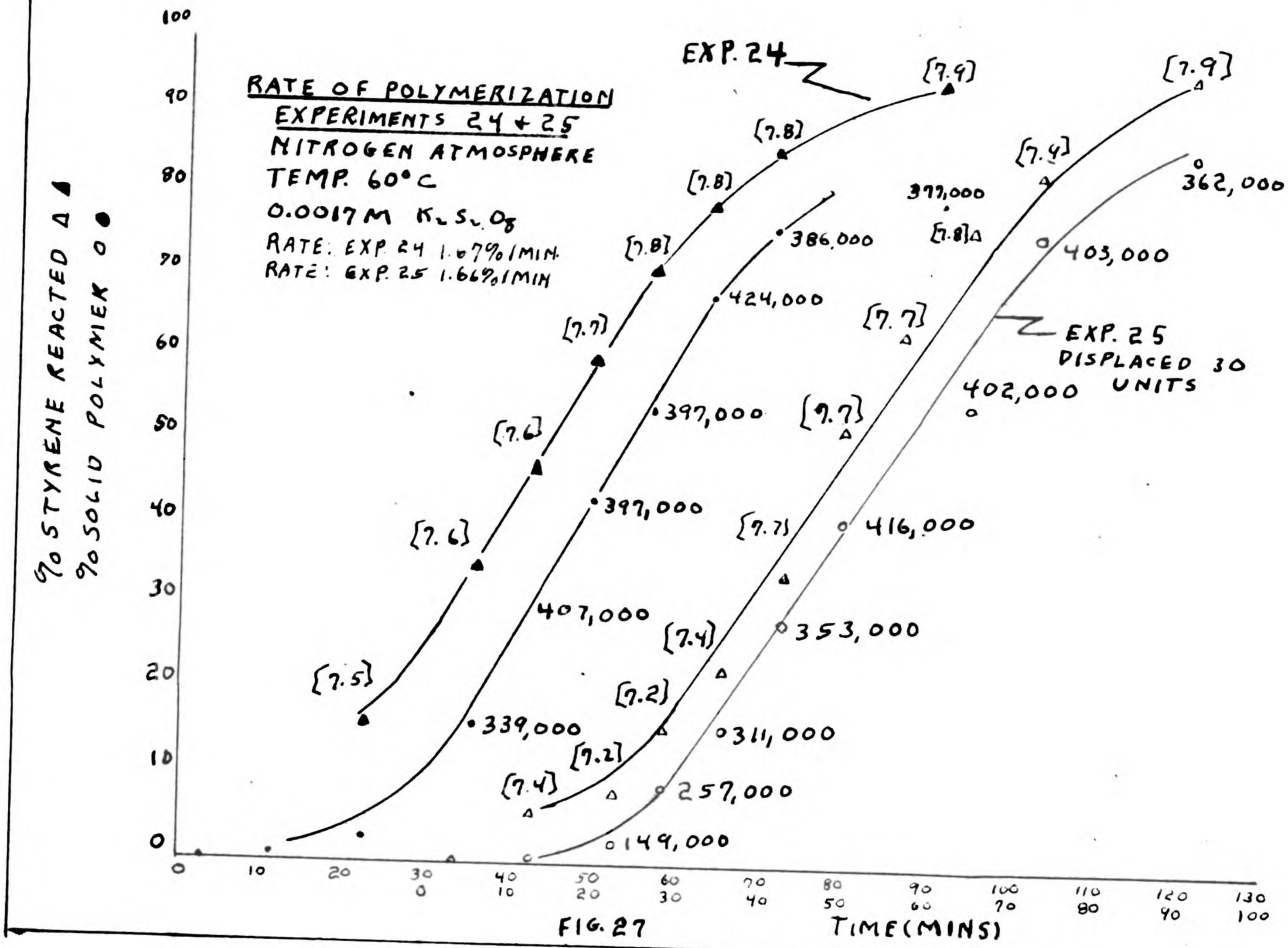

RATE OF POLYMERIZATION
EXPERIMENTS 24 + 25
NITROGEN ATMOSPHERE
TEMP. 60°C
0.0017M K₂S₂O₈
RATE: EXP. 24 1.67%/MIN.
RATE: EXP. 25 1.66%/MIN
% STYRENE REACTED △ ▲
% SOLID POLYMER ○ ●
EXP. 24
EXP. 25
DISPLACED 30 UNITS
TIME (MINS)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
0
10
20
30
40
50
60
70
80
90
100
[7.5]
[7.6]
[7.6]
[7.7]
[7.8]
[7.8]
[7.8]
[7.9]
[7.4]
[7.2]
[7.2]
[7.4]
[7.7]
[7.7]
[7.7]
[7.8]
[7.4]
[7.9]
339,000
407,000
397,000
397,000
424,000
386,000
397,000
149,000
257,000
311,000
353,000
416,000
402,000
403,000
362,000

FIG. 27

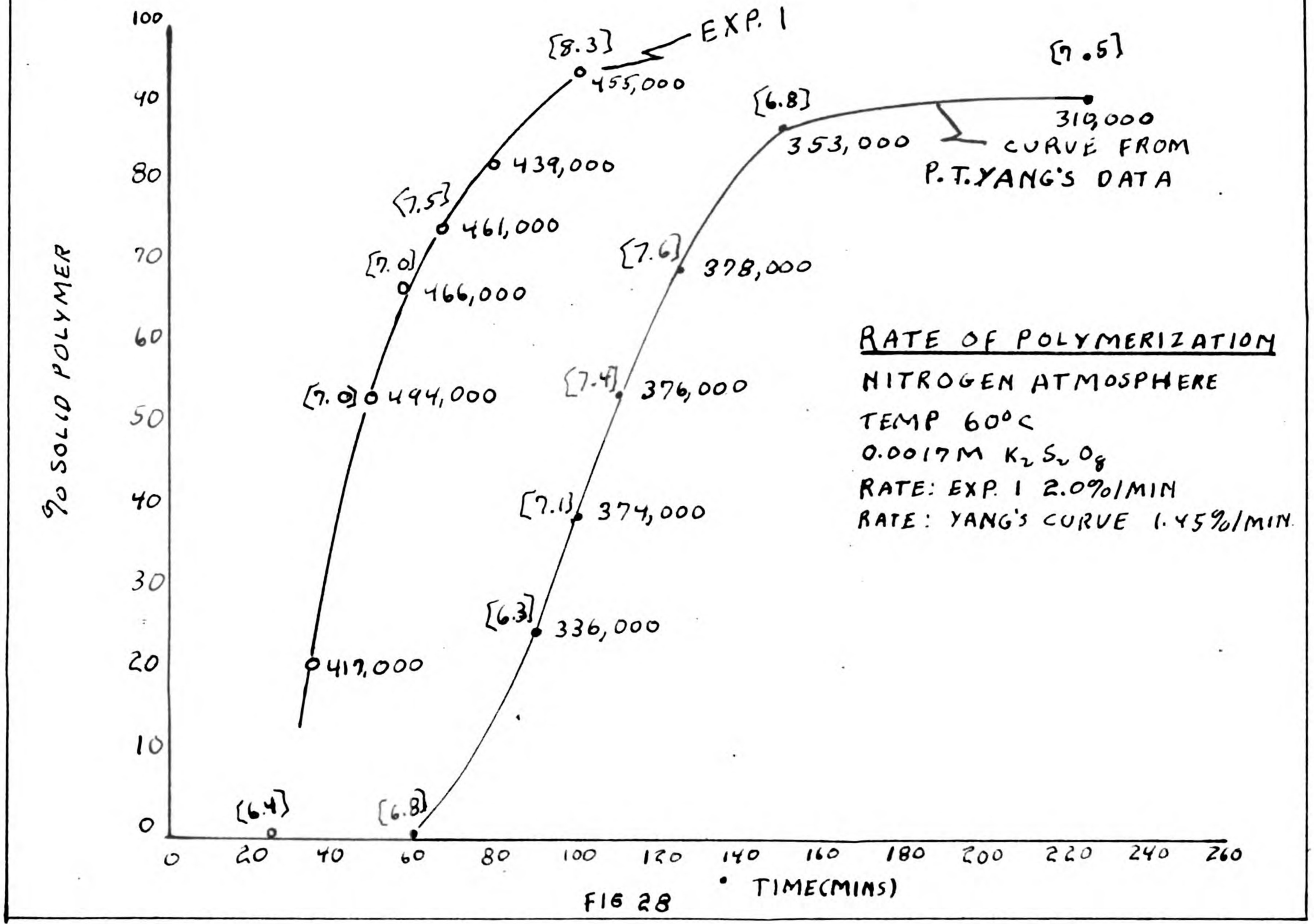

EXP. I
[8.3]
455,000
439,000
[7.5]
461,000
[7.0]
466,000
[7.0]
494,000
417,000
[7.5]
[6.8]
353,000
310,000
CURVE FROM
P. T. YANG'S DATA
[7.6]
378,000
[7.4]
376,000
[7.1]
374,000
[6.3]
336,000
[6.4]
[6.8]
RATE OF POLYMERIZATION
NITROGEN ATMOSPHERE
TEMP 60°C
0.0017M $K_2S_2O_8$
RATE: EXP. I 2.0%/MIN
RATE: YANG'S CURVE 1.45%/MIN.
% SOLID POLYMER
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
140
160
180
200
220
240
260
TIME(MINS)

FIG 28

THEORY AND DISCUSSION

The starting point for the growth of polymeric chains has frequently been postulated to be activated monomers from which polymeric chains are built up by the addition of single monomeric units. This particular growth of chains is inhibited by the presence of air, or more exactly, by oxygen. It was postulated, and later shown to be true, that the oxygen reacts preferentially with the activated monomer to form peroxides[26, 27,30]. Breitenboch[21] performed the emulsion reactions under nitrogen and obtained more consistent results.

In no case was there any mention of the fact that the carbon dioxide of the air had any effect on the polymerizing system. In order to determine whether or not carbon dioxide had any effect on an emulsion polymerization system, experiments were prepared conducting the reaction under an atmosphere of carbon dioxide and comparing it with those reactions conducted under an atmosphere of nitrogen, and a mixture of 95% nitrogen and 5% oxygen respectively.

The rate of polymerization and the induction period for Experiment #1 (Figure 1, nitrogen atmosphere) and Experiment #2 (Figure 2, carbon dioxide atmosphere) are almost identical, in contrast to the effect of Experiment #3 (Figures 3 and 4, oxygen atmosphere) which is to definitely decrease the rate of polymerization.

The most pronounced effect is on the average molecular weight. The polymer from Experiment #3 (oxygen atmosphere) was over 300,000 units lower than those of Experiments #1 (nitrogen atmosphere) and #2 (carbon dioxide atmosphere). This lowering must be attributed to the fact that the oxygen acts as a chain terminator and deactivator.

The average molecular weight of the polymer from Experiment #2 (carbon dioxide atmosphere) averaged 30,000 units less than that from Experiment #1 (nitrogen atmosphere). This lowering is probably due to the decrease in the pH of the former reaction resulting from the formation of carbonic acid. Since protons are known to act as chain terminators, a lowering of the molecular weight would be expected. However, since carbonic acid is a weak acid, it liberates only a few protons, thus accounting for the rather small lowering of the average molecular weight.

The pH lowering toward the end of the polymerization in Experiment #3 (oxygen atmosphere) may be attributed to the decomposition of the potassium persulfate to potassium bisulfate which is acidic. Ordinarily it was found that in a reaction under a nitrogen atmosphere, not exceeding two hours in duration, the potassium persulfate could be considered substantially stable, but on standing at 60°C the decomposition becomes apparent and appreciable.

Since the styrene in an emulsion polymerization forms peroxides in the presence of oxygen, a sample of the polymer obtained from Experiment #3 was tested by a procedure described by Nozacki[34]. The method consists of dissolving the polymer in acetic anhydride containing some chloroform. Sodium iodide is added and the solutions allowed to stand from 5 to 15 minutes. The development of a yellow color due to iodine indicates the presence of peroxides. The polymer which was tested formed a yellow colored solution showing the presence of peroxide in the polymer.

Since emulsion polymerization is initiated in the aqueous phase and the polymeric chains grow by addition of monomer, also in the aqueous phase, an increase in the solubility of monomer in the aqueous phase might tend to produce polymers of longer chains by making more monomer available at the site of the growing chains. In order to increase the solubility of monomer in the aqueous phase some solvent which dissolves styrene should be added to the aqueous phase.

In the case of solution polymerization the solvents must be such that both the monomer and polymer are dissolved, and therefore hydrocarbons, such as toluene and benzene, were used for this purpose. The use of alcohols was reported only in one case[9b]. They proved ineffective since, although the monomer was soluble in the alcohol, the polymer was insoluble and would precipitate in the course of polymerization.

In emulsion polymerization, hydrocarbons cannot be used due to their insolubility in the aqueous phase. Since a compound dissolving styrene and also soluble in water was necessary, the saturated alcohols with low molecular weights appeared satisfactory. The high molecular weight polymers may tend to precipitate in the presence of these alcohols, but in an emulsion polymerization the emulsifying agent keeps the polymer in suspension.

Use of an alcohol-water solution as the aqueous phase should increase the solubility of styrene, but as a consequence introduces another variable into the system. The alcohol may, in addition to increasing the solubility of monomer, act as a chain terminator or deactivator causing a decrease in the molecular weight.

Since the alcohols are soluble in both monomer and water, they would distribute themselves between the two phases, but would be concentrated principally in the aqueous phase because of the larger volume of the latter. Since dilute solutions were used, the amount dissolved in the monomer would be small and therefore its effect as a solvent or contaminant of the monomer was considered negligible.

It has been shown (Experiments 5-18) that the effect of using various water soluble alcohols in the aqueous phase of an emulsion polymerization was to lower the molecular weight and reduce the rate of overall polymerization. The rate of overall polymerization, as considered in this paper, is the percent theoretical yield of solid polymer formed per unit time. This rate was calculated for the "straight line" portion of the curves of percent theoretical yield versus time. This percent theoretical yield of solid polymer is termed "% solid polymer" on these graphs.

Flory[13a] was the first to suggest the possibility of chain transfer in polymerization whereby growing chains may be terminated by collision with solvent molecules. The activated solvent molecule may then initiate another chain by colliding with a monomer molecule and activate it or cause branching by colliding with a long chain.

It has been shown by many workers using non-catalyzed solution polymerization[35] that while the rate of formation of polymer was slower than that of bulk polymerization, the rate of chain growth was not affected by the solvent. The degree of polymerization, however, varied markedly with the solvent used.

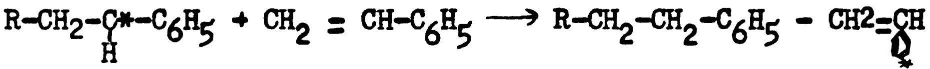
Mayo[36] interpreted the work of Suess[11a] and Schulz[25b] on solution polymerization on the basis of chain transfer. Although Mayo was dealing with non-catalyzed polymerization of styrene, his arguments may be applied to emulsion polymerization if the effect of the potassium persulfate is considered negligible due to its relatively small concentration. He states that the growth of polymer chains proceeds by addition of styrene units as follows:

(1) $R^* + C_6H_5CH = CH_2 \longrightarrow (R{-}CH_2\ {-}CH{-}C_6H_5)^*$

(*) designates an activated molecule

The reaction can then be terminated by one of the three following mechanisms:

(2) $2(R{-}CH_2{-}CHC_6H_5)^* \longrightarrow R{-}CH = CHC_6H_5 + R{-}CH_2{-}CH_2{-}C_6H_5$

(3) 

$R{-}CH_2{-}\underset{H}{C}^*{-}C_6H_5 + CH_2 = CH{-}C_6H_5 \longrightarrow R{-}CH_2{-}CH_2{-}C_6H_5 - CH2{=}\underset{Q^*}{CH}$

(4) $(R{-}CH_2{-}CH{-}C_6H_5)^* + S{-}H \longrightarrow S^* + R{-}CH_2{-}CH_2{-}C_6H_5$

Reaction (2) has been shown to occur but only to a small extent [15c]. The importance of reaction (3) has not been determined. Reaction (4) is that with solvent and is considered in detail in this paper.

If the activated solvent molecule reacts readily with styrene monomer, another chain would be started. Were this the only effect, the result would be a decrease in average molecular weight with no decrease in the overall rate of polymerization.

If upon formation the activated solvent molecules do not react readily with monomer, they will accumulate in the solution and, by a reaction analogous to (2), destroy the reaction chain. The effect would be to reduce the overall rate of polymerization and the average molecular weight.

The effect of reducing the overall rate of polymerization may be approached from a different point of view. If an activated monomer collides with a solvent molecule and this molecule absorbs part or all of the energy of activation, that monomer would be effectively terminated.

The solvent molecule in absorbing the energy of activation need not be activated to such a degree that it must react by a mechanism analogous to (2) in order to be deactivated, nor need it transfer the activation energy by reaction with monomer. It may instead, absorb the energy and retain it, remaining inert insofar as the polymerization reaction is concerned. The net effect of such a process could be called deactivation.

If deactivation occurs, the overall rate of polymerization would be decreased and the average molecular weight would be reduced; the latter resulting from the fact that growing chains would be terminated by solvent before a high molecular weight was attained. The lowering of the molecular weight would depend on the concentration of solvent since the probability of termination increases with increasing concentration of solvent.

Norrish and Smith[37] in the study of velocity constants of certain bimolecular reactions in solution observed that some solvents decrease the rate of reaction as compared to the same reaction in the gaseous state. The decrease in rate was explained by the collision of reactants with solvent molecules. A line of reasoning similar to that of the above authors was applied to reaction rate calculations in this paper.

Essentially the theory of reaction in the gaseous phase states that in order to have a reaction between two molecules it is necessary that they collide with a combined energy equal to or greater than, E, the energy of activation. The proportion of molecules for which the kinetic energy exceeds, E, is[39]:

$$\frac{\text{Number of effective collisions}}{\text{Total number of collisions}} = e^{-\frac{E}{RT}}$$

Norrish and Smith following the method of Lewis[38], calculated the average rate of collisions occurring between like atoms or molecules in the gaseous state by the equation:

(5) $Z = \sqrt{2}\,\pi\,\sigma^2 u\, n^2$

where: Z = number of molecules entering into collision per cc per second

σ = diameter of the molecule

u = root mean square velocity = $(3RT/M)^{\frac{1}{2}}$

n = number of molecules per cc

Designating the rate of effective collisions as "k", an expression is obtained which can be used to calculate the rate of reaction between like molecules in the gaseous state:

(6) $k = \pi\sigma^2 n^2\,(6RT/M)^{\frac{1}{2}}\, e^{-\frac{E}{RT}}$ where k = number of effective collisions per sec per cc

Substituting (5):

(7) $k = Z\, e^{-\frac{E}{RT}}$

This equation when applied to reactions in the gaseous state gave good agreement between the observed and calculated rates.

Norrish and Smith applied this equation to reactions in solutions assuming that the solvent acted only as free space. They found that the rate of reaction in some solvents was not affected as compared to that in the gaseous state, while other solvents lowered the rate. A probability factor, P, was introduced to account for the discrepancies that occur between the observed and calculated rates due to factors which are not taken into account in calculation of the term, Z. The expression (7) then becomes:

$$(8) \qquad k = P\,Z\,e^{-\frac{E}{RT}}$$

In the cases which Norrish and Smith studied the probability factor was used to compensate for the deactivating effect of the solvent. They considered this effect to be connected with the removal of energy of activation at the moment of collision, the amount absorbed being stated to be dependent on the molecular structure.

For collisions between unlike molecules the following expression was obtained by Hinshelwood[39] for gaseous phase reactions:

$$(9) \qquad k = N_A N_B \quad \sigma_{AB}^{a}\left[8\pi RT(1/M_A + 1/M_B)\right]^{\frac{1}{2}} \quad e^{-\frac{E}{RT}}$$

where: k = number of effective collisions per cc per second

N_A = number of molecules of A per cc

N_B = number of molecules of B per cc

σ_{AB} = mean molecular diameter, cm.

M_A = molecular weight of A

M_B = molecular weight of B

E = energy of activation, cals/mol

In the cases studied in this paper the polymerization of styrene in a non-alcoholic water phase was used as the "standard" of comparison. Any reduction in the rate of polymerization and average molecular weight would be attributed to the addition of alcohol to the aqueous phase. It is assumed that any effect which the presence of water may have on the reaction is constant in all the experiments due to its relatively great concentration as compared to any one of the other components in the system.

The results of this investigation show that the overall rate of polymerization is reduced by the addition of alcohols to the aqueous phase (Figures 6-11, 13-18, 30, 22-24), indicating that active centers are being removed from the reaction. Since, in order to effect a deactivation, it is necessary for an active center and an alcohol molecule to collide, the rate of effective collisions may be calculated from equation (9).

The implication is that two reactions are proceeding simultaneously in the alcoholic emulsion polymerization system: 1) the reaction of growing chains with monomer to lengthen the chain, and 2) the reaction of activated monomer with alcohol to remove activated centers. The rate of styrene polymerization was determined for both water and alcohol-water solutions. The observed decrease in the rate of polymerization of the alcohol-water systems is ascribed to the difference in rates of the two competing reactions.

Calculation of the theoretical rate of deactivation by alcohol using equation (9) gives results inconsistent with experimentally determined deactivation "reaction" rates. If it is assumed that rate of polymerization and rate of deactivation are independent and that deactivation occurs by reaction with activated monomer, it is possible to reconcile the calculated and experimental rates by the use of a specific probability constant, P. This probability factor has been found to have a reasonably constant value for each of the alcohols (Tables I, II, III, IV) investigated. The deactivation effect of the different alcohols based on the calculated values of P was found to decrease in the order isopropanol > t-butanol > ethanol > methanol.

A similar study by Norrish and Smith using the reaction of trimethylamine and p-nitrobenzyl chloride in methanol and ethanol solutions, gave calculated values for P which are remarkably close to those reported in this paper.

It is rather difficult to postulate a mechanism for deactivation. It may, however, be looked at in a qualitative way. At equi-molal concentrations the calculated rates for t-butanol and methanol are substantially identical. Such being the case, the larger deactivating effect observed for t-butanol may be attributed to the greater ability of the larger structure to absorb activation energy on collision.

TABLE I

Methanol Solution

$Z \times 10^{-28}$	Mols Alcohol	$K_2 \times 10^4$	Kc	$K \times 10^4$	$P \times 10^5$
20,489	1.4	2.4	2.24	0.7	3.2
40,969	2.8	2.3	4.08	0.8	1.96
61,410	4.2	1.9	6.61	1.2	1.81
82,178	5.6	1.84	9.11	1.26	1.38
121,859	8.4	0.5	14.46	2.6	1.79
				Average	2.03

TABLE II

Ethanol Solution

$Z \times 10^{-28}$	Mols Alcohol	$K_2 \times 10^4$	Kc	$K \times 10^4$	$P \times 10^5$
16,708	0.97	2.15	1.90	0.95	5.0
33,414	1.94	1.9	3.8	1.2	3.2
50,121	2.91	1.53	5.72	1.57	2.8
66,828	3.88	0.35	7.64	2.75	3.6
				Average	3.6

TABLE III

Isopropanol Solution

$Z \times 10^{-28}$	Mols Alcohol	$K_2 \times 10^4$	Kc	$K \times 10^4$	$P \times 10^5$
12,610	0.74	1.5	1.44	1.6	11.1
25,220	1.48	0.05	2.86	3.05	10.7
				Average	10.9

TABLE IV

t-Butanol Solution

$Z \times 10^{-28}$	Mols Alcohol	$K_2 \times 10^4$	Kc	$K \times 10^4$	$P \times 10^5$
10,479	0.60	2.19	1.19	0.91	7.6
20,958	1.20	0.14	2.39	2.96	12.0
				Average	9.8

(See Note - Next page)

Note: K_1 = "Standard" ratio of polymerization 3.1×10^{-4} mols per liter per sec.

Z = Number of collisions per cc per second

K_2 = Observed Polymerization rate, mols per liter per sec.

K_c = Calculated rate, mols per liter per sec.

K = Difference between "Standard" - observed rates, mols per liter per sec.

P = Specific probability factor = $\Delta K/K_c$

The molecular diameter[40], σ, of:

methanol = 4.57×10^{-8}

ethanol = 5.17×10^{-8}

isopropanol = 5.64×10^{-8}

t-butanol = 6.18×10^{-8}

styrene = 6.46×10^{-8}

Sample Calculation, 10% Ethanol

Data: Concentration of styrene is 0.95 mols/lit

$N_A = 5.72 \times 10^{20}$ molecules of styrene/cc

Concentration of ethanol is 1.94 mols/lit

$N_B = 11.69 \times 10^{20}$ molecules of ethanol/cc

$M_A = 104.1$ Molecular Weight of Styrene

$M_B = 46.07$ Molecular Weight of Ethanol

$\sigma_A = 6.46 \times 10^{-8}$ Molecular Diameter of Styrene

$\sigma_B = 5.17 \times 10^{-8}$ Molecular Diameter of Ethanol

$E = 17{,}000$ cals.[25h]

$T = 333^\circ K$

$$Z = (8\pi RT)^{\frac{1}{2}} \ (\sigma_A + \sigma_B/2)^2 \ (1/M_A + 1/M_B)^{\frac{1}{2}} \ (N_A N_B)$$

$$Z = (83.37 \times 10^4)\ (5.82 \times 10^{-8})^2 (.0262)^{\frac{1}{2}} (5.72)\ (11.69) \times 10^{40}$$

$Z = 33,414 \times 10^{28}$ number of collisions per cc per sec.

$k = Z\, e^{-\frac{E}{RT}}$ where k is the velocity constant

$$K_c = 33,414 \times 10^{28} \ e^{-\frac{17000}{661.34}}$$

$K_c = 2.291 \times 10^{21}$ collisions per second of molecules with an energy greater than 17000 cals in one cc

To convert to mols per lit per second multiple "k" by 1000 and divide by Avogadro's number 6.025×10^{23}. Then:

$K_c = 2.291 \times 10^{21}/6.025 \times 10^{20} = 3.80$ mols per lit per sec.

Rate of polymerization of styrene (K_1): 3.1×10^{-4} mols lit/sec
Observed Rate with 10% ethanol: (K_2) $\underline{1.9 \times 10^{-4}}$ " " "
Difference (ΔK): 1.2×10^{-4}

Deactivation Constant, P, or specific probability factor $= \dfrac{\Delta K}{K_c}$

$$= 1.2 \times 10^{-4}/3.80 = 3.3 \times 10^{-5}$$

The values obtained for P by Norrish and Smith[37] for a bimolecular reaction in methanol and ethanol are:

Methanol:	0.43×10^{-5}
Ethanol:	3.8×10^{-5} 2.1×10^{-5}

It has been shown that an increase of alcohol concentration causes the rate of polymerization to approach zero, at which point it might be assumed that any active centers formed are immediately deactivated.

The decrease of the average molecular weight with an increase of alcohol concentration in the aqueous phase (Figures, 12, 19, 21, 25) is consistent with the theory that the probability of chain termination is greater in the higher concentrations of alcohol.

Factors that were variable and which might effect the polymerization are the pH and decomposition of potassium persulfate. Each reaction was allowed to reach its own pH, no attempt being made to add any material to adjust the pH to a specific value. Addition of buffering agents was avoided as yet another variable would have been added to the system. With the exception of the experiment using carbon dioxide as the atmosphere the reactions remained between a pH of 6.7 and 7.7. Price[25b] has shown that the variation of the pH between these values has no effect upon the system. It has been assumed that the potassium persulfate does not decompose to any appreciable extent over the period of polymerization, and the data (Experiment #23) shows this to be a reasonable assumption. In no experiment, except those which ran for more than three hours, was there any appreciable decrease in the pH which might be attributed to the decomposition of the persulfate.

In the reactions using alcohols as part of the aqueous phase the decrease in unsaturation of the polymerizing system was determined by a titration method. These results calculated as reacted styrene monomer paralleled those of the percents of solid polymer formed. It should be noted that all the curves obtained for percent of reacted styrene lie 5-15% above those of the percent of solid polymer formed. The reason that they are not superimposed, as would be expected, may lie in the method of purifying the polystyrene. In this method 95% ethanol was used to wash the polymer and consequent leaching out of the alcohol soluble polymers.

The data (Experiments 19, 20, 21, 22) shows that the accuracy of the method of determining the amount of styrene in the system by reaction with mercuric acetate is ± 5%. In order to obtain reproducible results the order of addition of chemicals must be taken into account in addition to the time allowed between additions of the chemicals. It is not possible to interpret the values obtained from the titration scheme on any absolute basis, but since the curves for the percent of reacted styrene parallel those for the percent solid polymer formed, they are a check on the rate of overall polymerization. Any discussion of the effect of deactivation on the rate of polymerization as shown by the solid polymer curves applys equally well to the curves for the percent of reacted styrene.

It is possible to duplicate the polymerization reactions if the same chemicals are used under the same conditions. If it is necessary to use a new chemical, it is not possible to reproduce previous work exactly. The difference in rate of polymerization between the curves of Figure 27 and Figure 1, lies in the potassium persulfate used. The potassium persulfate used in both cases was from the same bottle, recrystallized on different occasions using identical procedures, but it was found that the recrystallized persulfates differed in catalytic properties. Reproducibility of results from a single crystal crop was good. Experiments 10 and 11 (Figure 14) were run with the same chemicals approximately three months apart and show an excellent duplication of the rates of polymerization.

The difference in rates of polymerization in Experiment 13 (Figure 16) and Experiment 14 (Figure 17) is attributed to the fact that in the former experiment freshly distilled styrene was used, while in the latter the same styrene, which had been stored for one week in the refrigerator, was used.

CONCLUSIONS

1. A carbon dioxide atmosphere has no effect on the rate of overall polymerization. Its effect is limited to the lowering of the pH of the system accompanied by a slight decrease in the average molecular weight of the polymer.

2. The water soluble alcohols studied are chain terminators. The average molecular weight of the polymer decreases with increasing concentration of alcohol in the aqueous phase.

3. The water soluble alcohols studied are inhibitors or deactivators. The rate of polymerization decreases with increasing concentrations of alcohol.

4. The relative deactivating effect as calculated is isopropanol > t-butanol > ethanol > methanol.

5. A "specific probability constant", P, is determined for each alcohol and is characteristic of that alcohol.

6. The amount of double bond which has reacted, calculated as the percent of styrene reacted per unit time, is the same as the rate of solid polymer formation.

7. It is possible to duplicate a particular polymerization reaction by using the same chemicals in the same manner.

LITERATURE CITED

1. Simon, E., Ann., 31, 267 (1839).

2. Berthelot, M., Ann., 141, 1818 (1867).
Centralblatt, 65, I, 1026 (1867).
65, I, 1081 (1867).

3a. Whitby, G. S., Trans. Faraday Soc., 32, 315 (1936).

b. Schulz, G. V. & Husemann, E., Z. Physik Chem., B34, 187 (1936).

c. Cohen, S. G., J. Am. Chem. Soc., 67, 17 (1945).

4. Taylor, H. S. & Vernon, A. A., J. Am. Chem. Soc., 53, 2527 (1931).

5. Bruson, H. & Staudinger, A., Ind. & Eng. Chem., 18, 38 (1929).

6. Sontag, D., Anal. Chem., 1359 (1934), C. A., 28, 4716 (1934).

7. Ziegler & Bohr, Ber., 61B, 253 (1928).

8a. Houtz, R. C. & Adkins, H., J. Am. Chem. Soc., 55, 1609 (1933).

b. Kawamus, H., C. A., 37, 4372 (1943).

9a. USP 1683404, Sept. 4, 1928.

b. Abere, J., Goldfinger, G., Naidus, U., & Mark, H., Jour. Phys. Chem., 49, 211 (1945).

c. Cohen, S. G., J. Am. Chem. Soc., 69, 1057 (1947).

10. Breitenboch, J. W., Springer, A., Abrahamczik, E., C. A., 6232 (1938).

11a. Suess, H., Pilch, K., Rudorfer, H., Z. Physik Chem., A179, 361 (1937).

b. Breitenboch, J. W. & Rudorfer, H., Monatsch., 70, 37 (1937).

12. Staudinger & Frost, Ber., 68, 2351 (1935).

13a. Flory, P. J., J. Am. Chem. Soc., 65, 372 (1943).

b. Chalmers, W., J. Am. Chem. Soc., 56, 912 (1934).

c. Staudinger, H., Trans. Faraday Soc., 32, 97 (1936).

d. Taylor, H. S. & Jones, W., J. Am. Chem. Soc., 52, 1111 (1930).

14. Schulz, G. V., Z. Physik Chem., A176, 317 (1936).

15a. Staudinger, H. & Hauer, W., "Die Hochmolekularen Organischen Verbindungen". Springer, Berlin 1932 p. 1179.

b. Staudinger & Schulz, Ber., 68B, 2320 (1935).

c. Schulz, G. V. & Husemann, E., Z. Physik Chem., B34, 194 (1936).

d. Kemp, A. R. & Peters, H., Ind. & Eng. Chem., 34, 1097 (1942).

16. Signer, H. & Gross, H., Helv. Chim. Acta., 17, 335 (1934).
C.A., 28, 3059 (1930).

17. Debye, Ewart, Roe & McCarinen, J. Chem. Phys., 14, 687 (1946).

18. Schulz, G. V., Z. Physik Chem., B30, 379 (1935).

19. Staudinger, H. & Husemann, E., Ber., 68, 1691 (1935).

20a. Mark & Raff "High Polymeric Reactions" Interscience, N. Y. 1941.

b. Hohenstein, W. P., Siggia, S. & Mark H.,
India Rubber World, 111, 173-177 (1944).

21. Breitenboch, J. W., Kolloid Z., 109, 119 (1944)
C.A., 41, 5338 (1947).

22. Fryling, C. F. & Harrington, E. W., Ind. & Eng. Chem., 36, 114 (1944).

23. Harkins, J., J. Chem. Phys., 13, 381 (1945)
14, 47, 215 (1946).

24. Montroll, E. W., J. Chem. Phys., 13, 337 (1945).

25a. Fikentscher, H., Angew. Chemie, 51, 433 (1938).

b. Schulz, Dinglinger & Husemann, Z. Physik Chem., B43, 385 (1939)

c. Price, C. C. & Durham, D. A., J. Am. Chem., Soc., 64, 2508 (1942).

d. Abere, J., Goldfinger, G., Naidus, U. & Mark H., J. Chem. Phys., 11, 379 (1943).

e. Pfann, H. F., Salley, D. J. & Mark,H., J. Am. Chem. Soc., 66, 983 (1944).

f. Price & Adams, J. Am. Chem. Soc., 67, 1674-80 (1945).

g. Corrin, M. L., J. Poly. Sci., 2, 257 (1947).

h. Frillette, W. J. & Hohenstein, W. P., J. Poly. Sci., 3, 22 (1948).

26. Barnes, J. Am. Chem. Soc., 67, 217 (1945).

27. Kolthoff, I. M. & Dale, W. J., J. Am. Chem. Soc., 69, 441 (1947).

28. Harman, R. A. & Eyring, H., J. Chem. Phys., 10, 557 (1942).

29. Kline, G. M., Brit. Plastics, 18, 101 (1946).

30a. Kolthoff & Dale, J. Am. Chem. Soc., 67, 1672 (1945).

b. Kolthoff, Guss, May & Medulia, J. Poly. Sci., 1, 340 (1946).

31. Yang, P. T., M. S. Thesis, Michigan State College (1947).

32. Kolthoff & Bovey, J. Am. Chem. Soc., 69, 2143 (1947).

33. Morgan, D. H., M. S. Thesis, Michigan State College (1946).

34. Nozacki, K., Ind. & Eng. Chem., Analyt. Edit., 18, 583 (1946).

35. Schulz, Dinglinger & Husemann, Z. Physik Chem., B43, 385 (1939)

36. Mayo, F. R., J. Am. Chem. Soc., 65, 2324 (1943).

37. Norrish & Smith, Trans. Chem. Society, 128, 129 (1928).

38. Lewis, W. C. M., Trans. Chem. Society, 113, 471 (1918).

39. Hinshelwood, C. N., "The Kinetics of Chemical Change" Oxford Press pgs. 14,17,46-47, 50-52 (1940).

40. Moelwyn-Hughes, E. A., Chem. Reviews, 10, 243 (1932).