SOME STUDIES ON THE EMULSION POLYMERIZATION OF STYRENE

Thesis for the Degree of M. S.
MICHIGAN STATE COLLEGE
Helen Deborah Morgan
1946

This is to certify that the

thesis entitled

Some Studies on the Emulsion
Polymerization of Styrene
presented by

Deborah Morgan

has been accepted towards fulfillment
of the requirements for

M. S. degree in Organic Chemistry

Ralph L Guile
Major professor

Date August 30, 1946

M-795

SOME STUDIES ON THE EMULSION POLYMERIZATION OF STYRENE

By

Helen Deborah Morgan

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

1946

[redacted]

ACKNOWLEDGEMENT

The author wishes to express her appreciation for the helpful counseling of Dr. R. L. Guile and Dr. R. C. Huston which they so willing gave during the course of this investigation.

TABLE OF CONTENTS

Historical

Experimental

INTRODUCTION:

In recent years the investigation of polymerization reactions has become of utmost importance from the commercial as well as the theoretical aspect. The products of these reactions have widespread usage in the preparation of synthetic rubber[1,2], shatterproof transparent windows, waterproof films for packaging food and machinery, and many other products. It is necessary in the preparation of these materials to have a uniform product. The properties of the final product derived from a polymer ~~is~~ are dependent primarily upon the molecular weight of the polymer, and the molecular weight varies greatly with the method of preparation. It is desirable to produce a polymer in an easily handled form which will have the proper molecular weight to give the desired properties in the finished product.

Attempts to accomplish this by use of mass and solution polymerizations led to products in the form of sticky cements or large hard lumps, difficult to handle.[3,4] It was found that through the use of emulsion polymerization products could be obtained in a latex form which could then be precipitated to form a fine powdered polymer which was easy to handle.[6,5] The use of an emulsion system, however, introduced more variables into the process. This made it more difficult to determine the effect each variable had upon the final product. The rate of formation of polystyrene in an emulsion system and the molecular weight of the product are dependent upon the following:[7,8,3] Type and amount of catalyst, type of atmosphere, type and amount of emulsifying agent, ratio of monomer to water, temperature and rate of stirring. To determine the effect of all of these variables would be a task too great for the scope of one investigation. This study was confined to the investigation of the effect of two different types of catalytic systems in two atmospheres, namely, nitrogen and air. All other conditions were kept as constant as was practically possible in laboratory procedure.

The analytical procedures for following the rate of reaction have been isolation of the polymer[9], titration of the monomer by bromine, change in volume, and most recently the change in rotation of polymerization of optically active monomers.[10,11] One method which has been widely applied is the running of duplicate reactions in sealed tubes, removing the tubes at various intervals and isolating the product. Many variations of the sealed tube technique have been reported. This method has not been too satisfactory as small differences between the tubes leads to inconsistent results.[7,8]

In this investigation the rates of polymerization were determined by withdrawing samples from a homogeneous polymerizing mixture at various time intervals and precipitating the samples immediately with alcohol. The precipitated polymer was centrifuged, washed thoroughly, dried and weighed. The molecular weights of the various polymeric samples were determined by viscosity methods using Staudingers rule.[12,13]

Some estimate of the molecular weight distribution within a sample may be made by titrating a solution of the sample with a nonsolvent and measuring the change in transmission of light from a constant light source through the solution by means of a photocell.[14] This procedure was carried out on numerous samples and showed observable differences in composition between them.

HISTORICAL:

Part I: Preparation of Polymers in Emulsion:

The field of emulsion polymerization is one of the newer fields of polymerization, yet it is widely applied. It is especially important in synthetic rubber manufacture.[1,5] It is a convenient method for obtaining an easily handled product which is in the form of a latex, in contrast to the sticky cements and solid lumps obtained as products from unemulsified polymerizations. It is more rapid and the rate of reaction is more easily controlled then in either bulk or solution polymerization.[3,15]

Mark and Raff[4] give a list of the ingredients necessary for an emulsion polymerization as: basic phase or emulsion medium, the main monomer, additional monomers, emulsifying agent or agents, stabilizer, regulator of surface tension, catalyst, and chain regulator. The more important of these ingredients are the monomer, catalyst, and emulsifying agents.

The material to be polymerized may consist of one or more monomers. The main monomer builds up the main part of the polymer and is usually 60-80% of the final polymer, the remainder being any additional monomer which is to be copolymerized with the main monomer. If only one monomer is to be used it makes up 30-35% of the emulsion system.[4]

The catalyst accelerates the formation of polymerization nuclei without affecting propagation. Most substances which have a catalytic effect also react toward the termination reaction, thus the addition of too much catalyst results in a low molecular weight product.[4] It has been shown by the experiments of Fryling and Harrington,[6] Fikentscher,[16] and also by Mark and others[6,8,17] that in systems catalysed by water soluble catalysts such as; inorganic peroxides, persulfates, percarbonates and perborates, the activation occurs in the aqueous phase rather than in the monomer phase or at the interface.

Fryling and Harrington[6] believe that with organic peroxides the initiation probably takes place in the organic phase and suggest that the locus of initiation of polymerization may provide an useful method of classification for various types of emulsion polymerizations.

The emulsifying agent is an important ingredient of the emulsion system for polymerization. It may in some cases catalyze the reaction as well as form the emulsion medium.[3] The polymerization velocity of some systems of low soap concentration is almost linearly proportional to the concentration of the soap. This catalytic effect appears to favor the theory of initiation of polymerization in the aqueous phase.[6] The more useful emulsifying agents for polymerizations are those that exhibit considerable solubilization of the monomer. Some of the more effective emulsifying agents are: aliphatic long chain carboxylic and sulfonic acids, sulfonated long chain alcohols and

and amines and aromatic alkyl sulfonic acids. The emulsifying agent consists of from 0.2-2% of the emulsion system.[4]

Part II: Characterization of the Product:

Viscosity Relationships:

There is a definite simple relationship between the specific viscosity of the solutions of different materials and their molecular weight. Experiments[18] show that with solutions of polymer homologs of the same concentration the specific viscosity varies greatly with the molecular weight, and that a few long molecules cause a much higher viscosity than numerous short ones. Using hemi colloidal and normal hydrocarbon products with known molecular weight 'M' Staudinger arrived at the following simple relationship:[12,18]

$$\frac{\eta_{sp}}{c} = k \cdot M$$

In this equation 'c' is the concentration of the solution in moles per liter of the basic unit of the polymer, 'k' is a characteristic constant for each series of polymer homologs, 'η_{sp}' is the specific viscosity which is the viscosity of the solution divided by the viscosity of the solvent minus one. This equation is valid only if applied to dilute solutions in which the individual chains, branched or not, are present as independent kinetic units and determine the character of the solution. Such solutions usually exhibit the property of normal viscosity, free from signs of elastic anomalies.[4] Every material which consists of threadlike molecules has in dilute solution a definite η_{sp}/c value, this value is dependent upon the same characteristics and essentially on the molecule length. This value is practically independent of the type of solvent used.[12]

In some cases the behavior of dilute solutions is also a help in distinguishing between straight and branched chains and is so used. The 'k' value, as calculated from the Staudinger viscosity equation, usually assumes its highest value for straight chains and decreases gradually as branching increases.[19] Polystyrene fractions of identical molecular weight prepared at low temperatures (20°C) show 'k' values around 1.5×10^{-4}, while corresponding molecular weight fractions for samples prepared at high temperatures (150°C) show values as low as 0.5×10^{-4}. Apparently this means that the capability of a long straight chain to produce viscosity in a solution is greater than that of a branched system.

There is a great deal of controversy as to the validity of the Staudinger equation and many correction factors have been applied to it.[20,21,22,23] Huggins[24] gives a comprehensive report on the development of several relationships between viscosity and molecular size, namely those of Einstein, Kuhn and Eisenschitz. It is generally recognized, however, that the Staudinger equation is a valuable and convenient tool for the comparison of different polymer samples under similar conditions of preparation.[13]

Precipitability Relationships:

The fact that polymers of different molecular weights have different solubilities has been used to fractionate polymer samples and thus determine the molecular weight distribution within the sample. This is a time consuming job and is impractical for a large number of samples.[25]

Adams and Powers,[14] using a method described by Mc Nally at the Gibson Island Conference 1942 for measuring the transmission ($-\log I/I_o$) of light through a solution of a synthetic resin during precipitation by a nonsolvent, developed a rapid method for estimating molecular weight distribution. A photronic cell was used to measure the transmission, which varied inversely with the amount of resin precipitated. They determined that the distribution of polymers in a resin could be estimated if the transmission during precipitation and the concentration of nonsolvent were known. To correlate titration data with polymer distribution a resin could be fractionated by partial solution and the molecular weight of each fraction determined. The amount of nonsolvent necessary to precipitate a known molecular weight fraction could then be determined.

Schulz[26] developed the following relationship:

$$\gamma^* = A + B/X$$

γ^* = concentration of nonsolvent
X = degree of polymerization
A and B are constants

which shows that the amount of nonsolvent required to precipitate a polymer is a measure of its degree of polymerization. By use of this Schulz equation the range in which a polymer fraction will be precipitated may be estimated. The amount in each fraction may be estimated by the differential of $-\log I/I_0$.

Adams and Powers[14] also found that this method would measure small differences in the composition of similar resin samples. That is samples that have the same average molecular weight but with different distribution of molecular weights within the individual samples would give different precipitability curves.

THEORETICAL:

The course of any polymerization reaction and the type of product formed is dependent upon three rate factors, nucleus formation, propagation and termination; which will be designated as k_1, k_2, and k_3 respectively.

Dostal and Mark[27] have formulated and solved the general differential equations for a chain-polymerization which occurs without breaking of the chain.

Nucleus formation is a relatively slow process which requires a definite amount of energy. In a homogeneous system there exist molecules of the monomer 'M' which can, by a certain process, form active nuclei. The formation of nuclei is characterized by a velocity constant k_1. Polymers may be formed by either mono or dimolecular reactions.[4] The relative amount of activation depends upon the number of monomers and the amount of heat added.

If the formation of nuclei is monomolecular the possibilities of activation are photochemical, catalytical, or purely thermal. The photochemical formation of nuclei, k_{11} is a measure both of the absorption of active radiation by the molecule 'M', and of the quantum yield of the irradiated light in respect to nucleus formation. Experimentally no monomolecular thermal activation has been definitely observed. However, in the case of large molecules, the interference of internal vibrations may accumulate sufficient energy to produce a polymerization nucleus.

It is thought that the bimolecular formation of nuclei is always the result of an activation due to collision between monomer molecules or monomer and catalyst molecule. These collisions are induced by thermal agitation and are represented by the constant k_{12}.[4]

Catalysts greatly influence the bimolecular nucleus formation and it is doubtful whether an uncatalysed thermal nucleus formation has been obtained. The types of substances which act as catalysts are metals (Na, K, Ni, Fe), halides (BF_3, $AlCl_3$, SiF_4, $ZnCl_2$), and oxygen compounds (H_2O_2, peroxides, persulfates, percarbonates, ozonides).

Burk[3] points out that in the presence of these substances the first step in nuclear formation is the addition of the catalyst to the monomer. Chalmers[28] suggests that the metal of the catalyst unites with the alpha carbon of vinyl derivatives to give a half-addition product such as $C_6H_5CHKCH_2$-. This could act as a starter for a polymerization chain reaction. The evolution of the polymeric molecule may be regarded as a chain reaction of the sort in which the units produced combine instead of maintaining separate existence.

If a polyreaction consists of nucleus formation, growth, and termination without branching of chains, the following relationships between time and concentration of monomer may be derived.[4]

For nuclear formation:

$$\frac{dc^*}{dt} = k_{11} \cdot c$$

$$\frac{dc^*}{dt} = k_{12} \cdot c^2$$

$$\frac{dc^*}{dt} = k_{13} \cdot c^3$$

'c' designates the molar concentration of the inactivated monomer 'H', 'c*' the concentration of the activated nuclei H_1, H_2, H_3. If it is assumed that the activation always proceeds in one definite manner, the possibility of the simultaneous occurrence of two activation reactions of different orders being excluded, the process of growth is represented by:

$$-\frac{dc}{dt} = k_{22} \cdot c^* \cdot c$$

This is a second order reaction between nuclei or chains c^* and the monomer c.

The growth process uses up monomer but the concentration of nuclei remains unaltered. This condition is accounted for by the fact that the activity of the nuclei, i.e. the velocity constant of the growth reaction, is independent of the length of the nuclei.

The chain-breaking reaction, which consumes nuclei, can be of the first or the second order. In the former case it can consist of the migration of a hydrogen atom along the chain to cause saturation of free valences. In the latter case, it can consist either of a reaction between a nucleus and a molecule of monomer or between two nuclei:

$$-\frac{dc^*}{dt} = k_{31}c^*$$

$$-\frac{dc^*}{dt} = k_{32}c^{*2}$$

$$-\frac{dc^*}{dt} = k_{311}c \cdot c^*$$

If there is a possibility of termination reactions of the first and second order occurring simultaneously, then the former would predominate at low concentrations and the latter at high concentrations.

These reactions describe the total conversion of monomer into polymer in the following way:

The starting reaction uses up monomer and produces active centers (or nuclei) in the system.

The propagation uses up more monomer, but leaves the number of the active centers unchanged because of the fact that the growth is of a type which regenerates the reactivity of the chain end after the addition of each new link.

The termination reaction destroys the active centers. It may or may not use up monomer for this purpose, but it does use up the nuclei.

The velocities of the different steps contribute to the rate of the total conversion. If $k_1 < k_3 \ll k_2$ each nucleus produced by the slow reaction k_1 will be caught immediately by the fast propagation process k_2 and extended into a long chain until this chain is stabilized by k_3. The rate of the conversion will depend only on k_1 and k_3; the distribution curve of the polymer will be determined by k_2 and k_3. The average molecular weight will remain practically constant during the reaction because the average life-time of the chains does not change; it is determined by the ratio of k_2 and k_3. This case has been observed in the thermal polymerisation of different vinyl derivatives. It has been called the radical chain mechanism.

If $k_1 > k_2 \gg k_3$ nuclei are rapidly produced by k_1, only slowly extended into chains by k_2 and slowly used up by k_3. Thus due to the ever growing number of active centers, no high polymeric material can be produced. It is possible by photochemical or catalytical action to produce very rapidly a certain number of active centers, and then to observe how they are gradually extended into chains by k_2, and how these chains are slowly converted into inactive molecules by k_3. The average life-time of the growing chains is long; the mean molecular weight of the material increases as the reaction proceeds; the distribution curve depends upon the interaction of k_2 and k_3 and the rate of total conversion is given by k_2. This type of polymerization follows the double bond chain mechanism.

The double bond mechanism is highly insensitive to all kinds of disturbances; it leads to extremely long chains, but the growth is very slow. The free radical mechanism is much faster, the high polymeric state is reached more rapidly, but the highly reactive intermediate products are very sensitive to external influences and chains are easily terminated.

Norrish and Brookman,[29] upon investigation of the catalysed thermal polymerization of styrene and methacrylate, drew the following conclusions. The molecular weight of the polymer obtained will be proportional to the time of the reaction, and inversely proportional to the concentration of the catalyst. This substantiates the earlier conclusions of Mark and Raff.[30]

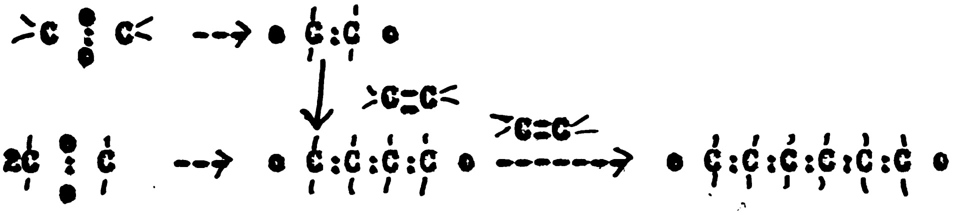
The compounds which undergo chain polymerization reactions are those which contain unsaturation. The types of unsaturation which may produce polymerization are $-C=C-$; $-C\equiv N$; $-C\equiv C-$; $=C=O$; and $=C=N$. The proximity of two or more of such groups is an important factor in determining the ease with which a compound will polymerize.

The analysis of the $-C=C-$ double bond according to quantum mechanics gives rise to the following concept: each valence dash of this linkage represents a pair of electrons in the sense of the Lewis valence theory. For each of these electron pairs there is a corresponding charge distribution which can be mathematically represented by suitable eigenfunctions.[4] The eigenfunctions of the two electron pairs can be characteristically distinguished. To make the distinction between the two clear, the terms; electrons or eigenfunctions of the first order (σ- functions), and electrons of the second order (π- functions) have been introduced.

The σ eigenfunction is that of the inner electrons, and closely corresponds to a normal single carbon to carbon bond. The π eigenfunction is that of the outer electrons, and is the decisive factor in the behavior of the double bond during polymerization.

The eigenfunctions of the second order may correspond to electrons of either anti-parallel or parallel spin. In the former case the double bond is closed and represents the fundamental state of ethylene; in the latter, the double bond is open and represents an excited state of ethylene. The double bond may be represented by the following symbol $>C \overset{\circ}{\underset{\circ}{:}} C<$ in which the electrons of the first order are designated by points and those of the second order by small circles.

For thermal polymerization in the absence of added catalytic agents, it has been suggested that the activation process might consist in the formation of a biradical[9] either unimolecular or bimolecular.



Mechanism I

For the benzoyl peroxide catalysis of the polymerizations of styrene, Schulz and Husemann[9] conclude that the propagation and termination reactions remain unaffected by the catalyst. The catalyst serves merely to increase the rate of the initiation reaction. Schulz suggests a mechanism for the initiation reation in the presence of peroxides involving the equilibrium formation of a complex between the catalyst and styrene, this then decomposes to give an activated styrene molecule. His data shows the rate to be proportional to the wquare root of the catalyst concentration. Price and Kell[10] postulate that the specific nature of this unimolecular chain-initiating reaction of peroxides is most probably their decomposition into free radicals. This suggestion offers an excellent explanation for many of the unusual catalytic effects of peroxides.

The free-radical mechanism of peroxide catalysis may be illustrated by the following simple equations, in which 'M' represents the monomer molecule, and the circle indicates the odd electron of the free radical:[11]

Initiation:

$$(ArCO_2) \longrightarrow 2\ ArCO_2 \circ$$

$$ArCO_2 \circ \longrightarrow CO_2 + Ar \circ$$

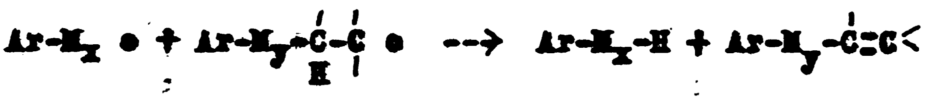
Propagation:

$$Ar \circ + M \longrightarrow Ar{-}M \circ$$

$$Ar{-}M \circ + M \longrightarrow Ar{-}M_2 \circ$$

$$Ar{-}M_x \circ + M \longrightarrow Ar{-}M_{x\ 1} \circ$$

Termination:



$$Ar{-}M_x \circ + Ar{-}M_y{-}\underset{H}{C}{-}C \circ \longrightarrow Ar{-}M_x{-}H + Ar{-}M_y{-}C{=}C<$$

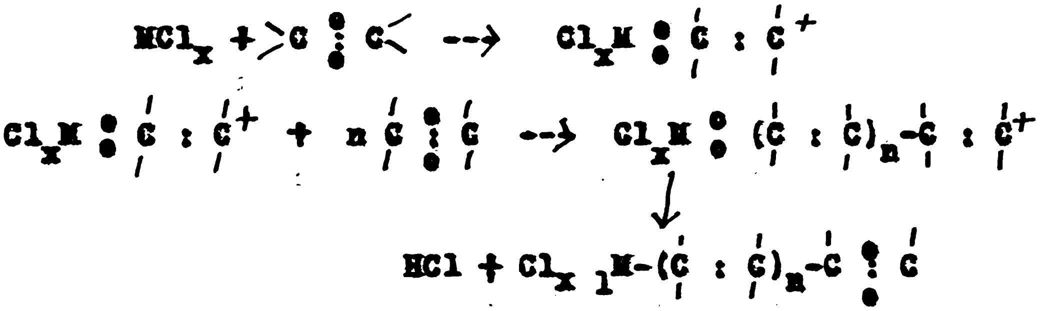
or

$$2\ Ar{-}M_x \circ \longrightarrow Ar{-}M_xM_x{-}Ar$$

Mechanism II

The nature of addition polymerization in the presence of such catalysts as boron fluoride, aluminum chloride, stannic chloride, or antimony pentachloride involve a different sort of mechanism.

Polymerization under these conditions may involve a polar chain mechanism, initiated by reaction of the catalyst with a monomer molecule. Hunter and Yohe[31] have suggested that the chain-initiating action of such catalysts depends upon their electrophilic nature, and consists in the acquisition by the catalyst of a pair of electrons from the double bond of the monomer.



$$MCl_x + {>}C \vdots C{<} \longrightarrow Cl_xM : C : C^+$$

$$Cl_xM : C : C^+ + n\,C \vdots C \longrightarrow Cl_xM : (C : C)_n - C : C^+$$

$$\downarrow$$

$$HCl + Cl_{x\ 1}M - (C : C)_n - C \vdots C$$

Mechanism III

This mechanism is analogous to the one suggested by Whitmore[32] for acid-catalyzed polymerization, in which the electron-deficient catalyst consists of a proton. Under conditions in which propagation is rapid compared with the loss of a proton from the active polymer, long-chain polymers will result; under conditions in which the reverse is true, dimers and trimers will be formed.

In general, there have been two essentially different viewpoints on the nature of the propagation reaction of polymer formation. That originally proposed by Staudinger[33] and supported by others[10] indicates a specific mechanism involving addition of an active free radical to the double bond of a monomer molecule generating a new free radical, which can in turn add again to another monomer molecule. (See mechanisms I and II) As a free radical chain reaction, polymerizations of this type should be subject to strong inhibition by small amounts of such substances as hydroquinone or diphenylamine. These substances are capable of preserving such monomers as methyl methacrylate, styrene, vinyl acetate, and dienes.

The second viewpoint regards the propagation reaction as an "energy chain," in which an "activated" monomer molecule adds to a normal molecule yielding an activated dimer which can add another monomer molecule the process continuing until the activation is nullified in some manner. (See mechanism III)

Individual active polymeric chains may be terminated into stable polymer molecules in several ways. The free radical may lose a hydrogen atom from the adjacent carbon atom to give a polymer molecule terminated by a double bond, or it may acquire a hydrogen atom from some other molecule in the reaction mixture to give a saturated polymer. Either of these processes, is merely a transfer of the active free radical, not its destruction, since one of the products in each case is a radical capable of generating a new active chain. Other ways by which termination may occur are; by the reaction of one chain end with another chain end, (see mechanism II) the reaction of a chain end with impurities, and the formation of polymembered rings in the molecule.[11]

The observation of Williams,[34] that the rate is directly dependent upon catalyst concentration, while the degree of polymerization is independent of catalyst concentration, would be accounted for if the termination reaction were the unimolecular loss of a proton. The polymer would be an organometallic compound, which might account for the difficulty encountered in freeing such polymers from the catalyst.

EXPERIMENTAL:

Part I: Preparation of the polymer:

Materials:

Aerosol OT

Polyvinyl alcohol (Dupont 52A-22)

Duponol G

Potassium persulfate

Sodium bisulfite

Ethyl alcohol 95%

Styrene (Eastman B.P. 33-35°/8mm)

The styrene was distilled from hydroquinone into a receiver containing hydroquinone collecting the fraction 143-144°C/743 mm. This fraction was then uninhibited by washing with cold 5% sodium hydroxide solution until the wash solution was colorless. The styrene was then washed until neutral with distilled water, dried with anhydrous sodium carbonate and stored in a refrigerator. The unhibited monomer was not allowed to stand for more than three days before use.

Equipment:

The polymerization reaction was carried out in a three necked round-bottom flask with 24/40 ground glass joints. The flask was equipped with a water sealed mechanical stirrer, a vacuum sampler, a thermometer and reflux condenser, which were attached to the same neck of the flask by means of an offset adapter. The flask was set in a constant temperature water bath which was kept at 40°C by means of a knife blade heater and a thermoregulator.

Procedure:

The basic ingredients of the emulsion system, which were kept constant, consisted of a water to monomer ratio of eight to one, and an emulsifying system consisting of 0.3% Aerosol OT, 0.3% polyvinyl alcohol and 0.3% Duponol C. This system was selected from many which were tried because it seemed to give the best emulsion throughout the reaction; that is, it kept both the monomer and polymer phases in an emulsified form. All percentages were based upon the water content of the system. The temperature was kept standard at 40°C and all reactions were stirred continuously during the polymerization reaction.

The emulsifying agents were added to 620 cc. of distilled water in the flask and the mixture stirred until a clear solution was obtained. Eighty cubic centimeters of styrene were then added and the mixture stirred until an emulsion was formed. The catalyst was dissolved in twenty cubic centimeters of distilled water and added immediately to the emulsion. Time of reaction was measured from the addition of the catalyst. Samples were withdrawn at various intervals during polymerization by means of a vacuum sampler. The samples were precipitated immediately by pouring them into 95% ethyl alcohol. They were then centrifuged, washed at least six times with water and six times with alcohol, filtered by suction and dried. The precipitation was carried out directly in graduated fifty cubic centimeter centrifuge tubes. The tubes were filled to thirty-five cubic centimeters with alcohol and fifteen cubic centimeters of the emulsion poured into them. Each sample taken has a volume of sixty cubic centimeters so four tubes were used for each sample. After the samples were dried they were then weighed and the percent polymerization calculated. Total polymerization would give a yield of six grams of polymer in sixty cubic centimeters of emulsion.

The variations in conditions used were: 1% potassium persulfate (0.023 moles/640 cc water) in an atmosphere of air, 1% potassium persulfate in an atmosphere of nitrogen, 1% potassium persulfate with an equal molar quantity of sodium bisulfite (0.023 moles) in an atmosphere of air, and 1% potassium persulfate with and equal molar quantity of sodium bisulfite in an atmosphere of nitrogen. A few runs were made using smaller amounts of the catalytic systems and were recorded in Table I.

In the use of the nitrogen atmosphere the nitrogen was bubbled through an aqueous solution of pyrogallic acid to remove all traces of oxygen and then into the reaction mixture through the sampling tube. The nitrogen was bubbled through the reaction mixture before addition of the monomer for approximately fifteen minutes and continuously during the reaction period.

Part II: Characterization of the Polymer:

The dried samples were ground in a mortar and sifted through a fine screen in order to make them go into solution more readily. Solutions of the polymer samples were made up in volumetric flasks at a concenrration of 0.02 molar (0.24%) in toluene which had been redistilled and collected at 108-109°C at 743 mm. The viscosities were determined at 20°C by means of a Cannon-Fenske-Ostwald viscosity pipette and the molecular weights were calculated according to the Staudinger equation:

$$M = \frac{\eta_{sp}}{kc}$$

In which

M = molecular weight

η_{sp} = specific viscosity

c = concentration in moles per liter of the basic unit of the polymer.

k = constant = 1.8×10^{-4}

The specific viscosity was determined by dividing the time of flow of the solution by the time of flow of the pure solvent and substracting one.

The molecular weights determined are tabulated in Table I.

An example of data and calculation of molecular weight of a typical sample.

Sample: Run# V - 50.8% polymerization.

Time in Sec.	
Solvent	Solution
32.8	77.6
32.6	77.4
32.7	77.5
32.8	77.5
32.8	77.5
32.8	77.5
	77.5

Relative Viscosity = 2.3628

Specific Viscosity = 1.3628

Concentration = 0.02 M

k = 1.8×10^{-4}

$$M = \frac{\eta_{sp}}{kc} = \frac{1.3628}{1.8 \times 10^{-4} \times 0.02}$$

M = 378,500

Table I

Run #	Catalyst	Time Hr.	% Polymer.	Molecular Weight (Viscosity)
I	$K_2S_2O_8$ 1%	1	10.0	
	in	5	27.3	35,500
	Air	17	62.6	37,200
		20	65.3	
II	$K_2S_2O_8$ 1%	2	8.0	
	in	3	9.6	
	Air	9 1/4	27.1	23,600
		23	57.6	27,000
		26	76.3	33,800
III	$K_2S_2O_8$ .5%	6 3/4	3.0	
	in	10	8.8	
	Air	23 1/4	51.0	28,700
		28	64.1	32,116
		33 3/4	90.0	
IV	$K_2S_2O_8$ 1%	2 1/6	64.0	398,000
	in	2 3/4	65.5	345,500
	Nitrogen	4	87.0	261,300
		7	98.0	182,000
V	$K_2S_2O_8$ 1%	3/4	17.5	160,000
	in	1 1/2	50.8	378,500
	Nitrogen	2 1/4	67.5	331,900
		Some small lumps formed in the emulsion		
		6	90.0	159,100

Table I (Con't)

Run #	Catalyst	Time Hr.	% Polymer.	Molecular Weight (Viscosity)
VI	$K_2S_2O_8$ .5%	1	6.1	
	in	1 1/2	19.0	
	Nitrogen	2	25.6	165,000
		3	43.3	
		4	63.3	229,500
		5	86.0	
		5 1/2	96.6	182,000
VII	$K_2S_2O_8$ 1%	1	20.0	15,200
	with	2	25.0	,
	$NaHSO_3$ .5%	3	41.3	17,000
	in	5	56.1	18,600
	Air	6	58.3	
		7	83.3	55,200
VIII	$K_2S_2O_8$ 1%	1 1/6	11.7	
	with	2 1/2	19.7	
	$NaHSO_3$ .5%	4	39.7	22,700
	in	5 1/2	51.7	25,400
	Air	7	93.5	
		9	94.3	35,500
IX	$K_2S_2O_8$ .5%	5/6	23.0	64,300
	with $NaHSO_3$ .25%	1 1/2	41.3	71,100
	in Air	Lumps formed and the reaction did not remain in an emulsion.		

Table I (Con't)

Run #	Catalyst	Time Hr.	% Polymer.	Molecular Weight (Viscosity)
XII	$K_2S_2O_8$ .125% with $NaHSO_3$ .0625% in Air	1	5.0	
		2		70,000
		Lumps formed and the reaction did not remain in an emulsion.		
XIII	$K_2S_2O_8$ .0625% with $NaHSO_3$ .0312% in Air	1	0	
		2	0	
		4	91.6	131,900
X	$K_2S_2O_8$ 1% with $NaHSO_3$ .5% in Nitrogen	1/2	10.1	
		1 1/2	21.3	24,600
		4 3/4	81.5	30,400
		6 1/4	96.7	
		7 1/4	97.5	30,400
XI	$K_2S_2O_8$ 1% with $NaHSO_3$ .5% in Nitrogen	5/6	14.5	
		2 1/3	27.1	
		3 1/3	43.0	47,400
		4 1/3	84.5	51,400
		5 1/3	96.3	45,700

One run made with 1% sodium bisulfite resulted in only 12% polymerization in 30 hours. The product was sticky and very hard to filter and wash as it adhered to the filter paper.

One run made using 1% $K_2S_2O_8$ in an atmosphere of oxygen gave very little polymer in 20 hours. The product was sticky and very difficult to handle.

Precipitability measurements were made on the various samples following a procedure described by Adams and Powers.[14] The apparatus used consisted of a light source, a specially constructed cell, a photocell, and a galvanometer.

The cell was constructed of stainless steel and measured seventeen centimeters in height, and was approximately four centimeters square. There were windows on two opposite sides which were held in place by special brass fittings, one of which fitted the lens of the light source and the other fitted the photocell. The other two sides and the bottom were enclosed with a water jacket through which water was circulated from a constant temperature bath which was kept at 20°C. When in use the light passed through the solution in the cell and struck the photocell on the opposite side. The photocell was connected to a galvanometer by means of a variable resistance so that the deflection of the galvanometer could be adjusted to stay on the scale.

Through the top of the cell was inserted a mechanical stirrer which was adjusted so that it gave thorough mixing but caused no bubbling in the solution; a thermometer, and the tip of a siphon burette which contained the nonsolvent.

Samples of the same solutions which were made up for the determination of viscosity were used. One hundred sixty cubic centimeters of the solution were placed in the cell, the light passed through and the galvanometer adjusted to a deflection of approximately one hundred by means of the variable resistance. Upon the addition of nonsolvent, 95% ethyl alcohol, an immediate turbidity occured which was due to the mixing of the alcohol and toluene alone and not due to the precipitation of any of the polymer. After approximately twenty cubic centimeters of alcohol were added the solution again became clear and the galvanometer was readjusted to approximately one hundred and the I_o reading taken. The solution was then titrated with the nonsolvent and deflections of the galvanometer recorded, which were the I readings. The factor $-\log I/I_o$ was then calculated and plotted against the percent nonsolvent, this resulted in the precipitability curve of the sample.

Tangents were then drawn to these curves at numerous points and these tangents plotted against percent nonsolvent. The tangent curves formed a peak at that percent nonsolvent which represented the greatest increase in extinction per unit of nonsolvent added, that is where the greatest amount of polymer precipitated with the addition of one unit of nonsolvent. Different molecular weights would precipitate at different concentrations of nonsolvent therefore, these peaks indicate the point at which the largest molecular weight fraction of the sample precipitated.

An example of the data obtained from a typical precipitation of a toluene solution of the polymer with 95% ethyl alcohol.

Sample: Run # VIII - 51.7% polymerization

Solution concentration: 0.02M

C_2H_5OH cc.	Deflection	- log I/I_o	% C_2H_5OH
49	95 = I_o		30.62
50	94	.00459	31.25
52	92	.01393	32.50
54	88	.03324	33.75
56	79	.08009	35.00
58	71	.12646	36.25
60	66	.15817	37.50
62	60	.19957	38.75
64	55	.23736	40.00
66	50	.27875	41.25
68	47	.30562	42.50
70	45	.32451	43.75
73	41	.36494	45.62
76	38	.39794	47.50
79	35	.43365	49.37
82	32	.47257	51.25
86	29	.51532	53.75
90	26	.56275	56.25
95	24	.59751	59.57
100	22	.63530	62.50
110	22	.63530	68.75
120	22	.63530	75.00

FIG I

RATE OF POLYMERIZATION

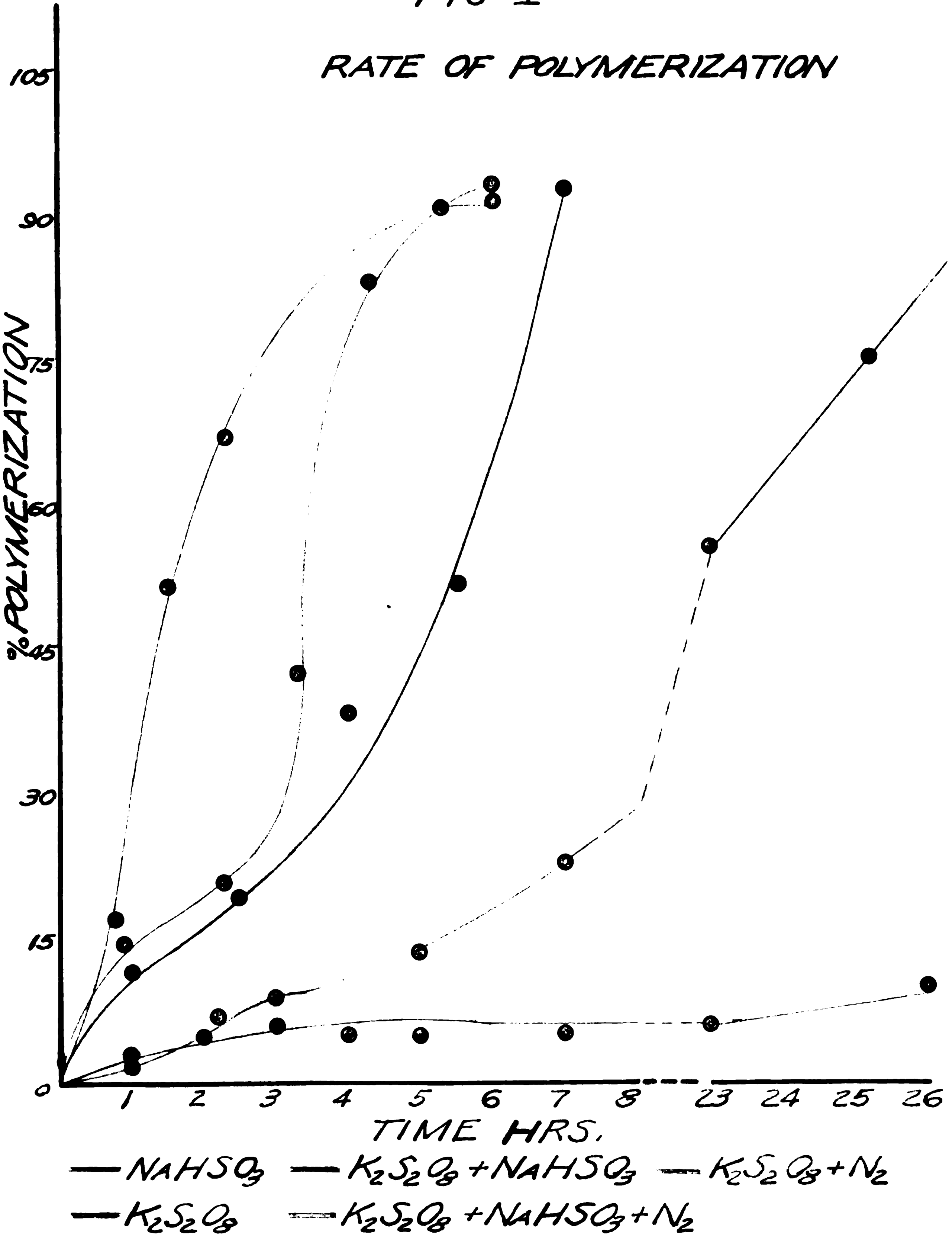


FIG I

RATE OF POLYMERIZATION

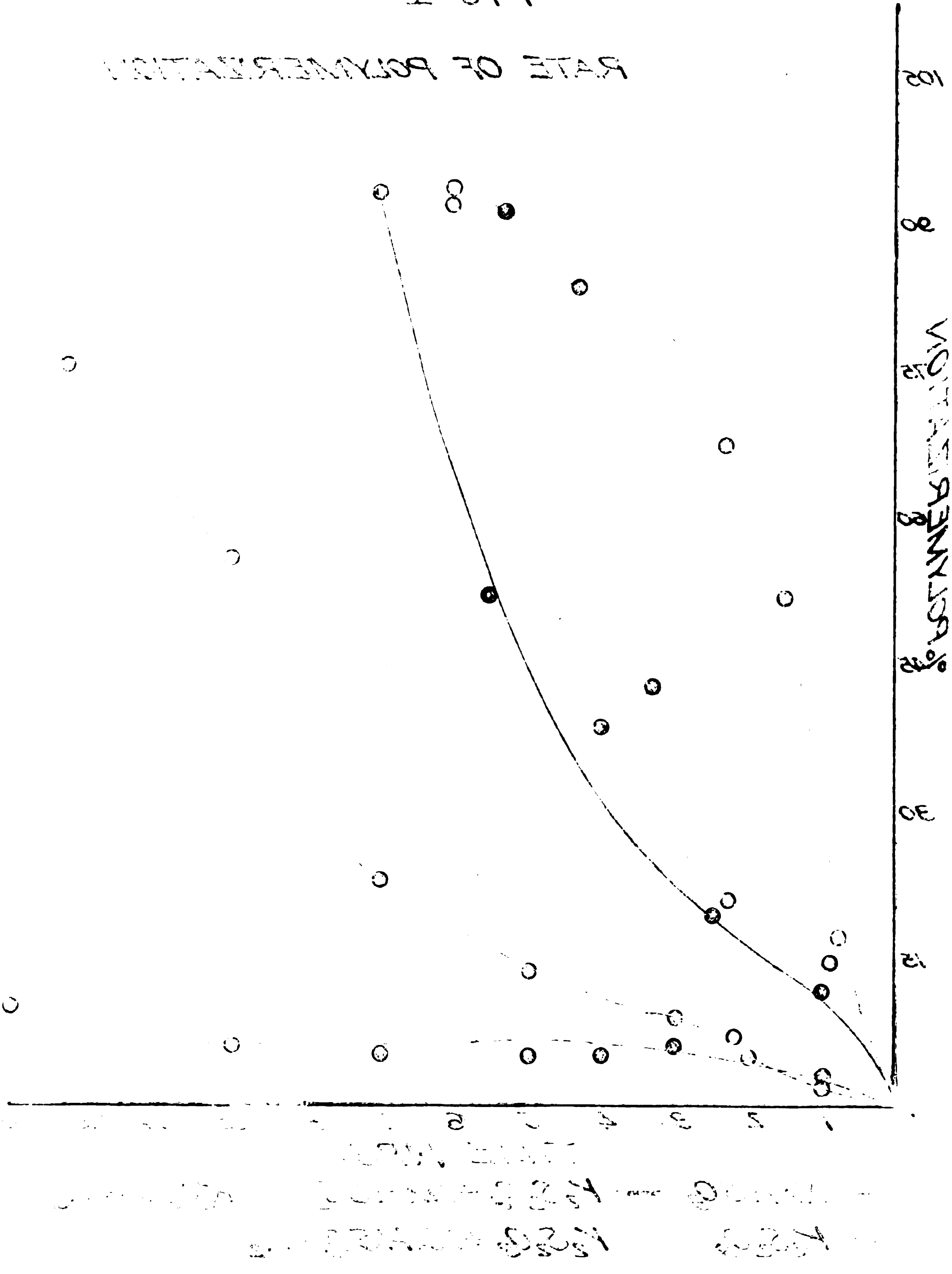


FIG II

MOLECULAR DISTRIBUTION

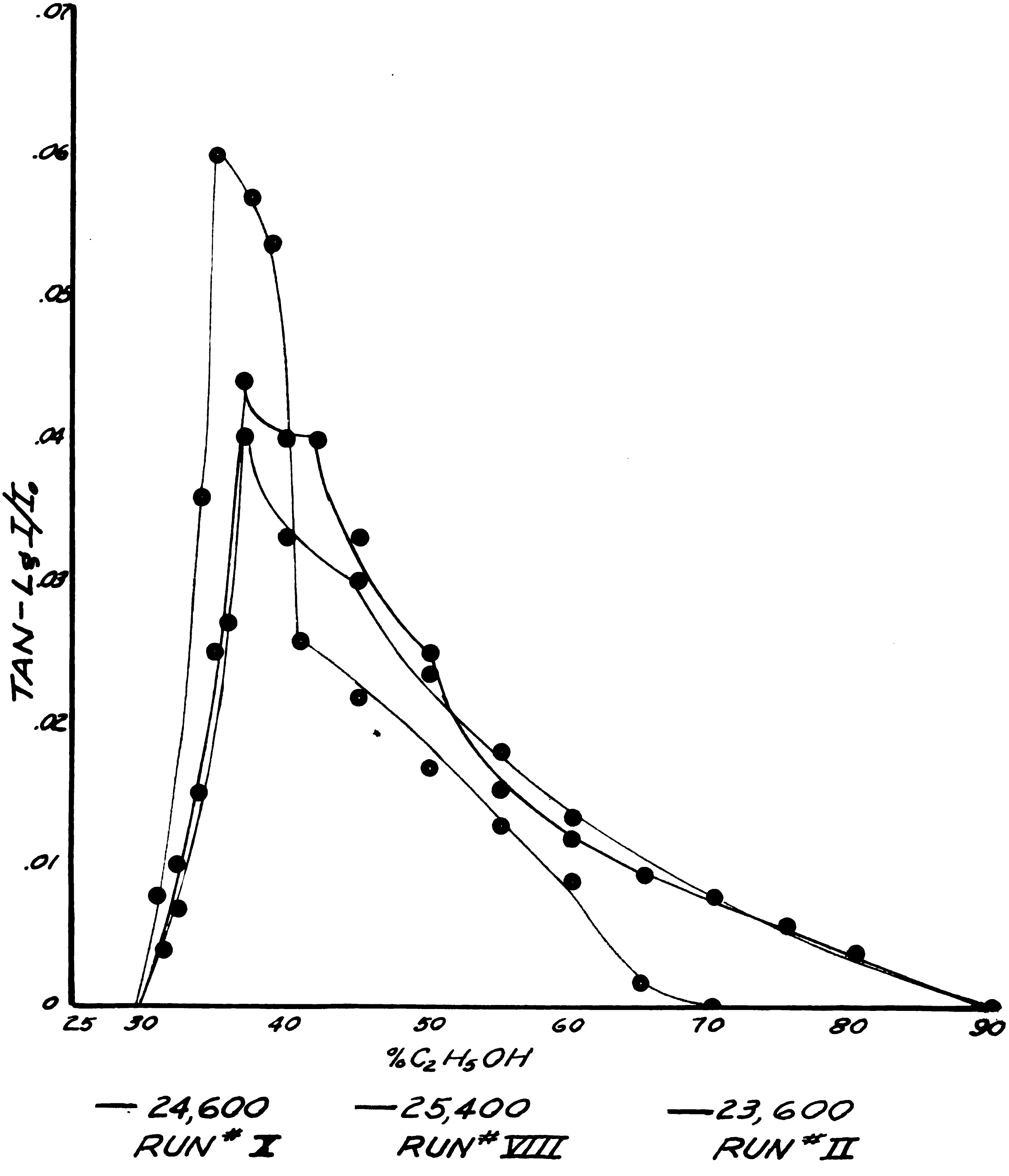


FIG II

MOLECULAR DISTRIBUTION

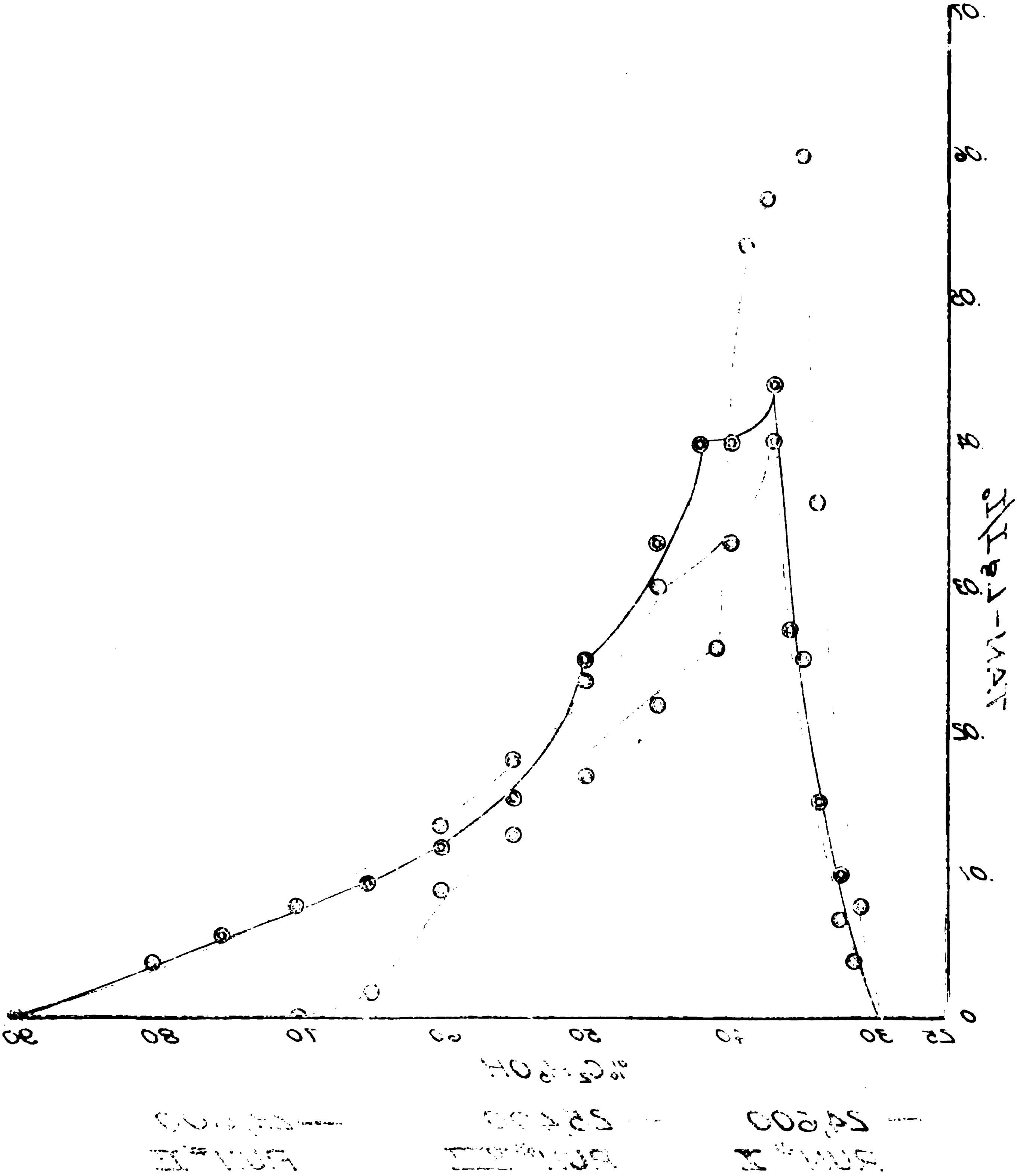
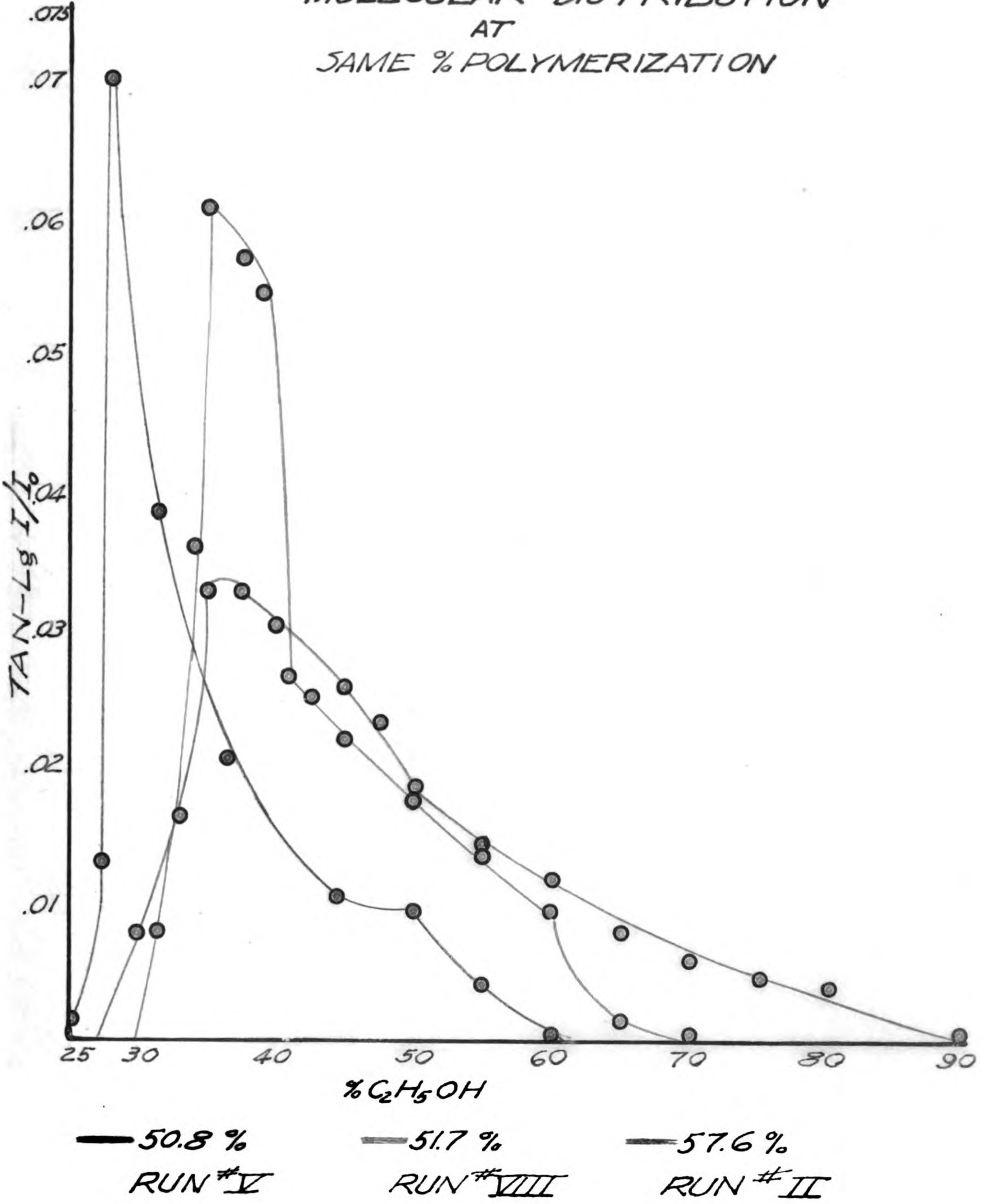


FIG. III



MOLECULAR DISTRIBUTION
AT
SAME % POLYMERIZATION

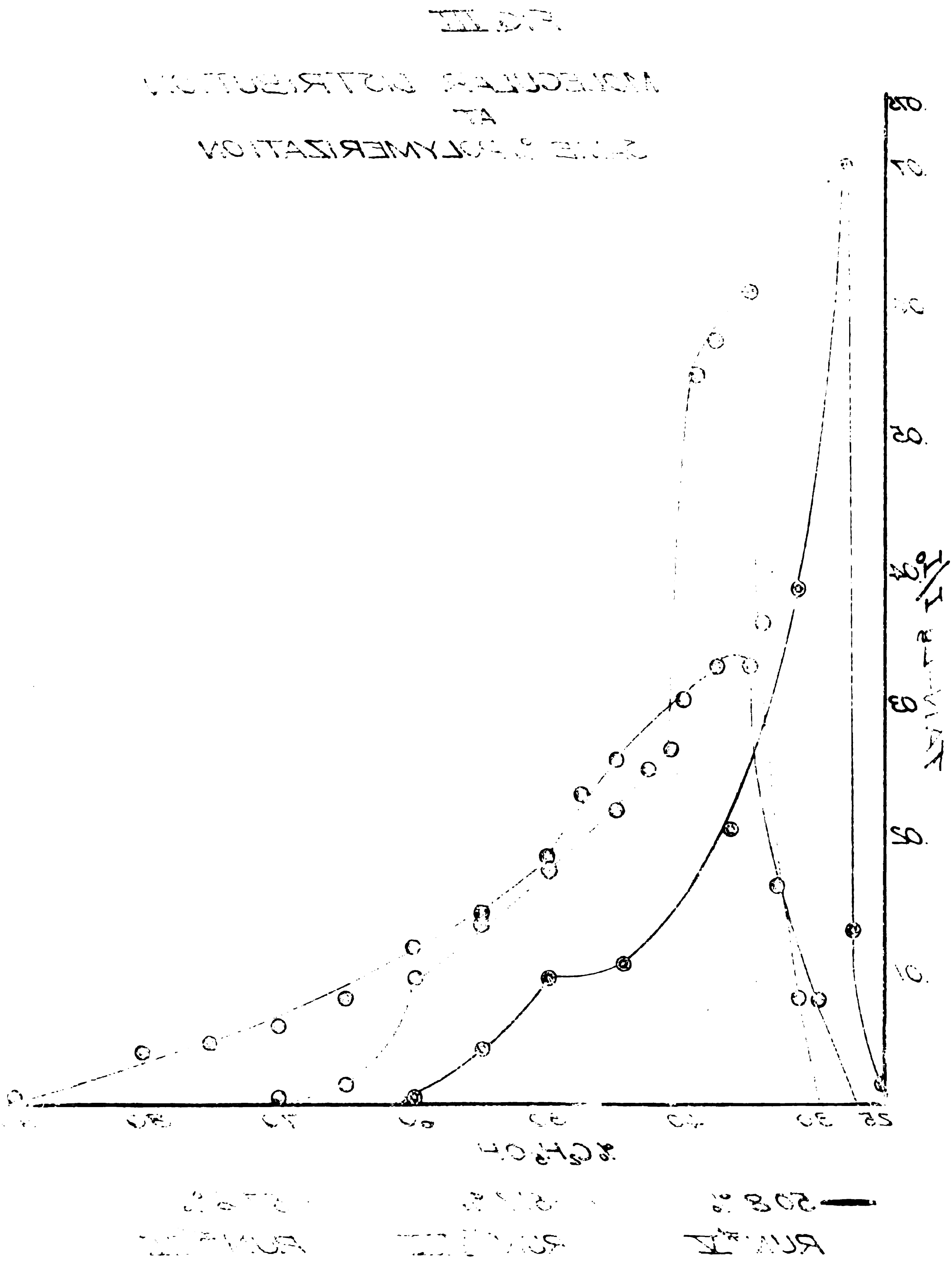
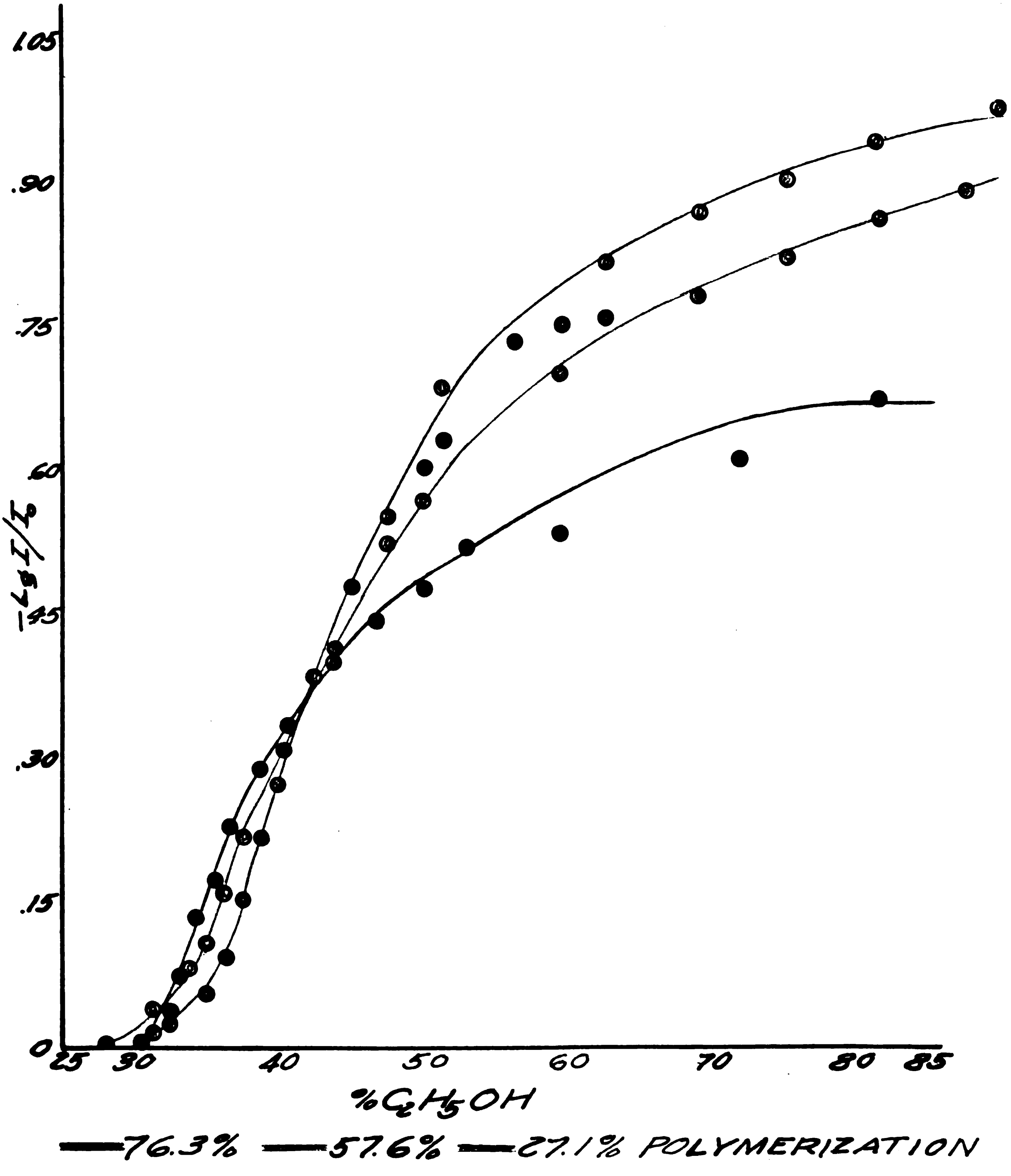


FIG. IV

PRECIPITABILITY ON RUN #II



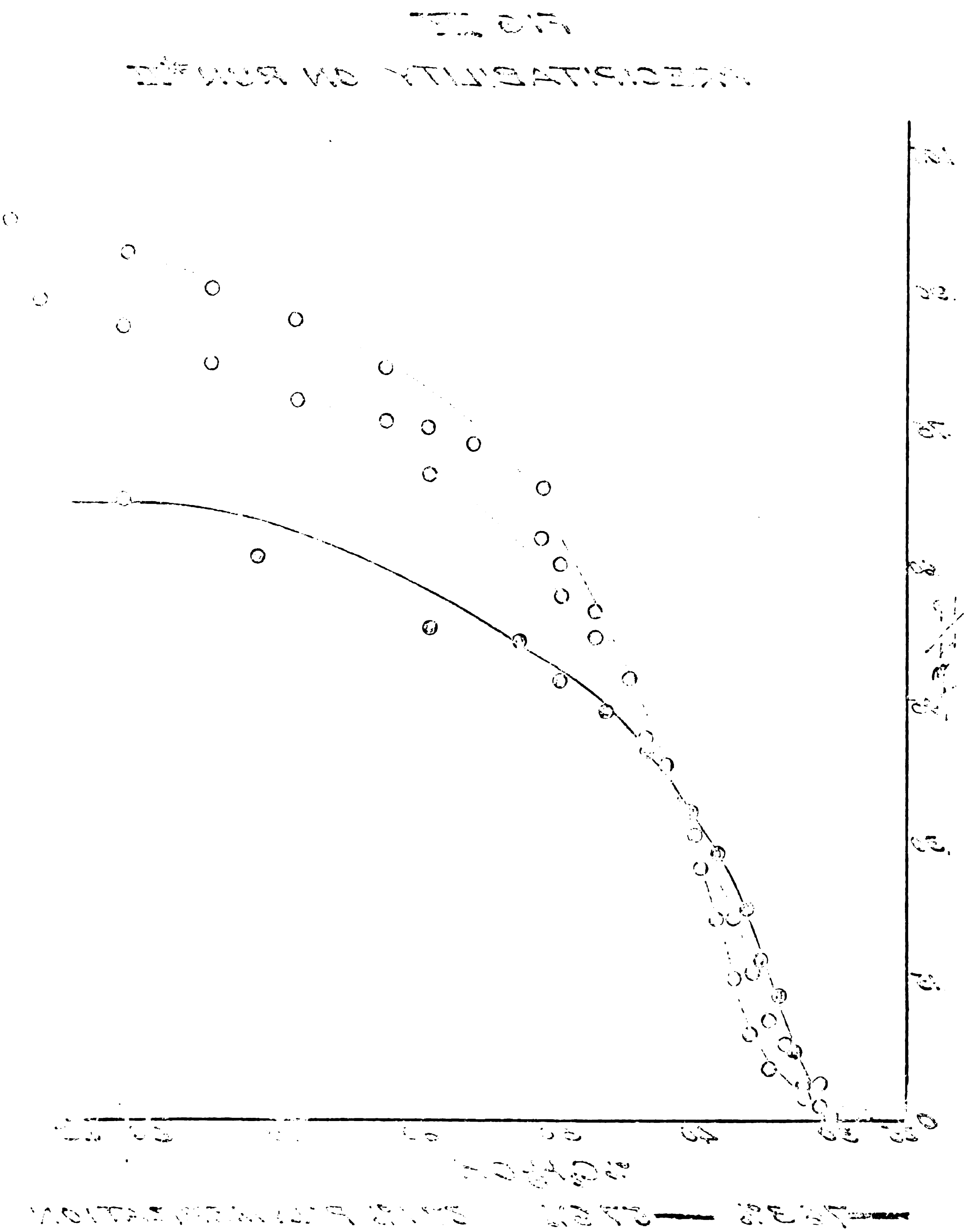


FIG. V

MOLECULAR DISTRIBUTION
RUN # II

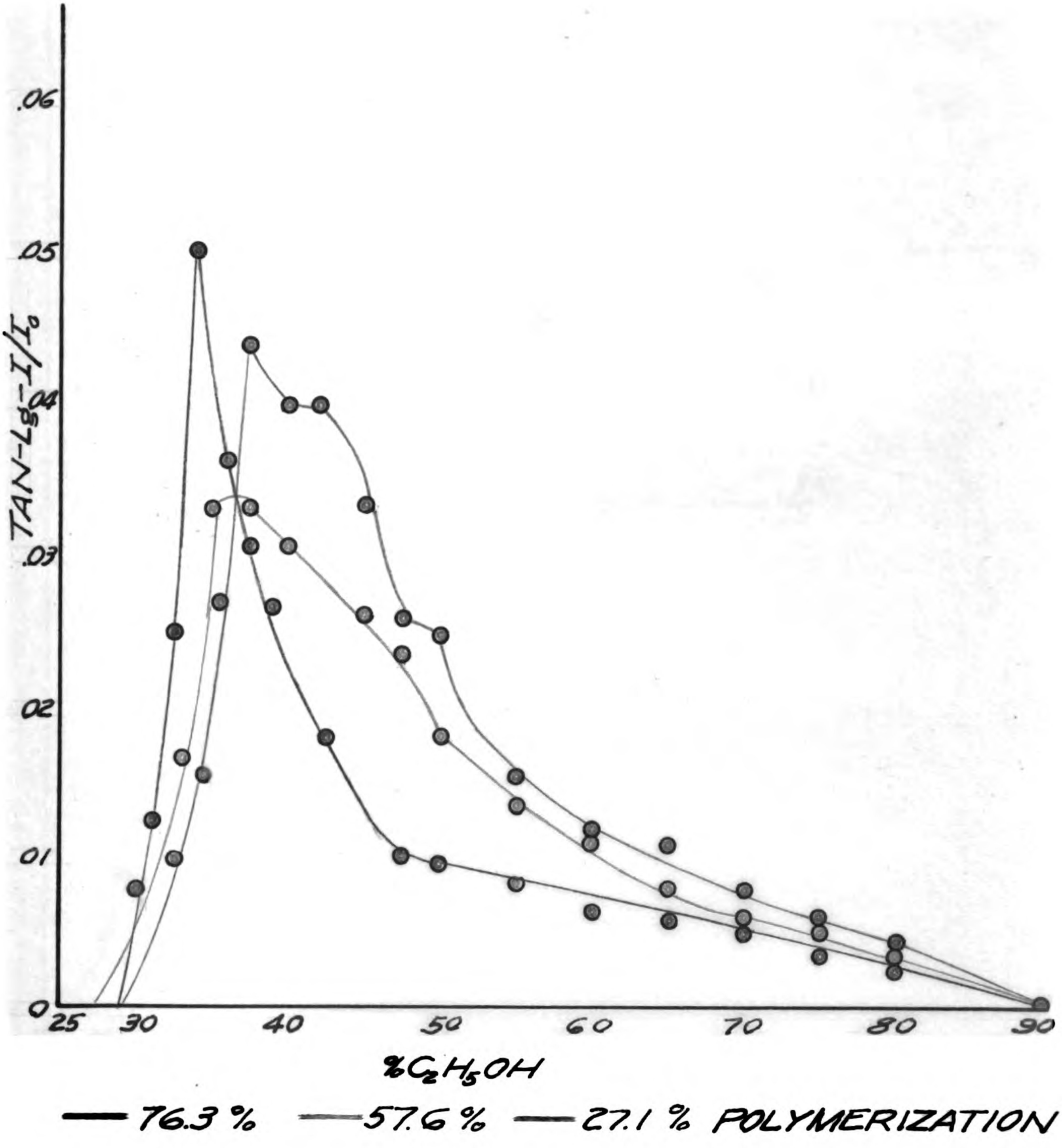


FIG. II

MOLECULAR DISTRIBUTION

RUN #II

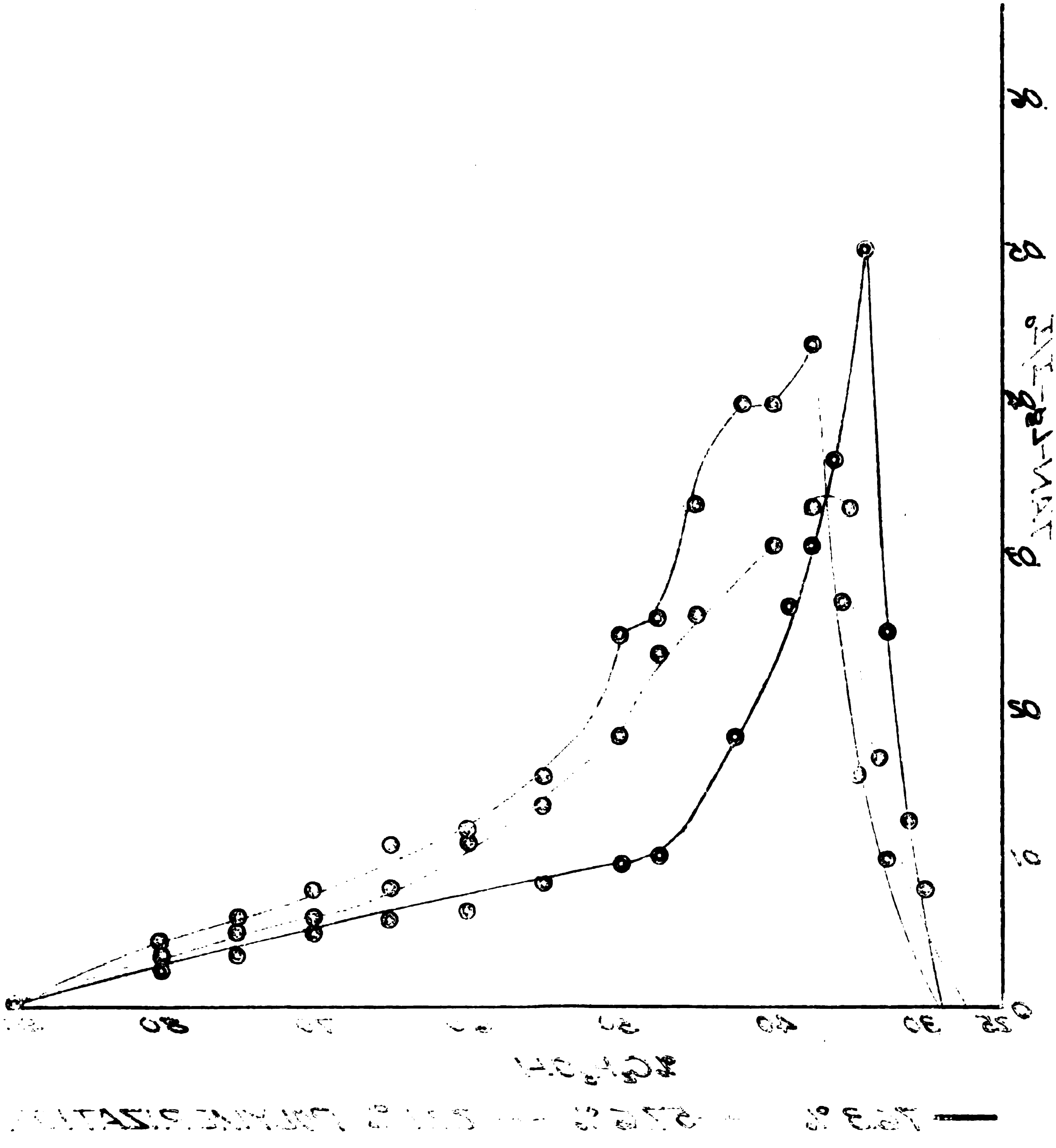


FIG. VI

PRECIPITABILITY ON RUN # IV

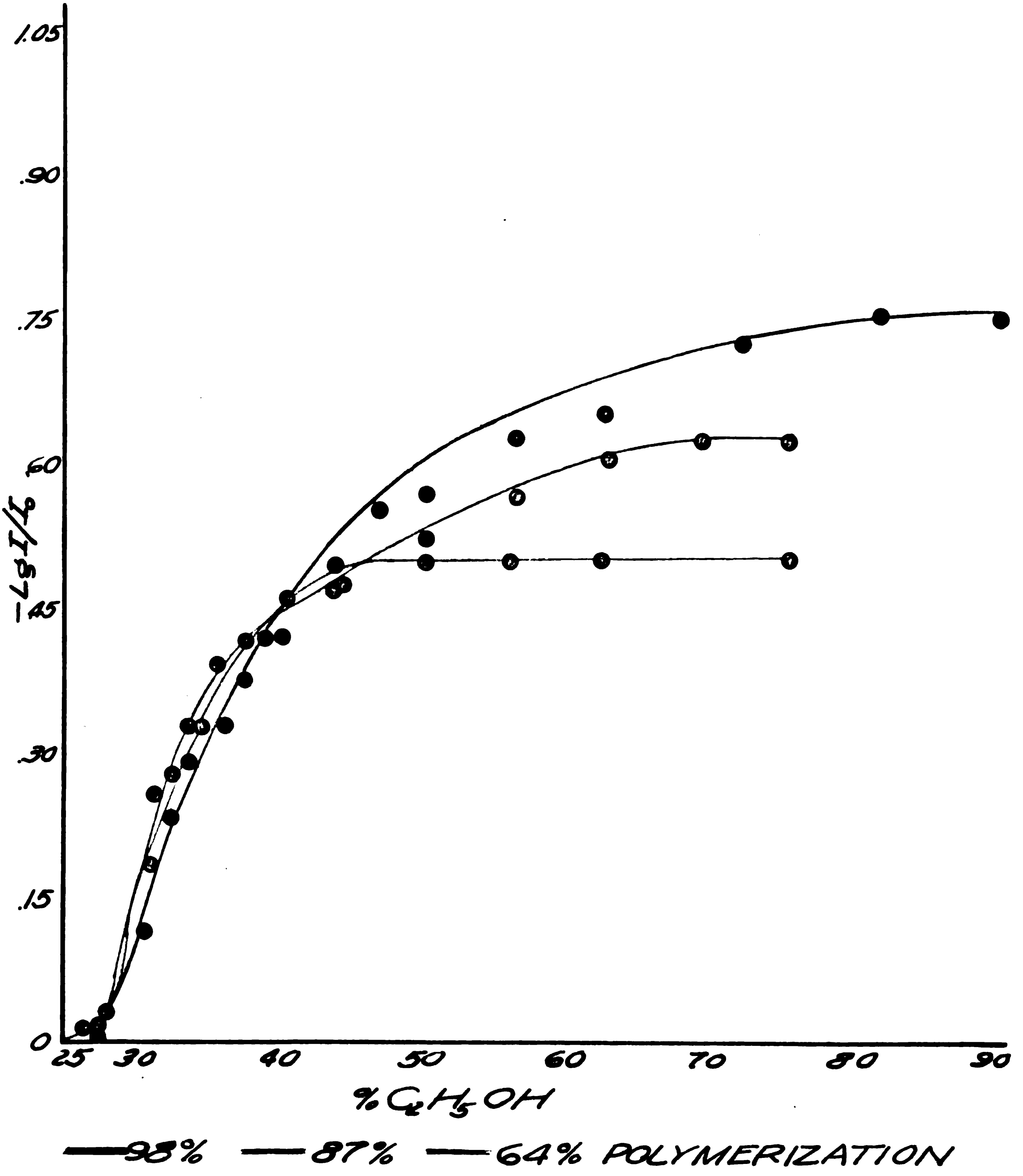


FIG III

PRECIPITABILITY ON RUN #II

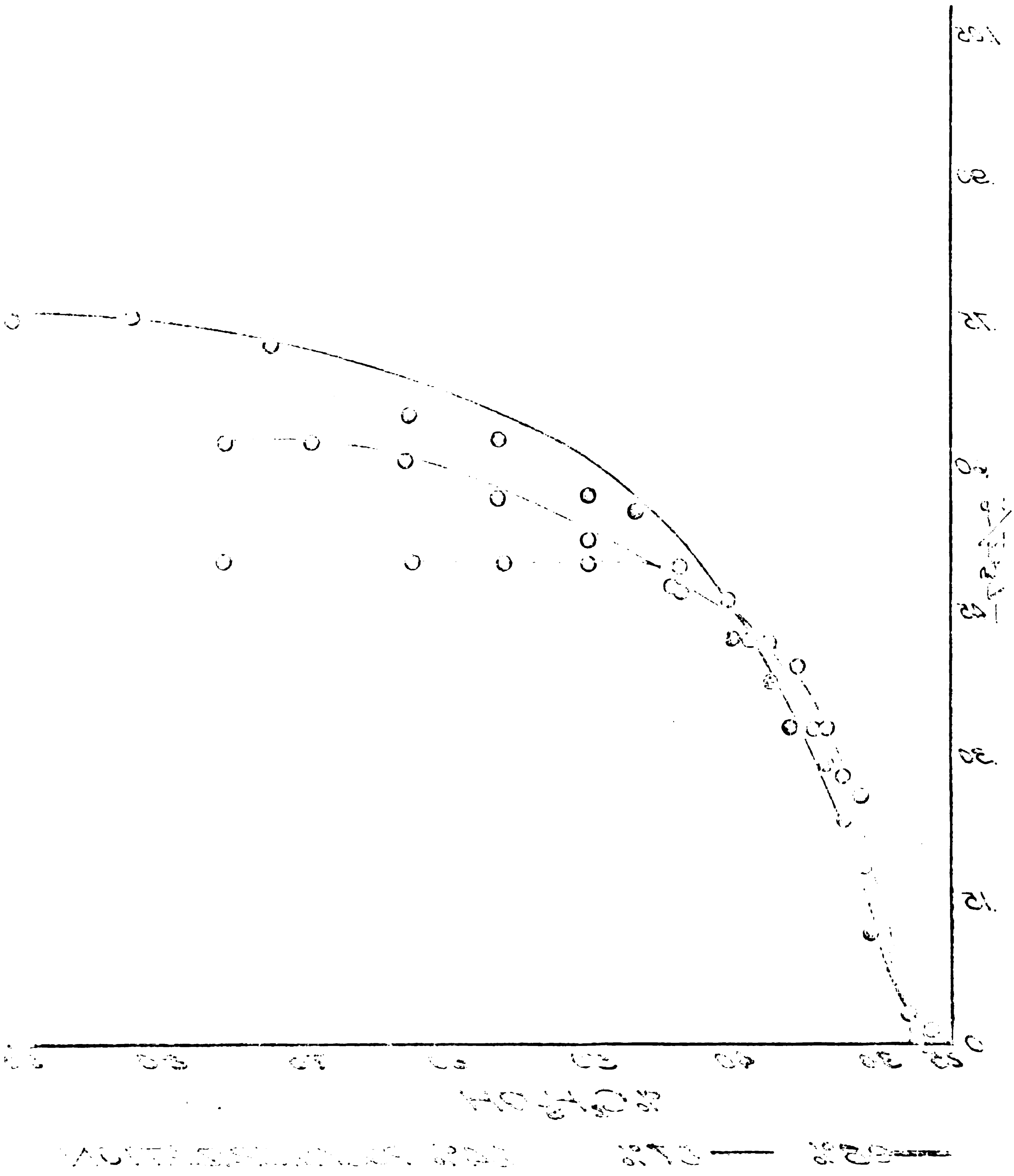


FIG. VII
PRECIPITABILITY ON RUN # V

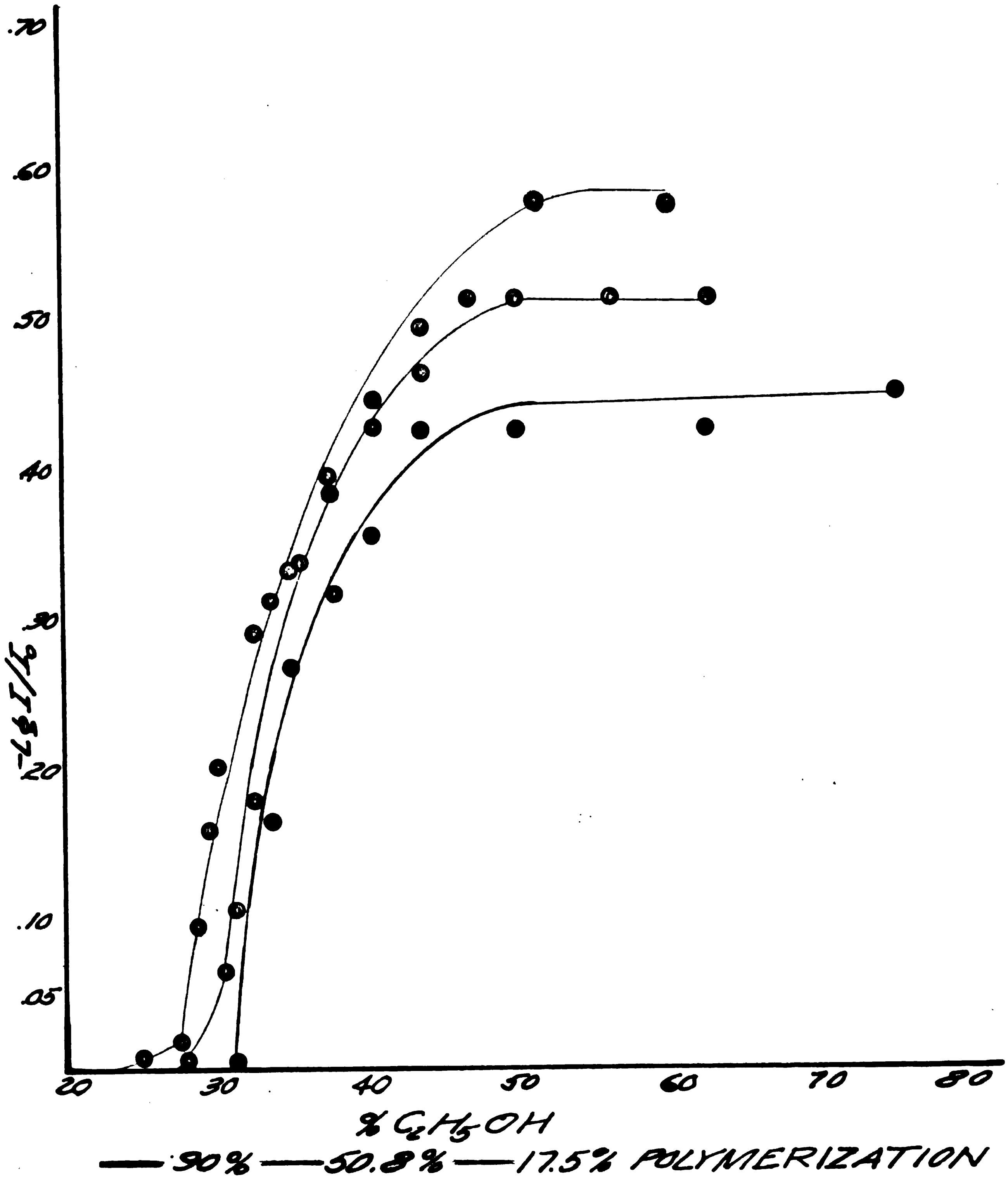


FIG. III

PRECIPITABILITY ON RUN # II

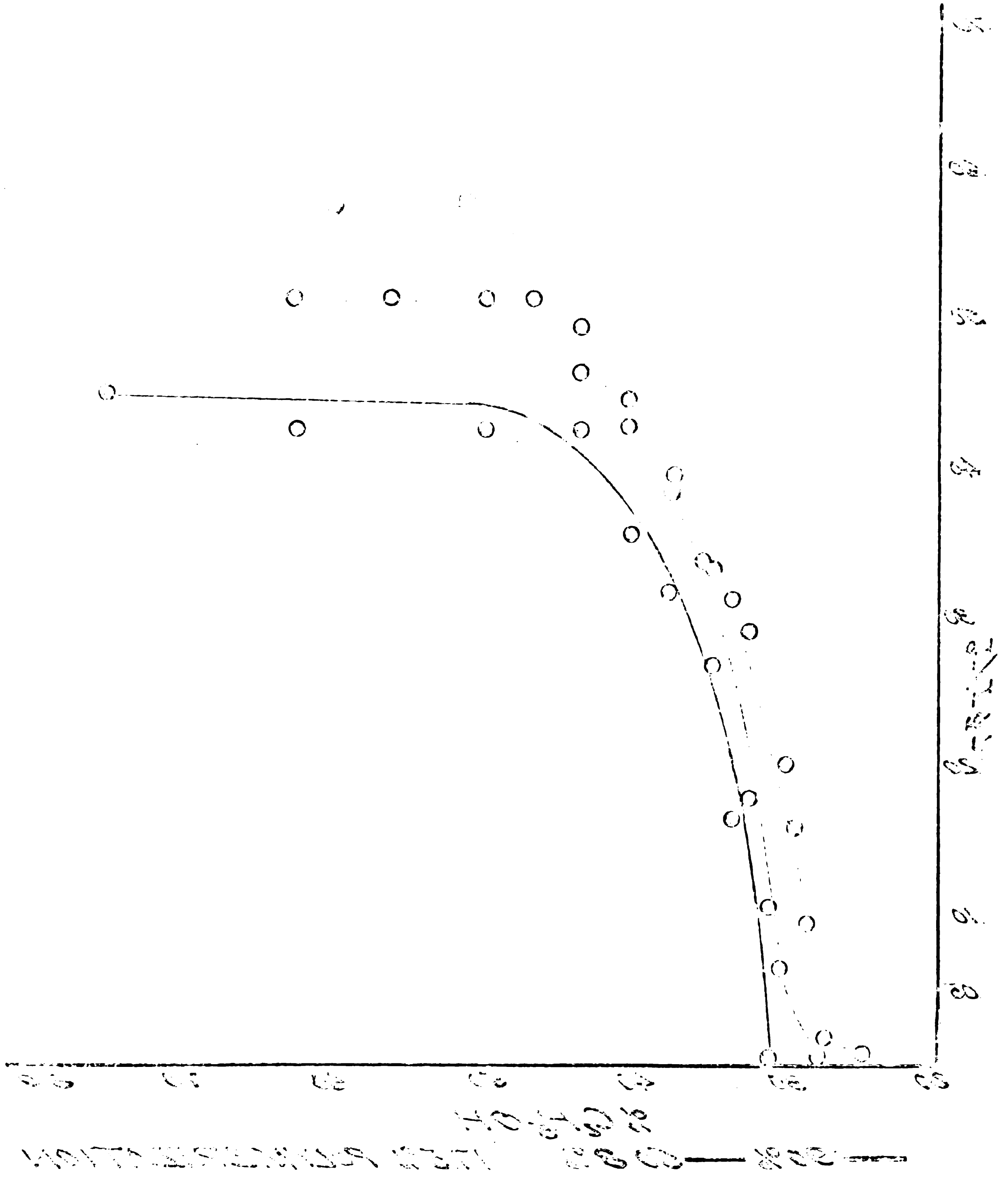
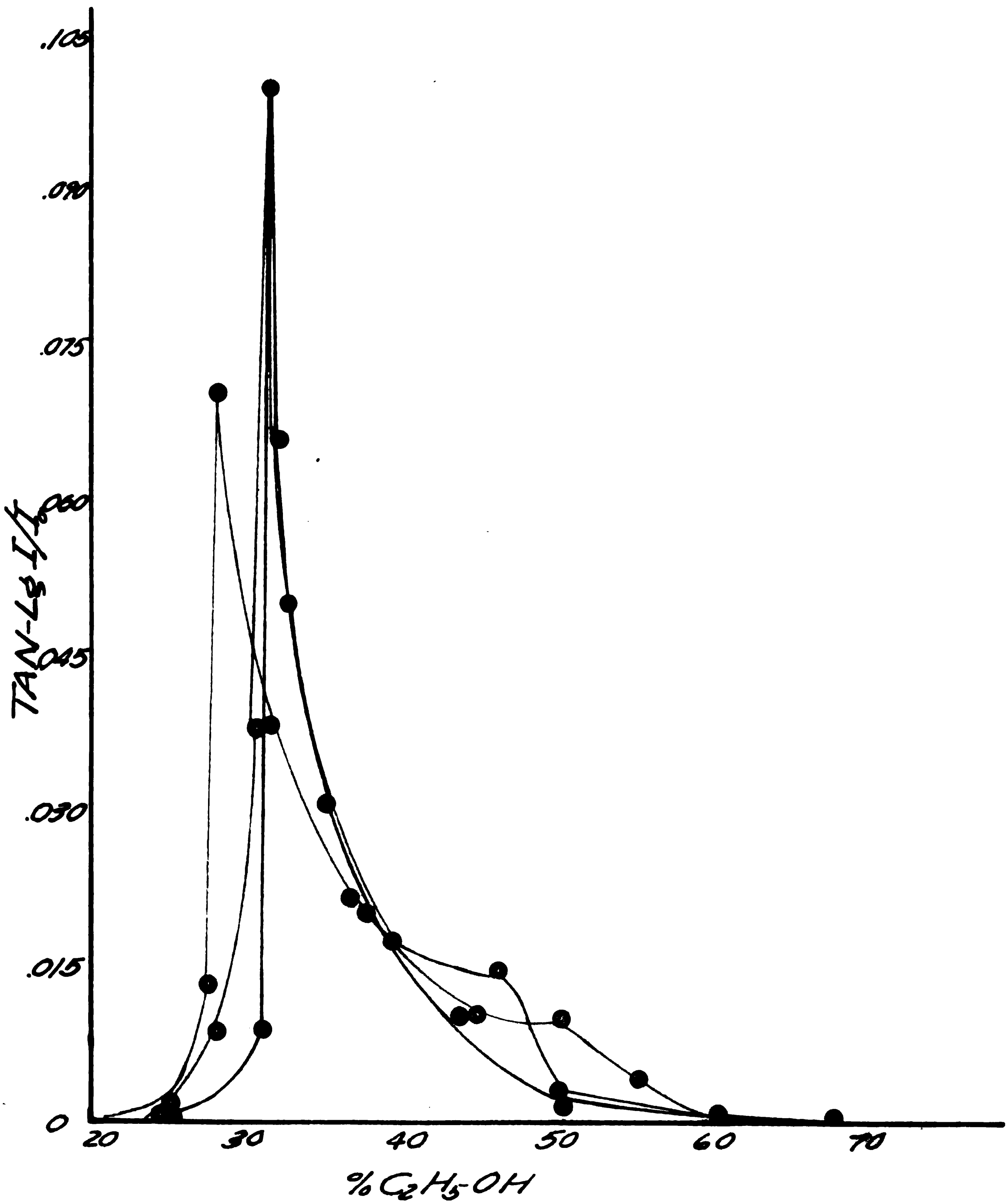


FIG VIII

MOLECULAR DISTRIBUTION RUN # V



— 90% — 50.8% — 17.5% POLYMERIZATION

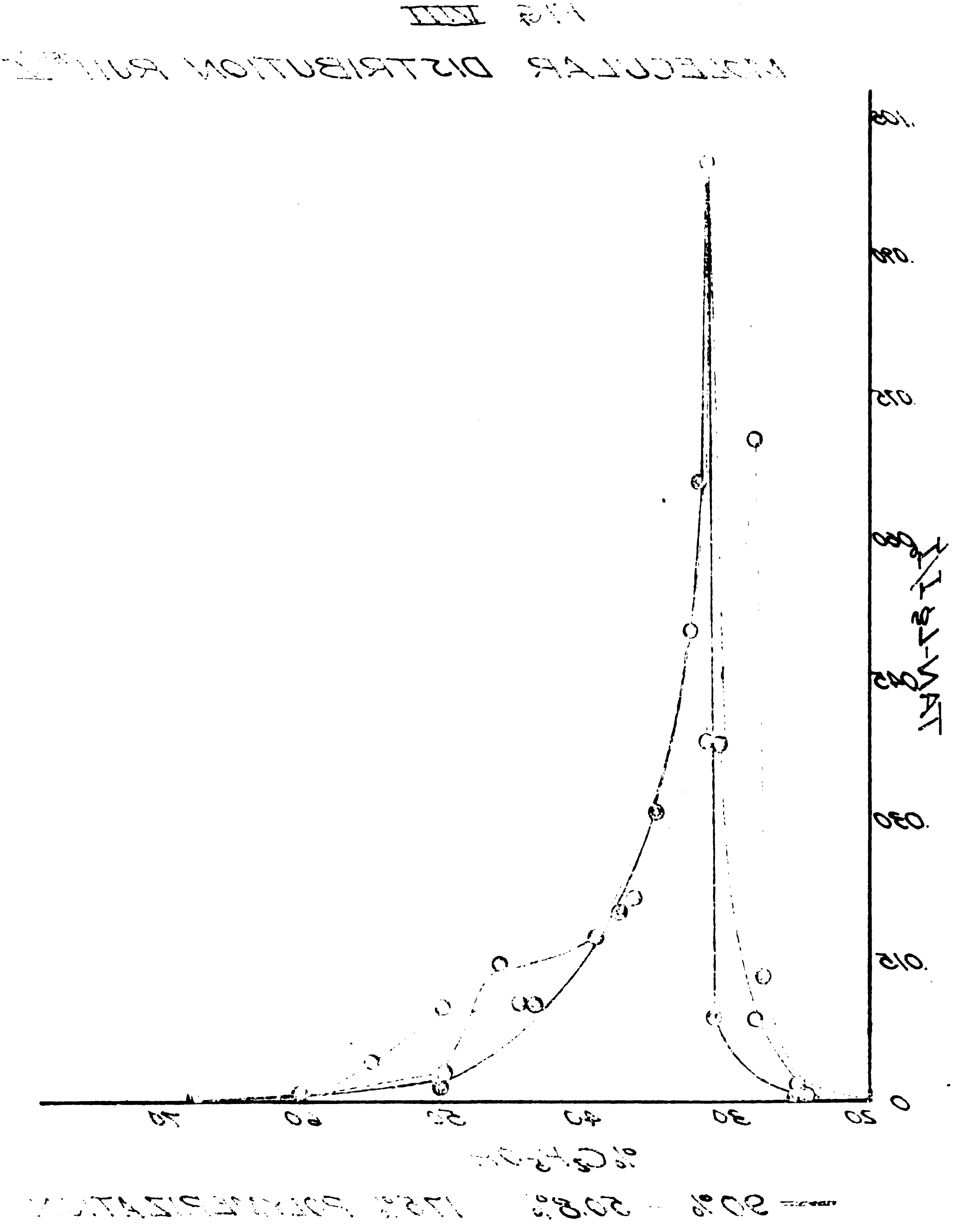


FIG XXIII
MOLECULAR DISTRIBUTION RUN
0
.015
.030
.045
.060
.075
.090
.105
20
30
40
50
60
70
% C2H5OH
50% - 50.8% 175° POLYMERIZATION

FIG. IX

PRECIPITABILITY ON RUN # VII

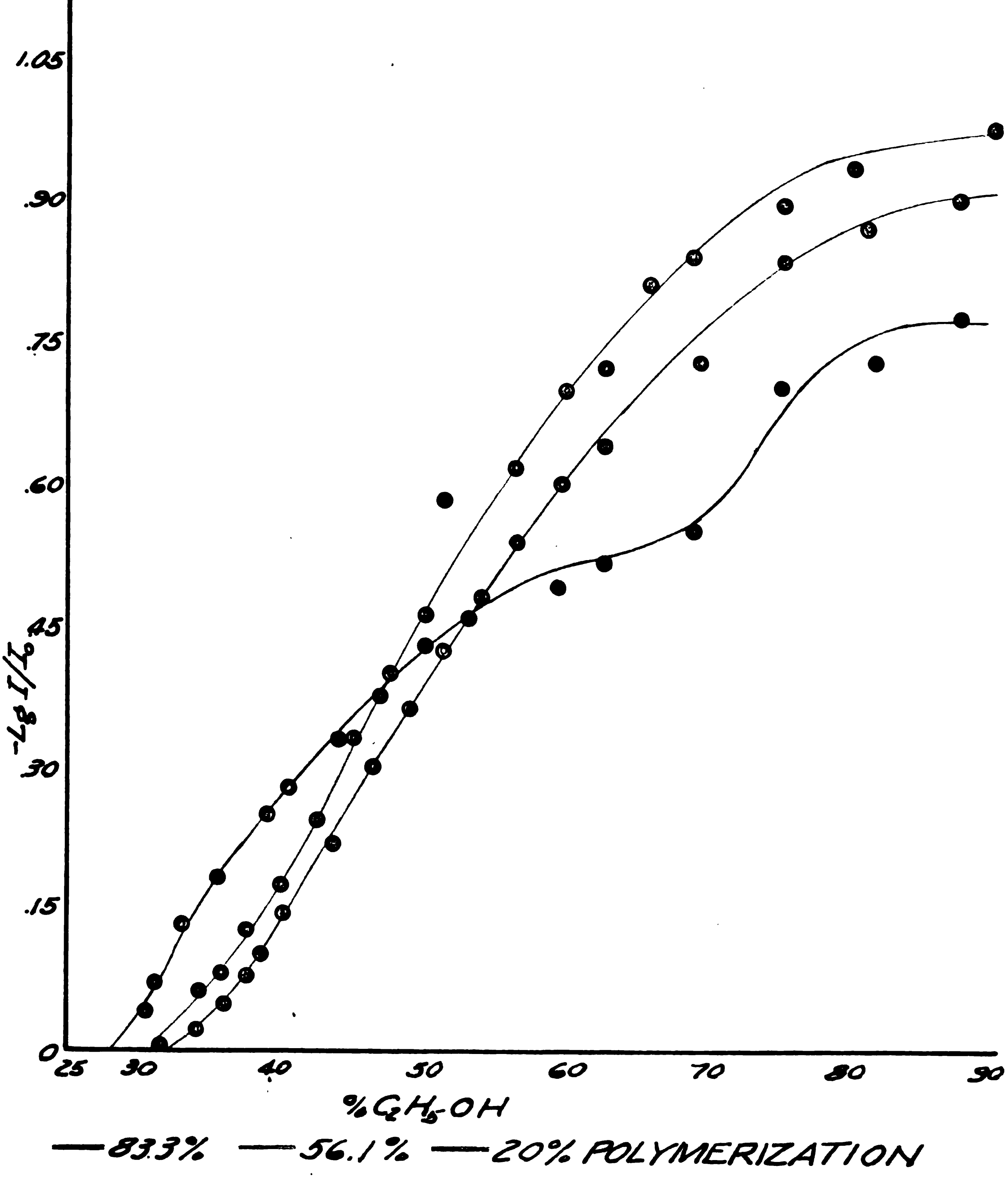


FIG. II

PRECIPITABILITY OF RUN # II

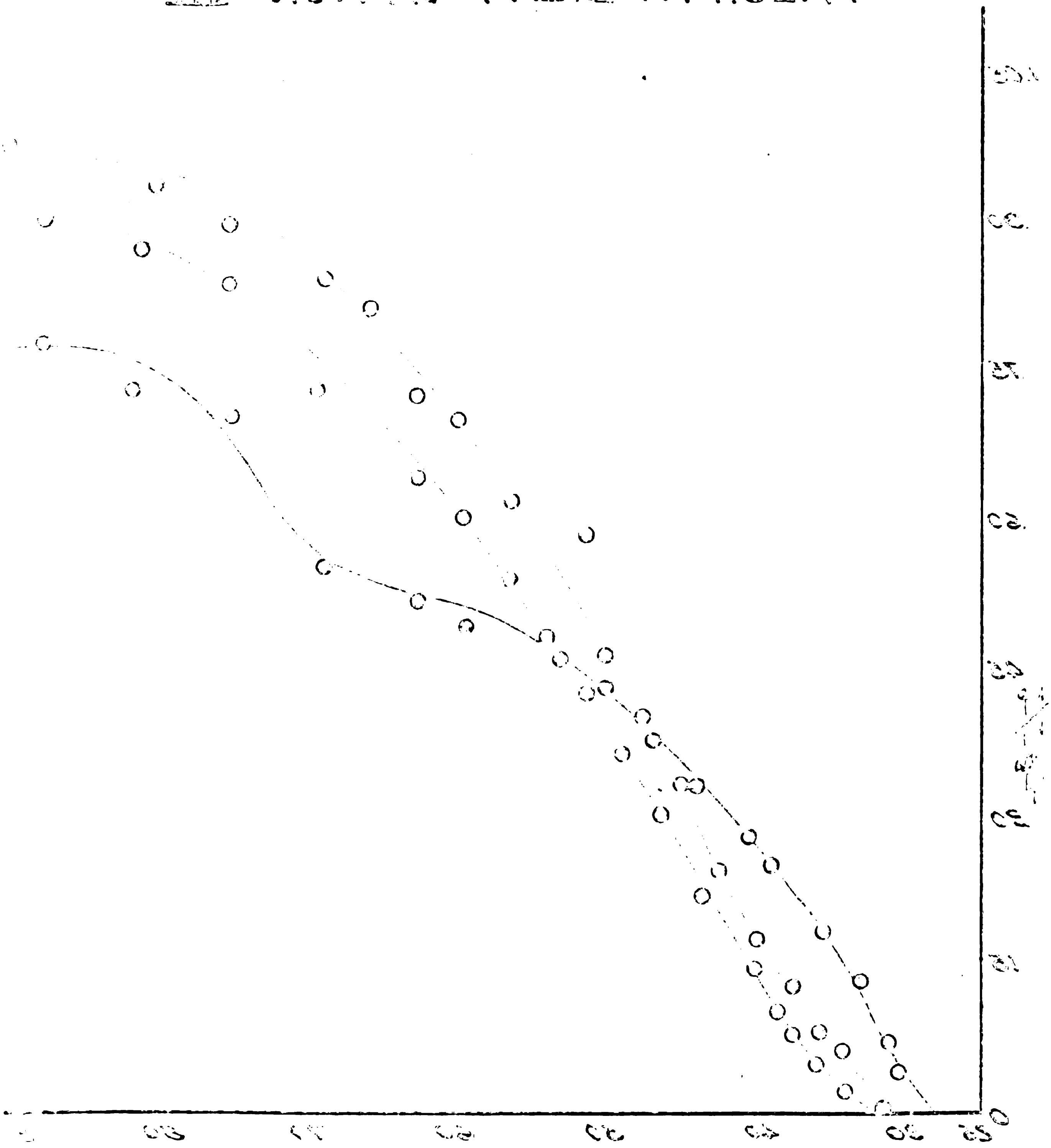
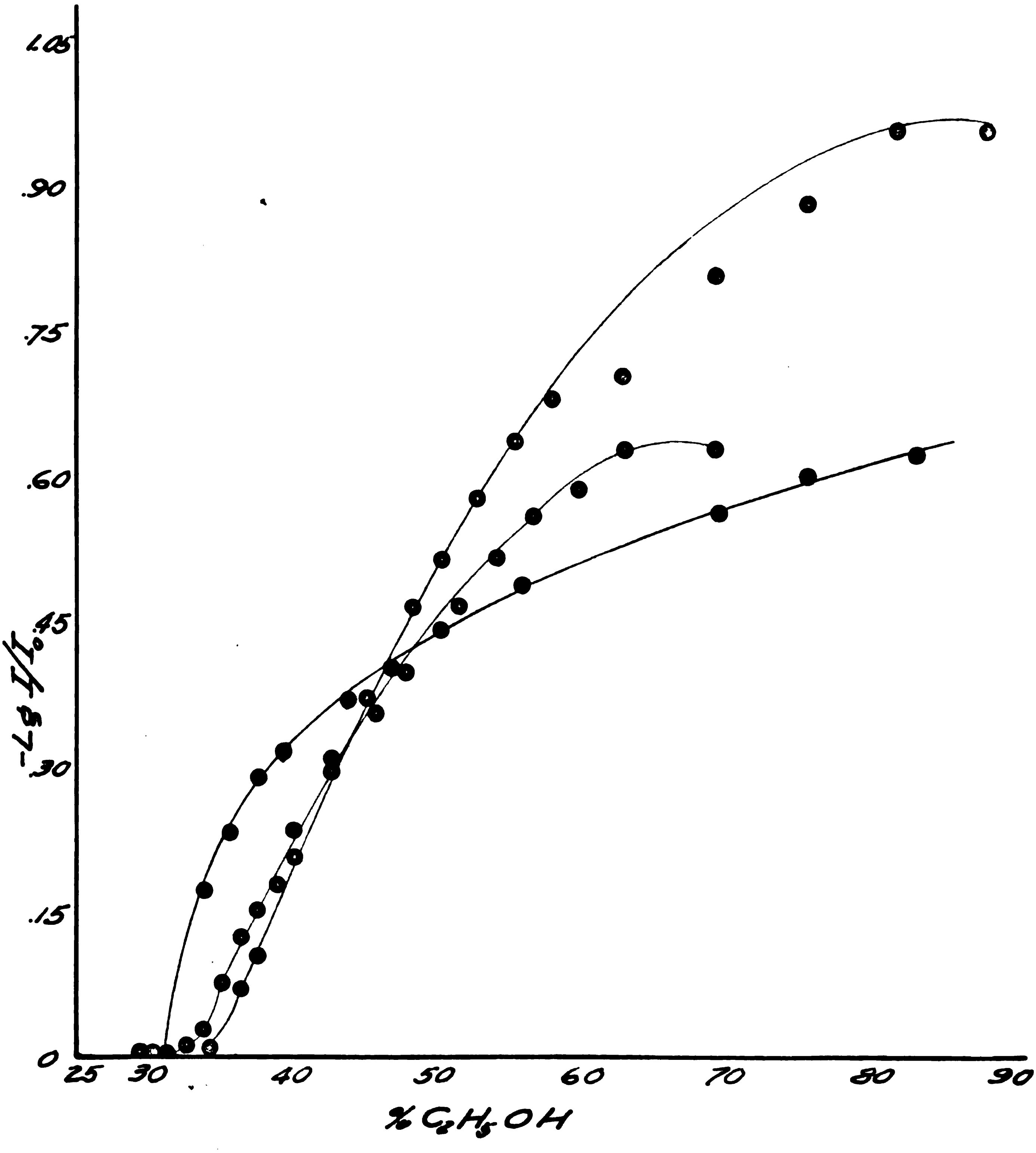


FIG. X

PRECIPITABILITY ON RUN # VIII



— 94.3% — 51.7% — 39.7% POLYMERIZATION

FIG. II

PRECIPITABILITY ON RUN #III

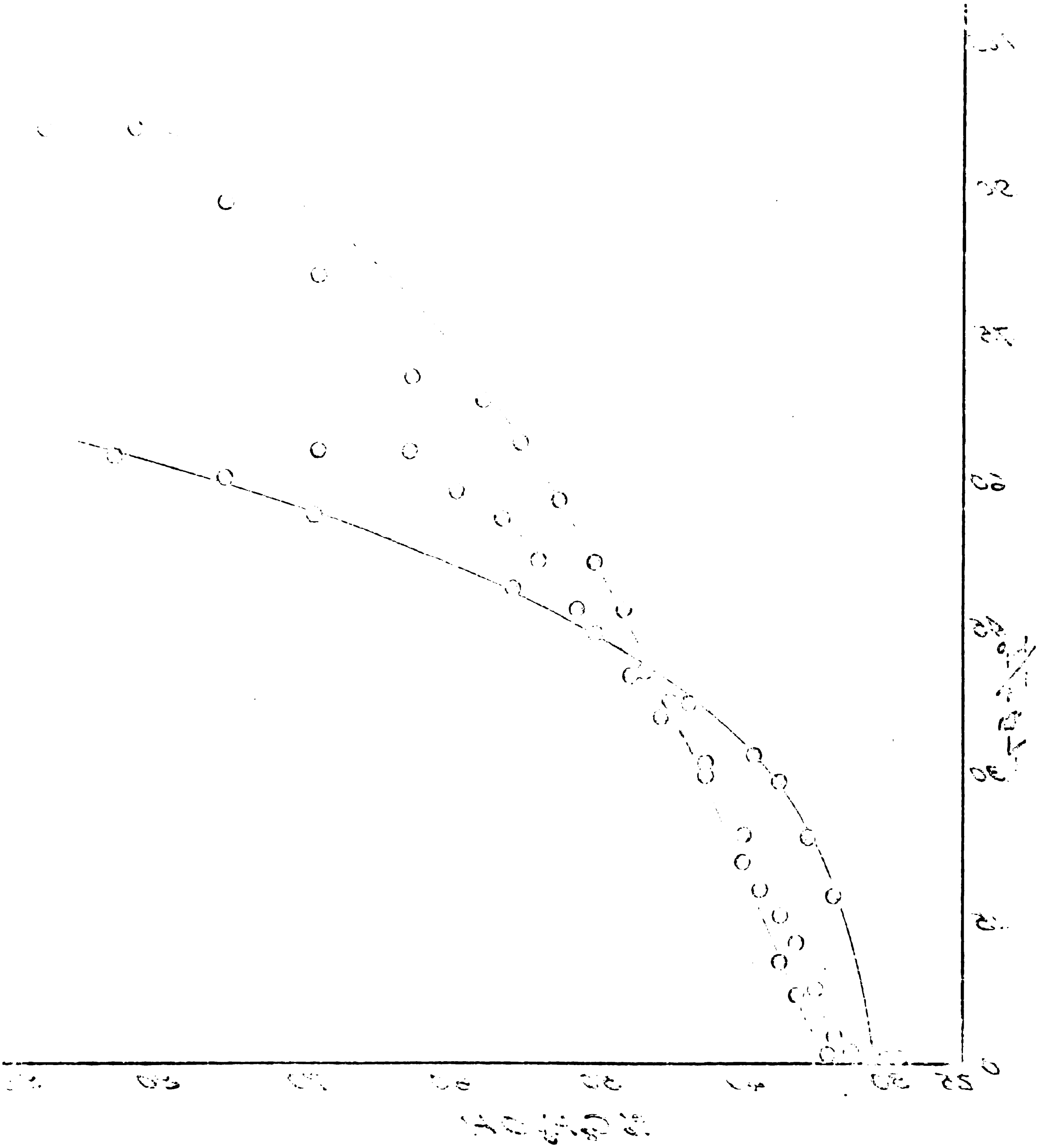
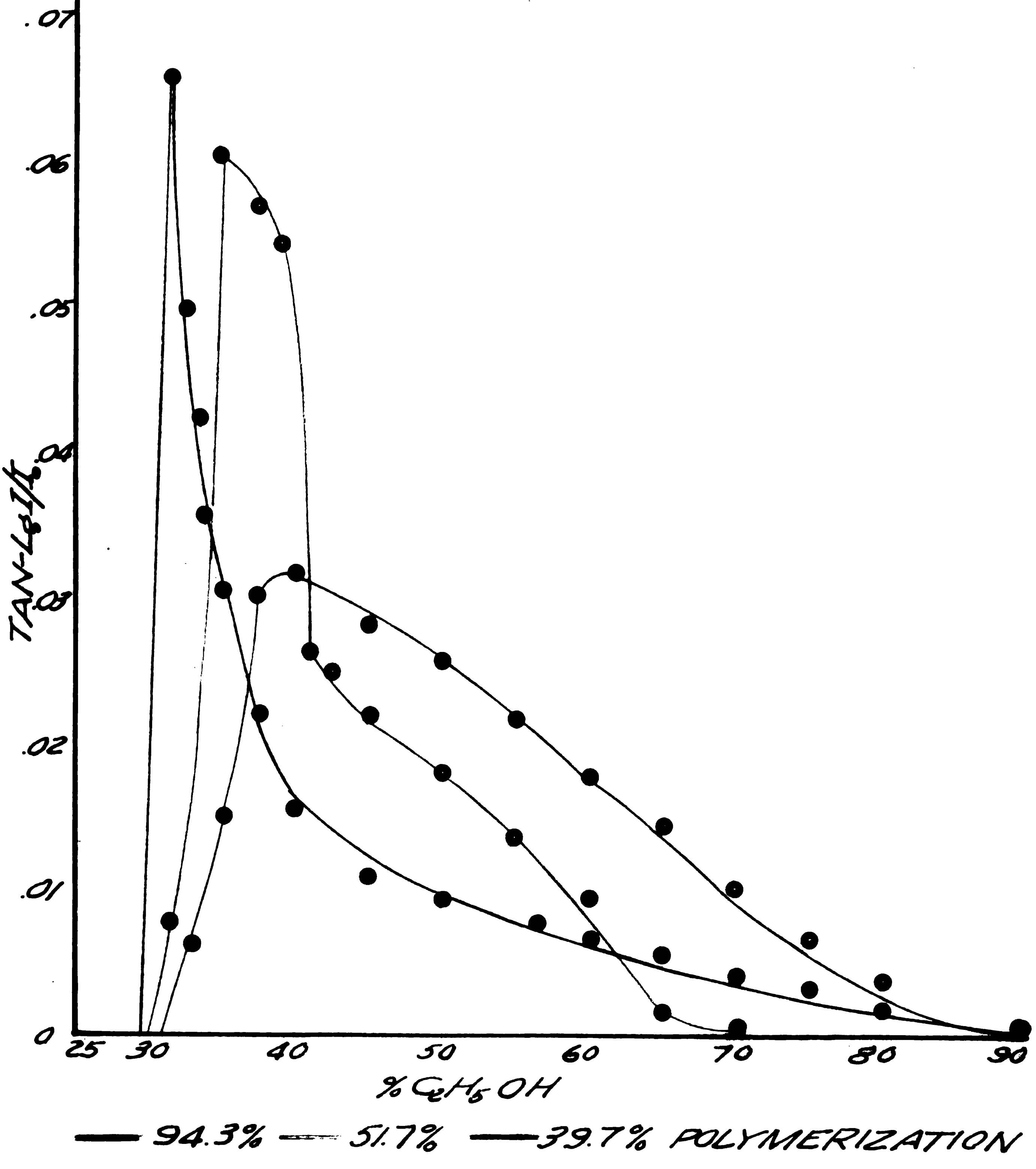


FIG. XI

MOLECULAR DISTRIBUTION RUN #VIII



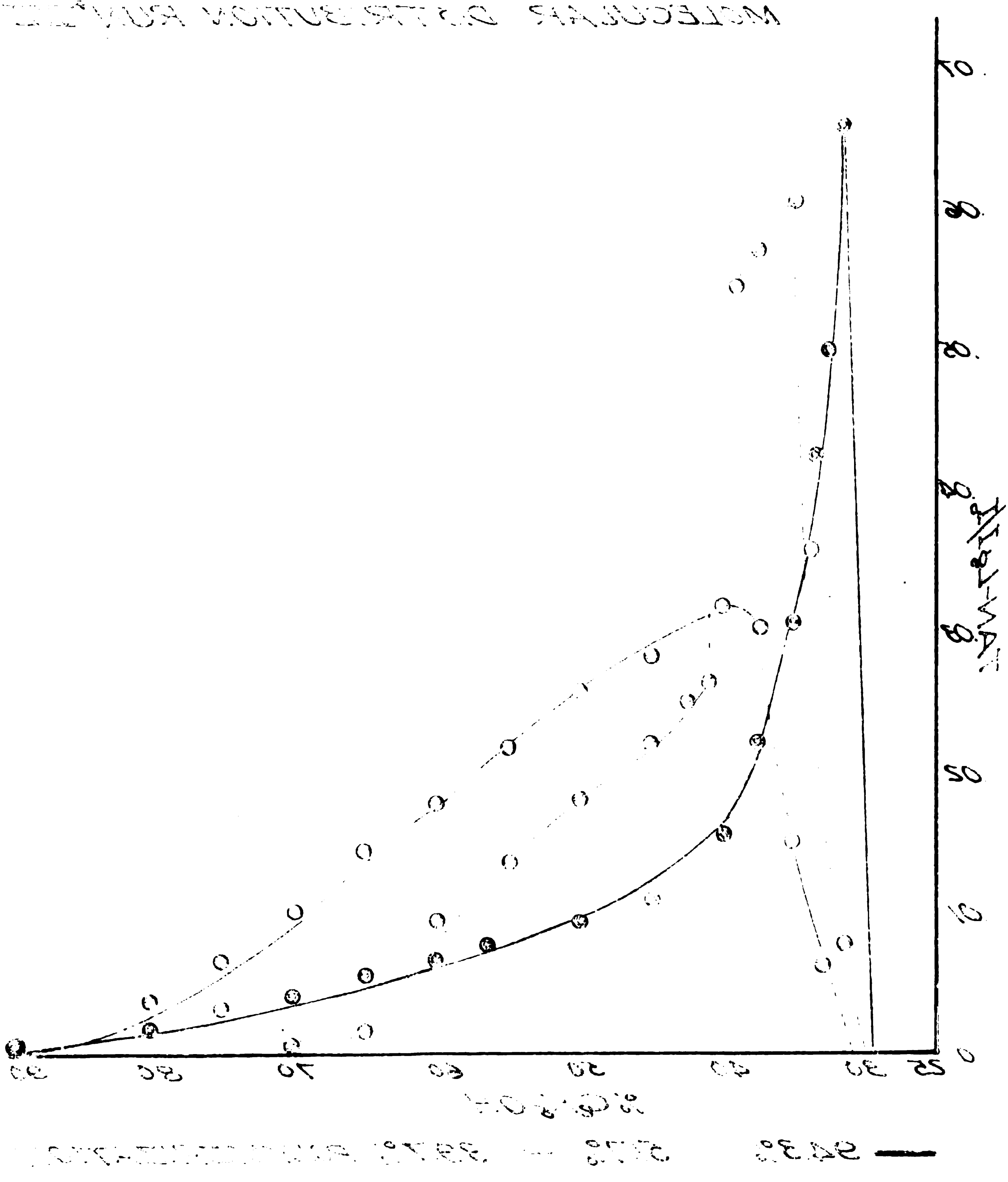
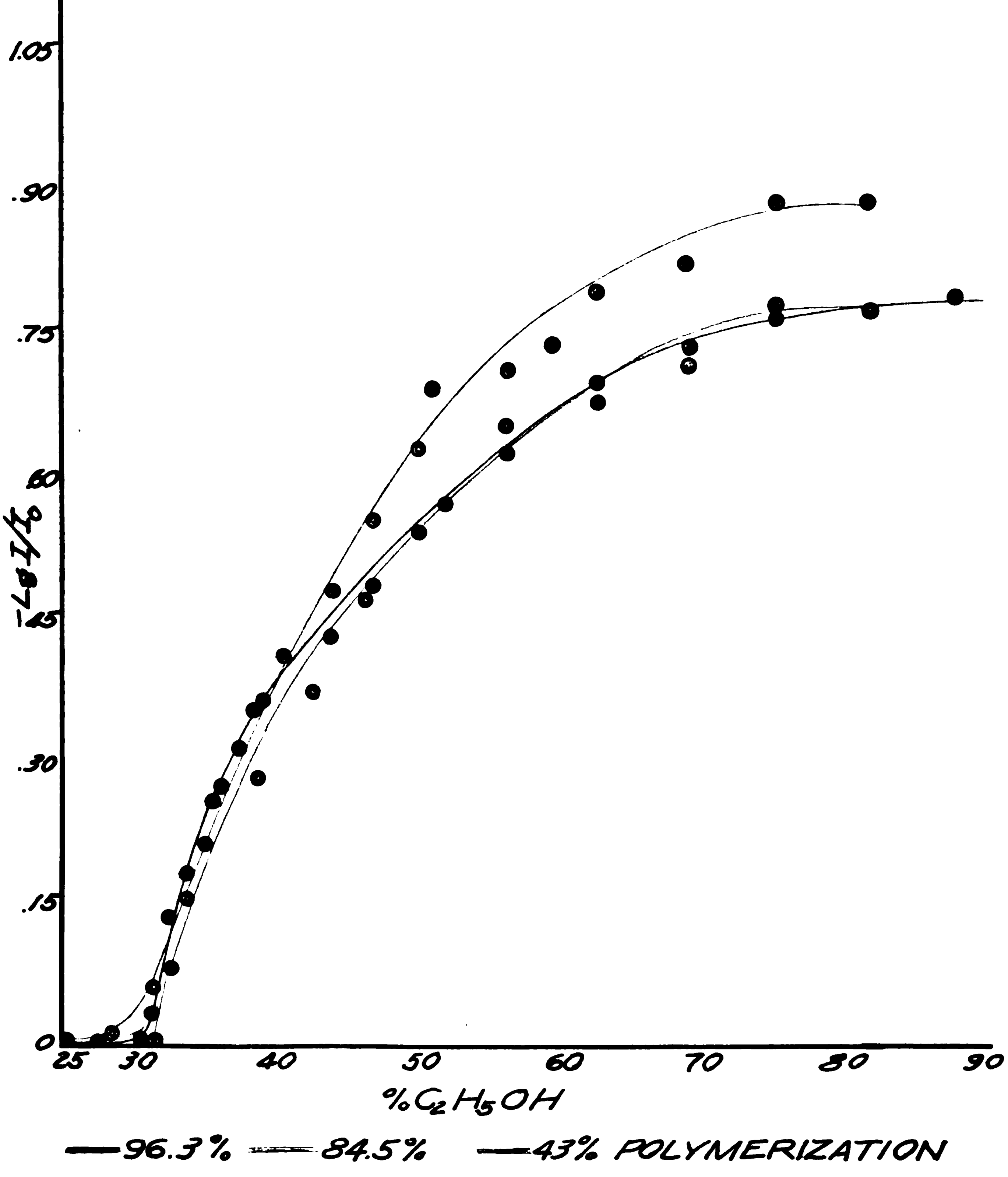


FIG. XII

PRECIPITABILITY ON RUN #XI



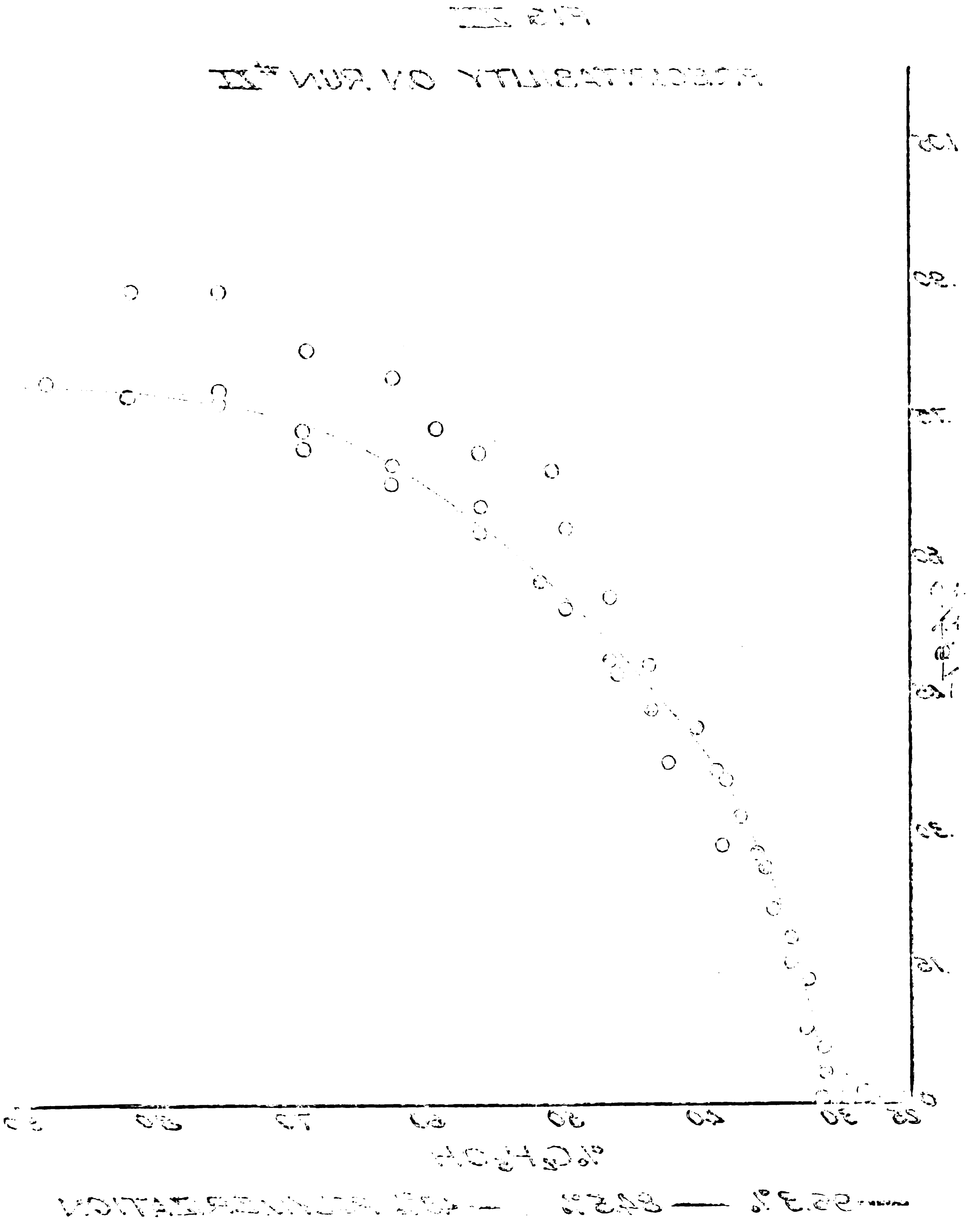


FIG XII
RECTIFIABILITY ON RUN #XI
1.05
.90
.75
.60
.45
.30
.15
0
85
80
70
60
50
40
30
25
% C2H5OH
95.3 % — 84.5 % — CONCENTRATION

DISCUSSION:

From a study of Table I and Fig. I it develops that there is a great difference in rate of reaction among the different catalytic systems. Sodium bisulfite alone has very little catalytic effect but increases the rate of polymerization greatly when used with potassium persulfate. The replacement of air with an atmosphere of nitrogen increases the rate even further. The molecular weights of the final products however are of the same order of magnitude.

Nitrogen atmosphere, used with potassium persulfate without the presence of sodium bisulfite, gives the most rapid reaction. The molecular weight of the final product is many times greater than that formed in the other systems.

It is also interesting to note that in the formation of very large molecules the greatest average molecular weight occurs at approximately fifty percent polymerization. This would seem to indicate that the decrease in the amount of monomer available toward the end of the reaction causes the formation of low molecular weight compounds which reduce the total average molecular weight of the final product. This type of maximum does not seem to occur in the formation of the lower molecular weight compounds. This could be explained by the fact that although there is the same decrease in the amount of monomer available, the chain length throughout the reaction is low so that there is not the contrast between the molecules formed at the beginning and end of the reaction.

Fig. VIII shows the molecular distribution curves of the samples taken from a run using potassium persulfate in nitrogen. It agrees with the molecular weight determinations in that the first and last samples which have approximately the same molecular weight have also almost identical distribution curves. The intermediate sample, however, which has a larger molecular weight has its peak at a smaller percentage of nonsolvent.

If an atmosphere of molecular oxygen is used with potassium persulfate practically no polymerization occurs over a long period of time.

The fact that an atmosphere of nitrogen gives rapid polymerization with the formation of long chains indicates that oxygen acts as an inhibitor and possibly a chain terminator. The running of a reaction under an oxygen atmosphere confirmed this idea.

The rapid rate of polymerization using potassium persulfate with sodium bisulfite could be accounted for if the sodium bisulfite, acting as a reducing agent, took up the oxygen present in the emulsion. This would remove the inhibitory and chain terminating effect of the oxygen. The presence of the sodium bisulfite in the system, however, could act as a chain terminator so that low molecular weights would be obtained.

The fact that placing this system under a nitrogen atmosphere gave little increase in the rate of polymerization seemed to support this conclusion.

By examining Fig. II it is apparent that there is little correlation between precentage polymerization and molecular distribution. This is not surprising considering the different rates at which the products were formed.

By plotting the molecular distribution curves of samples haveing approximately the same molecular weight on the same axis as in Fig. III, it can be seen that samples of the same molecular weight may not have the same molecular distribution. However, the peaks for these curves all occur at approximately the same percentage of nonsolvent.

By studying the various graphs on precipitability and molecular distribution it can be seen that the molecular weight and the molecular distribution change considerably as polymerization proceeds.

CONCLUSIONS:

1. Potassium persulfate catalyst in an atmosphere of air gives slow polymerization and a product with a molecular weight of approximately 35,000.

2. Potassium persulfate catalyst in a nitrogen atmosphere gives rapid polymerization and a product with a molecular weight of approximately 200,000at total polymerization. At fifty percent polymerization it gives a product of approximately 380,000 molecular weight.

3. Potassium persulfate with sodium bisulfite in an atmosphere of air gives rapid polymerization and a product with a molecular weight of approximately 40,000.

4. Potassium persulfate with sodium bisulfite in an atmosphere of nitrogen gives rapid polymerization and a product with a molecular weight of approximately 40,000.

5. Sodium bisulfite alone is ineffective in the catalysis of polymerization.

6. Molecular oxygen has an inhibitory effect upon polymerization in this system.

7. The smaller the amount of catalyst used in the potassium persulfate - sodium bisulfite system the higher the molecular weight of the product.

BIBLIOGRAPHY:

1. Powers, P. O., "Synthetic Resins and Rubbers", John Wiley and Sons, Inc. - New York
2. Carothers, W. H., Chem. Rev., Vol. 8, 353 (1931)
3. Burk, R. E., Thompson, H. E., Weith, A. J., Williams,I, "Polymerization" - New York 1937
4. Mark, H. and Raff, R., "High Polymers" Vol. III Interscience - New York - 1941-
5. Fryling, C. F., Ind. Eng. Chem. Anal. Ed. 16, 1 (1944)
6. Fryling, C. F., and Harrington, E. W., Ind. Eng. Chem. Ind. Ed., 36, 114 (1944)
7. Hohenstein, W. P., Siggia, S. and Mark, H., India Rubber World 111, 173 (1944) II
8. Hohenstein, W. P., Siggia, S. and Mark, H., India Rubber World 111, 436 (1945) III
9. Schulz, G. V. and Husemann, E., Z. physik. Chem. B 39, 246 (1938)
10. Price, C. C. and Kell, R. W., J. Am. Chem. Soc. 63, 2798 (1941)
11. Gilman, H.,"Organic Chemistry", 771 - New York 1943
12. Staudinger, H., "Die hochmolekularen organischen Verbindungen", Berlin 1932
13. Irany, E. P., J. Am. Chem. Soc. 61, 1734 (1939)
14. Adams, H. E. and Powers, P. O., Ind. Eng. Chem. Anal. Ed. 15, 711 (1943)
15. Staudinger, H. and Husemann, E., Ber. 68, 1691 (1935)

16. Fikentscher, H., Angew. Chem. 51, 433 (1938)

17. Hohenstein, W. P., Vingiello, F. and Mark, H., India Rubber World 110, 291 (1944) I

18. Rohrs, W., Staudinger, H. and Vieweg, R., "Fortschritte der Chemie, physik and technik der makromolekularen Stoffe" Vol. I - Berlin 1939

19. Mark, H., "High Polymers" Vol. II, New York 1940

20. Alfrey, T., Bartovics, A., and Mark, H., J. Am. Chem. Soc. 65, 2319 (1943)

21. Bartovics, A. and Mark, H., J. Am. Chem. Soc. 65, 1901 (1943)

22. Flory, Pl J., J. Am. Chem. Soc. 65, 272 (1943)

23. Kemp, A. R. and Peters, H., Ind. Eng. Chem. 34, 1097 (1942)

24. Huggins, M. L., I - Jour. Phys. Chem. 42, 911 (1938)
II - Jour. Phys. Chem. 43, 439 (1938)

25. Alfrey, T. and Mark, H., Paper presented at Division of Paint, Varnish and Plastics Chemistry - 1942

26. Schulz, G. V., Z. physik. Chem. A179, 321 (1937)

27. Dostal, H. and Mark, H., Z. physik; Chem. 29, 299 (1935)

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

29. Norrish, R. G. W. and Brookman, E. F., Proc. Roy. Soc. London (A) 171, 147 (1939)

30. Mark, H. and Raff, R., Z. physik. Chem. 31, 275 (1936)

31. Hunter, W. H. and Yohe, R. V., J. Am. Chem. Soc. 55, 1248 (1933)

32. Whitmore, F. C., Ind. Eng. Chem. 26, 94 (1934)

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

34. Williams, G., J. Chem. Soc. 775 (1940)