SOME STUDIES OF THE EMULSION
POLYMERIZATION OF STYRENE

Thesis for the Degree of M. S.
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Homer Robert Arthurs
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By

Homer Robert Arthurs

AN ABSTRACT

Submitted to the School of Graduate Studies of Michigan
State College of Agriculture and Applied Science
in partial fulfillment of the requirements
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MASTER OF SCIENCE

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HOMER ROBERT ARTHURS ABSTRACT

This thesis is a continuation of the work in emulsion polymerization, which has been previously carried out by workers in this laboratory. The equipment and technique employed in this research was similar to that used by these other workers.

The basic polymerization recipe which was employed in these experiments is as follows:

Temperature: 40° C. ± 0.1° C.

Nitrogen Atmosphere

Water: 686.0 grams

Potassium Persulfate: 0.1854 grams (0.001 M based on the aqueous phase)

Sodium meta Bisulfite: 0.0652 grams (0.0005 M based on the aqueous phase)

Styrene: varied

Dupanol G: varied (percent is based on the aqueous phase)

The ratio by weight of styrene to water which was used in these experiments was 1:14, 1:12, 1:10, 1:8, 1:6, and 1:4. The percent dispersing agent was held at a value of 1.0 percent when the concentration of the monomer was changed. The ratio of styrene to water was held at 1:8 when the percent dispersing agent was 1.5, 1.0, 0.75, 0.50, and 0.25.

The time-conversion curves were obtained for these various conditions and the rate of conversion determined from the straight-line portion of these curves. It was found that the emulsion polymerization of styrene was 3/2 order with respect to the monomer concentration. When the amount of dispersing agent was increased, it was found that the rate of conversion was also increased. The rate of polymerization is related to the percent dispersing agent by

$$-dm/dt = K(\%\ \text{dispersing agent})^{1/3} - 0.32K$$

where K is a constant.

The molecular weights were also obtained, and it was found that the molecular weight increased when the percent dispersing agent was increased or the styrene concentration was increased.

It was also found possible to determine styrene in the aqueous phase of polymerization mixtures by the mercuric acetate method if aluminum chloride was absent.

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INTRODUCTION

Research in emulsion polymerization in this laboratory began in the year 1946 with preliminary work by Morgan.[1] In 1947, Yang,[2] using potassium persulfate as a catalyst for styrene polymerization, observed a minimum limit of catalyst concentration for obtaining high-molecular-weight polymers. Early in 1948, Hallenbeck[3] found a stirring effect on the polymerization rate of styrene catalyzed by hydrogen peroxide. Later in the same year, Mihina[4] presented his thesis work on alcohols as deactivation agents for the emulsion polymerization of styrene. In 1948, Loring[5] studied the effect of one redox system on emulsion polymerization of styrene. The redox system employed was that of meta sodium bisulfite with potassium persulfate.

This paper reports the results of the first attempt in this laboratory to closely examine the effect of the monomer (styrene) concentration and emulsifying agent (Dupanol G) concentration on the rate of conversion of the monomer. The redox system employed was that of meta sodium bisulfite with potassium persulfate.

HISTORICAL

Prior to 1927, the majority of polymerization reactions were carried out as either a bulk or a solution process. Then Dinsmore,[6] and Luther and Heuck[7] described a method for polymerizing unsaturated monomers in an aqueous emulsion. This method, due to certain features (namely, the ease of temperature control, formation of high-molecular-weight products, and increased rate of reaction), came into widespread use in the production of polymers. There have been numerous patents issued concerning the polymerization of styrene in an emulsion system.[8-15]

Mark and Raff[16] have described a typical emulsion polymerization as one which contains a purified monomer, a basic phase (emulsion medium), emulsifying agent, stabilizer, regulator of surface tension, catalyst, chain regulator, and a buffer. Examples of the various substances which can be used for such an emulsion system are:

1. purified monomer—almost any substituted ethylenic compound.
2. basic phase—usually water free from impurities

3. emulsifying agent—aliphatic long-chain carboxylic and sulfonic acids, sulfonated long-chain alcohols and amines, or aromatic alkyl sulfonic acids.

4. stabilizer—casein, dextrin, or soluble starch.

5. catalyst—peroxides, free radicals, etc.

6. regulator of surface tension—aromatic or aliphatic alcohols.

7. chain regulator—mercaptans, other organic sulfur compounds, or chlorinated hydrocarbons.

The most important of these are the monomer, catalyst, and the emulsifying agent.

The mechanism of emulsion polymerization is not fully understood at this time, although several workers have contributed greatly to the clarification of some of the aspects. Fikentscher[17] advanced the hypothesis that polymerization in an aqueous suspension takes place essentially in the aqueous phase, and not inside the monomer droplets. Venograd and his collaborators[18] observed the behavior of small droplets of styrene in aqueous solutions of peroxides under the microscope. They found that the radii of these globules decreased by an amount which was roughly proportional to the time of immersion, and that the polymer was slowly formed in the aqueous phase surrounding the droplets. Hohenstein and Mark[19] also supported the concept of polymerization in the aqueous phase. They added the monomer to a water solution of hydrogen peroxide and observed: (a) the monomer stayed on top, (b) in a short time the water became opaque due to the formation of the polymer, and (c) none of the polymer could be detected in the monomer. These reports would seem to indicate that the hypothesis of Fikentscher is correct.

When soap solutions are used instead of pure water, the mechanism is significantly changed. Fryling and Harrington[20] stated that the addition of monomers to aqueous soap solutions is accompanied by two changes in pH. The initial decrease is due to the formation of micelles in the aqueous phase. With further addition of monomer, the pH is increased. This change in pH has been attributed to the interaction of the soap and monomer. Since soap is a salt of an organic acid, it will hydrolyze to form a weak organic acid and a strong base. This can be represented by the following equation:

$$RCOO^- + Na^+ + H_2O \rightleftharpoons RCOOH + Na^+ + OH^-$$

The acid will react with the monomer, and thus be removed from the equilibrium system. This will shift the equilibrium to the right, and thereby increase the pH. They also stated that this phenomenon lends support to the theory that emulsion polymerization is initiated in the aqueous phase and not at the interface of the micelle and aqueous phase, or in the monomer phase.

By extending the work of Hess[21, 22] on the diffraction of X rays by soap solutions, Harkins and McBain[23-27] have obtained evidence which indicates the presence of lamellar micelles in aqueous soap solutions. These micelles are close packed, side by side, and placed end to end. When hydrocarbons were added to these concentrated (10 to 30%) soap solutions, it was shown by these workers that the average distance between adjacent lamellae was increased. In order to explain the accelerating influence of soap on the rate of polymerization, it is now assumed that lamellar micelles exist not only in the concentrated, but also in dilute (1 to 3%) soap solutions. These micelles contain solubilized monomer, and are highly swollen with water. Therefore, they permit a free diffusion of the water-soluble initiator. The formation of active centers takes chiefly in these micelles.[17, 27, 28]

Since the activation energy of the initiation in a soap solution of styrene by potassium persulfate was found to be around 17,000 calories per mole,[28] which is about 8,000 calories less than in bulk or homogeneous solution, it is apparent that the activation of the double bond by the persulfate inside a soap micelle requires less energy than in the monomer phase or in a solvent.

Oxygen is recognized as an inhibitor[29] in polymerization reactions. Therefore, various reducing agents have been added to polymerization systems in order to remove gaseous oxygen. It has been found that not only are the induction periods eliminated, but in many cases the subsequent rates of polymerization are increased. These facts were discovered in England and Germany at just about the same time and have opened the field of redox catalysis of polymerization reactions.

Initiation of polymerization by redox systems was first noticed in England by Bacon,[30] who termed it "reduction activation." He made a systematic study of the rates of polymerization of various monomers, in aqueous solution, in the presence of various oxidizing and reducing agents. A detailed study of the kinetics and mechanism of redox polymerization systems with persulfate as the oxidizing agent was carried out by Morgan.[31] Both authors, Bacon and Morgan, reported that initiation in the systems which they studied was much more effective with acrylonitrile and its derivatives than with butadiene and its derivatives, with styrene occupying an intermediate position.

Probably the best quantitative study of a redox system which is capable of initiating vinyl polymerization was carried out by Baxendale, Evans, and Park,[32] who studied the catalytic effect of hydrogen peroxide on the polymerization of acrylonitrile in the presence of ferrous sulfate. These authors accepted the mechanism of Haber and Weiss[33] for the decomposition of this redox system.

1. $H_2O_2 + Fe^{++} \longrightarrow HO^- + HO\cdot + Fe^{+++}$
2. $HO\cdot + Fe^{++} \longrightarrow HO^- + Fe^{+++}$
3. $HO\cdot + H_2O_2 \longrightarrow H_2O + HO_2^{\cdot}$
4. $HO_2^{\cdot} + H_2O_2 \longrightarrow HO\cdot + H_2O + O_2$

In addition, Baxendale and co-workers suggested the following steps:

5. $HO\cdot + M \longrightarrow HOM\cdot$
6. $HOM\cdot + nM \longrightarrow$ polymer

These workers have shown that under the conditions used, reaction 3 is almost negligible and reaction 2 is only 20 percent of 5. Therefore, in the competitive reaction for the hydroxyl radical, the reaction of the hydroxyl radical with the monomer is much more important than the other two reactions.

According to previous studies by King and Steinbock,[34] and to the recent systematic investigation by Morgan,[31] the interaction between persulfate and thiosulfate can be described as follows:

$$S_2O_8^{--} + S_2O_3^{--} \longrightarrow SO_4^{--} + SO_4^{\cdot -} + S_2O_3^{\cdot -}$$

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

$$HO\cdot + M \longrightarrow HOM\cdot$$

$$SO_4^{\cdot -} + M \longrightarrow {}^{-}O_4SM\cdot$$

$$S_2O_3^{\cdot -} + M \longrightarrow {}^{-}O_3S_2M\cdot$$

Morgan[31] also pointed out the fact that addition of cupric ion in the persulfate-thiosulfate system increased the rate of conversion.

Loring[5] has studied the redox system of persulfate and meta bisulfite in the emulsion polymerization of styrene.

In studying emulsion polymerization systems, the German workers[41] found that the addition of various organic reducing agents to alkaline recipes containing agents such as benzoyl peroxide, hydrogen peroxide, or ammonium persulfate, frequently gave a marked increase in the rate of polymerization, and that a further increase was, in many cases, brought about by the addition of metallic salts. In most cases this increase took place only if some complexing agent were present.

With the development of these oxidation-reduction catalysts there has been a great deal of work carried out in the preparation of butadiene-styrene copolymers used in the manufacture of artificial rubber.

Baxendale and co-workers[32, 35] have studied the polymerization of methacrylate in aqueous solution, using the ferrous-hydrogen peroxide system as the initiator. They found the rate of polymerization to be proportional to the monomer concentration up to about 40-percent conversion, after which the rate became slower than corresponded to first-order kinetics. This retardation was attributed to the coagulation of the polymer formed. The addition of an emulsifying agent had the effect of increasing both the rate and the extent of polymerization. The kinetics of the reaction remained unchanged by the addition of the emulsifying agent (cetyl trimethyl ammonium bromide).

Morgan[31] has studied the polymerization of acrylonitrile in aqueous suspension, using ammonium persulfate as the initiator.

He found that the rate was approximately proportional to the 1.5 power of the monomer concentration, and to the square root of the persulfate concentration. Deviations were observed, however, particularly above 50-percent conversion of monomer.

Kolthoff and Bovey[36] have found that, in a water system of styrene and potassium persulfate, the rate of polymerization is bimolecular in respect to the styrene. Deviations from this are obtained at higher rates of conversion. These deviations are attributed to the effect of the polymer particles formed in the system. They also carried out the styrene-persulfate polymerization in the presence of dodecylamine hydrochloride, and again found that the reaction was bimolecular in respect to styrene. However, if potassium palmitate or potassium laurate is used as the dispersing agent, an approximately first-order reaction with respect to styrene is obtained.

Josefowitz[37] has recently carried out a number of initial-conversion measurements of acrylonitrile in aqueous suspension and of styrene in aqueous emulsion, using the persulfate-thiosulfate system as initiator. He found that the rate of conversion depends upon the monomer concentration in the range of powers of from 1.5 to 2.0.

Since a soap micelle is the point of initial polymer growth, it would be expected that the amount of emulsifying agent should affect the rate of conversion.

Kolthoff and co-workers[38] have studied the effect of the amount of soap upon the rate of polymerization of styrene. They found that the rate is proportional to the square root of the amount of soap. However, Hutchinson[39] has reported that when styrene is polymerized in aqueous potassium laurate solution with benzoyl peroxide, the rate is proportional to the cube root of the soap concentration. The direct proportionality of rate to square root of the soap concentration was observed by other workers in this field.[40]

EXPERIMENTAL

Reagents

Styrene. The monomer used in these experiments was styrene, which was obtained from the Dow Chemical Company. Before each run it was vacuum distilled. The boiling points for two pressure ranges are shown below.

41° to 43° C. at 14 to 16 mm.
55° to 58° C. at 30 to 33 mm.

These fractions had a refractive index of 1.544 at 20° C.

Water. The water used in these experiments was prepared by refluxing it with alkaline permanganate for two hours in an atmosphere of nitrogen, and then distilling off the purified water. The alkaline permanganate was made by dissolving 300 grams of potassium hydroxide and 18 grams of potassium permanganate in enough water to make one liter of solution. Fifty milliliters of this solution was added to two liters of distilled water and refluxed for two hours in an atmosphere of nitrogen. The water was then distilled off, discarding the first and last 10 percent. The water was purified not more than five hours before use, and it was kept under a positive pressure of nitrogen until it was used.

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

Sodium bisulfite (meta). Merck's reagent grade.

Duponol G. A DuPont emulsifying agent described as being an alcohol amine sulfate. The particular alcohol was lauryl. The reagent was used without purification, but the same lot was used throughout the experiments. It was stored at 60° C. in order to facilitate weighing.

Ethanol. USP 95 percent (B.P. 76° to 77° C.).

Aluminum chloride. Baker and Adamson's C.P. grade ($AlCl_3 \cdot 6\ H_2O$).

Nitrogen (water pumped). The nitrogen was passed through two columns containing alkaline pyrogallol solutions before use. This solution was made by adding 5 grams of pyrogallic acid to 100 milliliters of water containing 50 grams of potassium hydroxide.

Toluene. J. T. Baker's C.P. grade purified by distillation.

Mercuric acetate. J. T. Baker's C.P. grade.

Carbon tetrachloride. J. T. Baker's C.P. grade.

Sodium chloride. Baker and Adamson reagent grade.

Sodium hydroxide. Standard (0.1 N.) carbonate-free solution.

Methanol. Anhydrous Merck reagent grade.

Procedure

The equipment and technique employed in this work was similar to that used by other workers[1-5] in this laboratory. The polymerization was carried out in a four-neck 1-liter round-bottom flask with standard ground-glass joints. This flask was fitted with a mercury-sealed swivel stirrer, a sampling tube that extended to the bottom of the flask, and two addition tubes. A thermometer which extended into the reaction flask and a short bulb-type water condenser was connected to one of these addition tubes. A small double water trap was connected to the condenser in order to permit the nitrogen to escape and prevent air from sucking back into the system. Through the second addition tube, there was placed a nitrogen intake tube that permitted the flow of nitrogen over the top of the emulsion, and a calibrated addition cylinder. This calibrated cylinder was used for the addition of conductance water and styrene. A diagram of this apparatus is shown in the literature.[42]

All reactions were conducted under a nitrogen atmosphere; the flow of nitrogen was regulated to one bubble per second. The temperature was maintained constant by a water bath controlled to 40° C. ± 0.1° C. The rate of stirring was not recorded, but it was maintained rapid and constant throughout the reaction period.

The equipment was thoroughly cleaned before each run. The desired amount of dispersing agent was added to the reaction vessel. The equipment was assembled and then completely flushed free of air by nitrogen which had been passed through alkaline pyrogallol solution. During this time the water was purified in the manner indicated previously (page 12). This water was drawn into the calibrated addition cylinder and added to the reaction flask. The water was allowed to come to operating temperature. The weighed amounts of catalyst and cocatalysts were added to the system, and after allowing five minutes for these to go into solution, the styrene was added. The styrene was not preheated before use because a negligible temperature drop of less than one degree was observed on the addition of the styrene. The initial time of polymerization was recorded as the time of the monomer addition.

Ten-gram samples were withdrawn periodically throughout the run. These were removed by means of an aspirator and transferred to a tared flask which contained a weighed amount of ethanol (40 gm.) and aluminum chloride (0.1 gm.). These flasks and their contents were chilled to 0° C. before use. The purpose of the alcohol and the aluminum chloride was to quench the reaction and coagulate the polymer. The chilling of the solution assists in quenching by the rapid reduction of the temperature. The weight of the sample removed was determined by weight difference. All weighings were carried out to the nearest milligram.

These samples were then quantitatively transferred to centrifuge bottles and the polymer separated from the liquid by centrifuging. The solid polymer was filtered and washed with ethanol and distilled water. This washing was for the purpose of removing residual emulsifier, water-soluble material, monomer, and other alcohol-soluble material. The polymer was allowed to dry for 48 hours at 60° C., and then weighed.

The percent conversion was calculated as follows:

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

The percentage of styrene in the sample is the same as that in the reaction flask. Therefore, it is possible to calculate the amount of styrene in the samples. The theoretical weight of polystyrene is equal to the weight of styrene in the sample. An example of this method of calculation is as follows:

ratio by weight of styrene to water in reaction flask 1:8

weight of sample . . . . 9.000 gm.

weight of polymer . . . . 0.500 gm.

$$\%\ \text{conversion} = \frac{0.500 \times 100}{[1/(1+8)][9.000]} = 50\%$$

Determination of average molecular weight. The viscosity of a solution containing polystyrene in toluene was used to determine the average molecular weight of the polymer.

Fifty-milliliter volumetric flasks containing approximately 45 milliliters of toluene and 0.05 gram of polystyrene were prepared. These flasks were allowed to stand 48 hours at 60° C. in order to obtain complete solutions of the polymer. At the end of the 48 hours, the volumetric flasks were cooled to 20° C., and filled to the mark with toluene, and the contents thoroughly mixed.

A Connon-Fenske-Ostwald viscosity pipette was used to determine the time of efflux of the polystyrene solutions and also of the pure toluene. The time of efflux at 20° C. ± 0.1° C. was determined to 0.1 second by a stop watch. The specific viscosity was calculated from the following relationship:

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

The average molecular weight can be calculated from the specific viscosity by means of Staudinger's equation. This equation is:

$$M = N_{sp}/K(C)$$

where

M = average molecular weight

N_{sp} = specific viscosity

K = 1.8×10^{-4}

C = moles of polymer per liter of solution

A mole of polystyrene is equal to the weight of the recurring unit, which is the molecular weight of styrene.

During this investigation, it was thought advisable to repeat some of the work of Loring.[5] He reported that the mercuric-acetate method for the titrametric determination of styrene was unsuccessful for this polymerization system, but he gave no reasons why unsatisfactory results were obtained. Therefore, it was decided to attempt to find out why this method was unsatisfactory.

The mercuric acetate method[43] is based upon the reaction of mercuric acetate with a double bond to liberate one molecule of acetic acid. This acid is then titrated with standard sodium hydroxide to a phenolphthalein end point. The amount of double bond, calculated as styrene, was obtained from the number of milliequivalents of standard sodium hydroxide used.

In order to check the work of Loring, various standard emulsions of styrene were prepared. These emulsions contained some or all of the following ingredients:

1% Dupanol G

0.001 M potassium persulfate

0.00027 M sodium bisulfite (meta)

based on the water phase, and/or

0.4 gm. aluminum chloride

10 ml. ethanol

0.4 gm. monomeric styrene

The amount of styrene in these mixtures was determined by the mercuric-acetate method. The results are shown below.

Titration of monomeric styrene.

1. Styrene and ethanol:

% styrene	100.6	101.3
	100.3	100.0
	100.9	99.9

2. Styrene, ethanol and Dupanol G:

% styrene	99.9	99.9
	100.7	101.5
	100.2	100.5

3. Styrene, ethanol, Dupanol G, potassium persulfate, and sodium meta bisulfite:

% styrene	101.0	100.5
	99.4	99.4
	100.4	100.6
	98.7	99.8

98.4	98.0
100.5	101.0
99.2	100.1
99.8	98.8
99.1	99.5
98.4	100.0
100.1	99.8

4. Styrene, ethanol, Dupanol G, potassium persulfate, sodium meta bisulfite, and aluminum chloride (the results were high and erratic):

% styrene	148.3
	161.2
	152.3

Data

All experiments had the following ingredients and factors in common:

Water: 686.0 grams

Potassium persulfate: 0.1854 grams (0.001 M based on the aqueous phase)

Sodium meta bisulfite: 0.0652 grams (0.0005 M based on the aqueous phase)

Nitrogen atmosphere

Temperature: 40° C.

Indication is made in each experiment of the grams of styrene and the percent (based on the aqueous phase) Dupanol G present.

EXPERIMENT 1

1.0% Dupanol G and 49.0 grams of Styrene

Sample	Time (minutes)	Percent Solid Polymer	Average Molecular Weight
1	9	12.0	-
2	18	28.6	680,000
3	27	42.2	742,000
4	36	54.8	773,000
5	45	66.5	690,000
6	54	74.5	-
7	63	80.9	-
8	72	82.4	-
9	81	84.5	-
10	90	85.9	-

EXPERIMENT 2

1.0% Dupanol G and 57.3 grams of Styrene

Sample	Time (minutes)	Percent Solid Polymer	Average Molecular Weight
1	9	8.2	-
2	18	17.9	-
3	27	29.6	770,000
4	36	42.1	796,000
5	45	52.8	883,000
6	54	62.4	790,000
7	63	70.7	-
8	72	77.0	-
9	81	82.0	-
10	90	84.3	-

EXPERIMENT 3

1.0% Dupanol G and 68.6 grams of Styrene

Sample	Time (minutes)	Percent Solid Polymer	Average Molecular Weight
1	9	5.3	-
2	18	13.7	-
3	27	24.3	-
4	36	35.0	810,000
5	45	45.3	946,000
6	54	55.1	921,000
7	63	63.8	855,000
8	72	70.8	-
9	81	76.2	-
10	90	80.6	-

EXPERIMENT 4

1.0% Dupanol G and 85.8 grams of Styrene

Sample	Time (minutes)	Percent Solid Polymer	Average Molecular Weight
1	9	8.1	-
2	18	12.6	-
3	27	21.9	-
4	36	29.7	644,000
5	45	39.4	834,000
6	54	51.1	884,000
7	63	55.5	801,000
8	72	64.5	733,000
9	81	72.4	-
10	90	76.4	-

EXPERIMENT 5

1.0% Dupanol G and 114.3 grams of Styrene

Sample	Time (minutes)	Percent Solid Polymer	Average Molecular Weight
1	9	-	-
2	19	4.4	-
3	28	11.7	-
4	37	18.9	-
5	46	27.0	-
6	54	34.6	-
7	64	40.0	1,100,000
8	73	46.8	1,151,000
9	82	52.6	1,132,000
10	91	57.4	1,073,000

EXPERIMENT 6

1.0% Dupanol G and 172.5 grams of Styrene

Sample	Time (minutes)	Percent Solid Polymer	Average Molecular Weight
1	9	1.8	-
2	18	3.8	-
3	27	6.6	-
4	36	10.4	-
5	45	13.6	-
6	54	18.1	-
7	63	22.1	-
8	72	27.3	916,000
9	81	32.2	1,034,000
10	90	38.3	1,250,000
11	99	42.7	1,280,000
12	108	47.0	1,330,000
13	117	51.5	1,306,000
14	126	54.2	1,222,000
15	135	58.3	1,173,000

EXPERIMENT 7

1.50% Dupanol G and 85.8 grams of Styrene

Sample	Time (minutes)	Percent Solid Polymer	Average Molecular Weight
1	9	6.1	-
2	18	14.3	-
3	27	25.1	-
4	36	36.0	1,101,000
5	45	46.4	1,122,000
6	54	56.5	1,243,000
7	63	64.2	1,291,000
8	72	71.5	1,230,000
9	81	76.5	-
10	90	79.0	-

EXPERIMENT 8

0.75% Dupanol G and 85.5 grams of Styrene

Sample	Time (minutes)	Percent Solid Polymer	Average Molecular Weight
1	9	3.2	-
2	18	7.7	-
3	27	13.0	-
4	36	20.4	816,000
5	45	28.9	880,000
6	54	37.4	931,000
7	63	45.1	990,000
8	72	52.4	1,027,000
9	81	59.4	965,000
10	90	64.9	885,000

EXPERIMENT 9

0.50% Dupanol G and 85.8 grams of Styrene

Sample	Time (minutes)	Percent Solid Polymer	Average Molecular Weight
1	9	3.7	-
2	18	6.7	-
3	27	11.0	-
4	36	16.1	609,000
5	45	21.6	729,000
6	54	28.2	805,000
7	63	33.8	855,000
8	72	40.3	911,000
9	81	45.8	931,000
10	90	51.9	890,000

EXPERIMENT 10

0.25% Dupanol G and 85.8 grams of Styrene

Sample	Time (minutes)	Percent Solid Polymer	Average Molecular Weight
1	9	0.2	-
2	18	-	-
3	27	3.6	-
4	36	6.6	-
5	45	11.2	-
6	54	15.6	-
7	63	19.5	546,000
8	72	23.0	574,000
9	81	24.4	612,000
10	90	28.4	662,000

EXPERIMENT 11

1.0% Dupanol G, 85.8 grams of Styrene and 0.4529 grams of Potassium Persulfate

Sample	Time (minutes)	Percent Solid Polymer	Average Molecular Weight
1	83	10.0	-
2	115	23.0	-
3	145	38.3	920,000
4	175	51.5	1,051,000
5	205	64.4	984,000
6	237	74.2	929,000
7	265	81.4	-
8	295	85.6	-
9	325	87.3	-

EXPERIMENT 12

0.50% Dupanol G, 85.8 grams of Styrene and 0.4529 grams of Potassium Persulfate

Sample	Time (minutes)	Percent Solid Polymer	Average Molecular Weight
1	90	13.6	-
2	136	32.3	927,000
3	168	44.7	1,040,000
4	198	55.1	1,104,000
5	228	66.5	1,040,000
6	258	74.3	990,000
7	288	80.8	-
8	318	83.3	-

Graphs

The results of the preceding experiments, and some calculations made from them, are in the following twenty-one graphs. The word "ratio" on these graphs is the weight ratio of styrene to water.

Graphs 1 to 7 show the rate of polymerization (percent conversion versus time) in experiments where the concentration of styrene was varied.

Graphs 8 and 9 give evidence that this polymerization is a 3/2 order reaction with respect to monomer concentration.

Graph 10 shows how the molecular weight of the polymer changes with the percent conversion, using different concentration of styrene.

Graphs 11 to 15 show the rate of polymerization (percent conversion versus time) in experiments where the amounts of dispersing agent was varied.

Graph 16 shows how the molecular weight of the polymer changes with the percent conversion, using different amounts of dispersing agent.

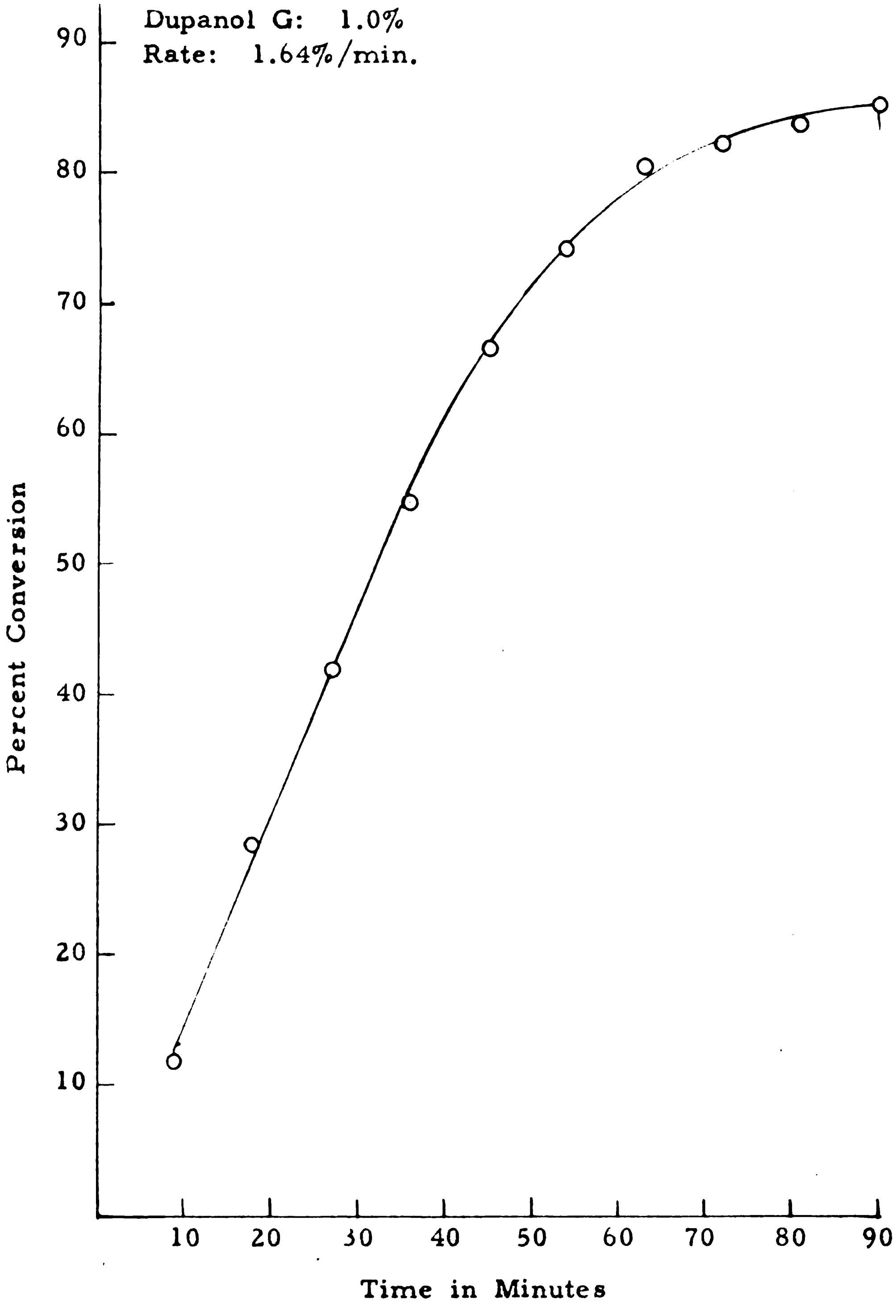
Graph 17 shows the relation between the amounts of dispersing agent and the rate of conversion.

Graph 18 shows that the rate of conversion is a 1/3 order with respect to the dispersing agent.

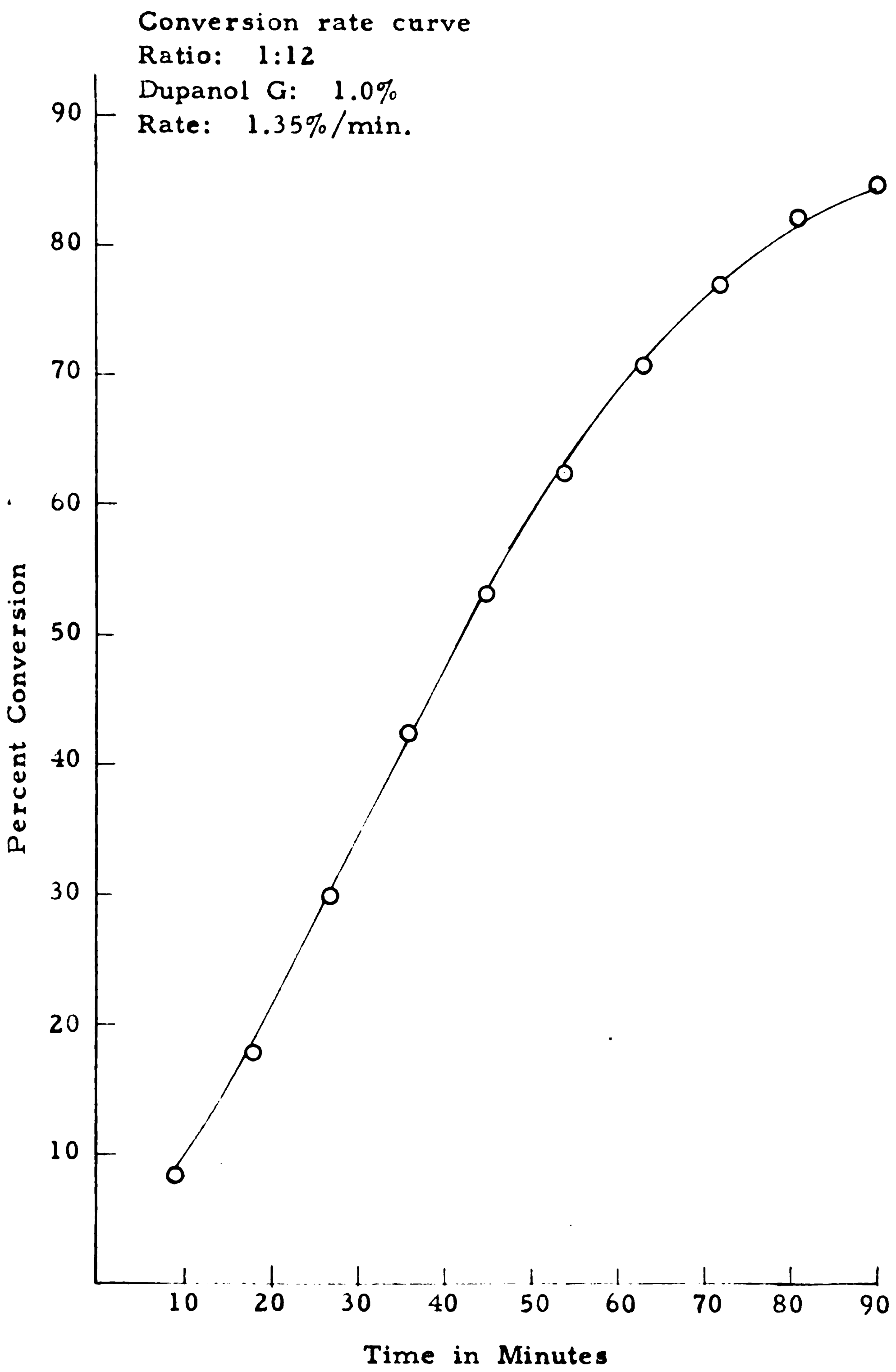
Graphs 19 to 21 show the conversion rate-time curves for systems in which the meta bisulfite was absent, using different amounts of dispersing agent.

GRAPH 1

Conversion rate curve
Ratio: 1:14
Dupanol G: 1.0%
Rate: 1.64%/min.

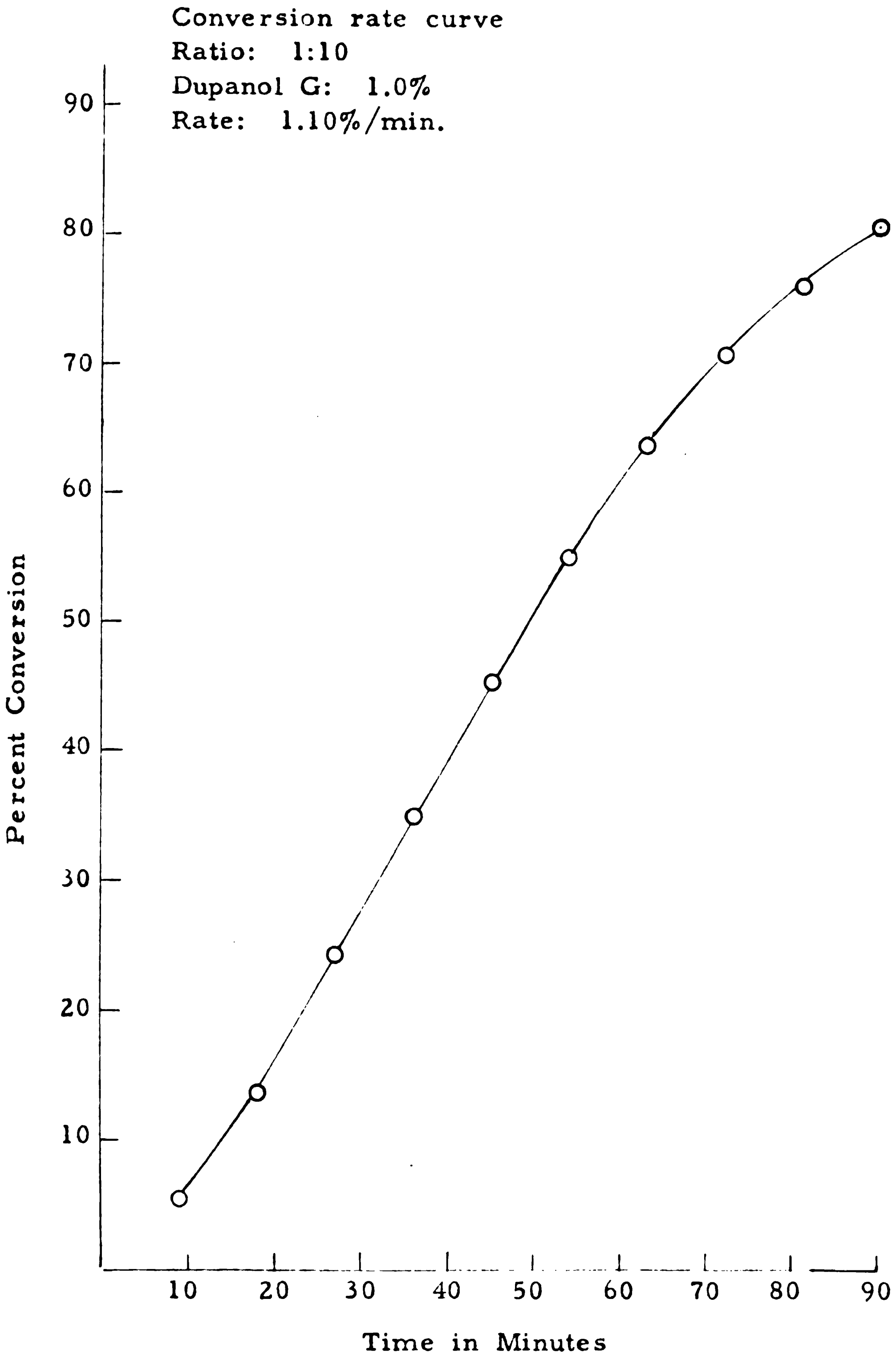


GRAPH 2



Conversion rate curve
Ratio: 1:12
Dupanol G: 1.0%
Rate: 1.35%/min.

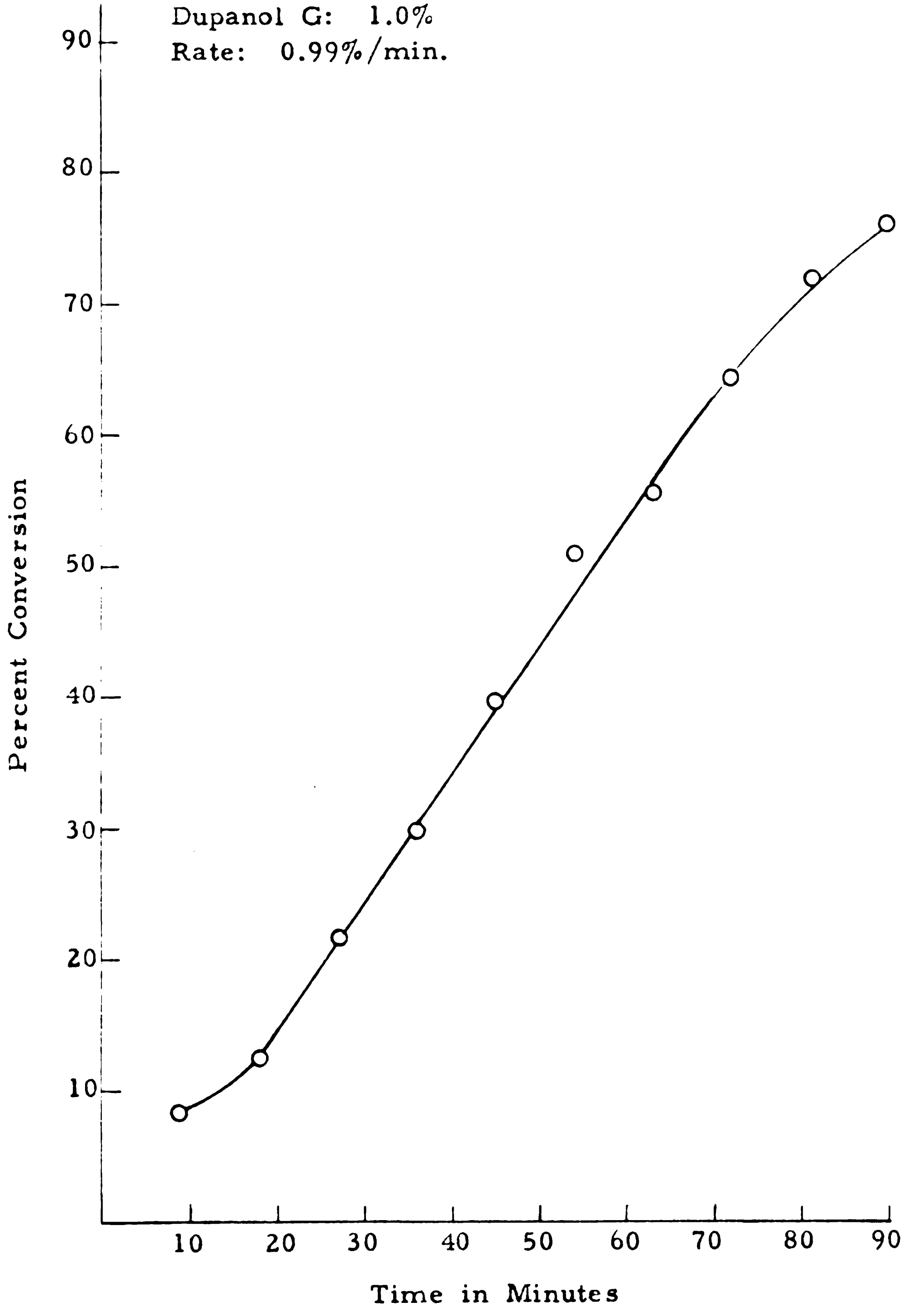
GRAPH 3



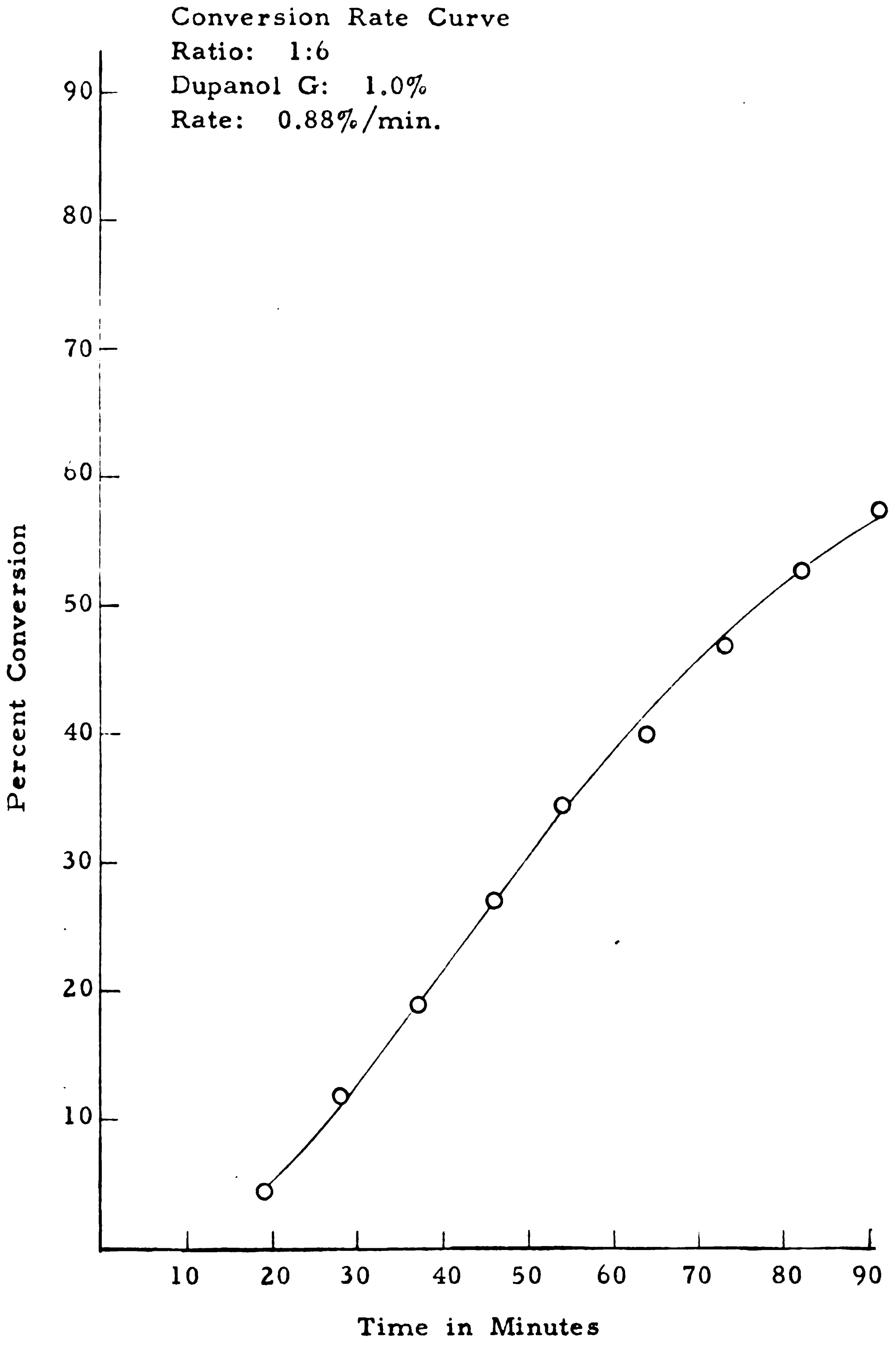
Conversion rate curve
Ratio: 1:10
Dupanol G: 1.0%
Rate: 1.10%/min.

GRAPH 4

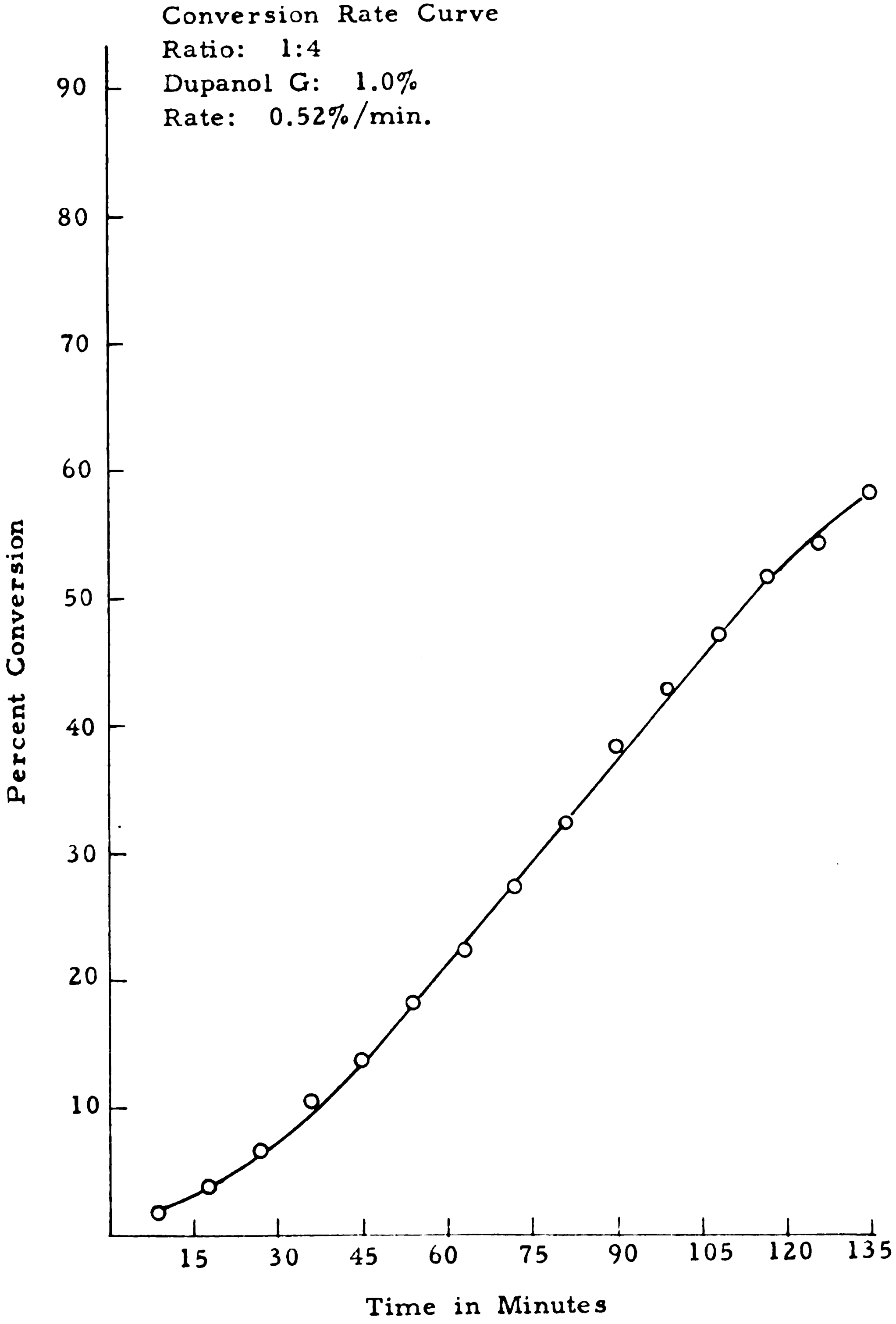
Conversion Rate Curve
Ratio: 1:8
Dupanol G: 1.0%
Rate: 0.99%/min.



GRAPH 5

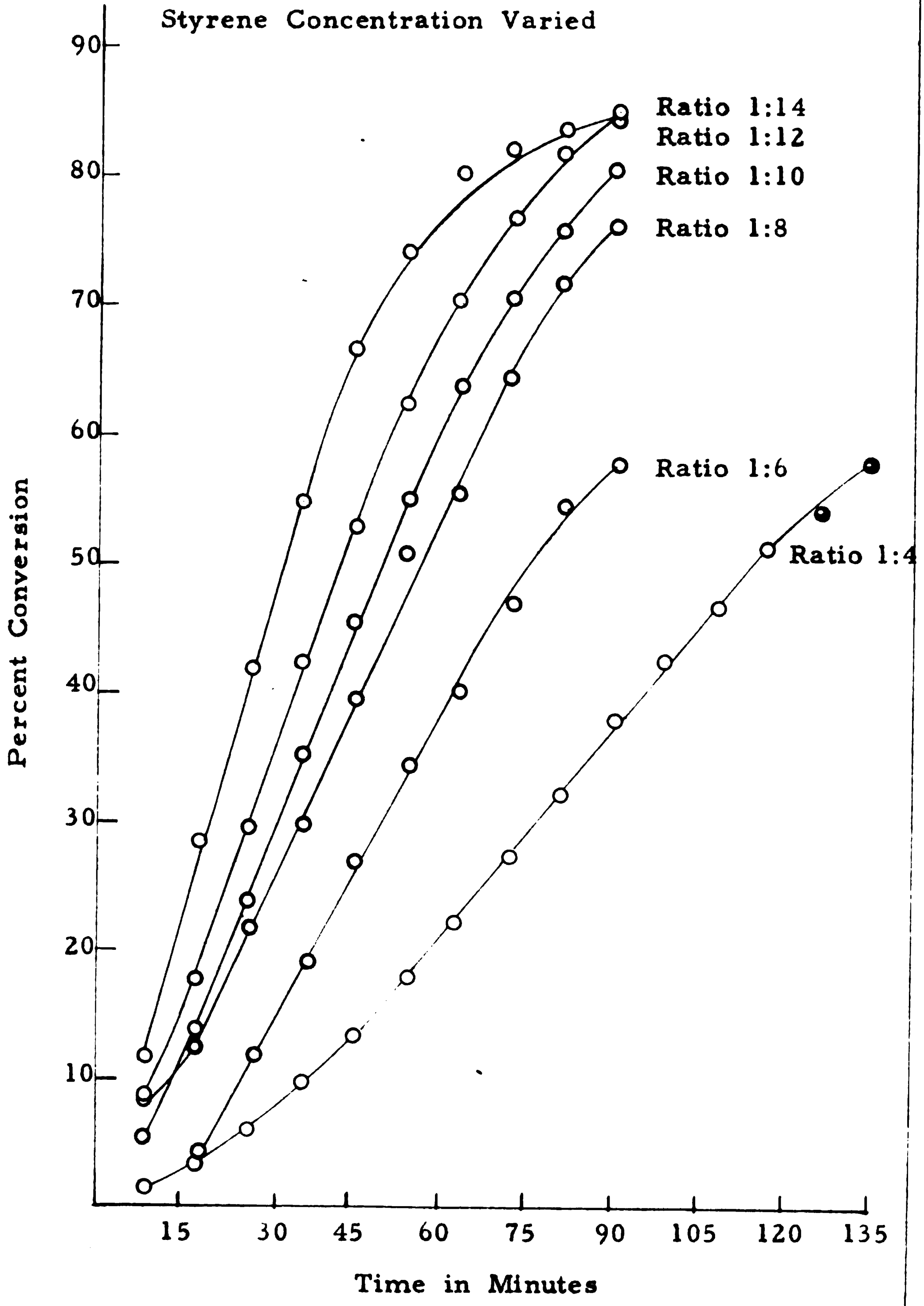

Conversion Rate Curve
Ratio: 1:6
Dupanol G: 1.0%
Rate: 0.88%/min.
Percent Conversion
90
80
70
60
50
40
30
20
10
10
20
30
40
50
60
70
80
90
Time in Minutes

GRAPH 6


Conversion Rate Curve
Ratio: 1:4
Dupanol G: 1.0%
Rate: 0.52%/min.
Percent Conversion
90
80
70
60
50
40
30
20
10
15
30
45
60
75
90
105
120
135
Time in Minutes

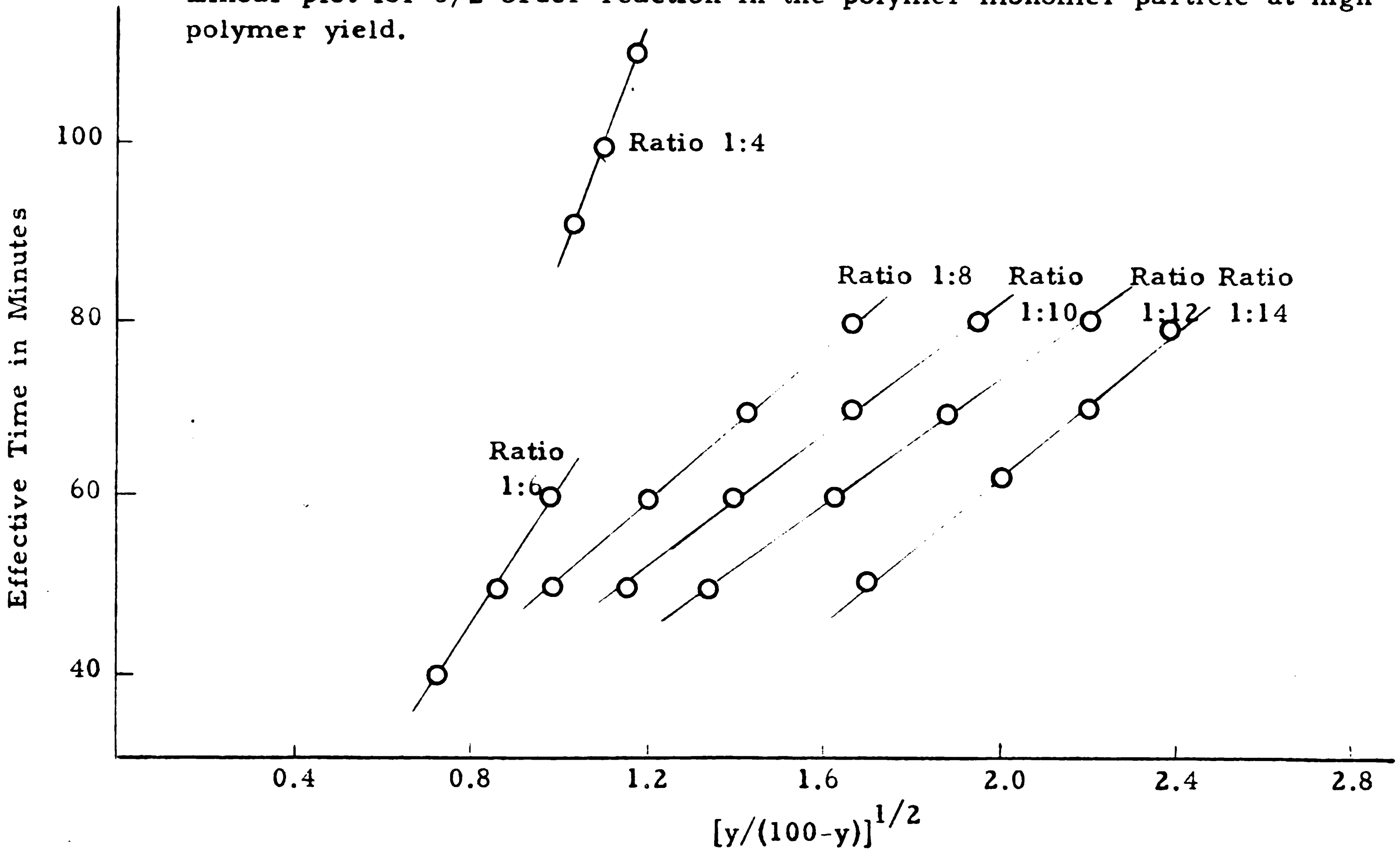
GRAPH 7

Conversion Rate Curves
1 to 6
Styrene Concentration Varied



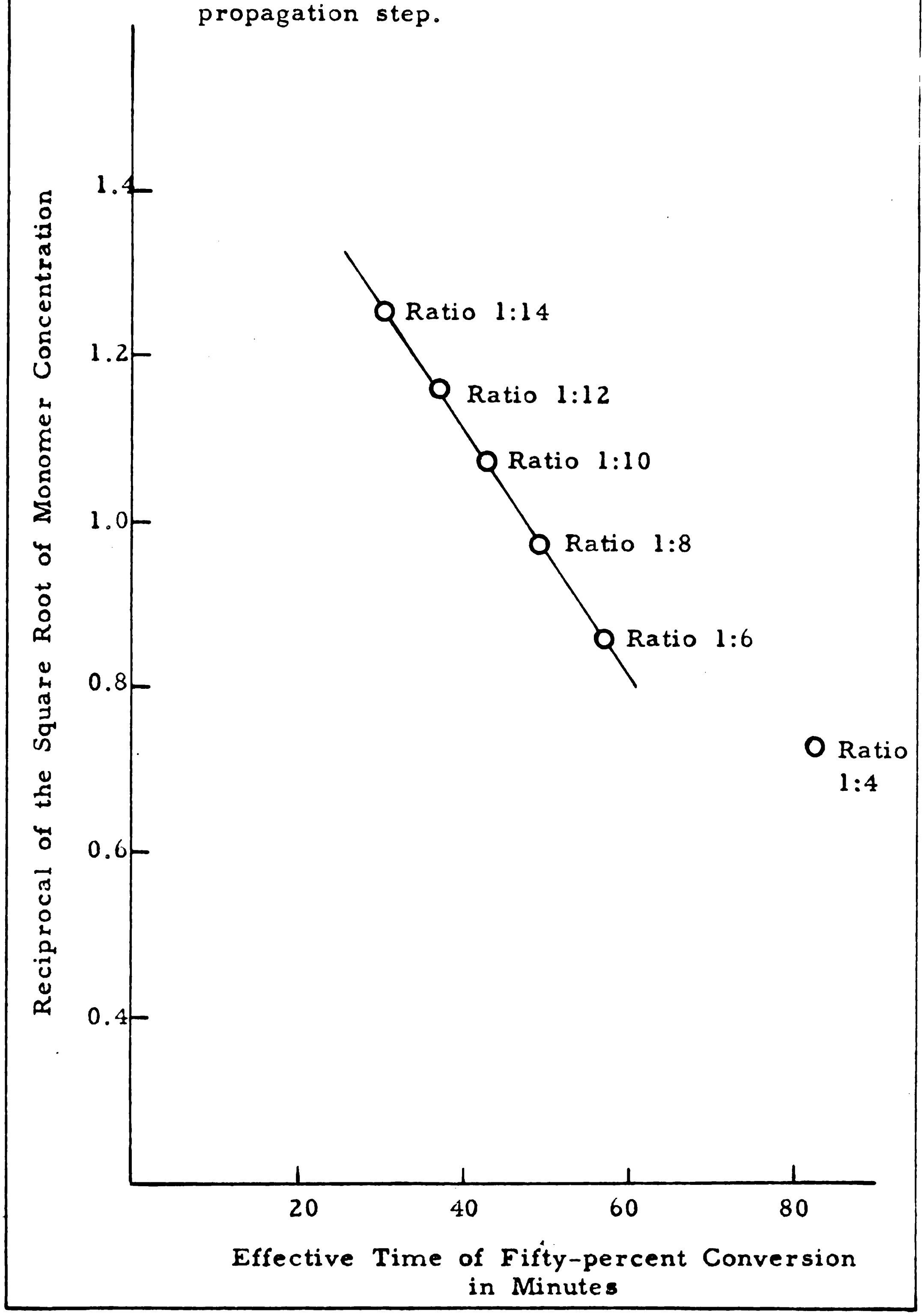
GRAPH 8

Linear plot for 3/2 order reaction in the polymer-monomer particle at high polymer yield.



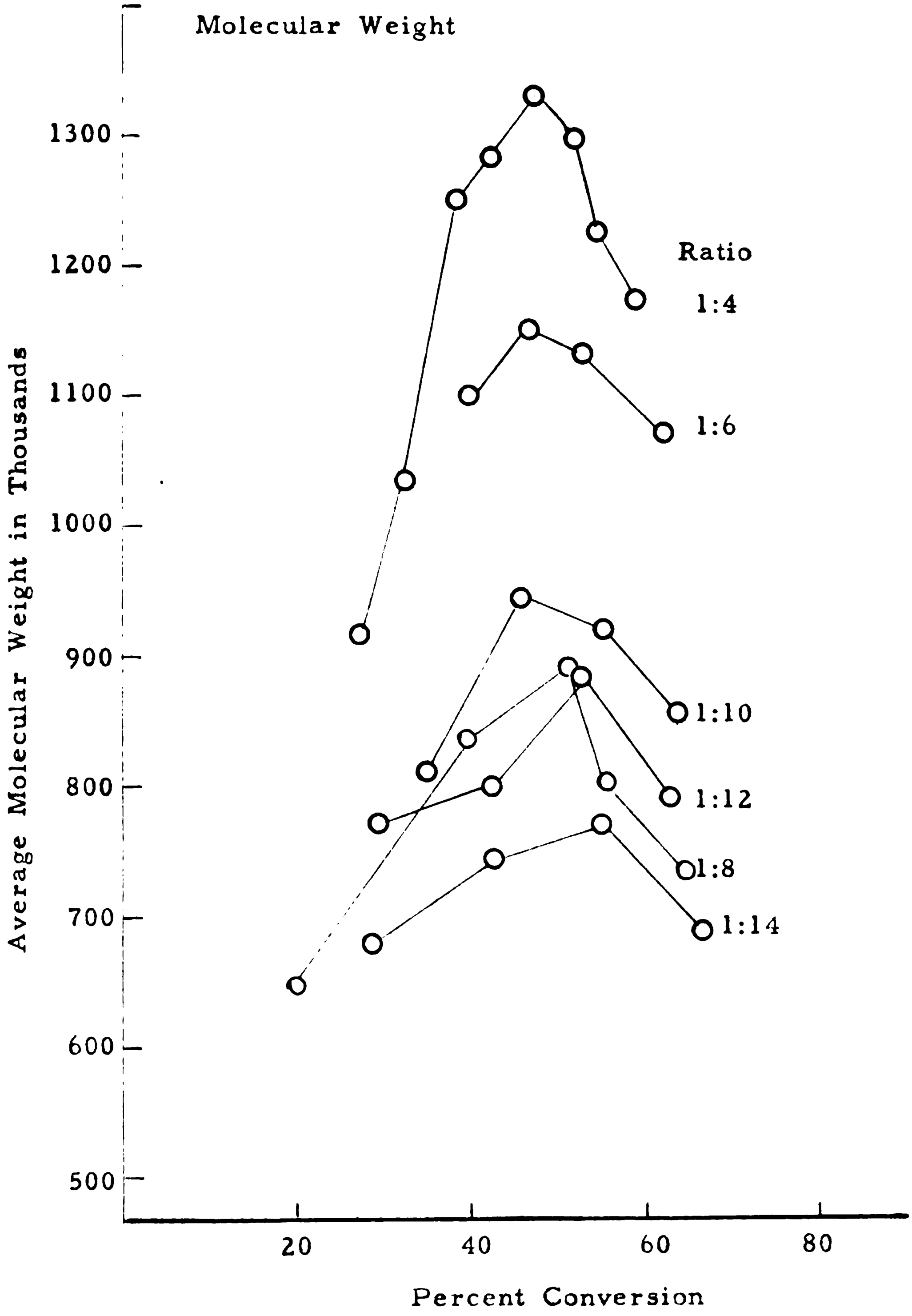
GRAPH 9

Linear plot for 3/2 order reaction in propagation step.

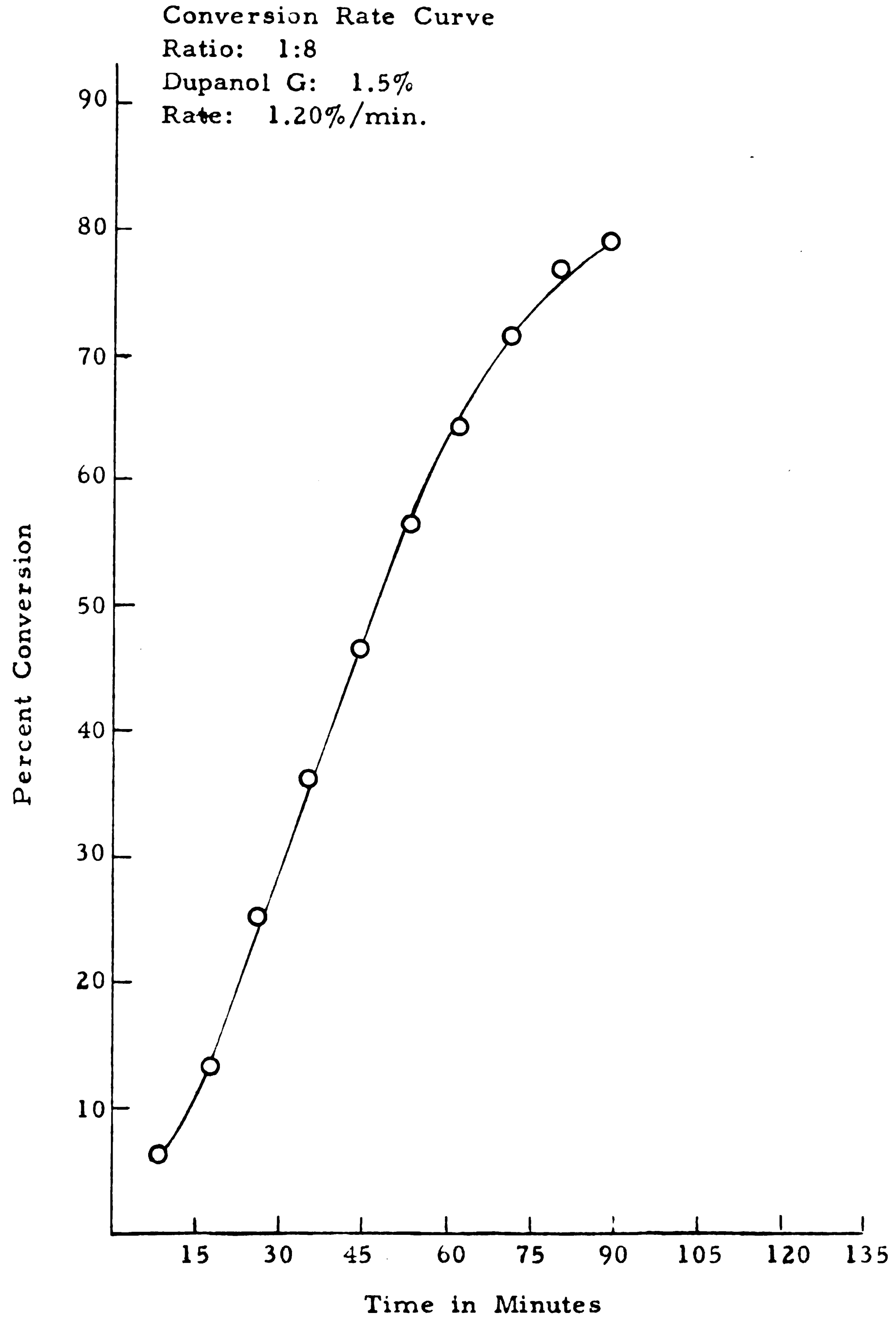


GRAPH 10

Percent Conversion
versus
Molecular Weight

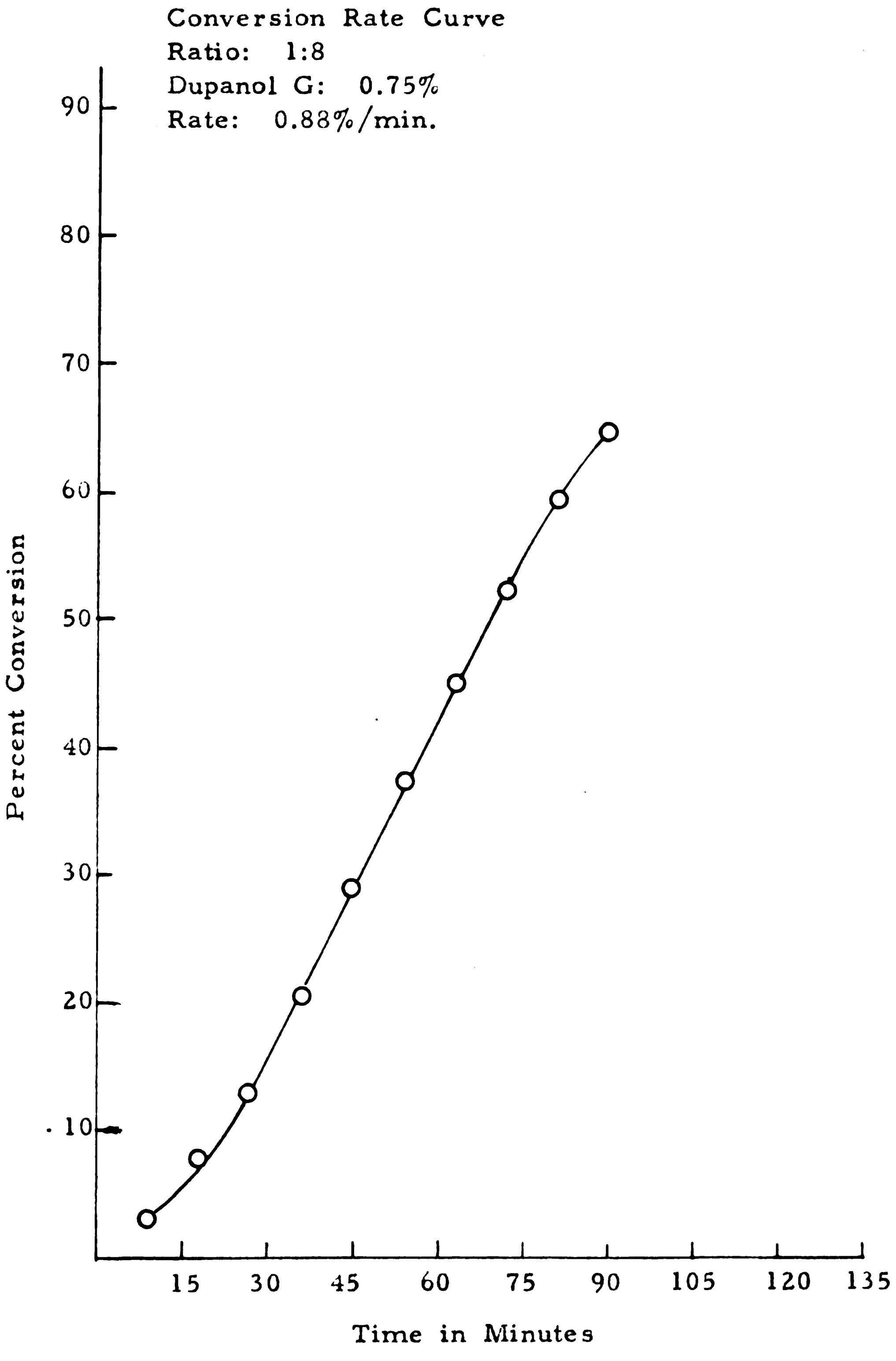


GRAPH 11



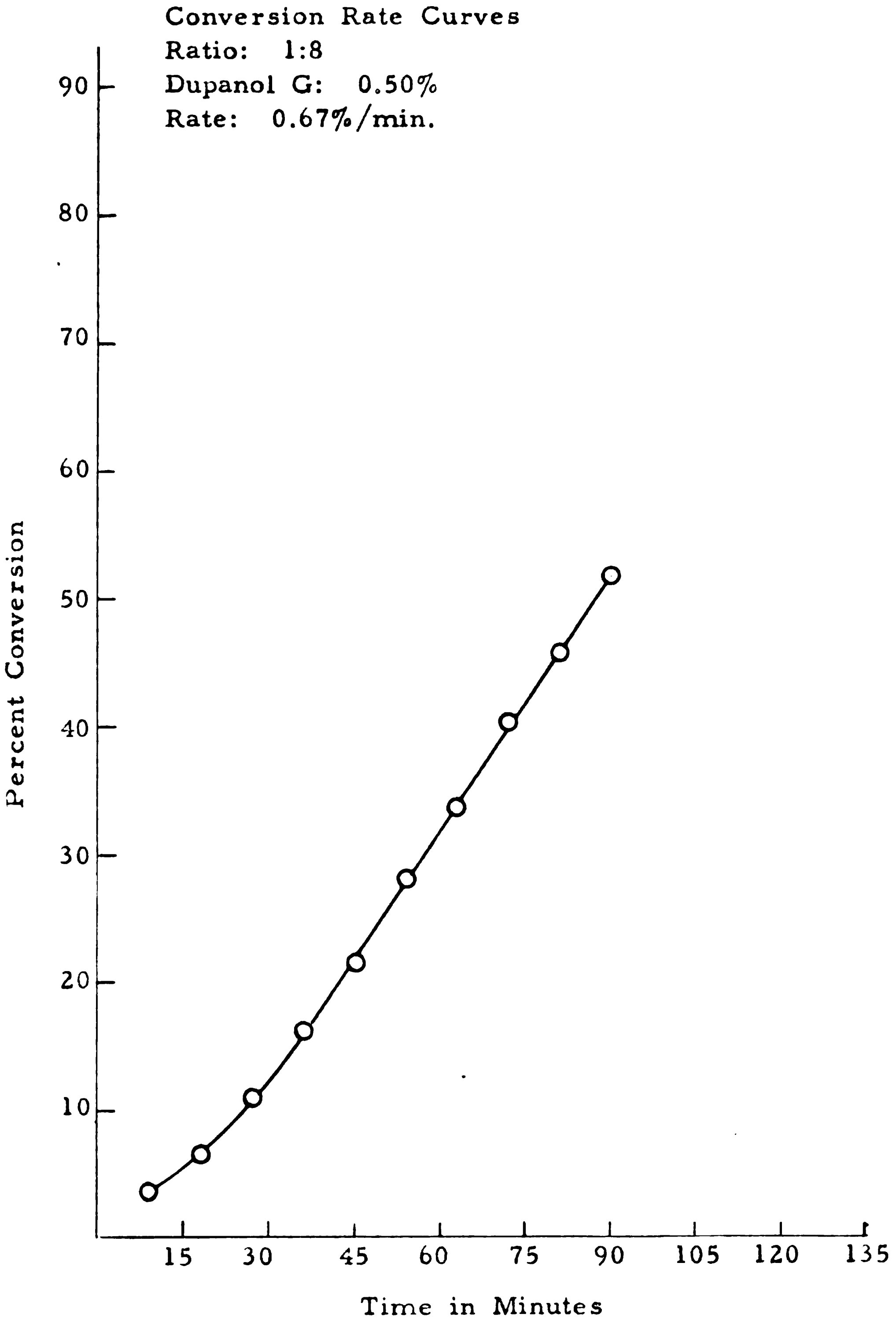
Conversion Rate Curve
Ratio: 1:8
Dupanol G: 1.5%
Rate: 1.20%/min.

GRAPH 12



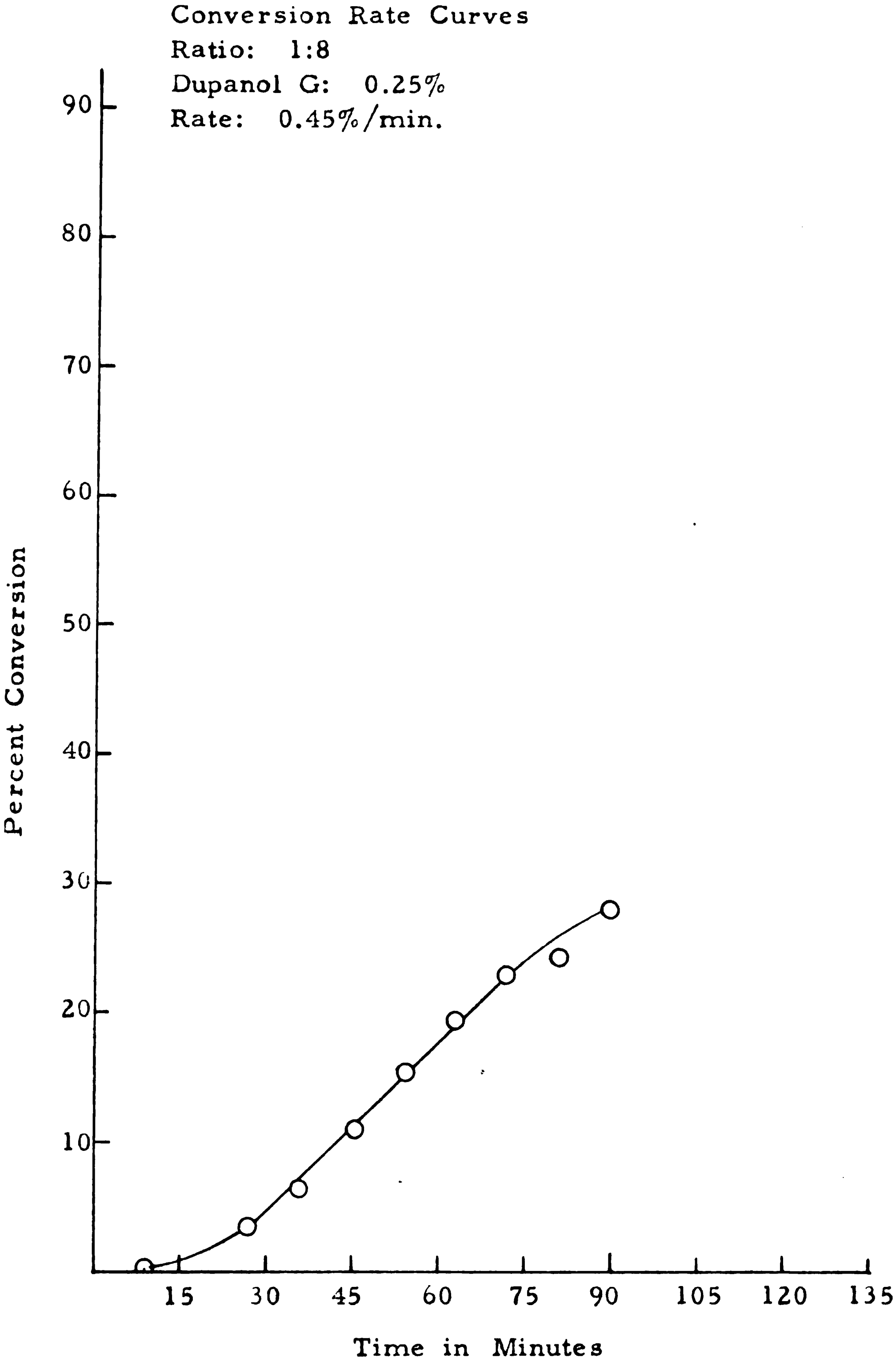
Conversion Rate Curve
Ratio: 1:8
Dupanol G: 0.75%
Rate: 0.88%/min.

GRAPH 13



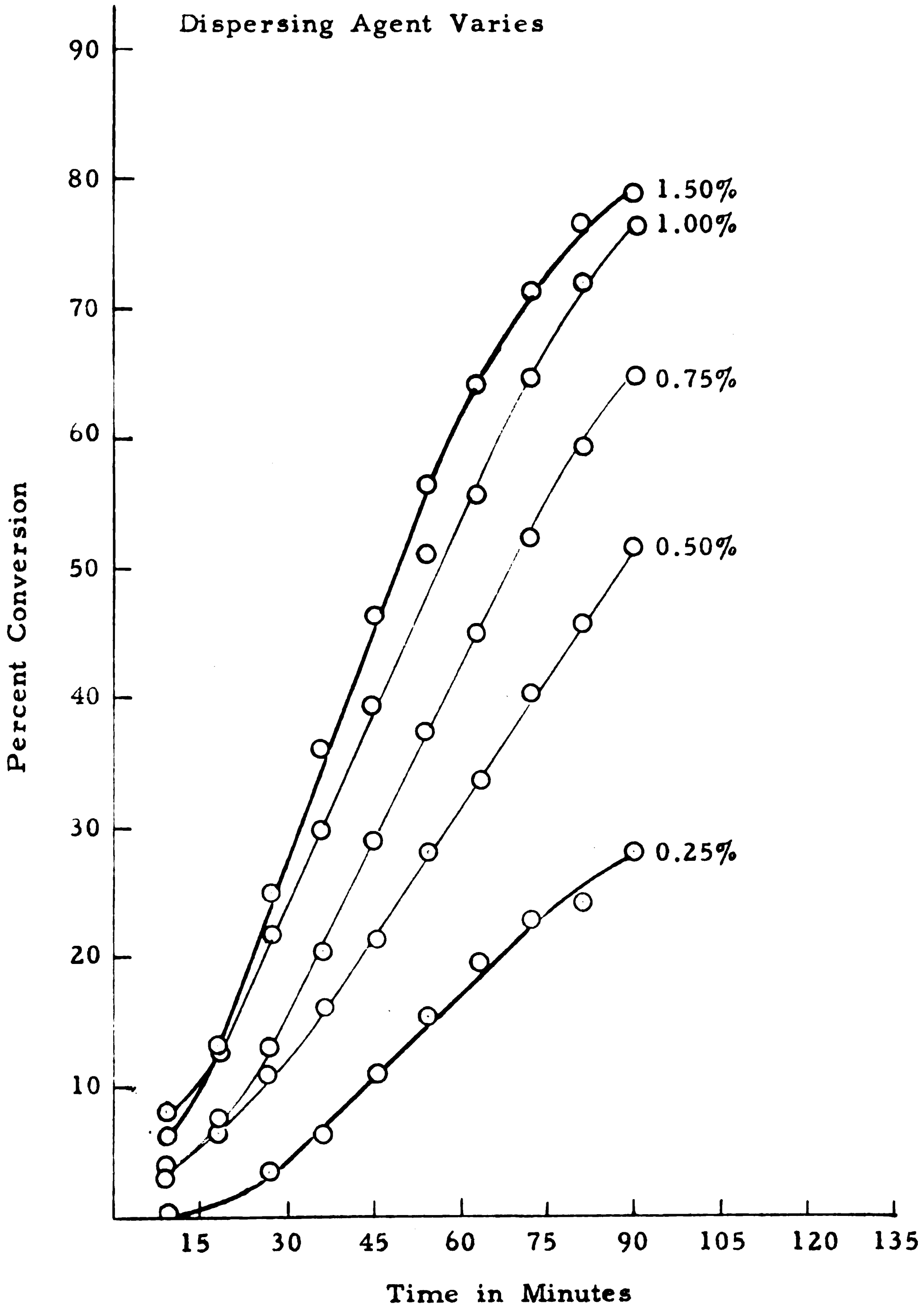
Conversion Rate Curves
Ratio: 1:8
Dupanol G: 0.50%
Rate: 0.67%/min.

GRAPH 14

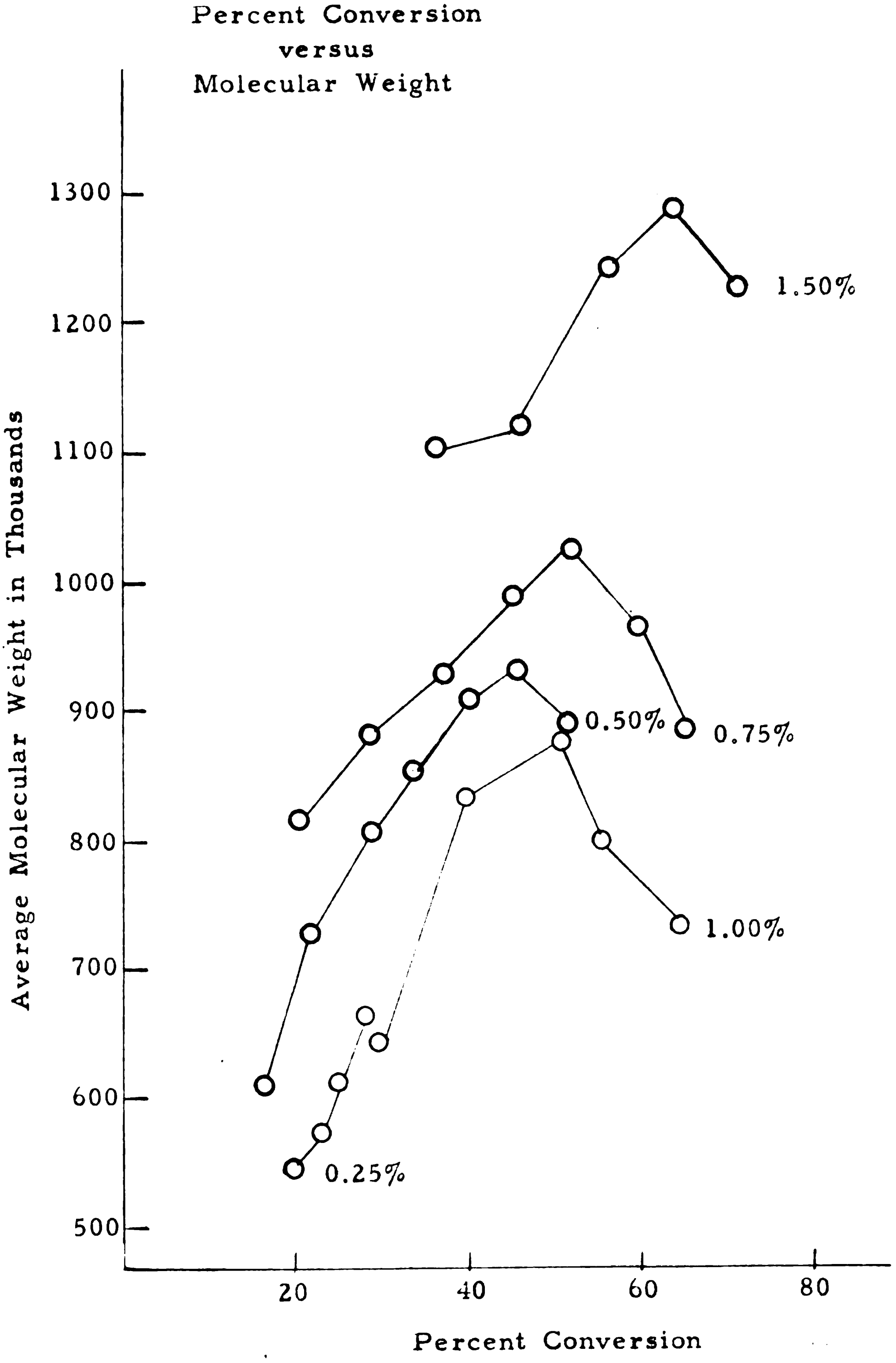


Conversion Rate Curves
Ratio: 1:8
Dupanol G: 0.25%
Rate: 0.45%/min.

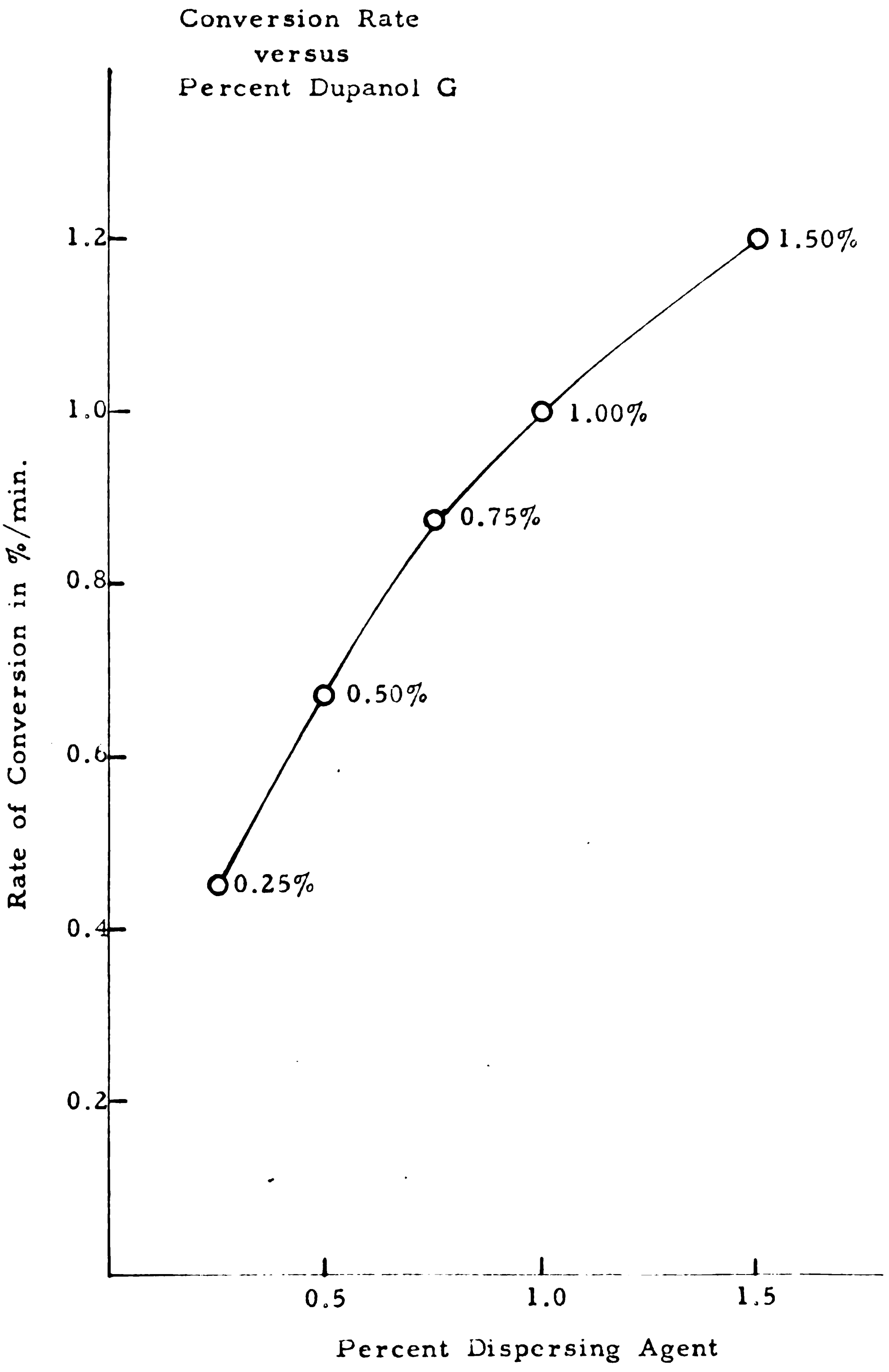
GRAPH 15


Conversion Rate Curve
4 11-14
Dispersing Agent Varies
Percent Conversion
90
80
70
60
50
40
30
20
10
15
30
45
60
75
90
105
120
135
Time in Minutes
1.50%
1.00%
0.75%
0.50%
0.25%

GRAPH 16

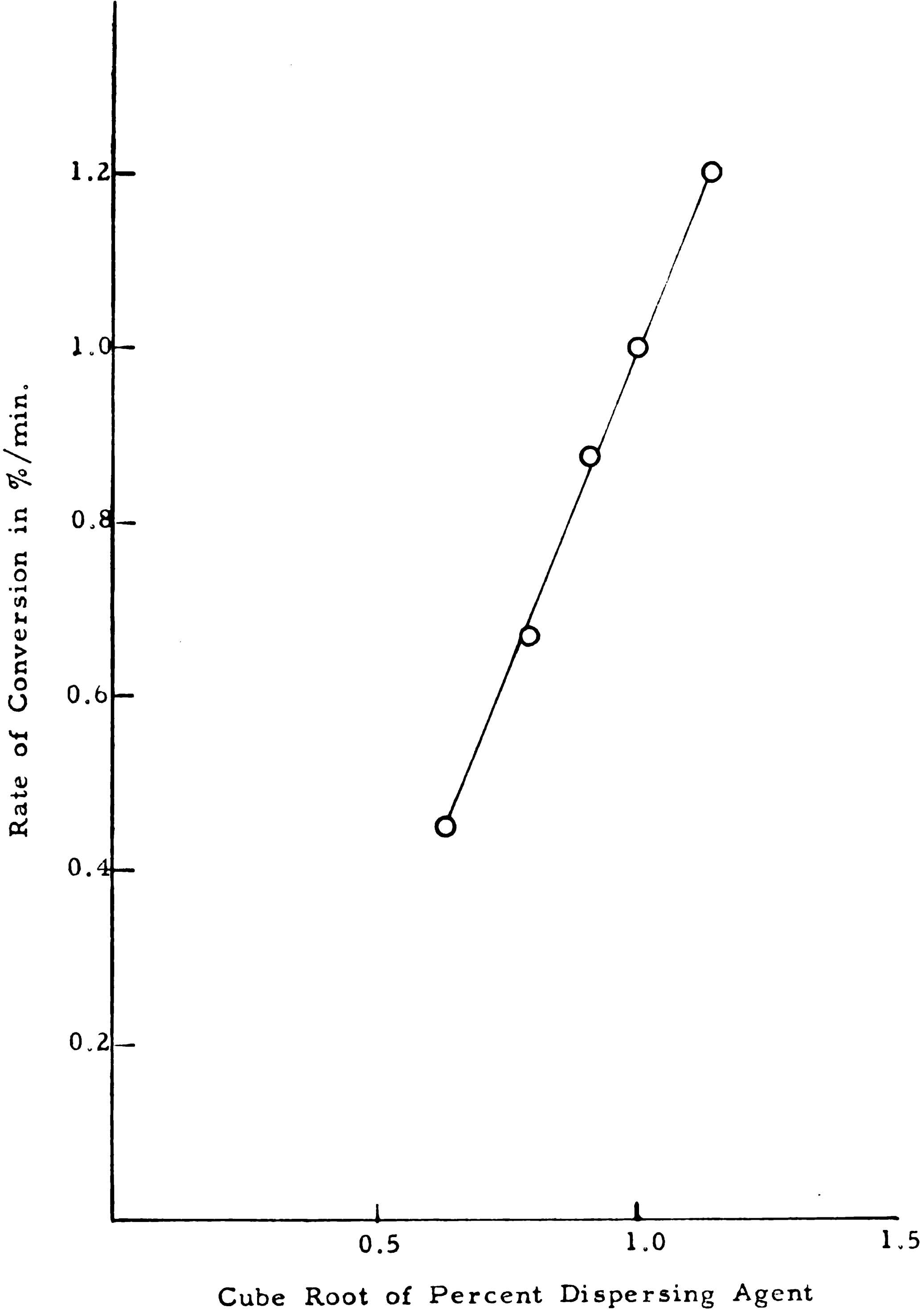

Percent Conversion
versus
Molecular Weight
Average Molecular Weight in Thousands
1300
1200
1100
1000
900
800
700
600
500
20
40
60
80
Percent Conversion
1.50%
0.75%
0.50%
1.00%
0.25%

GRAPH 17

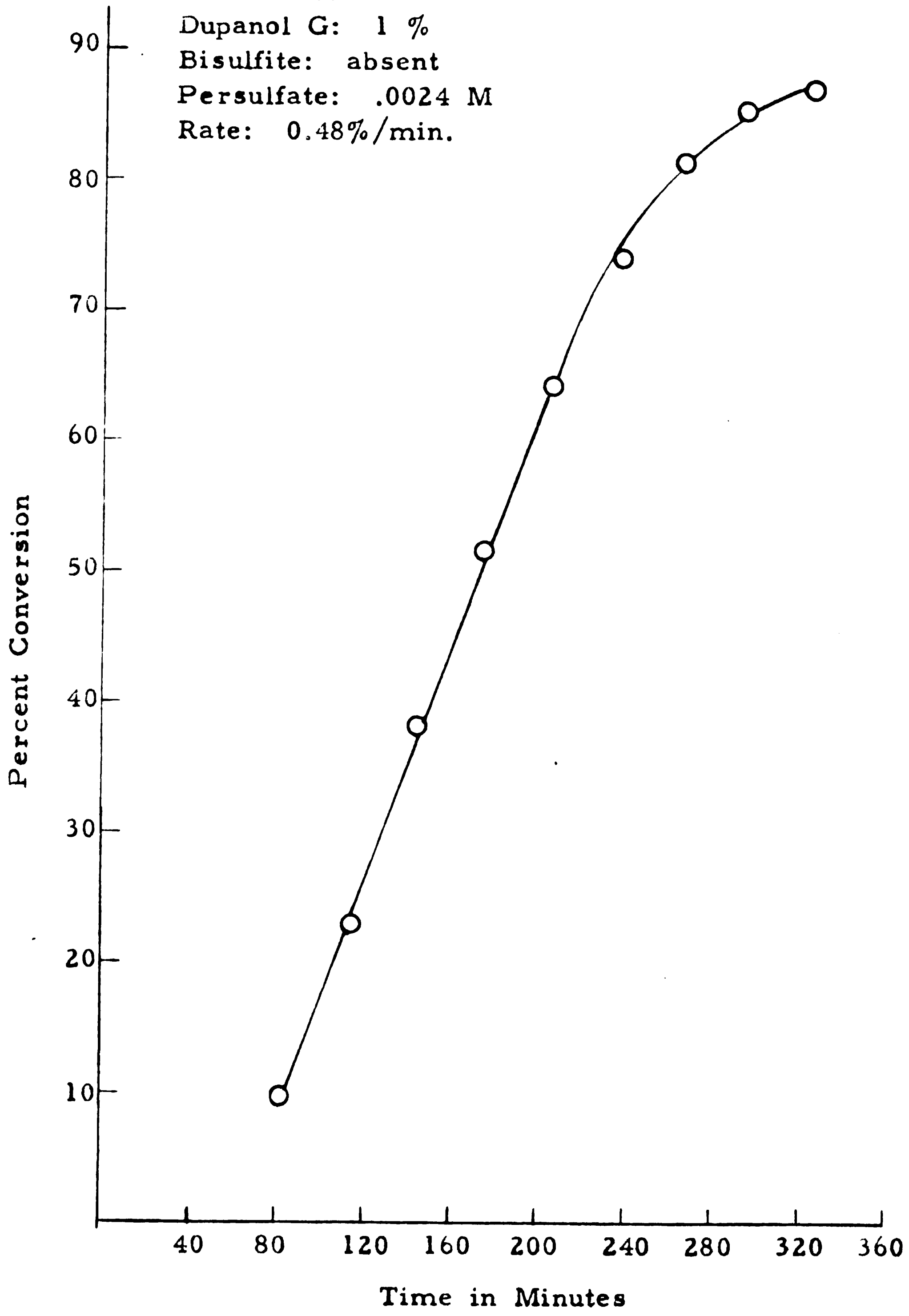

Conversion Rate
versus
Percent Dupanol G
Rate of Conversion in %/min.
1.2
1.0
0.8
0.6
0.4
0.2
0.25%
0.50%
0.75%
1.00%
1.50%
0.5
1.0
1.5
Percent Dispersing Agent

GRAPH 18

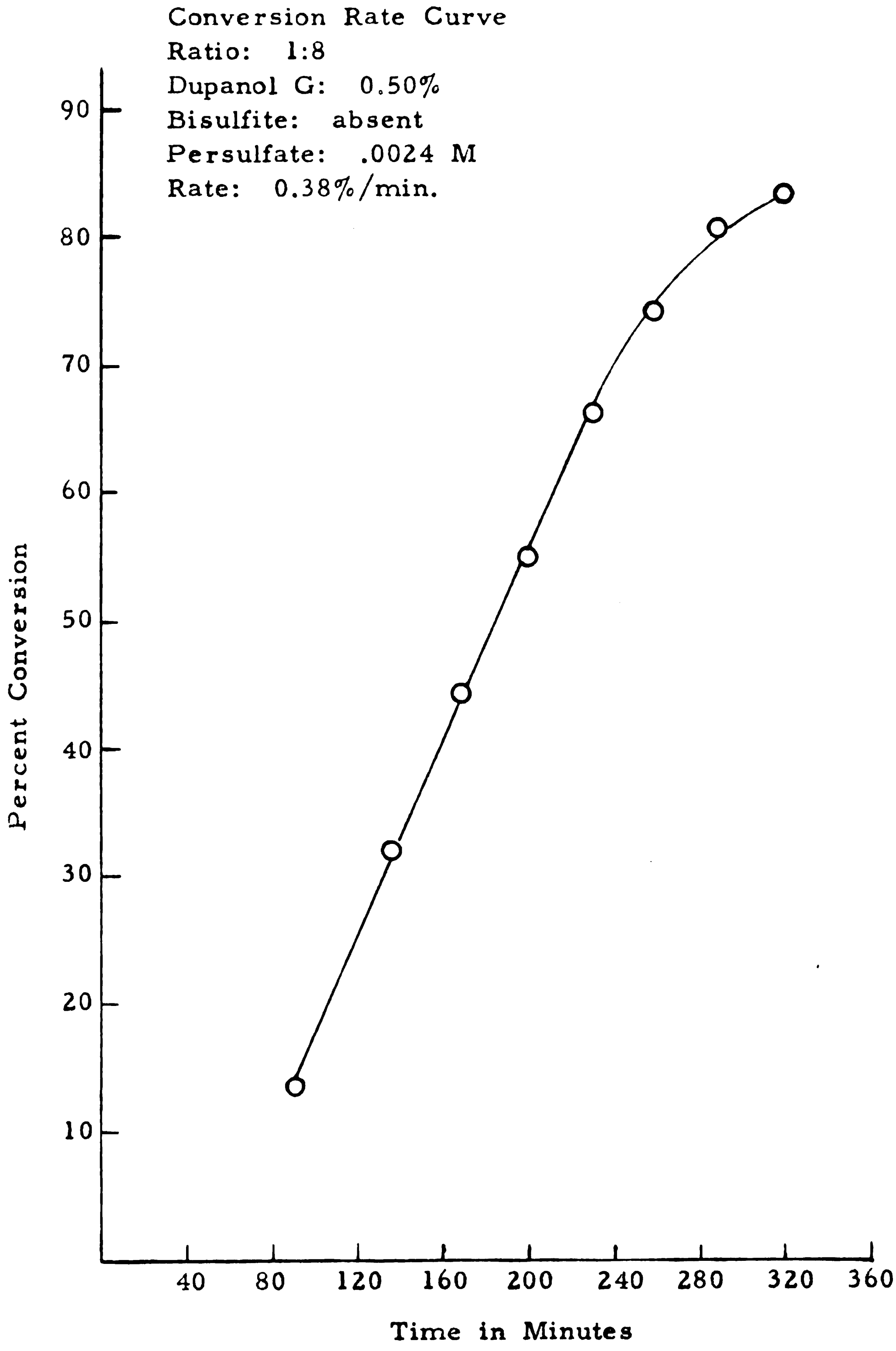
Linear plot for rate of conversion versus cube root of percent dispersing agent.



GRAPH 19

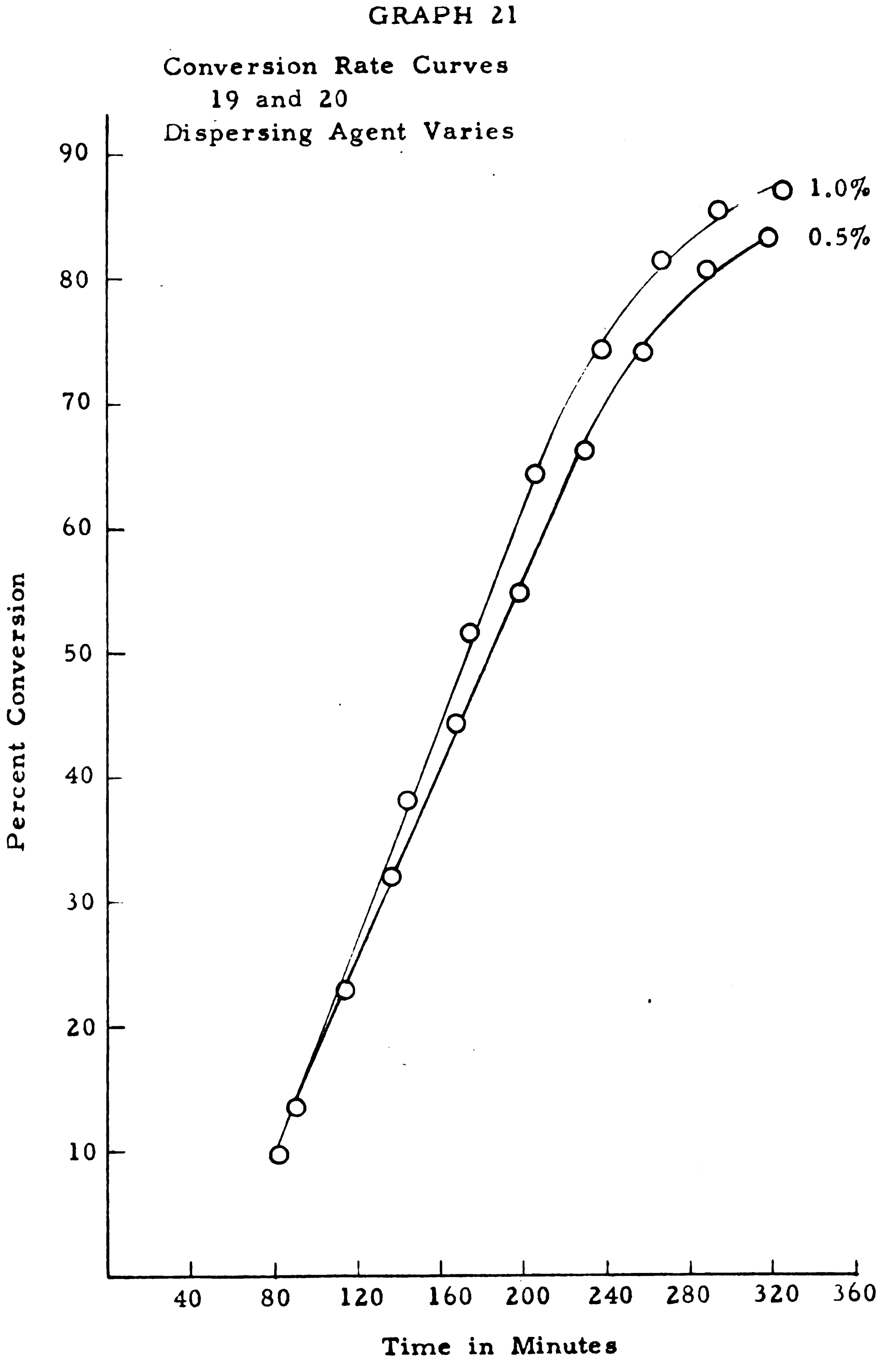

Conversion Rate Curve
Ratio: 1:8
Dupanol G: 1 %
Bisulfite: absent
Persulfate: .0024 M
Rate: 0.48%/min.
Percent Conversion
90
80
70
60
50
40
30
20
10
40
80
120
160
200
240
280
320
360
Time in Minutes

GRAPH 20



Conversion Rate Curve
Ratio: 1:8
Dupanol G: 0.50%
Bisulfite: absent
Persulfate: .0024 M
Rate: 0.38%/min.

GRAPH 21


Conversion Rate Curves
19 and 20
Dispersing Agent Varies
1.0%
0.5%
90
80
70
60
50
40
30
20
10
Percent Conversion
40
80
120
160
200
240
280
320
360
Time in Minutes

DISCUSSION

A series of reaction-rate curves were obtained for the redox catalyzed polymerization of styrene by plotting the percent solid polymer versus the time of reaction for each of the experiments. The straight-line portion of each curve represents the true rate of reaction (the propagation step). In all cases the straight-line portion is preceded by a curve representing the induction period. This period is caused by the inhibiting effect of oxygen and other impurities. After approximately 50-percent conversion, the curve falls off from the straight line and the termination step shows its effect. All polymerization rates used in this work were obtained by evaluating the slopes of the straight-line portion of these curves.

In this particular investigation it was found that as the concentration of the monomer was decreased, the rate of conversion was increased. The rates of conversion were from 0.45 to 1.64 percent per minute when the ratio, in grams, of styrene to water was from 1:4 to 1:14 (Graphs 1 to 6).

The emulsion polymerization can be divided into two stages: (1) the presence of monomer droplets, and (2) the disappearance of the monomer droplets (all the remaining monomer is dissolved in the polymer-monomer particle). At yields in the neighborhood of 40 to 60 percent conversion, the monomer phase disappears. This is represented on the time-conversion curve by the point where the reaction curve departs from the straight line. Whatever monomer is now present will be dissolved in the polymer-monomer particle and in the free water. The amount present in the water will be extremely small in the case where the monomer is styrene, and it will contribute very little to the rate of polymerization. Now the monomer-polymer particle may be treated as a system of styrene dissolved in a nonpolar solvent, which is the polymer. The polymer may be considered to act as a hydrocarbon of considerably lower molecular weight.

The oxidation-reduction polymerization of styrene in a hydrocarbon solvent may be approximated by a rate equation of 3/2 order with respect to the monomer concentration.[44] This rate equation for polymerisation of styrene in the polymer takes the form:

$$-dm/dt = k\ m^{3/2}$$

where

-dm/dt is the rate of removal of the monomer or the rate of formation of the polymer;

m is the concentration of the monomer in the hydrocarbon, or, in this case, the concentration of the styrene in the polymer.

When this equation is integrated between the limits m and m^o, the following expression is obtained:

$$m^{-1/2} - m^{o-1/2} = k/2\ (t - t^o)$$

where

m^o is the monomer concentration at the percent yield y^o where the monomer phase initially disappears;

m is the monomer concentration above which a separate monomer phase no longer exists. The polymer yield is y^o at this monomer concentration.

t is the effective time of polymerization (the over-all time minus that of the induction period). The induction period is the time obtained when the straight-line portion of the reaction rate curve is extended to the x axis.

t^o is the effective time to obtain the percent yield y^o.

The quantity y^o/Rp can be substituted for t^o where Rp is the true rate of conversion before attaining a yield of y^o. Now for that portion of reaction in which a separate monomer phase no longer exists, expression (1) reduces to:

$$2/k\ [y/(100-y)]^{1/2} - 2/k\ [y/(100-y)]^{1/2} + y^o/Rp = t$$

where y is the percent polymerization at the time t. Thus, according to the above treatment, a plot of $[y/(100-y)]^{1/2}$ should be linear with respect to time. When the data obtained in this investigation were plotted according to the above scheme, straight lines were obtained in every case (Graph 8). Therefore, it would seem likely that the kinetics treatment is approximately correct. If the above discussion were applied to the straight-line portion of the curves, then again the rate should be 3/2 order with respect to the monomer concentration. The half life, the effective time for 50-percent conversion, will be related to the monomer concentration by the following relationship:

$$t_{1/2} = K/m^{1/2}$$

A plot of $t_{1/2}$ versus $1/m^{1/2}$ will be a straight line. This plot resulted in a straight line except for the monomer-water ratio of 1:4 (Graph 9). This discrepancy was probably due to the lack of dispersing agent; that is, a separate monomer phase was present.

The monomer concentration will also affect the molecular weight of the products formed. This is represented in Graph 10. It will be noted that, as the monomer concentration in the basic polymerization recipe is increased, the molecular weight is also increased. The molecular weight is low for the ratio 1:8.

According to the generally accepted theory of polymerization proposed by Harkins,[25-27] the soap micelles are the main loci for the initial formation of latex particles. Therefore, after the micellar soap is gone, due to adsorption on the large number of latex particles, no new particles are formed, and the polymerization proceeds largely in the latex particles. If this mechanism is correct, the rate of polymerization will be affected by the amount of emulsifying agent present. Time-conversion curves were obtained for the redox polymerization of styrene, using varying amounts of dispersing agent (Graphs 11 to 15). It will be noted that, as the concentration of the Dupanol G is increased, the rate of conversion is also increased. This is to be expected, since with the increased dispersing agent, more latex particles will be formed before the micellar soap is depleted. Therefore, with more points of reaction, the monomer will be depleted at an increased rate. A straight line is obtained when the rate, as determined from the straight portion of the time-conversion curve, is plotted against the cube root of the percent dispersing agent (Graph 18). Therefore, for the particular system under consideration the kinetic equation is of the 1/3 order with respect to the dispersing agent. This equation takes the form of

$$-dm/dt = K(\%\ \text{dispersing agent})^{1/3} - 0.32K$$

where

-dm/dt is the rate of removal of monomer;

K is the constant which contains the effect of redox catalysis concentration, monomer concentration, and the specific rate constant.

Apart from the effect on the rate of conversion, the concentration of the dispersing agent has some effect on the molecular weight of the polymer formed. As the amount of soap is increased, the molecular weight is also increased (Graph 16). The one exception to this was when the 1-percent soap solution was used. However, if this run is neglected, the increase in molecular weight can be explained by the following: The monomer which diffuses into the polymer particle will find a condition of high polymer concentration. Therefore, the polymer growth within such a particle proceeds in a system of high viscosity. This condition favors a decrease in the termination rate but does not greatly affect the rate of propagation, with the result that the reaction rate and the molecular weight of the polymer are high. Since the termination reaction is dependent upon diffusion for the mutual collision of the active ends of the large molecules, it appears reasonable to assume that increased viscosity of the medium will hinder the diffusion of large polymer molecules. However, the propagation, which involves diffusion of small monomer molecules, will remain unaffected. With increased concentration of the emulsifying agent, many more polymer particles compete for the monomer in the water, and therefore there will be a higher polymer-monomer ratio within the particle; that is, a system of higher viscosity. If the polymer concentration in a latex particle remains at a higher level throughout most of the reaction, the molecular weight of the polymer will be higher than if it were formed in a latex particle where the polymer concentration is lower. If the assumption that with increasing number of polymer particles less monomer is available per particle is correct, then the concentration range within the particle will vary within narrow limits. Conditions of this type will favor an increased rate of conversions and molecular weight. In the absence of radium meta bisulfite, the rate of conversion is decreased when the dispersing agent is decreased (Graphs 19 and 20).

The polymer samples are centrifuged, filtered, washed with alcohol and water, and dried. During this procedure the amount of solid polymer will be decreased because some of the lower-molecular-weight products, such as the dimers and trimers, are soluble in the alcohol. Therefore, it was thought advisable to determine the amount of styrene in the polymer filtrate. The sum of the percent solid polymer and the percent styrene in the filtrate, should be equal to 100 percent. These percentages were based on the theoretical amount of styrene in the polymer sample. If the percentages do not add up to 100 percent, the difference, neglecting experimental error, would be due to the low-molecular-weight products in the filtrate.

Loring[5] attempted to determine the styrene in the filtrate by means of the mercuric-acetate method[43] for ethylenic linkages. This method is based upon the reaction of mercuric acetate with a double bond to liberate one molecule of acetic acid. This acid is then titrated with standard sodium hydroxide to a phenolphthalein end point. Loring found that the results were not reproducible, but he gave no reason for this. It was thought advisable to repeat this work. In order to accomplish this, several emulsion samples were prepared which contained some or all of the reagents of the polymerization recipe. The results obtained were acceptable for every case except when aluminum chloride is present. The average result for 34 titrations was 99.8 percent styrene, with a range of values of 101.3 to 98.0 percent. The low results can be attributed to the rapid formation of the dimers and trimers in the samples by a redox system. Also the range of values can be attributed to the difficulty in detecting the end point.

When the amount of styrene in an emulsion sample which contained aluminum chloride was determined, it was found that the amount of styrene found was always too great. This can be explained by the hydrolysis of the aluminum chloride to form hydrochloric acid. Therefore, the sample will contain acetic acid and hydrochloric acid, and the titration will give a high result.

CONCLUSIONS

1. The emulsion polymerization of styrene, using potassium persulfate-sodium meta bisulfite as the redox system, has been shown to be of the 3/2 order with respect to the monomer concentration.

2. It was shown that the rate of polymerization is increased when the amount of dispersing agent is increased. The rate of conversion is related to the percent dispersing agent by

$$-dm/dt = K(\% \text{ dispersing agent}) - 0.32K$$

3. The molecular weight of the polymer is a function of the dispersing agent. As the dispersing agent concentration is increased, the molecular weight increases. The maximum molecular weight is obtained at 40 to 60 percent conversion for the polymerization recipes studied.

4. It is possible to determine styrene in the aqueous phase of polymerization mixtures by the mercuric-acetate method if aluminum chloride is omitted.

REFERENCES

1. Morgan, M.S. Thesis, Michigan State College (1946).

2. Yang, *ibid*. (1947).

3. Hallenbeck, *ibid*. (1948).

4. Mihina, *ibid*. (1948).

5. Loring, *ibid*. (1948).

6. Densmore, U. S. Pat., 1732795, Sept. 13, 1927.

7. Luther and Heuck, German Pat., 558,890, Jan. 8, 1927.

8. British Pat., 355,573, Jan. 28, 1930.

9. British Pat., 366,944, Sept. 30, 1930.

10. German Pat., 570,986, Feb. 27, 1933.

11. German Pat., 573,586, April 3, 1933.

12. German Pat., 676,585, Feb. 28, 1936.

13. French Pat., 844,073, July 18, 1939.

14. German Pat., 727,955, Oct. 15, 1942.

15. U. S. Pat., 2,005,295, Jan. 18, 1935.

16. Mark and Raff, "High Polymers," Vol. III, Interscience, New York, 1941.

17. Fikentscher, Angew. Chem., *51*, 433 (1934).

18. Venograd, Abstracts of 108th. Meeting of the American Society, New York, Sept. 13, 1944.

19. Hohenstein and Mark, J. Polymer Sci., 1, 150 (1946).

20. Fryling and Harrington, Ind. Eng. Chem., 36, 114 (1944).

21. Hess, Ber., 70, 1800 (1937).

22. Hess, ibid., 70, 1808 (1937).

23. McBain, "Advances in Colloid Sci.," Vol. I, Interscience, New York, 1942, p. 124.

24. Harkins, J. Chem. Physics, 13, 381 (1945).

25. Harkins, ibid., 14, 47 (1946).

26. Harkins, ibid., 14, 215 (1946).

27. Harkins, J. Am. Chem. Soc., 68, 220 (1946).

28. Hohenstein, India Rubber World, 111, 173 (1944).

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

30. Bacon, Trans. Faraday Soc., 52, 140 (1946).

31. Morgan, ibid., 52, 169 (1946).

32. Baxendale, Evans, and Park, ibid., 52, 155 (1946).

33. Haber and Weiss, Proc. Roy. Soc. London, A147, 233 (1939).

34. King and Steinbeck, J. Am. Chem. Soc., 52, 4779 (1930).

35. Baxendale, Evans, and Kitham, Trans. Faraday Soc., 52, 688 (1946).

36. Kolthoff and Bovey, J. Polymer Sci., 5, 487 (1950).

37. Josefowitz and Mark, Polymer Bull., 1, 140 (1945).

38. Kolthoff, Meehan and Carr, J. Polymer Sci., 6, 73 (1951).

39. Staudinger, Chem. and Ind., 563 (1948).

40. Bovey and Kolthoff, J. Am. Chem. Soc., 69, 2143 (1947).

41. Kern, Die Makromolekulare Chemie, 1, 199 (1947); C. A., 42, 4234 (1948).

42. Yang and Guile, J. Polymer Sci., 6, 681 (1951).

43. Martin, Anal. Ed. 21, 921 (1949).

44. Schulz and Huseman, Z. Physik. Chem., B 39, 246 (1938).