



110
383
THS

EFFECT OF STIRRING ON THE
EMULSION POLYMERIZATION OF
STYRENE WHEN CATALYZED BY
HYDROGEN PEROXIDE CATALYSTS

Thesis for the Degree of M. S.
MICHIGAN STATE COLLEGE
Victor Lee Hallenbeck

1948

3.2



**EFFECT OF STIRRING ON THE EMULSION POLYMERIZATION
OF STYRENE WHEN CATALYZED BY
HYDROGEN PEROXIDE CATALYSTS**

By

VICTOR LEE HALLENBECK

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

6-29-56

7

331679

ACKNOWLEDGMENT

The author wishes to express his deep appreciation for the help and encouragement of Dr. R. L. Guile during the course of this investigation.

TABLE OF CONTENTS

	Page
INTRODUCTION	1
HISTORICAL	2-6
EXPERIMENTAL	
Reagents	7
Equipment	9
Procedure	10-13
Data Tables	14-18
Graphs	19-29
DISCUSSION	30-34
CONCLUSION	35
BIBLIOGRAPHY	36-37

INTRODUCTION

Within recent years emulsion polymerization has been intensely investigated both commercially and from the theoretical viewpoint. These investigations have been concerned with various aspects of the reaction: the effects of temperature, the effects of concentration of catalyst, and the effects of different types of inhibitors, on the rate of polymerization and the molecular weight of the polymer. One of the most interesting studies has been on the question of whether or not the polymerization proceeds in the emulsified monomer droplets or in the aqueous phase.

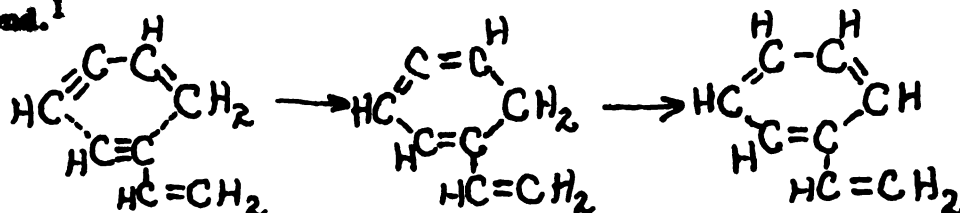
Considerable differences in the results of various workers investigating similar polymerizing systems have been noted and are usually attributed to the extreme sensitivity of such systems. Comparison of results from investigator to investigator and even within the work of a single investigator has been difficult or impossible. Of the many investigations carried out the effect of stirring or shaking has been least mentioned in the literature. Since almost without exception stirring or shaking is a part of the technique used in emulsion polymerizing systems, its effect is of interest.

This work was started as an investigation of the minimum amount of catalyst, H_2O_2 , necessary to cause polymerization of styrene in a particular emulsion system. The author observed a stirring effect. This effect was investigated and is the subject of this thesis.

Historical:

Styrene was first isolated by distillation of Gum Storax. Polystyrene when first mentioned in 1839 was thought to be an oxidation product produced upon the application of heat.

In 1867 Berthelot synthesized styrene by the condensation of acetylene and by the dehydrogenation of ethylbenzene.² Styrene can also be considered as a dimer of vinylacetylene formed by an addition in a 1, 4-sense, of the acetylenic portion of one molecule of vinylacetylene to the conjugated system of another and then a rearrangement of one double bond.¹



The most important source of styrene today is from ethylbenzene,³ a dehydrogenation reaction.

Polymerization of styrene has been carried out in bulk, in solution and in emulsion.⁴ The tendency for styrene to polymerize is typical of all unsaturated compounds since they exhibit a natural urge to saturate themselves.⁷ The process of emulsion polymerization which is highly important was first mentioned in 1915. Emulsion polymerization is more rapid than bulk or solution, and the rate of reaction is more easily controlled.⁸ Styrene polymerization has also been studied in solutions of various organic solvents (solution polymerization) such as alcohol, toluene, carbon tetrachloride, and benzene.^{5,7}

Mark and Raff describe a system for emulsion polymerization which consists of an emulsifying agent, a purified monomer, a stabilizer,

a surface regulator, a catalyst, a chain regulator, and a buffer.⁶ The emulsifying agent can be ammonium soaps, saponin, organic sulfonates of long chain alcohols, and albumen.⁸

Many workers have investigated the question of whether or not the polymerization takes place in the aqueous or the monomer phase. Fryling and Harkins stated that styrene polymerized in the aqueous phase and suggested that the monomer oriented and polymerized within soap micelles. They postulated this idea through interpretation of pH changes. Upon addition of monomer to an emulsifying solution there were two changes of pH i.e. when the monomer was added during polymerization. The changes were considered to be due to the passage of the monomer into the aqueous phase, although interference in pH values may be caused by oxidation, hydrolysis and adsorption of emulsifier on the formed polymer.^{9,12}

Direct x-ray evidence has been obtained which indicates the presence of lamella micelles in aqueous soap solutions. These micelles are close-packed side by side and placed in pairs end to end.¹⁰ Micellar formation may be responsible for a drop in activation energy from 25 Kcal per mole in solution polymerization to about 17 Kcal per mole in emulsion polymerization. Very little polymer is formed in the monomer emulsion particles due to the small number of free radicals present at this site.¹¹ McBain also supported the concept of polymerization in the aqueous phase. He added monomer to a water solution of peroxide and observed, first, monomer stayed on top, second, in a short while the water layer became opaque due to the formation of the polymer and

third, none of the polymer could be detected in the monomer. Fibentschen reported polymerization to be in the aqueous phase on observation that the emulsified particles decreased in size as polymerization proceeded.¹⁰

The emulsion polymerization of styrene is considered to take place in three steps; an activation inhibition period, a steady reaction or propagation period and then a termination period. The rate of propagation in dilute emulsifier concentration is nearly linear with respect to the concentration of the emulsifier. The best concentration of emulsifying agents is between 0.2-2%.

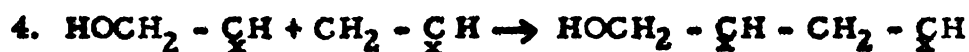
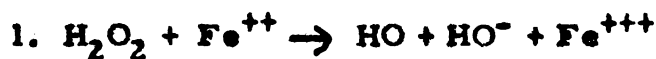
Price stated there are two methods of activation namely the free radical and the ionic. The fact that the activation period is decreased by using pure styrene, by excluding oxygen, and by increasing the temperature is an indication that impurities in the aqueous phase inhibit polymerization.

Many types of catalysts have been described for the polymerization of styrene. Some of these are heat, light, ozone, peroxides, alkali, the metal chlorides (B, Sb, Sn), diazonium compounds, hydrogen fluorides, perborates and phosphates. The catalyst used in emulsion polymerization is usually of the water soluble type such as hydrogen peroxide or potassium persulfate, the latter being the more widely used.

Bacon describes the use of reducing agents as co-catalysts claiming polymerization can be conducted at lower temperatures and at much greater speed when various reduction "activators" such as sulphurous acid, sulphites, bisulphites and sulfur addition products of aldehydes and ketones are used. The concentration of catalyst has a distinct effect on polymerization. The rate of polymerization has been

reported to be proportional to the square root of the concentration of the catalyst.

Evans has carried out considerable work with hydrogen peroxide and with ferrous iron as a catalytic aid. A trace of ferrous iron greatly decreases the activation period and increases the rate of propagation. The hydrogen peroxide and ferrous iron team works in the following manner:



Step two is almost entirely eliminated if the hydrogen peroxide is in excess over the ferrous iron.²⁴

Since the usual methods for determining molecular weights (freezing point depression, etc.) are entirely unreliable above molecular weights of 10,000, molecular weights of high polymers are determined by methods involving osmotic pressure, viscosity and the use of the ultra-centrifuge.²³

Staudinger has postulated an equation for obtaining molecular weights by viscosity:

$$\text{M. W.} = N_{sp}/KC$$

where N_{sp} is the specific viscosity which is defined as the increase in viscosity produced in a solvent by dissolving a unit amount of a substance in a unit volume of the solvent, K is a constant, C is the concentration of polymer in the solvent. However, at best, the Staudinger viscosity method

gives only relative molecular weights. Freezing points, osmotic pressures, and end-group methods lead to values which are termed number average molecular weights.

Often the values obtained with the ultracentrifuge vary greatly from those obtained by viscosity. The ultracentrifuge gives more nearly an absolute determination but due to availability of the equipment for viscosity determinations, the viscosity method is the most frequently used.²² It can be said that the viscosity molecular weight of a typical unfractionated polymer would not be very seriously in error unless the polymer were extensively branched. No reliable conclusions about molecular weight distribution can be drawn from molecular weight data alone without fractionation of the polymer sample.²¹

Experimental:

Reagents:

The reagents used were as follows:

**Styrene
Duponol G
Hydrogen Peroxide
Ethanol
Aluminum Chloride
Mercuric Acetate
Sodium Chloride
Methyl Alcohol
Carbon Tetrachloride**

The styrene was obtained from the Dow Chemical Company, distilled under vacuum (15mm) and only that portion having an index of refraction of 1.5450 was used for the polymerizations. It was stored in the refrigerator for no longer than a week before use.

Duponol G, a sulfonated derivative of lauryl alcohol (Dupont Co.) was used in 1 % as the emulsifier, since previous experiments have shown it to maintain a stable emulsion between monomer and water, and polymer and water at this concentration.

The hydrogen peroxide (Merck 30 %) was used in varying concentration from .003 molar to .75 molar.

The ethanol used in coagulation of the polymer was commercial 95 % grade.

Aluminum chloride was technical grade; and mercuric acetate, sodium chloride, methanol, and carbon tetrachloride were Baker's C. P. grade.

All water used was specially purified being distilled from a KMnO_4 solution in all glass equipment directly into the reaction flask.

Equipment:

All experimental polymerizations were carried out in a four neck, one liter flask equipped with 24/40 ground glass joints. The flask was equipped with a thermometer, a vacuum sampler, and a mercury sealed stirrer propelled by a variable speed motor. A 200 cc erlenmeyer was attached to the vacuum sampler and when the vacuum was applied a sample was collected in the flask.

The nitrogen was passed through a train which contained two 500 cc bottles of alkaline pyrogallol to absorb any traces of oxygen and was introduced into the system above the solution.

The flask was immersed in a constant temperature water bath adjusted to a temperature of 40°C and finally to 60°C.

A Beckmann pH meter was used throughout each polymerization to follow the pH value of the emulsion.

A cannon-Fenske-Ostwald viscosity pipette was used to determine the specified viscosity used in calculating the average molecular weights.

Procedure:

Seventy-five grams of styrene were added to 600 grams of a 1% solution of Duponol G. This gave a one to eight ratio between monomer and water. The above mixture of styrene and dispersing solution was added to the reaction flask which had been previously immersed in the constant temperature water bath at 40°C or 60°C. The pH value was then taken. Hydrogen peroxide was added in amounts varying from .003 molar up to .75 molar concentration.

Sample flasks were prepared by adding approximately 25 cc of ethyl alcohol and a trace of AlCl_3 to twelve weight (to 1/100 of a gram) erlenmeyer flasks.

After addition of catalyst the induction time was determined by treating very small samples of the reaction mixture with alcohol until appearance of an opaque solution which was considered the end of the induction period. At suitable intervals samples were collected in the weighed sample flasks, the amount of each sample being determined by weight difference. At each sampling the pH value of the emulsion was determined and recorded.

The coagulated polymer was separated by use of a centrifuge, the supernatant liquid was poured off and a 15 cc sample of the supernatant was taken to determine the unreacted monomer by the mercuric acetate method. This method consisted of adding 4 grams of mercuric acetate to a 15 cc sample, allowing to stand for one minute and then adding 20 cc of methanol. After a further period of standing (approximately 5 minutes) 20 cc of a saturated solution of sodium chloride was

1. The first part of the document is a letter from the President of the United States to the Congress, dated January 1, 1862.

2. The second part is a report from the Secretary of the Treasury, dated January 1, 1862.

3. The third part is a report from the Secretary of the Interior, dated January 1, 1862.

4. The fourth part is a report from the Secretary of the Navy, dated January 1, 1862.

5. The fifth part is a report from the Secretary of the War, dated January 1, 1862.

6. The sixth part is a report from the Secretary of the State, dated January 1, 1862.

7. The seventh part is a report from the Secretary of the War, dated January 1, 1862.

8. The eighth part is a report from the Secretary of the Navy, dated January 1, 1862.

9. The ninth part is a report from the Secretary of the War, dated January 1, 1862.

10. The tenth part is a report from the Secretary of the Navy, dated January 1, 1862.

11. The eleventh part is a report from the Secretary of the War, dated January 1, 1862.

12. The twelfth part is a report from the Secretary of the Navy, dated January 1, 1862.

13. The thirteenth part is a report from the Secretary of the War, dated January 1, 1862.

14. The fourteenth part is a report from the Secretary of the Navy, dated January 1, 1862.

added followed by 20 cc of carbon tetrachloride. The liberated acetic acid was then titrated with .1N NaOH using phenolphthalein indicator. Each liberated mole of acetic acid represents one mole of unreacted monomer. The amount of unreacted monomer was calculated as follows:

$$\text{Wt. of monomer in sample} = \frac{(\text{Wt. of ethanol} + \text{Wt. of sample})(N.V.\text{meq.})}{15}$$

N = normality of NaOH used

V = volume of NaOH used

meq. = milliequivalents of styrene (.104)

$$\% \text{ Monomer} = \frac{\text{Wt. of monomer}}{\text{Wt. of sample}} \cdot \frac{\text{Wt. of mixture}}{\text{Wt. of styrene}}$$

The coagulated polymer was washed from the centrifuge tubes with 95 % alcohol and collected by suction filtration. The polymer was then washed several times with alcohol, dried at 75°C for 24 hours and weighed.

The percent polymer was then calculated as follows:

$$\% \text{ Polymer} = \frac{\text{Wt. of polymer}}{\text{Wt. of sample}} \cdot \frac{\text{Wt. of mixture}}{\text{Wt. of styrene}} \times 100$$

The average molecular weight was determined by Staudinger's viscosity method. One tenth of a gram of the polymer sample was placed in a 100 cc volumetric flask, and about 50 cc of toluene was added. This in turn was placed in a hot room for a twenty-four hour period to assure complete solution of the polymer. The volumetric flask was then filled so that it contained about 90 cc of toluene and then immersed in a constant temperature water at 20° (.2°) C. The flask was allowed to come to temperature and then filled up to the mark.

Viscosities were determined in the usual fashion by use of a Cannon-Fenske-Ostwald modified pipette. The viscosity data obtained was used in the Staudinger's equation to calculate the average molecular weight.

Staudinger's equation:

$$M.W. = N_{sp}/KC$$

Where: M.W. = average molecular weight

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

C = molar concentration of polystyrene in toluene solution

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

A paddle type, pyrex glass stirrer of the J-2174A type, the Scientific Glass Apparatus Company, with a 2 and 2/3 inch blade was used for agitation of the emulsion system. Stirring conditions were of three types: Continuous stirring, intermittent stirring and non-stirring. Also two rates of stirring were studied. Continuous stirring was that condition where the stirrer was run throughout the reaction. Intermittant stirring was that condition where the stirrer was alternately run for ten minutes and stopped for ten minutes throughout the reaction. Non-stirring was that condition where the stirrer was only used to make the emulsion and then not used throughout the rest of the reaction. In the case concerning rate of stirring, the rate was determined by use of a stop watch and a wax pencil. The number of rings traced on the turning stirrer by the wax pencil in ten seconds was taken as the rate.

Since even slight traces of oxygen have been discovered by previous workers to inhibit the reaction, refluxing and distillation of the

water to be used in the experiment was carried out in an atmosphere of nitrogen freed of oxygen by passing through alkaline pyrogallol.

Using the above procedure many polymerization were carried out and the results tabulated.

Experimental Data:**General:**

Amount of Styrene 75gm
 Amount of 1% Duponol G Solution 600gm
 Nitrogen Atmosphere

Table 1

Sample	Time	pH	%Polymer	M.W. (ave.)
1	1590 mins	6.85	9.74%	132,000
2	1625	6.75	10.98	251,300
3	1750	6.85	--	353,350
4	1805	7.10	--	304,500
5	1840	7.10	18.98	475,500
6	2025	6.85	23.20	337,600
7	2745	6.85	26.14	337,400
8	2805	6.80	30.85	429,800

Water Bath Temperature 40°C; Intermittant Stirring
 Catalyst Concentration .10 molar Hydrogen Peroxide

Table 2

Sample	Time	pH	%Polymer	M.W. (ave.)
1	150 mins	6.60	0.95%	--
2	180	6.50	0.81	--
3	235	6.55	0.66	--
4	265	6.55	2.98	--
5	320	6.75	7.48	215,800
6	355	6.65	11.56	299,800
7	500	7.20	47.19	379,800
8	560	7.20	62.37	351,100
9	1295	7.20	66.96	340,500
10	1350	7.20	71.33	309,500

Water Bath Temperature 40°C; Intermittant Stirring
 Catalyst Concentration .25 molar Hydrogen Peroxide

Table 3

Sample	Time	pH	%Polymer	M.W.(ave.)
1	140 mins	6.05	4.37%	--
2	170	6.20	7.91	--
3	235	6.60	16.56	137,700
4	295	6.73	29.94	241,100
5	353	6.75	--	242,800
6	395	6.70	50.81	254,900
7	520	6.70	69.54	272,100
8	575	6.60	76.87	275,500
9	600	6.60	80.00	248,000
10	1320	6.00	89.02	230,000

Water Bath Temperature
Catalyst Concentration

40°C; Intermittant Stirring
.75 molar Hydrogen Peroxide

Table 4

Sample	Time	pH	%Polymer by Precipitation	% Polymer Values	M.W.(ave.)
1	110 mins	6.70	0.55%	1.66%	--
2	140	6.85	2.98	1.50	--
3	170	6.90	4.59	--	--
4	205	--	8.80	11.67	34,100
5	265	6.30	20.81	17.30	55,500
6	295	6.30	24.67	19.62	72,800
7	325	6.40	36.49	31.67	79,800
8	386	6.80	52.94	49.22	95,400
9	445	6.90	64.44	58.93	--
10	485	6.65	84.79	71.46	86,700

Water Bath Temperature
Catalyst Concentration

60°C; Constant Stirring
.75 molar Hydrogen Peroxide

Table 5

Sample	Time	pH	% Polymer	M.W.(ave.)
1	55 mins	6.60	5.30 %	--
2	80	6.50	6.60	--
3	95	6.70	9.60	62,800
4	110	6.65	15.86	127,300
5	140	6.80	36.63	162,000
6	170	--	62.24	175,800
7	205	6.80	82.91	173,000
8	260	6.80	89.18	166,900
9	330	6.50	90.82	140,500
10	385	6.30	87.23	130,600

Water Bath Temperature 60°C; Non-stirring
 Catalyst Concentration .75 molar Hydrogen Peroxide

Table 6

Sample	Time	pH	% Polymer	M.W.(ave.)
1	40 mins	6.70	3.60 %	--
2	55	7.10	2.40	--
3	70	7.00	3.10	--
4	100	7.00	6.60	67,200
5	160	6.60	35.90	132,800
6	220	7.00	58.10	158,700
7	275	6.70	84.20	136,200

Water Bath Temperature 60°C; Intermittant Stirring
 Catalyst Concentration .75 molar Hydrogen Peroxide

Table 7

Sample	Time	pH	% Polymer	M.W.(ave.)
1	300 mins	6.5	2.07 %	--
2	360	6.2	2.16	32,800
3	420	6.4	2.79	38,400
4	480	6.1	8.36	44,000

Water Bath Temperature 60° C; Rate of Stirring 540 rev./min
 Catalyst Concentration .75 molar Hydrogen Peroxide

Table 8

Sample	Time	pH	%Polymer	M.W.(ave.)
1	70 mins	6.9	2.47%	--
2	140	6.7	4.94	--
3	210	7.2	12.71	64,500
4	270	7.1	27.45	64,500
5	300	7.2	24.29	78,100
6	330	7.1	32.39	71,300
7	360	7.0	40.14	52,600
8	390	7.0	52.69	--

Water Bath Temperature 60°C; Rate of Stirring 300 Rev./min
 Catalyst Concentration .75 molar Hydrogen Peroxide
 Nitrogen used only to sweep system and during sampling.

Table 9

Sample	Time	pH	%Polymer	M.W.(ave.)
1	88 mins	7.20	5.59%	--
2	148	7.20	12.37	56,000
3	203	7.20	31.11	83,200
4	268	7.10	48.12	106,100
5	298	7.16	56.57	107,100
6	328	6.90	62.17	101,800
7	358	6.90	71.37	93,300
8	388	6.70	77.56	35,600

Water Bath Temperature 60°C; Rate of Stirring 300 rev./min
 Catalyst Concentration .75 molar Hydrogen Peroxide

Table 10

Sample	Time	pH	%Polymer	M.W.(ave.)
1	40 mins	7.60	6.60%	--
2	70	8.10	16.86	356,700
3	100	7.90	36.00	406,000
4	115	7.90	43.88	416,200
5	130	7.90	65.18	431,500
6	145	8.30	84.50	431,500
7	175	8.30	96.64	360,100
8	205	7.90	94.79	329,500

Water Bath Temperature 60°C; Non-stirring
 Catalyst Concentration .10 molar Hydrogen Peroxide

Table 11

Sample	Time	pH	%Polymer	M.W.(ave.)
1	45 mins	7.1	7.63%	309,700
2	75	7.7	29.26	446,500
3	90	7.7	42.91	462,000
4	105	8.0	58.46	493,000
5	120	7.9	71.02	492,000
6	135	8.2	81.83	462,000
7	165	8.2	92.13	389,000
8	195	7.9	94.23	392,000

Water Bath Temperature

60°C; Non-stirring

Catalyst Concentration

.05 molar Hydrogen Peroxide

Table 12

Sample	Time	pH	%Polymer	M.W.(ave.)
1	25 mins	7.0	10.71%	449,800
2	40	7.1	18.82	529,900
3	55	7.3	33.73	688,400
4	70	7.6	46.12	732,700
5	85	7.7	62.30	792,300
6	100	7.7	79.27	782,100
7	115	7.6	83.25	744,600
8	145	7.4	83.66	686,700

Water Bath Temperature

60°C; Non-stirring

Catalyst Concentration

.01 molar Hydrogen Peroxide

Fig I

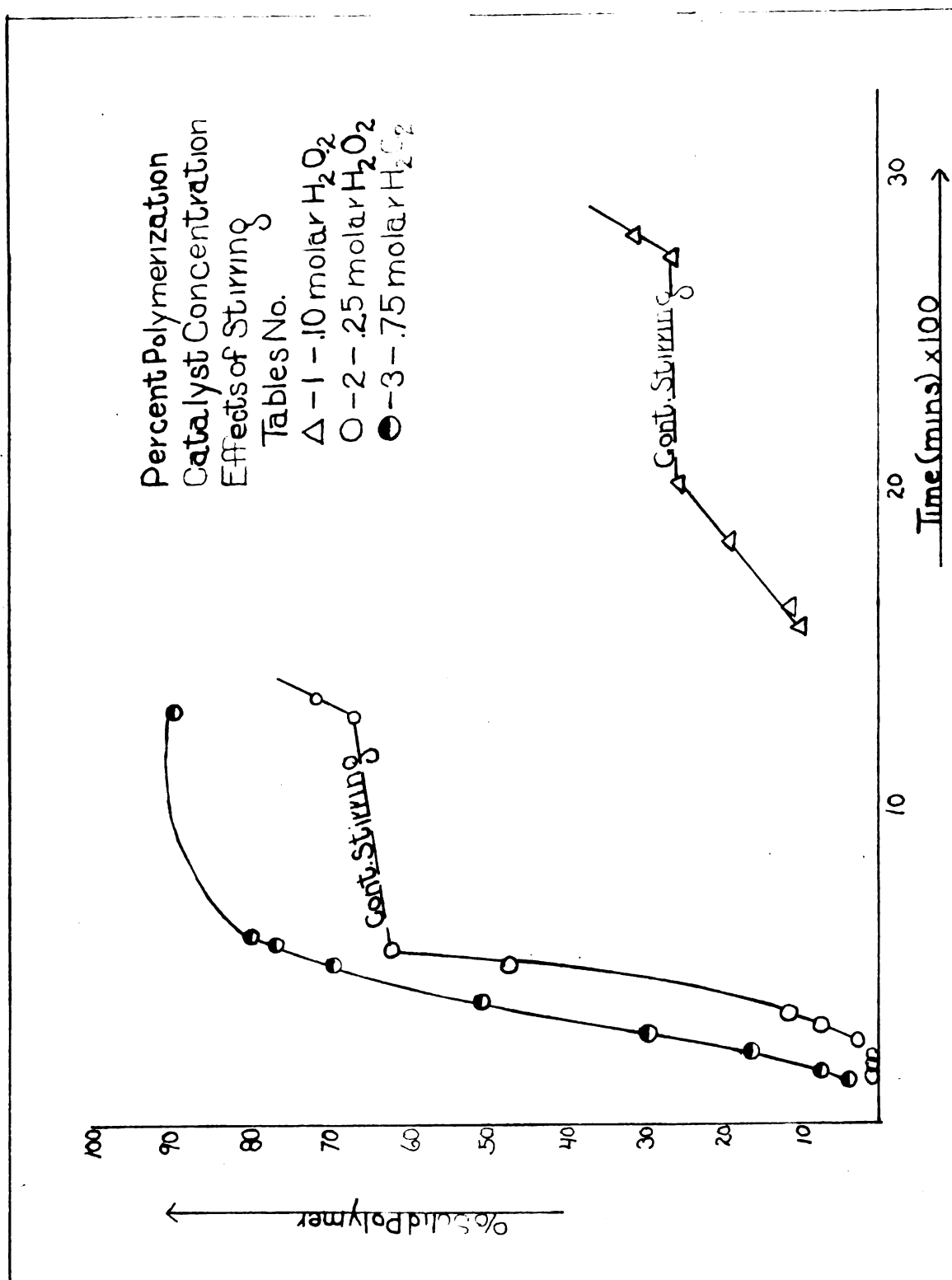


Fig II

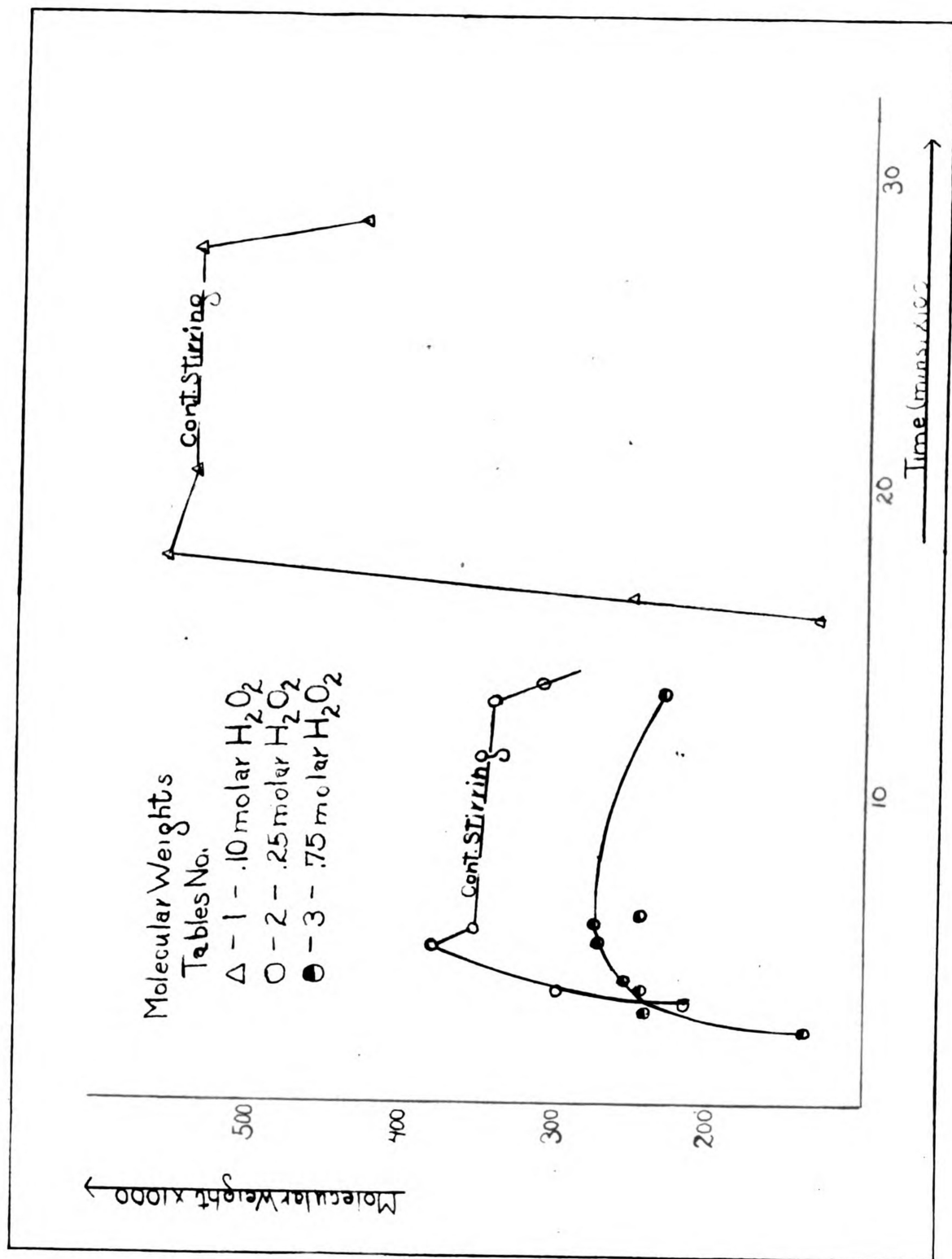


Fig. III

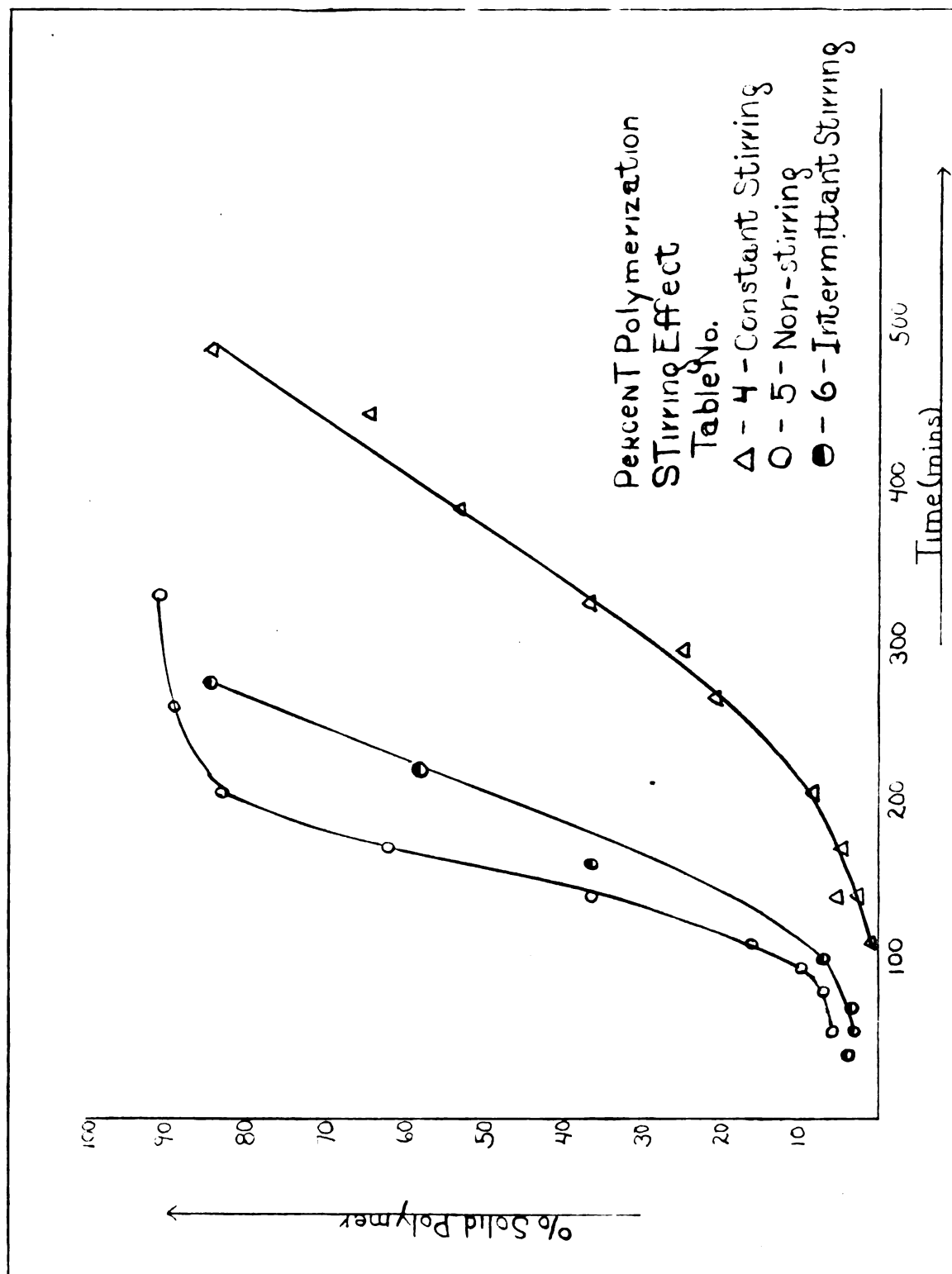


Fig IV

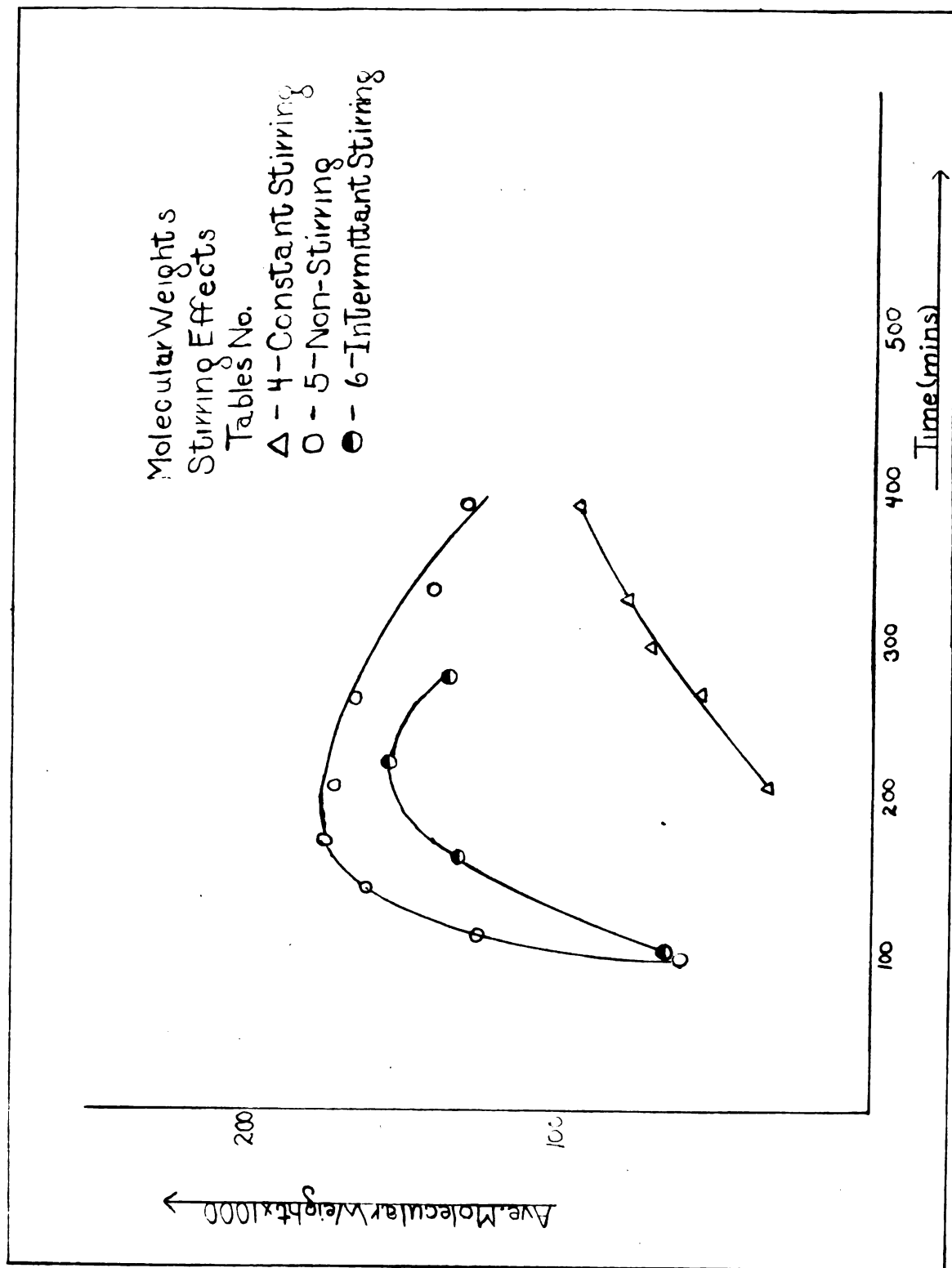


Fig V

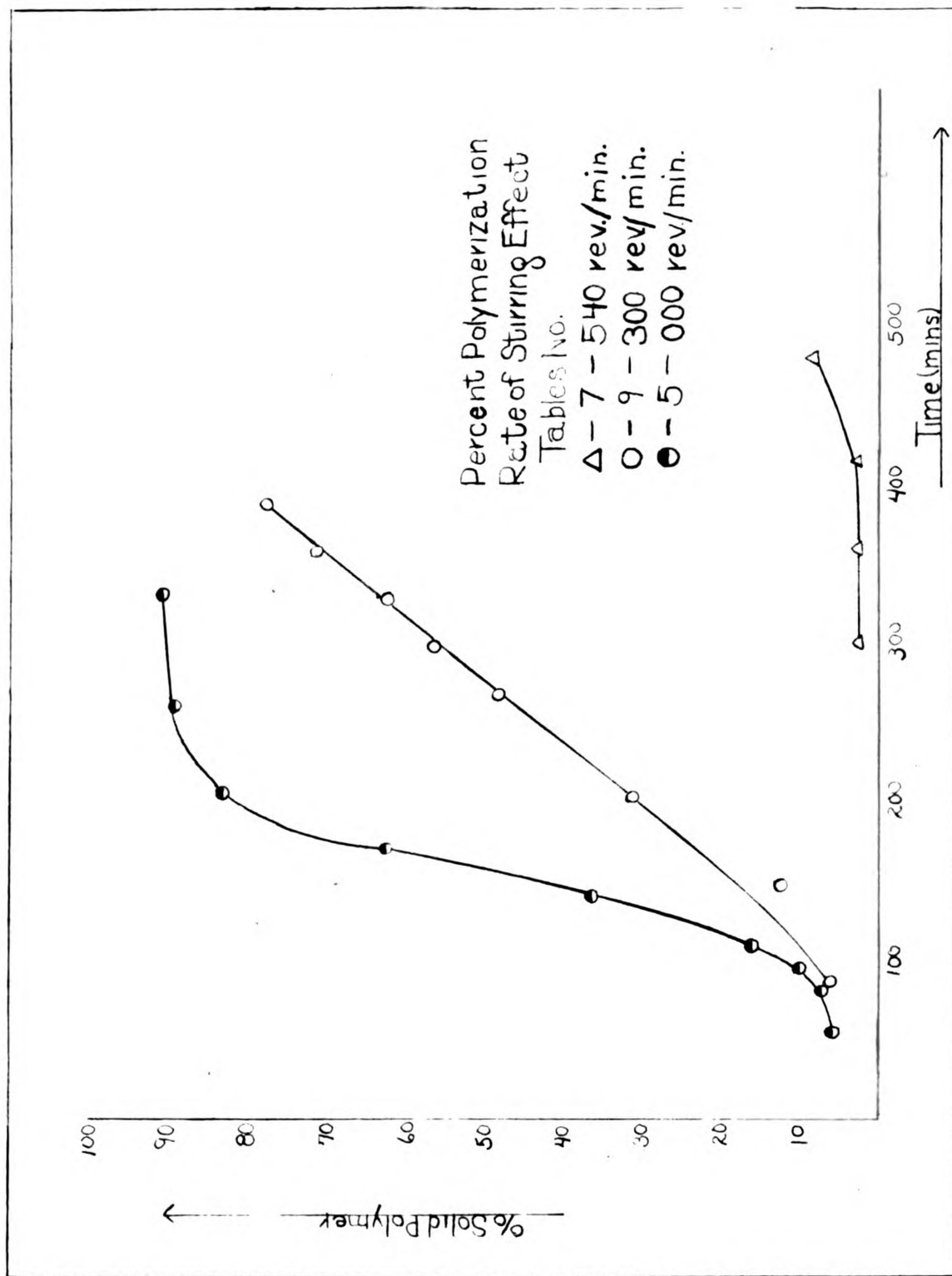


Fig VI

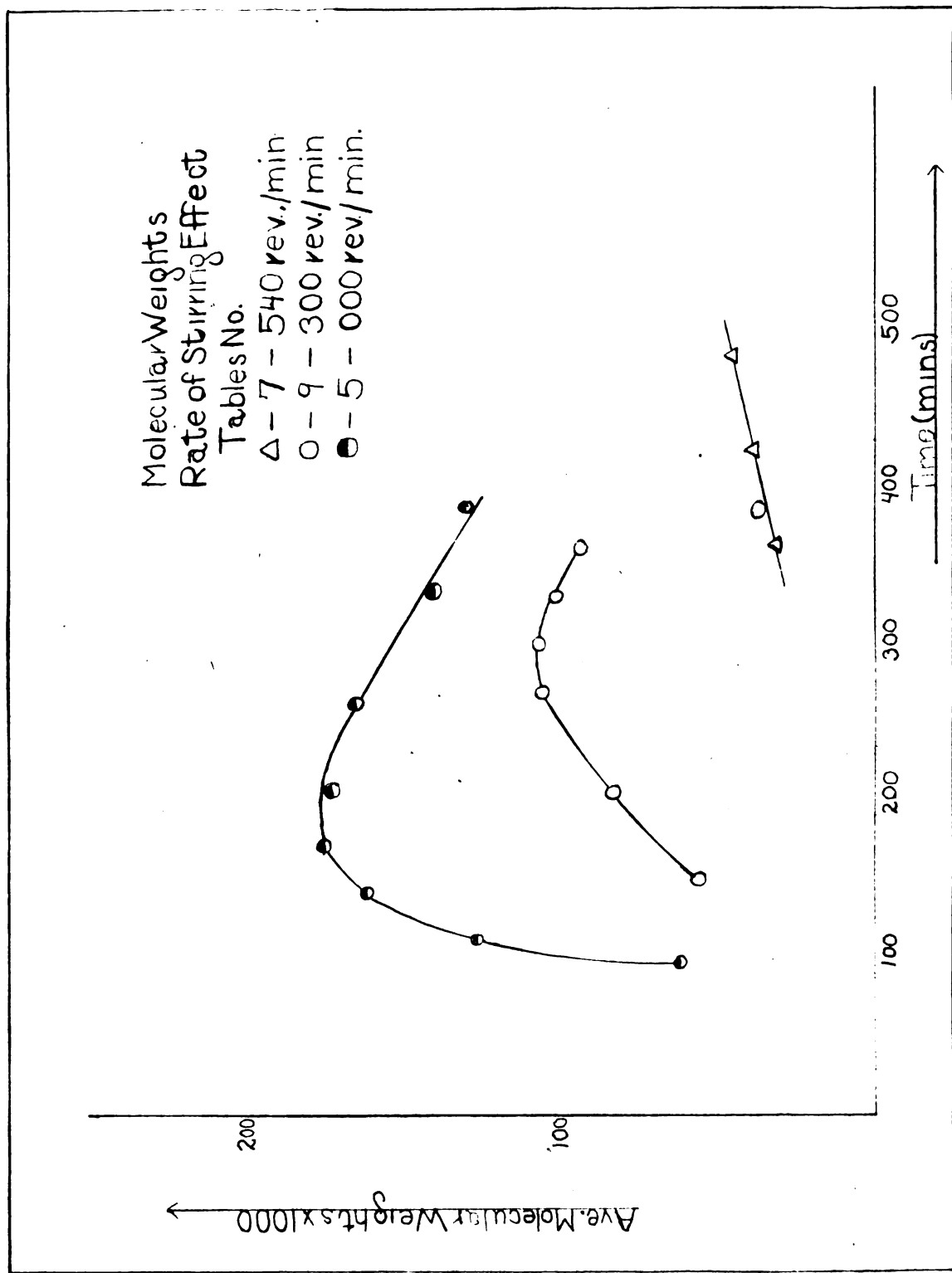


Fig VII

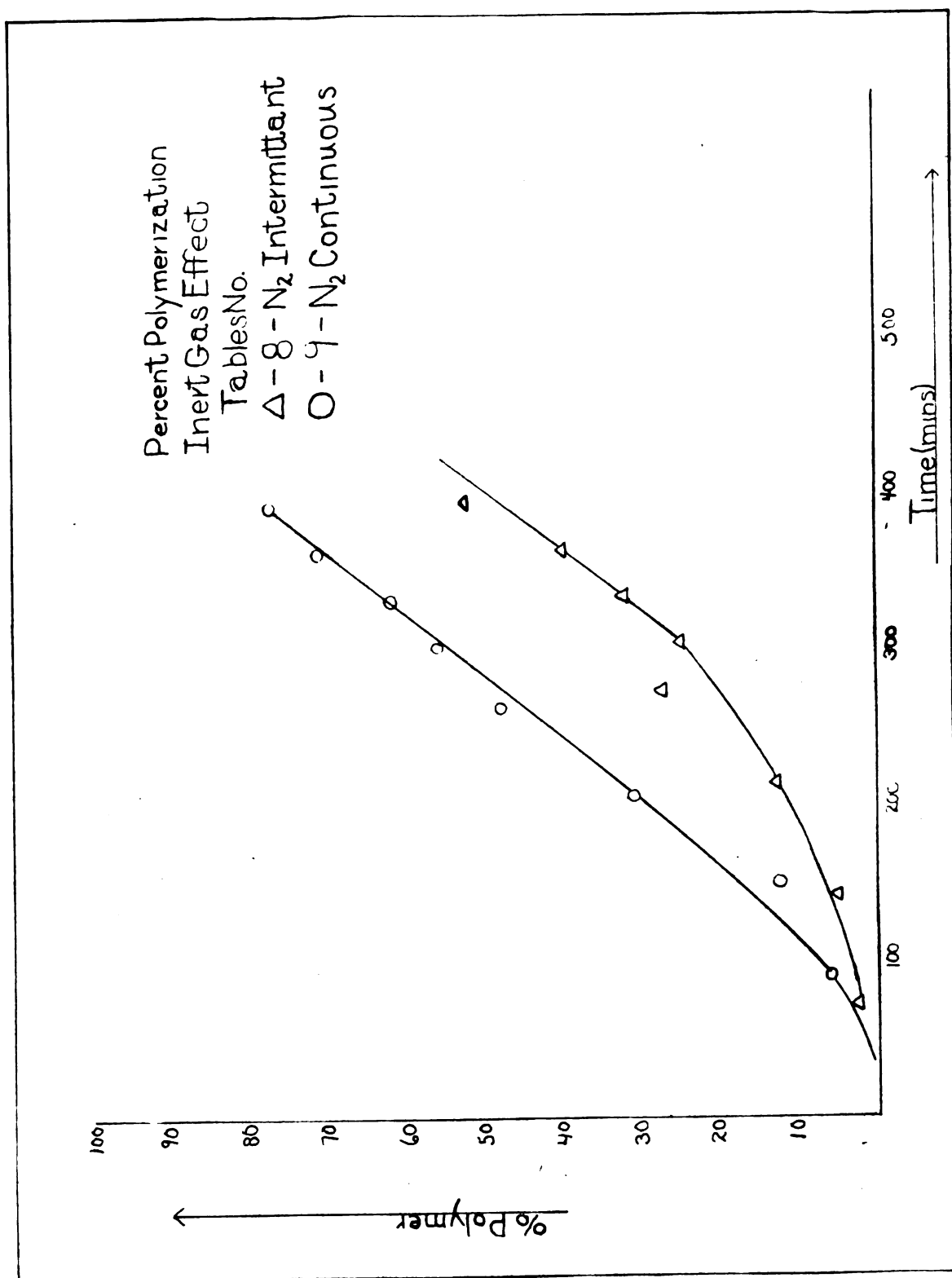


Fig VIII

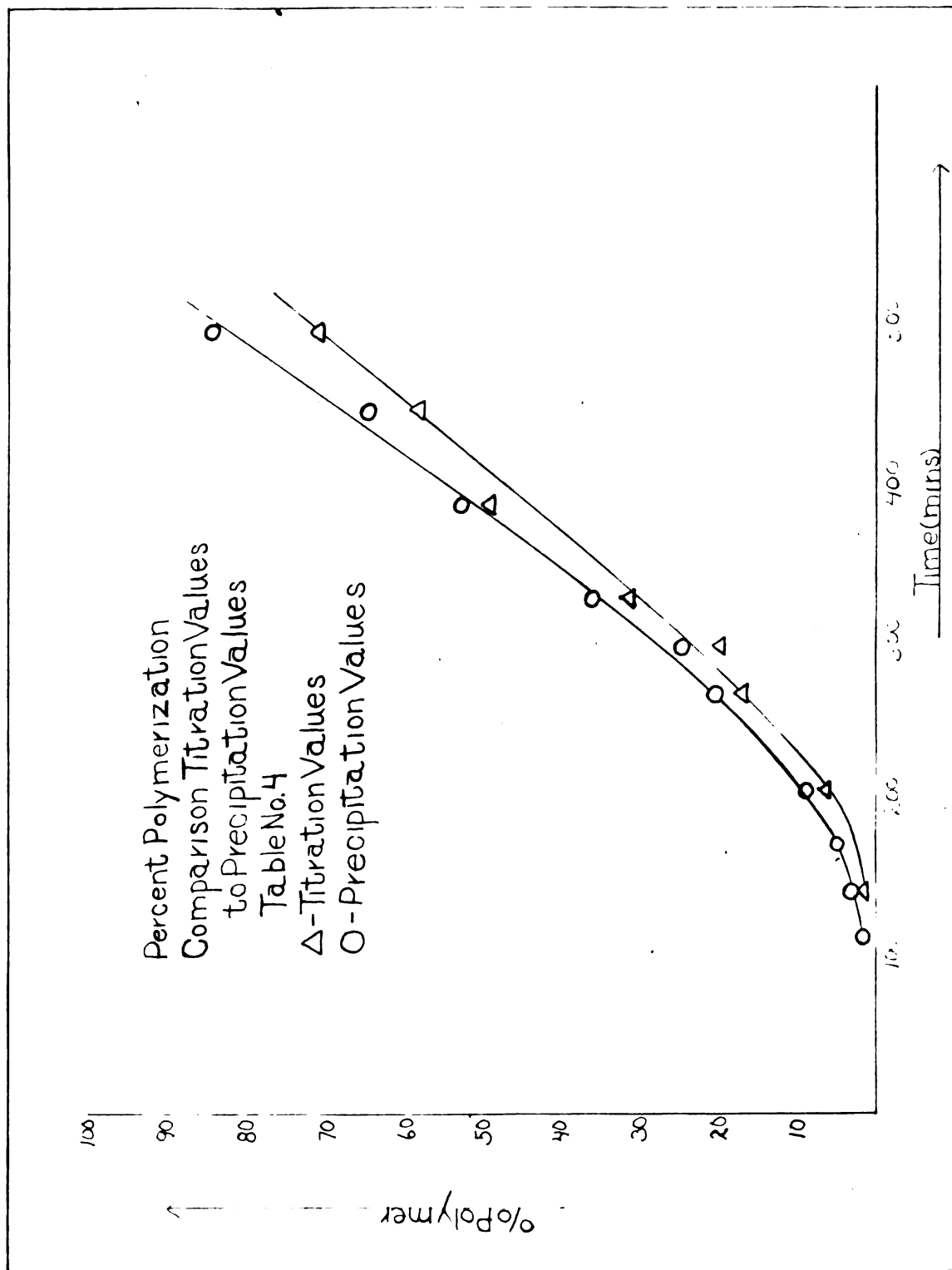


Fig IX

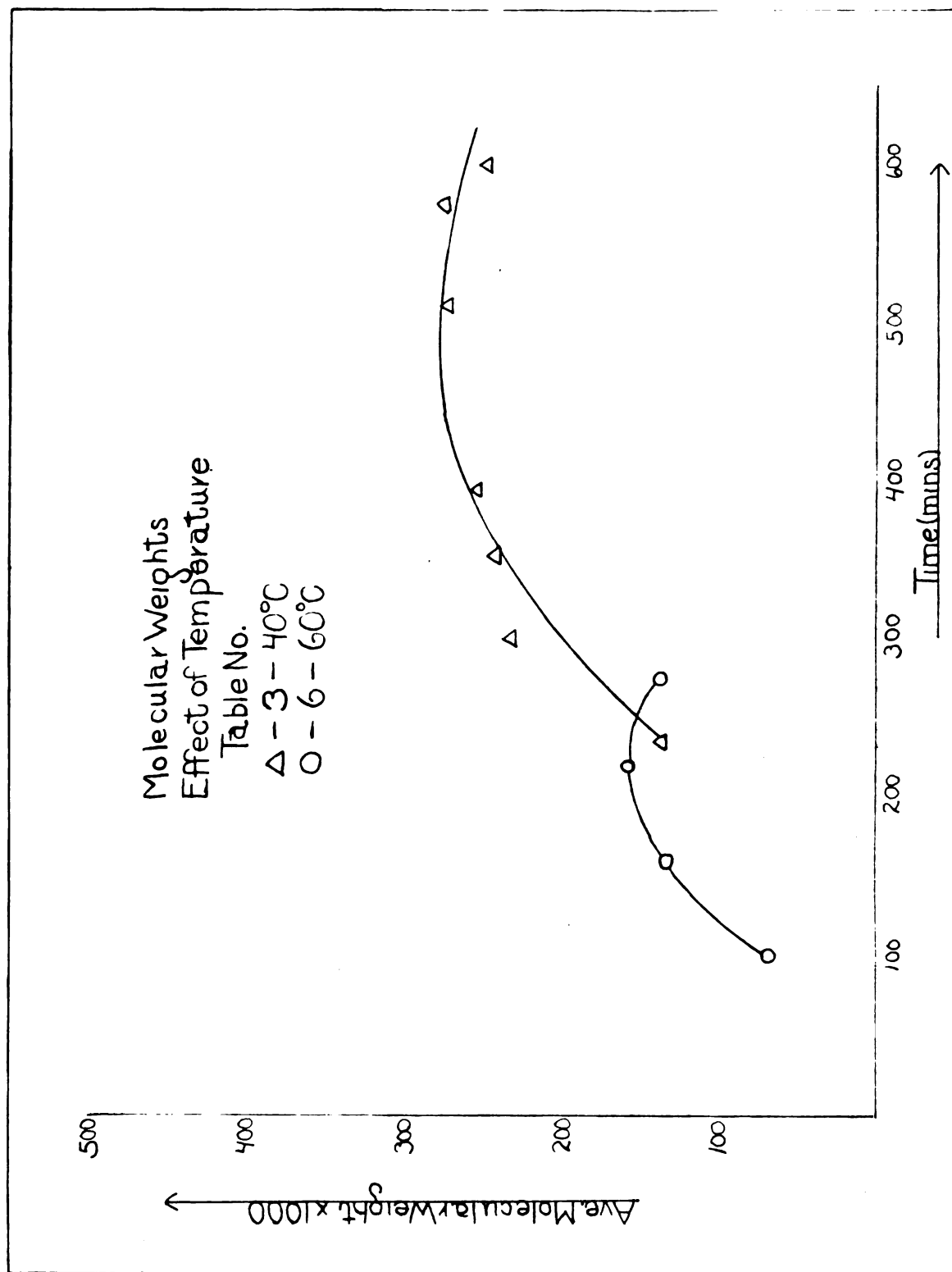


Fig X

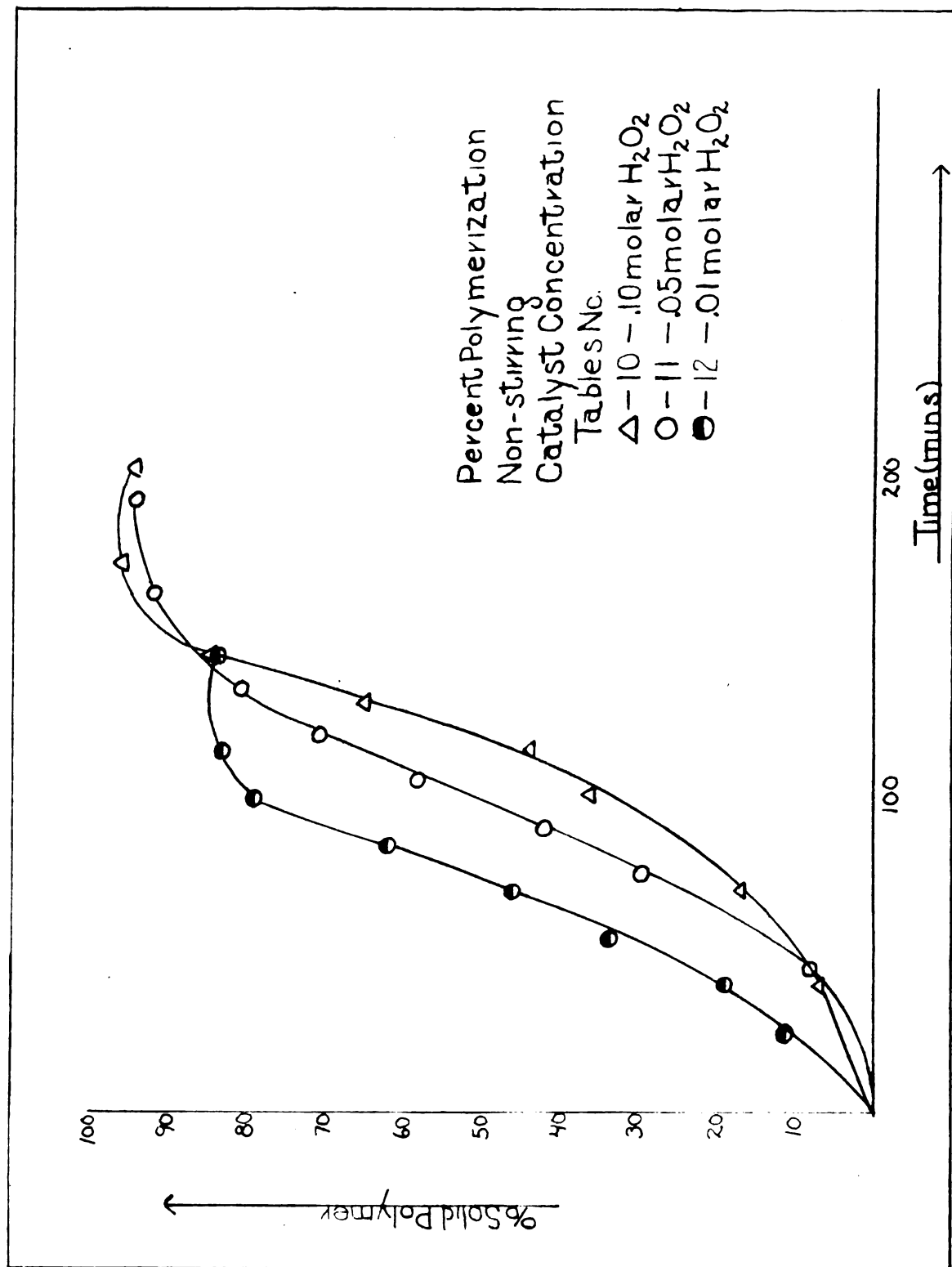
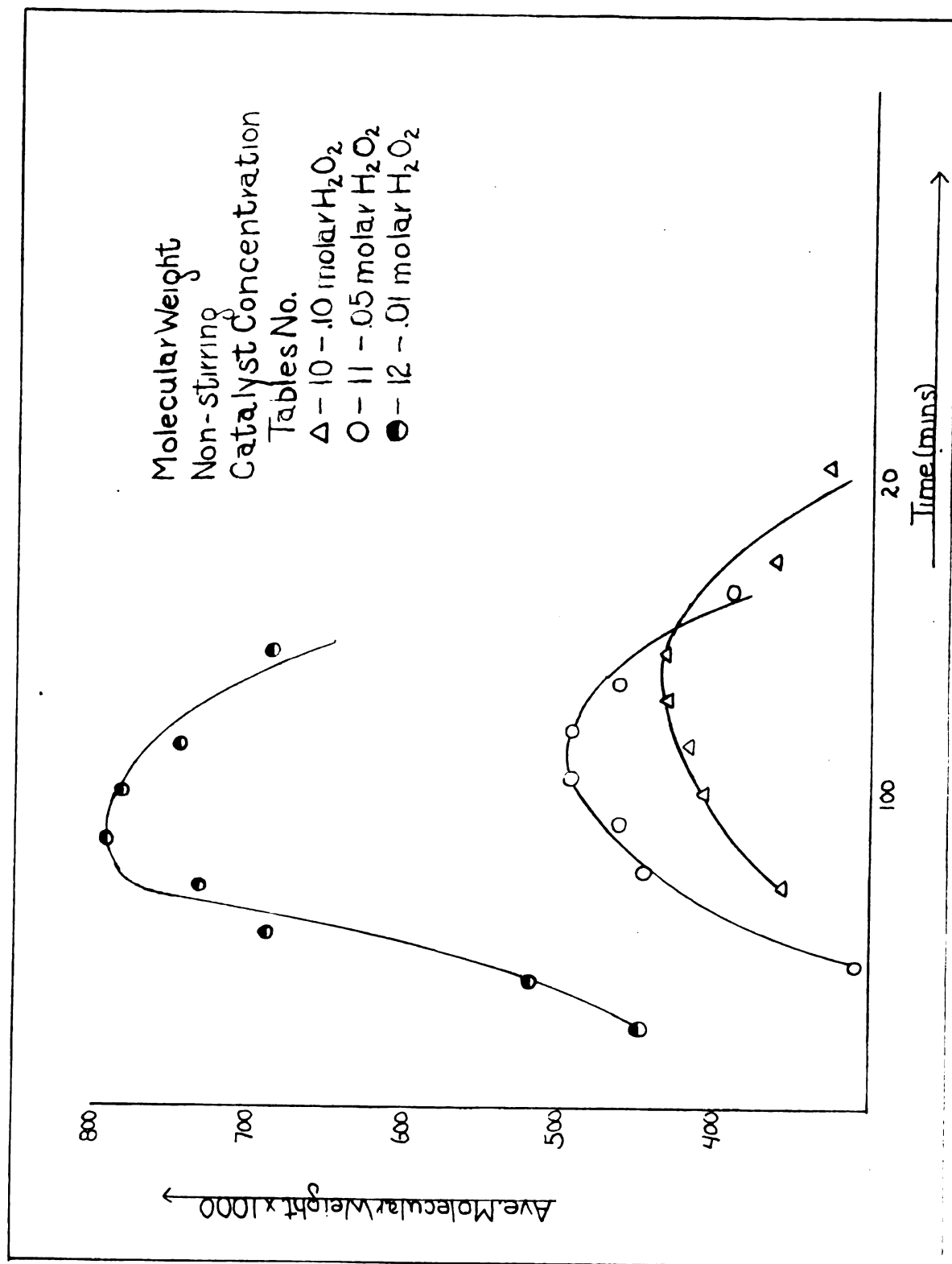


Fig. XI



Discussion:

This work was started with the intention of investigating the effect of hydrogen peroxide as catalyst on the polymerization of styrene. Since the first experiments carried out at room temperature and at low concentrations of catalyst proved to be unsatisfactory (over a twenty-four hour period or longer no polystyrene was detected) the temperature of the polymerization system was raised to 40°C at which temperature polymerization was found to occur. Because the induction time and the rate of polymerization were dependent upon the concentration of catalyst, varying amounts of catalyst were used in an attempt to find the optimum concentration. It was at this time that stirring was observed to have a noticeable effect in that it prolonged the induction time and caused the formation of lower molecular weight polymers. This was found to be especially true at the lower concentration of catalyst. The temperature of the system was then raised to 60°C to overcome the stirring effect, but the stirring effect was still noticeable. Only the degree and rate of polymerisation increased. A study of this stirring effect with all other conditions constant, i.e. the ratio of monomer to water, the styrene with a boiling point of 38°-39°C/15 mm and an index of refraction of 1.5450, and the concentration of emulsifying agent, was initiated.

It was observed that the water must be free from any dissolved salts especially those of iron for in a comparison of two early experiments, one in which the distilled water used was taken directly from the distilled water tap, and the other in which the water was redistilled from

a KMnO_4 solution, a wide deviation of results occurred.

Experiments 1, 2, and 3 were carried out at 40°C , and experiments 4 through 12 were carried out at 60°C .

From a study of Fig. I and Fig. II, the effect of stirring can be seen. The effect of stirring can be shown by comparison between samples 6 and 7 of experiment 1 and between samples 8 and 9 of experiment 2. During the interval between the taking of samples 6 and 7 and samples 8 and 9, the stirring was continuous. During the intervals between the taking of the other samples the stirring was intermittent over ten minutes periods. With continuous stirring the polymerization reaction stopped, and the molecular weights and percent polymerization remained the same. As soon as intermittent stirring was reapplied the reaction returned to its previous rate of polymerization and previous change of molecular weights.

The induction time is greatly reduced and the rate of propagation is increased with an increase in catalyst concentration. Differences in molecular weight that are also noticed indicates that as concentration of catalyst was increased the molecular weight decreased. This is probably due to the increase in the number of free radicals with the increase in catalyst concentration. The free radicals act as chain terminators as well as initiators causing a decrease in molecular weight with an increase in catalyst concentration.

Fig. III and Fig. IV give a picture of the results obtained when continuous, intermittent, and non-stirring are used. The induction times were reduced and the average molecular weights were increased

with a decrease in the amount of agitation. The average molecular weight curves indicates that decreased stirring increase the maximum average molecular weights. In two respects, namely that concerned with percent polymerization and that concerned with molecular weight, the stirring can be interpreted as a definite chain terminator in its effect on percent polymerization and on average molecular weights of the polymer formed.

The effect of stirring rate may be seen in Fig. V and Fig. VI. The induction time is almost infinite with a rapid rate of stirring (500 rev./minute). As the rate of stirring is decreased, the induction time is reduced and the propagation rate is increased. A comparison of molecular weights indicate the chain terminating power of stirring. With an increased stirring rate the molecular weights are decreased.

Perhaps the chain terminating effect of the stirring may be due to the inert atmosphere (N_2) being mixed into the system. An investigation of Fig. VII shows that the effect of stirring is not due to increased N_2 in the system. Experiment 9 is that system where nitrogen is run through continuously during the reaction. Experiment 8 is that system where nitrogen was only used to flush atmospheric oxygen out of the system and then turned off. A comparison of the two experiments indicate that nitrogen does not have a significant inhibiting effect. If the nitrogen were to have an inhibiting effect, it would increase the induction time when the amount being introduced into the system was increased. This was found not to be true in fact an opposite effect was observed. Thus it can be concluded that the inhibiting effect of nitrogen

is insignificant. The actual increase in induction time was probably due to oxygen getting into the system.

Fig. VIII is a comparison of mercuric acetate titration values of unreacted monomer as compared to the values for unreacted monomer calculated from the coagulated polymer. The values for unreacted monomer calculated from the coagulated polymer is based on the difference between the weight of the coagulated polymer and the theoretical weight of polymer if all the monomer in the sample had polymerized. The method of determining the unreacted monomer is based on the reaction between mercuric acetate and the unreacted double bond of the monomer. Thus if some of the monomer has reacted to form dimers or trimers which are too low in molecular weight to be precipitated by the alcohol used to coagulate the polymer, the reaction between the double bond and mercuric acetate could not take place. This would mean the titration values will be lower than those for the coagulated polymer.

A relation of average molecular weights to the temperature may be seen in Fig. IX. The average molecular weights of the polymerization products obtained from reactions at higher temperature are lower than those calculated from the polymerization products obtained at lower temperature. The two curves in this case were obtained from reactions run at temperatures of 40° and 60° C. The higher molecular weights came from the reaction at 40° C; the lower molecular weights came from the reaction at 60° C. This is due to the fact that at the higher temperature many more nuclei are activated at one time to

cause formation of many more short chains. This is in conformity with the results of previous investigators.

Most of the polymerizations discussed up to this point were carried out with a catalyst concentration of .75 molar. With concentration of catalyst below .75 molar, experiments were inhibited so much by stirring they could not be studied. As shown previously some experiments were carried out using a concentration of hydrogen peroxide at .75 molar with non-stirring. Experiments were then carried out with non-stirring and with lower concentration of catalyst. The results as seen in Fig. X and Fig. XI show the induction time to be practically eliminated and show the molecular weights to increase with a decrease in catalyst concentration.

Conclusion:

- 1. Stirring causes an increase in induction time and a decrease in molecular weight. This is especially true at the lower concentration of catalyst.**
- 2. At 60° C. with elimination of stirring the lower concentration of catalyst reduces the induction time to practically zero and increases the molecular weight (800,000).**
- 3. Lower temperature causes an increase in molecular weights and an increase in induction time.**
- 4. A comparison of mercuric acetate titration values with those values based on the coagulated polymer indicates the amount of styrene existing as dimers or trimers.**
- 5. The effect of an inert gas (N₂) on the system is slight.**

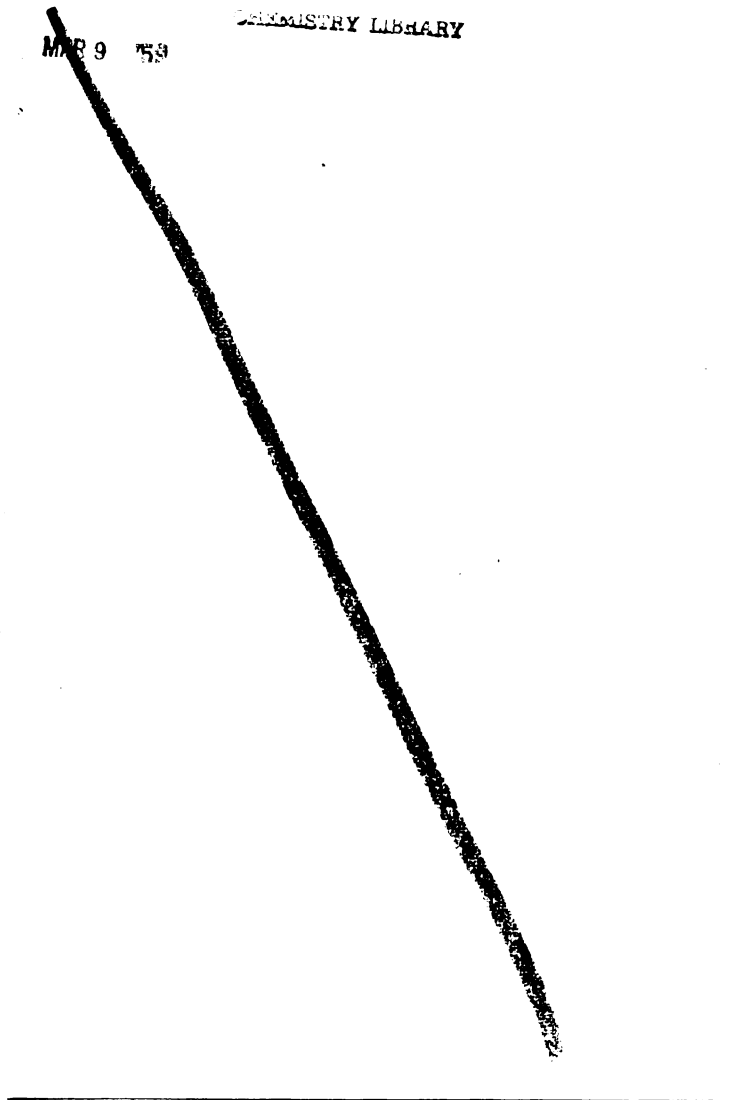
Bibliography:

1. Mark, H., and Whitby, High Polymers, I, 278, Interscience Publishers, New York, 1940.
2. Berthelot, M., Ann., 141, 181 (1867).
3. Ellis, The Chemistry of Synthetic Resins, I, 232, Reinhold Publishers, New York, 1935.
4. Hohenstein, W. F., Vingiello, F. and Mark, H., India Rubber World, 110, 291 (1944).
5. Abere, J., Goldefinger, G., Naidus, H. and Mark, H., J. Phys. Chem., 49, 211 (1945).
6. Mark, H. and Raff, R., High polymeric Reactions, 81, Interscience Publishers, New York, 1941.
7. Carothers, W. H., Chem. Rev., 8, 392 (1931).
8. Burk, R. E., Thimpson, H. E., Weith, A. J., Williams, Polymerization, Interscience Publishers, New York, 1937.
9. Fryling, C. F., and Harrington, K. W., Ind. Eng. Chem., 36, 114 (1944).
10. McBain, J. W., Solubilization and other factors in Detergent Action, in Advances in Colloid Science, I, 124 (1942).
11. Harkins, W. D., Paper at Meeting of A.C.S., Chicago, 1946.
12. Harkins, W. D., J. Am. Chem. Soc., 69, 1428 (1947).
13. Flery, P. J., J. Am. Chem. Soc., 59, 241 (1937).
14. Price, C. C., Ann. N. Y. Acad. Sc., 44, 351 (1943).
15. Powers, P. C., Synthetic Resins and Rubbers, 156, John Wiley and Sons, London, 1944.
16. Williams, G., J. Chem. Soc., 1940, 775.
17. Cohenand Saul, G., J. Am. Chem. Soc., 67, 17, (1945).
18. Bacon, R. G. R., Trans. Faraday Soc., 42, 140 (1946).
19. Pice, C. C., J. Am. Chem. Soc., 67, 1674 (1945).
20. Kline, G. M., Br. Plastics, 18, 101 (1946).

21. Gee, G., *Trans. Faraday Soc.*, 40, 261 (1944).
22. Burk, R. E., Thompson, H. E., Wieth, A. E., and Williams, V., *Polymerization*, Reinhold Publishers, New York, 1947.
23. Baxendale, J. H., Evans, M. G., and Park, G. S., *Trans. Faraday Soc.*, 42, 156 (1946).
24. Staudinger, H., *Die Hochmolekularen Organischen Verbindungen*, 156, Julius Springer, Berlin, 1932.

MAR 9 1958

PARLIAMENTARY LIBRARY



MICHIGAN STATE UNIVERSITY LIBRARIES



3 1293 03062 1852