

UNCLASSIFIED

AD NUMBER
AD036925
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to DoD only; Administrative/Operational Use; 09 JUL 1954. Other requests shall be referred to Office of Naval Research, Arlington, VA 22203. Pre-dates formal DoD distribution statements. Treat as DoD only.
AUTHORITY
ONR ltr dtd 13 Sep 1977

THIS PAGE IS UNCLASSIFIED

Armed Services Technical Information Agency

Because of our limited supply, you are requested to return this copy WHEN IT HAS SERVED YOUR PURPOSE so that it may be made available to other requesters. Your cooperation will be appreciated.

AD

36925

NOTICE: WHEN GOVERNMENT OR OTHER DRAWINGS, SPECIFICATIONS OR OTHER DATA ARE USED FOR ANY PURPOSE OTHER THAN IN CONNECTION WITH A DEFINITELY RELATED GOVERNMENT PROCUREMENT OPERATION, THE U. S. GOVERNMENT THEREBY INCURS NO RESPONSIBILITY, NOR ANY OBLIGATION WHATSOEVER; AND THE FACT THAT THE GOVERNMENT MAY HAVE FORMULATED, FURNISHED, OR IN ANY WAY SUPPLIED THE SAID DRAWINGS, SPECIFICATIONS, OR OTHER DATA IS NOT TO BE REGARDED BY IMPLICATION OR OTHERWISE AS IN ANY MANNER LICENSING THE HOLDER OR ANY OTHER PERSON OR CORPORATION, OR CONVEYING ANY RIGHTS OR PERMISSION TO MANUFACTURE, USE OR SELL ANY PATENTED INVENTION THAT MAY IN ANY WAY BE RELATED THERETO.

Reproduced by
DOCUMENT SERVICE CENTER
KNOTT BUILDING, DAYTON, 2, OHIO

UNCLASSIFIED

AD No. 36425
ASTIA FILE COPY

OFFICE OF NAVAL RESEARCH

Contract Nonr. 736 (00) Project NR 330-027

TECHNICAL REPORT 6

July, 1954

"STERIC" PROTECTION OF COLLOIDAL PARTICLES I

by

Thomas L. Pugh

Submitted By

Wilfried Heller

Project Director

Chemistry Department, Wayne University

Detroit, Michigan

OFFICE OF NAVAL RESEARCH

Contract Nonr. 736(00) Project NR 330-027

Research on the Size and Shape of Large
Molecules and Colloidal Particles

Technical Report No. 6

PROTECTIVE ACTION OF HYDROPHILIC
POLYMERS ON GOLD SOL

By

Thomas L. Pugh

Submitted by

W. Heller
Project Director
Dept. of Chemistry
Wayne University
Detroit, Mich.

July 9, 1954

Introductory Remarks

This Technical Report is an exact copy of part of the Master Thesis of Mr. Thomas L. Pugh. The main part, to be brought in a subsequent Report, was concerned with the determination of the densities and refractive indices of the polymer particles contained in the lattices used for light scattering measurements within the frame work of the objectives of this project. The present material was collected as a fill-in of the various waiting periods involved in the execution of the principal work.

The results contained in this report appear significant because they indicate the possibility of a new and very promising method for stabilizing colloidal solutions, including lattices--which were not used in this preliminary work. This method is based upon inter particle "steric hindrance" and the name to be proposed for this method of stabilization is "steric stabilization."

In order to make a prompt dissemination of these results possible, the thesis was not revised for the purpose of this report. Major changes, including condensation of the material, elimination of details, method of presentation and enlargement of the theoretical section, will be made prior submitting the material for publication which is planned within the next two months.

Wilfried Heller

TABLE OF CONTENTS

	Page
LIST OF TABLES	111
LIST OF FIGURES	iv
PROTECTIVE ACTION OF HYDROPHILIC POLYMERS ON GOLD SOL	
Chapter	
I. INTRODUCTION	1
II. THE LITERATURE SURVEY	3
III. EXPERIMENTAL	7
A. Equipment	7
B. Preparation of the Materials.	8
C. Experimental Procedure.....	20
IV. DATA AND GRAPHS	27
V. DISCUSSION OF RESULTS	31
VI. REFRACTIVE INDEX OF POLYMER SOLUTIONS	34
VII. SUMMARY.....	43

LIST OF TABLES

Table	Page
I. Refractive Index vs. Concentration, $\bar{M}$ -600...	14
II. Refractive Index vs. Concentration, $\bar{M}$ -6000..	14
III. Refractive Index vs. Concentration, $\bar{M}$ -9000..	15
IV. Conversion of Tanaka's Data	19
V. Comparison of $\Delta n/c$ of Three Independent Sources	19
VI. Sample Table of a Typical "Run"	25
VII. Polymer Concentration vs. Coagulation Values Blank	27
VIII. Polymer Concentration vs. Coagulation Values $\bar{M}$ -600	27
IX. Polymer Concentration vs. Coagulation Values $\bar{M}$ -6000	28
X. Polymer Concentration vs. Coagulation Values $\bar{M}$ -9000	28
XI. $\bar{M}$ and $\sqrt{\bar{M}}$ vs. Concentration of Polymers: 0.100 g./100 ml	28
XII. Refractive Index vs. Polymer Concentration, $\bar{M}$ -300	36
XIII. Refractive Index vs. Polymer Concentration, $\bar{M}$ -400	36
XIV. Refractive Index vs. Polymer Concentration, $\bar{M}$ -1000	36
XV. Refractive Index vs. Polymer Concentration, $\bar{M}$ -4000	36
XVI. $\bar{M}$ vs. $\Delta n/c$, n_D 25.00°C, $c = \text{g./100 ml}$	41
XVII. $\bar{M}$ vs. $\Delta n/c$, $n_{5461 \text{ \AA}}$ 25.00°C, $c = \text{g./100 g.}$	41

LIST OF FIGURES

Figure		Page
1.	Refractive Index vs. Polymer Concentration, $\bar{M}$ -600	16
2.	Refractive Index vs. Polymer Concentration, $\bar{M}$ -6000	17
3.	Refractive Index vs. Polymer Concentration, $\bar{M}$ -9000	18
4.	Coagulation Values vs. Polymer Concentration..	29
5.	$\bar{M}$ and $\sqrt{\bar{M}}$ vs. Coagulation Values	30
6.	Refractive Index vs. Polymer Concentration, $\bar{M}$ -300	37
7.	Refractive Index vs. Polymer Concentration, $\bar{M}$ -400	38
8.	Refractive Index vs. Polymer Concentration, $\bar{M}$ -1000	39
9.	Refractive Index vs. Polymer Concentration, $\bar{M}$ -4000	40
10.	$\Delta n/c$ vs. $\bar{M}$, This Investigation	42
11.	$\Delta n/c$ vs. $\bar{M}$, Data of Tanaka	42

PROTECTIVE ACTION OF HYDROPHILIC
POLYMERS ON GOLD SOL

CHAPTER I

INTRODUCTION

When the electrolyte sensitivity of a hydrophobic colloid is reduced by the addition of a third substance which may also be a colloid, the phenomenon is known as protective action. The reagents which produce this protection are known as protecting agents and can be placed in one of two classes. (1) The protective agent may be a polymer charged by virtue of dissociating groups on its carbon skeleton. These groups may be -NH_2 or -COOH , for example. The addition of a positively charged polymer to a positive particle in a sol increases the charge of the particle by adsorption of the polymer ion on the surface. With this type of protection one may encounter a phenomenon called sensitization: This may take place in the event of a small addition of negative polymer ion to a positive colloidal particle. (2) If the hydrophilic colloid is non-ionic, it merely protects a hydrophobic particle from coagulation by completely enveloping it with a protective coating. Coagulation is then prevented due to the inability of the "gegenions" to "reach" the charge on the particle. It was thought

that a third type might exist: (3) If a protecting agent consists of long-chain polymers of which the "head" is adsorbed into the surface of the colloidal particle, the protection is due to steric hindrance. That is, the long chain "tails" of the polymers are out in the solvent and prevent another protected particle from entering its sphere of influence. Thus it was decided to investigate this possibility.

Examples of case (1) are gelatin, proteins, etc. while (2) is represented by such substances as starch and dextrin. The last model (3) would be represented by non-rigid long-chain polymers which is the type of protection agent described in this thesis. A molecular weight series of polyethylene glycols were the polymers used; they have a basic structure of $\text{HO}(-\text{CH}_2-\text{CH}_2-\text{O}-)_n-\text{C}_2\text{H}_4\text{OH}$ where n may vary from 4-203.

The use of stabilizing agents in industry and in the laboratory is increasing. Therefore if the model suggested were true, then a whole new field of stabilizing agents would be opened. It was decided to fully investigate the protective properties of this polymer, that is, its minimum protecting concentration, sensitization and any effects due to molecular weight increase.

CHAPTER II

THE LITERATURE SURVEY

Very little work in the past has been done in actual connection with the theory of protective action. Most of the work done in the last few years has been of a practical nature. It has dealt with the gold numbers of polymeric, protein and carbohydrate substances, the effect of protective action on the Schultze-Hardy rule and patents for organic polymers which can be used as stabilizing agents.¹⁻⁶

A few recent investigations have been conducted, however, which definitely pertain to the problem of the protective action phenomenon. One which might be considered related to this problem was that of a group of Japanese

¹H. R. Kruyt and C. W. Horsting, Rec. trav. chim. 57, 737-40 (1938).

²A. A. Titov, Kino. Fote-Khim. Prom., 1938, No. 9, 44-50; Khim. Referal. Zhur. 2, No. 3, 129 (1939); C.A. 34, 921 (1940).

³H. J. C. Tendeloo, Rec. trav. chim. 60, 347-48 (1941).

⁴R. T. Nazzaro, Paper Trade J., 121, No. 21, 90, 94 (1945).

⁵R. Subramhanya, K. Doss and B. Rao, Proc. Indian Acad. Sci., 26A, 197-202 (1947).

⁶R. F. Stalzer, E. S. Dillon and W. C. Vosburgh, Anal. Chem., 22, 952-53 (1950).

research workers.¹ First, they defined a new type of gold number which was very similar to Zsigmondy's but in place of salt addition they froze their gold sol samples. They defined the freezing gold number as that number of mg. of protecting agent added to 10 ml. of gold sol that just prevents coagulation by freezing.

Using this type of a gold number these workers showed that with an increase in OH groups there was an increase in protective action.² They checked alcohols varying from methanol up to raffinose. Whether this type of protection is due to adsorption of the reagent (true protection) or due to the charge increase on the hydrophobe which has been noted by other investigators is not certain. Chatterji and Lodha confirmed the results of Krulyt and Van Duin which consisted of adding increasing amounts of non-electrolytes (organic compounds such as phenols, carbonyl compounds and alcohols) to As_2S_3 sols and checking the behavior towards salt additions.³ It was found that unless the concentration of the non-electrolyte was so high that dielectric constant of the solvent was affected, the result of the non-electrolyte addition led to an apparent stability of the hydrophobic colloid.

¹Shohei Uno and Naoji Ichiji, J. Chem. Soc. Japan, Pure Chem. Section, 72, 607-10 (1951).

²Ibid., 72, 877-80 (1951).

³A. C. Chatterji and H. R. Lodha, J. Indian Chem. Soc., 28, 131-34 (1951).

Doscher, Myers and Atkins prepared a compound from ethylene oxide and a fatty acid which gave them a polymer of this formula: $R-O-(C_2H_4O)_n-C_2H_5OH$ where R was the fatty acid residue and n had average values between three and twenty.¹ Using a Langes gold sol they found, at least for NaCl and $CaCl_2$, that the Schultze-Hardy rule was minimized. In fact, the coagulating power of the calcium ions was less than that of the sodium ions. They worked in a concentration region from 1.0×10^{-4} to 7.0×10^{-4} % of stabilizing agent and used from 0.5% to 3.5% salt concentrations to coagulate the protected sol.

In a case very similar to the model where long-chain polymers protect a hydrosol particle by "steric effects," a group of investigators in Holland have found that just such a model exists for a carbon dispersion in an organic solvent.^{2,3,4} For a stabilizer, they used an aromatic nucleus which contained alkyl side chains of varying length. They found by calculation and experiment that the longer the side chain the better the stability. Their theory and experiments showed that the aromatic nucleus as the "head" was adsorbed

¹T. M. Doscher, G. E. Myers and D. C. Atkins, Jr., J. Colloid Sci., 6, 223-35 (1951).

²M. van der Waarden, J. Colloid Sci., 5, 317-25 (1950).

³E. L. Mackor, J. Colloid Sci., 6, 492-96 (1951).

⁴E. L. Mackor and J. H. van der Waals, J. Colloid Sci., 7, 535-50 (1952).

on the surface of the organophobic particle while the side chain or "tail" was sticking out into the solvent. The stability can be accounted for by considering the decrease in the number of configurations of the adsorbed molecules when two stabilized particles approach each other. This decrease is said to be caused by an increase in "configurational free energy" and hence leads to a repulsive force which at short distances will counteract the relatively long range van der Waal-London attractive forces between colloidal particles.

CHAPTER III

EXPERIMENTAL

Section A. Equipment

In checking protective action a series of solutions all containing the same amount of protecting agent and gold sol can be used. The amount of coagulant is varied systematically in the series to determine the coagulation point. To accomplish this, pyrex 3/4" dia. x 6" test tubes were used in the test tube racks previously painted white in order to present a better background for comparison.

The specially purified water which is necessary for the preparation of a gold sol and which was also used for the solutions of polyethylene glycol was obtained by distillation from an all-pyrex glass distillation apparatus. The water was collected and stored until needed in pyrex, glass-stoppered, reagent bottles. During the collection of water the end of the condenser and the bottle neck were wrapped with tin foil in order to prevent any dust in the air from entering the system.

Buell showed in his work that the refractive index of polyethylene glycol solutions varied considerably with the concentration.¹ This variation, proved linear, was thus a

¹W. Buell, Thesis, Wayne University, 1949, p. 6.

convenient method for measuring the concentration of the solutions. For this purpose, as in the work of Buell, the dipping refractometer was used which allowed a measurement of the concentration to ± 0.007 g. per 100 ml. The refractive index itself was reproduced to ± 0.00001 units with a constant temperature bath which was held to a temperature of $\pm 0.01^\circ\text{C}$. The bath control unit which is capable of much higher precision ($\pm 0.001^\circ\text{C}$), with a suitable thermoregulator was built at a cost of \$30.00 and was patterned after that described by Garrett.¹

Section B. Preparation of the Materials

A gold sol was prepared with a slight modification according to the nuclear method mentioned by Rinde.² For a water supply throughout the experiment particularly in the preparation of the gold sol a dust-free, double-distilled water was used. The first distillation was through an ordinary commercial still, while the second was performed in the pyrex apparatus described in the previous section of this chapter. All the chemicals were reagent grade except the red phosphorus which was Merck ungraded. The solutions necessary for the gold sol preparation were made up as follows: 500 ml. of a saturated red phosphorus ethanol solution was prepared using 95% ethanol; it was then filtered

¹A. B. Garrett, Ind. Eng. Chem., 25, 355 (1933).

²H. Rinde, Inaugural Dissertation, Uppsala, 1928, p. 26.

three times to remove any undissolved material. The solution was diluted with 500 ml. of 95% ethanol and stored in a one-liter glass-stoppered, pyrex, volumetric flask.

0.014 M $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and 0.208 N K_2CO_3 solutions were also prepared using the double distilled water and were stored in the pyrex volumetric flasks.

The recipe which resulted in the most intense red sol was prepared by placing 110 ml. of the double distilled water into clean, unscratched 400 ml. beakers. 3.4ml. of the AuCl_3 solution, 1.0 ml of the K_2CO_3 solutions and 2.0 ml of the P in EtOH were added. At this point, the solution mixture is colorless and is placed over a flame and allowed to come to boil. Just as the boiling starts another 0.7 ml of K_2CO_3 solution is added. After boiling for 2 to 5 minutes the solution passes from colorless to blue and finally to a clear, intensely red sol. By no other method of addition of the K_2CO_3 was a clear sol obtained. And yet, if the extra addition of K_2CO_3 was left out, the sol did not form, indicating that the acidity was still a little too high. The sols were allowed to cool and then transferred to liter pyrex volumetric flasks. The stoppers were sealed with paraffin wax to prevent evaporation.

It was noted that if there were any scratches in the beakers they seemed to serve as precipitation points which led to the formation of an orange-brown precipitate. About one-half of the sols produced were discarded because of this

precipitate formation. Ten liters of gold sol were prepared using this method. When attempts were made to prepare large batches of sol at once, i.e. 500 mls, poor sols resulted. They were either too light in color or contained the orange-brown precipitate. After storing the sols for two months in liter volumetric flasks, they were all put together in one large reservoir. The container was a 12-liter, round bottom, pyrex flask, which was stored in a dark, cool cabinet. A rubber stopper wrapped in tin foil was used to stopper the flask. The large reservoir was used so that all the tests conducted would have the same concentration of gold sol. The gold concentration in the sol was approximately 11.5 mg per 100 ml of sol. The concentration in the actual tests was 8.85 mg/100 ml of sol.

Whether the P or the EtOH is the reducing agent in this method is difficult to determine, since both components have been used in other reduction methods.¹ Even after the boiling there is still a slight odor of the alcohol in the sol which could possibly be responsible for its high stability which has been 20 months, so far.

The polyethylene glycols, which were obtained from the Texas plant of the Dow Chemical Company, were purified by filtering the liquids and reprecipitating the solids from organic solvents. The polyethylene glycols are liquids up

¹The Svedberg, "Kolloider Lösungen," Dresden, Germany: Theoder Steinkopff, 1951, pp. 47, 50.

through the $\bar{M}$ -600. These liquid fractions were filtered twice through sintered pyrex glass filters with suction. They were then placed in a vacuum desiccator with P_2O_5 as a desiccant and evacuated until their weights were constant.

The solid members which ranged from $\bar{M}$ -1000 to $\bar{M}$ -9000 were dissolved in reagent grade acetone with a little heat to increase the solubility. The solutions were then filtered through the sintered glass filter and reprecipitated with redistilled hexane. Since hexane proved too difficult to be removed by the vacuum desiccator, the polymers were shaken three times with fresh portions of ether that had been dried over P_2O_5 and distilled onto sodium. Next, the polymers were placed on porous plates in vacuum desiccators and dried to constant weight.

Only three fractions of the molecular weight series were used in making this investigation: $\bar{M}$ -600, $\bar{M}$ -6000, and $\bar{M}$ -9000. Using the dipping refractometer, calibration curves were prepared giving the refractive index as a function of polymer concentration. Once these curves were available, one could produce any concentration of polymer without accurate weighing or constant weight drying. In order to conserve on dried material the various concentrations for the calibration curves were made from one stock solution which had been prepared by weighing the polymer directly, dissolving it in double-distilled water and diluting to 100 mls in pyrex, glass-stoppered volumetric flasks.

Since these polymers do not exhibit volume additivity in good solvents, it was necessary to check the error, if any, in diluting the stock solution. The advantage here was that a relatively low concentration was being diluted and there was the possibility that the error in volume additivity may not be greater than the dilution error.

A short experiment was carried out to check this error. Using the advantage of weighing a solid material, $\bar{M}$ -6000 was used in the experiment. Taking a 100 ml burette and a dry 100 ml volumetric flask, 5.000 g. of the polymer were placed in the flask. Enough distilled water was added to dissolve the $\bar{M}$ -6000. After the polymer had dissolved and while swirling the flask to ensure complete mixture of any added water, the volumetric flask was filled to the 100 ml mark. Thus, the flask contained 5.000 g of polymer and 95.8 ml of H_2O . Fifty ml of the solution which now contained 2.500 g of polymer and 47.9 ml of H_2O were pippetted into a dry volumetric flask. Again with swirling, distilled water was added to the 100 ml mark. It required 50.1 ml of H_2O , thus giving 2.500 grams of polymer with $50.1 + 47.9$ ml or 98.0 ml of H_2O . This result was compared with one obtained by placing 2.500 g of polymer in a dry flask and repeating the water adding procedure. It took 97.8 ml to fill the flask.

The difference between this and 98.0 ml is only 0.20% which is hardly detectable in a volumetric flask with an accuracy of 0.16%. Another check-point on the non-additivity

error, however, is found in the calibration curves or the experimental $\Delta n/c$ values. If a curved line, or a straight line with a scattering of the experimental points in the higher concentration regions were obtained, an error would be apparent. A similar comparison can be made of the $\Delta n/c$ values. $\Delta n/c$ is defined by:

$$\frac{\Delta n}{c} = \frac{n_s - n_m}{c}$$

n_s = refractive index of the solution

n_m = refractive index of the solvent

Δn = difference between the n values

c = concentration in g/100 ml of solution.

Using the data from Tables I-III the calibration curves shown in Figures 1-3 were constructed. As one can observe by the position of the points, there was no serious additivity error. These curves are nearly superimposable upon those developed by Buell for his work.^{1,2} A comparison of three independent research projects, including this one, shows that a fair reproduction of average $\Delta n/c$ values are possible, see Table IV.^{3,4} Table III was needed for the conversion of Tanaka's data which was originally determined

¹ Buell, op. cit., p. 6.

² See Chapter VI of this thesis for other refractive index data.

³ W. Tanaka, Thesis, Wayne Univ. 1951, pp. 47 and 50.

⁴ Buell, op. cit., p. 12.

using g/100 g for polymer concentrations.

TABLE I
REFRACTIVE INDEX vs. CONCENTRATION

$\bar{M} - 600$		
Concn. g/100 ml	n_D 25.00°C	$\frac{\Delta n}{c}$
0.000	1.33252	
0.679	1.33337	.001252
1.698	1.33467	.001266
2.548	1.33577	.001276
4.246	1.33796	.001283
5.095	1.33903	.001278

Ave. 001271

TABLE II
REFRACTIVE INDEX vs. CONCENTRATION

$\bar{M} - 6000$		
Concn. g/100 ml	n_D 25.00°C	$\frac{\Delta n}{c}$
0.000	1.33252	
0.539	1.33324	.001336
1.616	1.33470	.001349
2.694	1.33612	.001336
4.310	1.33830	.001341
5.388	1.33979	.001349

Ave .001342

TABLE III
REFRACTIVE INDEX vs. CONCENTRATION

$\bar{M} = 9000$

Conc. g/100 ml	n_D 25.00°C	$\frac{\Delta n}{c}$
0.000	1.33252	
0.580	1.33330	.001345
1.451	1.33446	.001337
2.419	1.33576	.001339
3.386	1.33705	.001338
4.837	1.33904	.001348

Ave .001341

n_D 25°C

FIG. 1 $\bar{M}$ -600

REFRACTIVE INDEX
VS.
POLYMER CONCN.

1.339

1.338

1.337

1.336

1.335

1.334

1.333

1.332

1.00

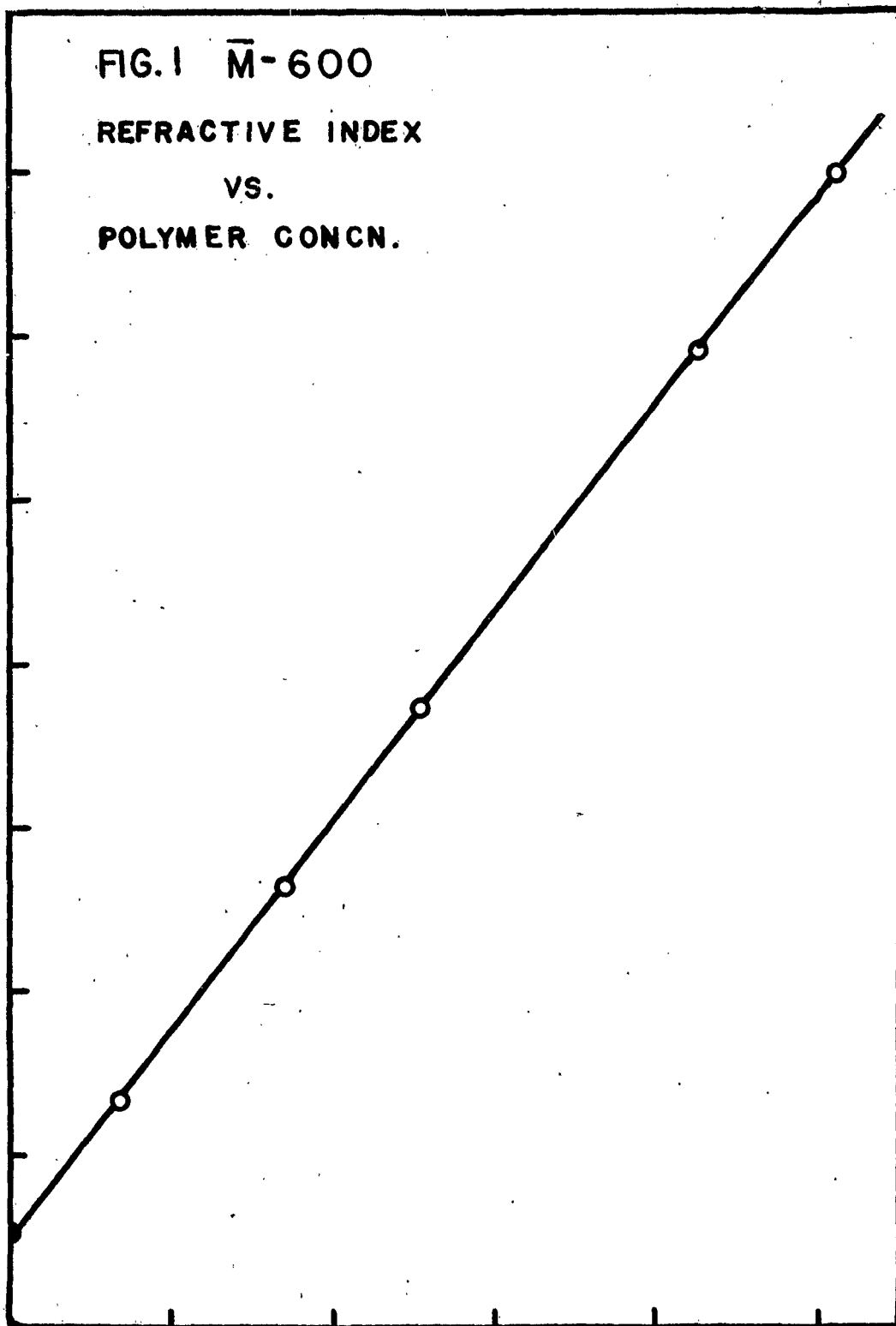
2.00

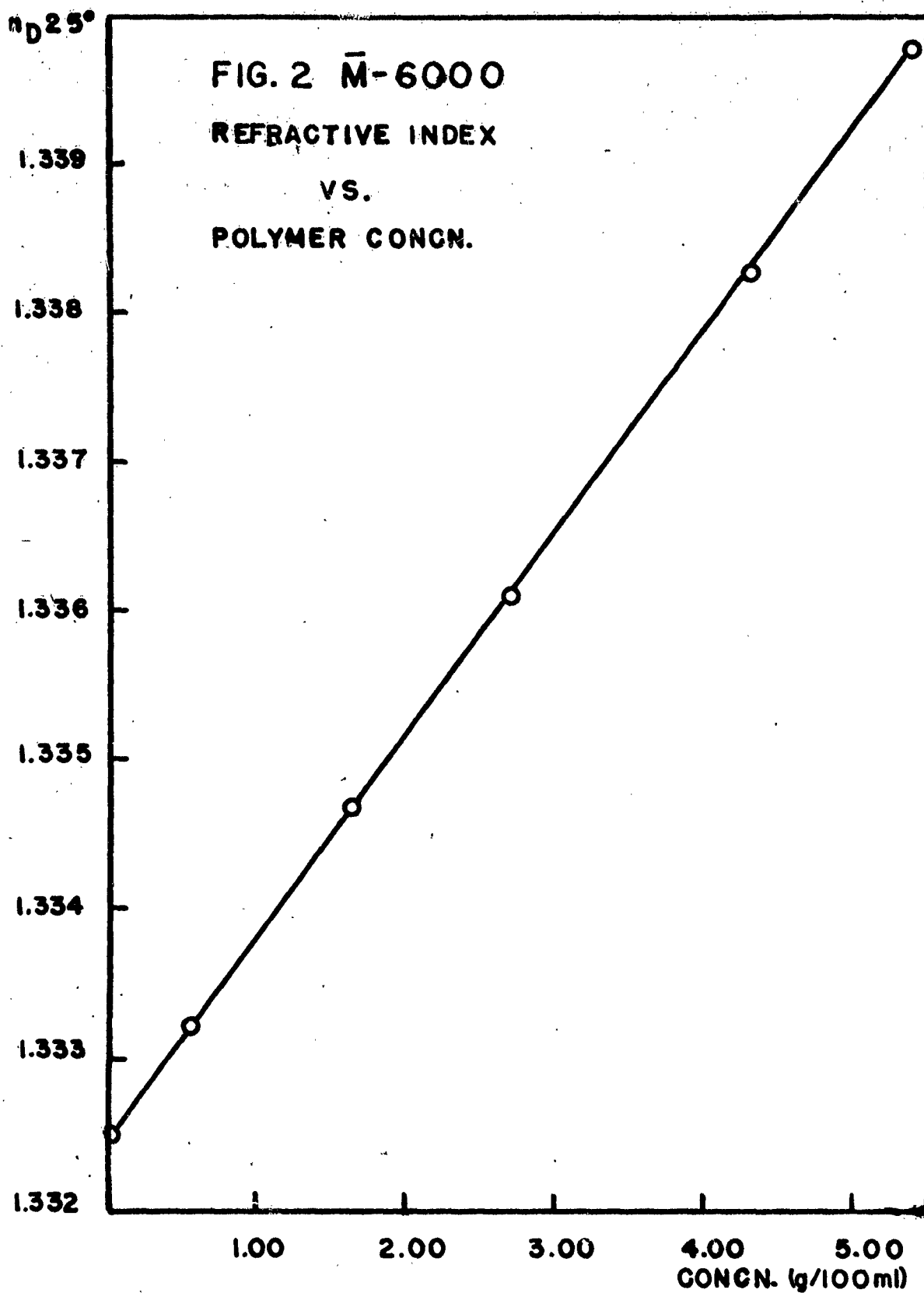
3.00

4.00

5.00

CONCN.(g/100ml.)





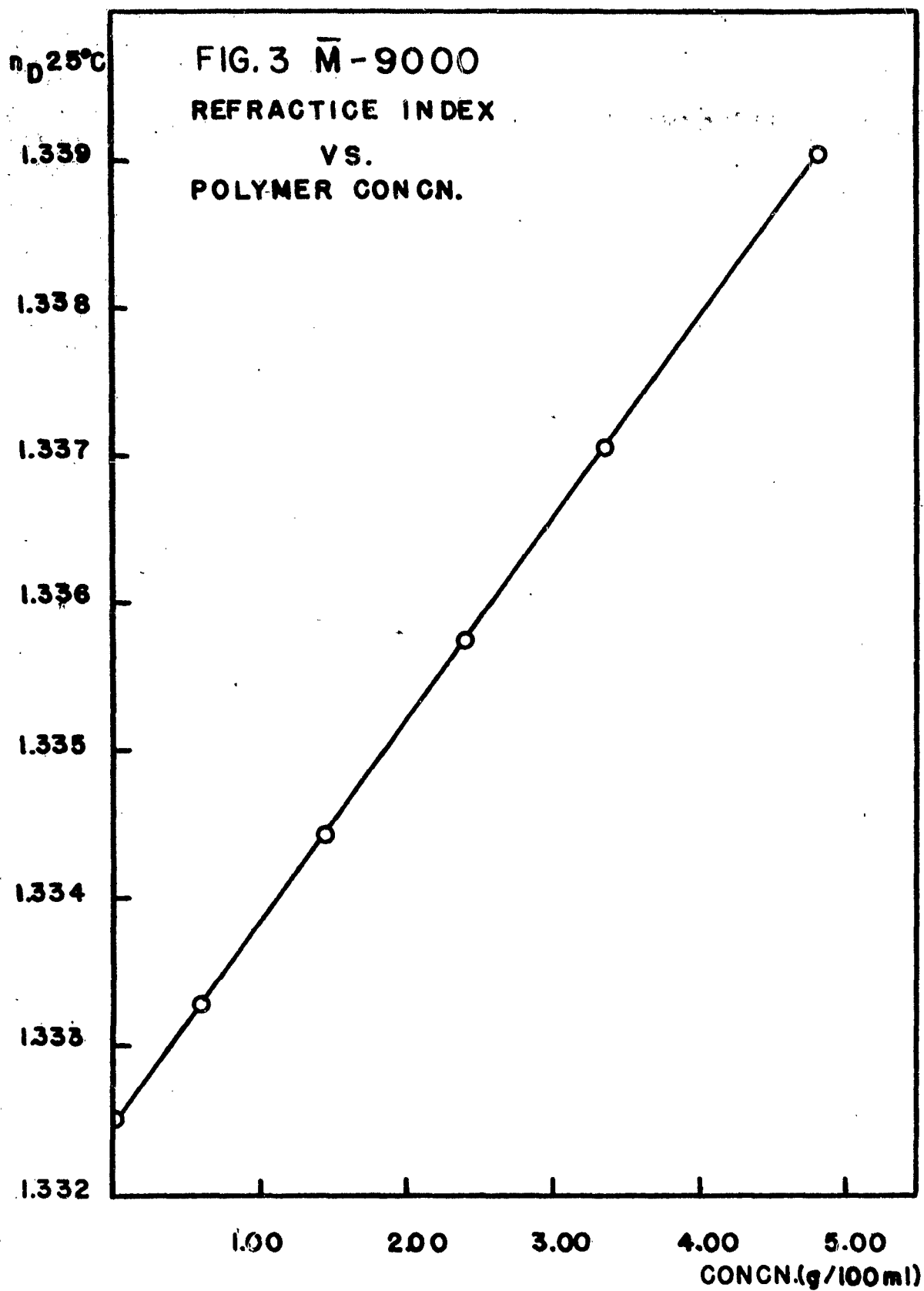


TABLE IV

CONVERSION OF TANAKA'S DATA¹

from g/100 g of soln. to g/100 ml of soln.

	$\bar{M}$ -300	$\bar{M}$ -600	$\bar{M}$ -6000
Ave concn. g/100 g	.2134	.2862	.2191
Δd of ave concn.	.001438	.001451	.001583
d of soln.	.9974	.9975	.9974
$(\Delta n/c)$ g/100 g	.001197	.001266	.001338
$(\Delta n/c)$ g/100 ml	.001200	.001269	.001341

TABLE V

COMPARISON OF $\frac{\Delta n}{c}$ OF THREE INDEPENDENT SOURCES

Polymer	Tanaka ² $\Delta n/c$	Buell ³ $\Delta n/c$	This Investigation $\Delta n/c$
$\bar{M}$ - 300	0.001200	-	.001243
$\bar{M}$ - 600	0.001269	0.001300	.001271
$\bar{M}$ - 6000	0.001341	0.001345	.001342

It is surprising that Tanaka's data was determined using a different wavelength of light (546 m μ) and still

¹Tanaka, op. cit., pp. 47 and 50.

²Ibid.

³Buell, op. cit., p. 12.

agrees fairly well. Both Tanaka's and Buell's average $\Delta n/c$ values were obtained by weighing dry polymer for all concentrations thus eliminating any additivity errors. However, by comparison, one can see that good results were obtained by using dilutions in this investigation.

Another surprising factor is that the two other investigators both used a supply of polymers from another source and despite the possibility of different fractionation and preparation techniques, the $\Delta n/c$ values for the different molecular weight fractions are similar.

Since the precision of the concentration was limited to ± 0.01 g/100 ml, on the graph, it was necessary to dilute from higher concentrations for anything needed below 0.50 g/100 ml.

Salt solutions of KCl in double distilled water were prepared by weighing KCl, placing it in volumetric flasks, and diluting to the required mark. Concentrations were expressed in mMoles per liter of solution.

Section C. Experimental Procedure

The "gold sol reaction" is really a misnomer for no true chemical reaction takes place in a coagulation experiment. When one produces a finely divided gold sol, the sol is an intense wine red. However, upon electrolyte addition the particles agglomerate due to the neutralization of the surface charge of the particle. When the particle size

increases due to coagulation, the sols change from red to blue, similar to an indicator when the end point of a reaction has been reached. If a protective agent is present the red sol exhibits a resistance to coagulation or turning blue. This resistance is a sign of protective action. It is measured by the concentration or number of mg of KCl it takes to just coagulate a predetermined volume of gold sol.

The advantages of using a gold sol for protective action tests are many. In the first place, the preparation and the uses of the gold sol have been repeated many times. The fact that many investigations have used the gold sol for protective action experiments allows, at least, a relative comparison of results of this work with that of the past. The gold sol is easily made and if prepared properly will be stable for long periods of time. (The sol in this laboratory has been stable for 20 months without any addition of stabilizing agent.) The main advantage for using gold sol, of course, is the red to blue "end point reaction."

Even though the gold sols themselves and sometimes the gold numbers are not reproducible in different laboratories, the results for relative protective action effects from one batch of gold sol cannot be denied. Thus the gold sol and the "gold sol reaction" ideally suit the purpose of this experiment.

In using the "gold sol reaction," several arbitrary factors must be established and carried throughout the

experiment if the results of each series of tests are to be compared. The first condition which must be set is the time of observation after the mixing of the salt solutions with the protected sols. All three polymer fractions were checked along with a blank in the same experiment. Often more than one experiment would be carried out in one day. So that the per cent error in the time of coagulation would be low and to allow the preparation of more than one experiment in one day, 24 hours was used as the time elapsing between the time of addition of coagulant and the time of observation.

Since all tests must be carried out on the same "stock solution" of gold sol, it had to be conserved wherever possible. On the other hand, a large enough sample must be placed in the test tubes so that it can be easily observed. A total sample of approximately 10 ml in a six-inch test tube satisfied this last condition. For experimental convenience 9.1 ml was used as the exact total volume used throughout the investigation. Seven ml of this total volume consisted of gold sol.

In this research, a "series" consisted of six or seven test tubes, all containing the same amounts of gold sol and one protecting agent, plus a systematically varied amount of KCl. A "run" consists of four "series": a blank, $\bar{M}$ -600, $\bar{M}$ -6000 and $\bar{M}$ -9000. For comparison reasons the concentrations of the polymers in one "run" were matched as closely as possible.

The procedure for a "run" was as follows: Qualitatively, the amounts of KCl were predetermined by a "titration" of the sol with the KCl solution to be used in that particular series. A table was then constructed, prearranging all the amounts of additives to the gold sol: water, polymer solution, and coagulant. Using automatic, gravity-feed burettes for the gold sol, water and coagulant, the solutions were added in the following order to a "run" of test tubes: Seven ml of gold sol were added to all 28 test tubes of a run. Next the water necessary to make all total volumes equal was added. The protective colloid solution was added or in the case of the blank, an appropriate volume of water was put in with the previous water addition. At this point, the solutions were stirred with a pyrex rod which contained a loop in the end. Then while stirring with the glass loop, the coagulant or KCl solution was added. The time of the addition of the coagulant to a particular "series" was noted when the coagulant was added to the central, or in this experiment, the fourth test tube. Thus for one "run," there were four times to be noted. If there was a mistake in time notation, as mentioned previously, the 24 hour time of coagulation resulted in a very small per cent error of time observation.

The coagulation values were first recorded as that test tube number which first showed signs of coagulation. Later,

the coagulation values were transformed to the limits within which the true coagulation value must lie. This value can be defined as that concentration of coagulant which just coagulates or just prevents coagulation of the gold sol. By taking the concentration of the last test tube unaffected by coagulation and the one which shows the first signs of coagulation, the coagulation value by either definition must fall within these bounds. The symbol γ is used for the coagulation values which are expressed as the KCl concentration in the test tube in mMoles per liter of sol. In most cases, it would be too time-consuming to expand a "series" between the uncoagulated and the coagulated test tube to obtain data a little more significant. In preparing another "series" which uses the uncoagulated tube as the lowest member of the new series and the coagulated as the highest, the differentiation from one tube to the next might be so little that the end point would be too indistinct to be of any value. Only in a case where there might be an overlapping of coagulation values of two polymer weight fractions would an expansion of a "series" be considered. A sample "run" can be seen in Table VI. The results of all the data and the graphs are shown in Chapter IV, while the discussion of their significance is reserved for Chapter V.

TABLE VI

SAMPLE TABLE OF A TYPICAL "RUN"

BLANK Time Started: 12:40 P.M. Time Checked: 12:40 P.M.

T.T. No.	Ml of 1 M KCl	Ml of H ₂ O	Concn. of KCl (moles/l)	Results
1	0.05	2.05	0.0055	tube No. 3 .010M < c < .020M
2	0.09	2.01	0.010	
3	0.18	1.92	0.020	
4	0.27	1.83	0.030	
5	0.36	1.74	0.040	
6	0.46	1.64	0.051	
7	0.55	1.55	0.060	

M-600 0.34 ml of 2.86 g/100 ml

Time Started: 12:45 P.M. Time Checked: 12:45 P.M.

T.T. No.	Ml of 1 M KCl	Ml of H ₂ O	Concn. of KCl (moles/l)	Results
1	0.05	1.71	0.0055	tube No. 5 .020 M < c < .025M
2	0.09	1.67	0.010	
3	0.14	1.62	0.015	
4	0.18	1.58	0.020	
5	0.23	1.53	0.025	
6	0.32	1.44	0.035	
7	0.41	1.35	0.045	

TABLE VI - Continued

M-6000 0.34 ml of 2.81 g/100 ml
Time Started: 12:50 P.M. Time Checked: 12:50 P.M.

T.T. No.	Ml of 1 M KCl	Ml of H ₂ O	Conc. of KCl (moles/l)	Results
1	0.20	1.56	0.022	tube No. 4 .044 M < c < .055 M
2	0.30	1.46	0.033	
3	0.40	1.36	0.044	
4	0.50	1.26	0.055	
5	0.60	1.16	0.066	
6	0.70	1.06	0.077	
7	0.80	0.96	0.088	

M-9000 0.36 ml of 2.69 g/100 ml
Time Started: 1:00 P.M. Time Checked: 1:00 P.M.

T.T. No.	Ml of 1 M KCl	Ml of H ₂ O	Conc. of KCl (moles/l)	Results
1	0.55	1.19	0.181	tube No. 6 0.445 M < c < 0.511 M
2	0.75	0.99	0.247	
3	0.95	0.79	0.313	
4	1.15	0.59	0.379	
5	1.35	0.39	0.445	
6	1.55	0.19	0.511	
7	1.75	0.00	0.577	

CHAPTER IV

DATA AND GRAPHS

Tables VII - X contain the results of the protective action experiments.

TABLE VII - BLANK

POLYMER CONCENTRATION
v.s.
COAGULATION VALUES

Run No.	Polymer Concn.	Coagulation Values mM/l KCl
1	0.00	15-20
2	0.00	10-20
3	0.00	10-15
4	0.00	10-15
5	0.00	10-15
6	0.00	10-15
7	-	Ave 10-15

TABLE VIII - M-600

POLYMER CONCENTRATION
v.s.
COAGULATION VALUES

Run No.	Polymer Concn. g/100 ml	Coagulation Values mM/l KCl
1	-	-
2	0.0056	10-15
3	0.0101	10-15
4	0.0314	16-22
5	0.0660	15-20
6	0.107	20-25
7	0.229	20-25

TABLE IX - $\bar{M}$ -6000

POLYMER CONCENTRATION
v.s.
COAGULATION VALUES

Run No.	Polymer Concn. g/100 ml	Coagulation Values mM/l KCl
1	-	-
2	0.0056	10-15
3	0.0101	15-20
4	0.0309	11-22
5	0.0648	22-33
6	0.105	44-55
7	0.230	60-80

TABLE X - $\bar{M}$ -9000

POLYMER CONCENTRATION
v.s.
COAGULATION VALUES

Run No.	Polmyer Concn. g/100 ml	Coagulation Values mM/l KCl
1	0.0011	10-15
2	0.0057	25-30
3	0.0103	44-55
4	0.0325	181-247
5	0.0650	379-445
6	0.106	445-511
7	0.230	508-659

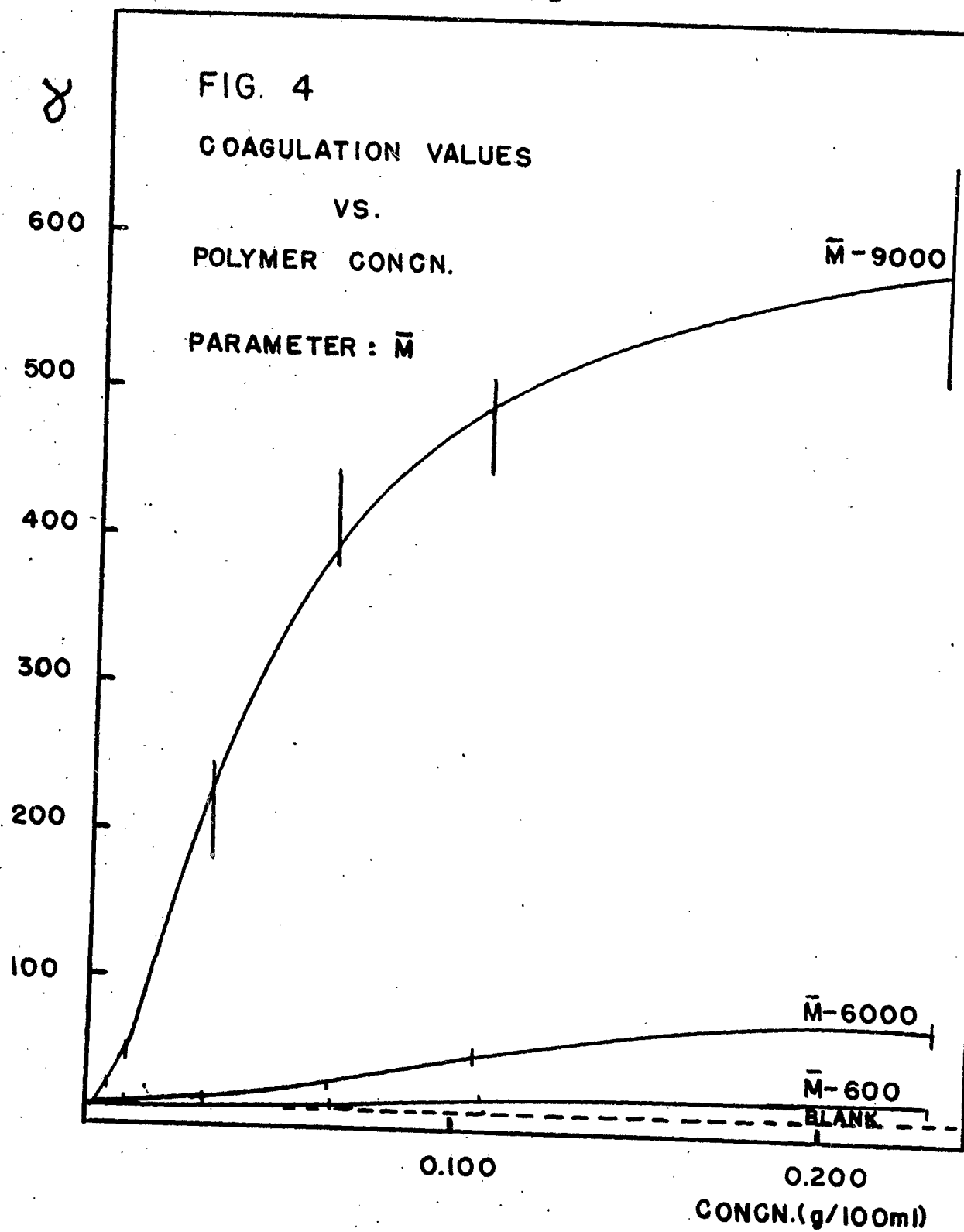
TABLE XI

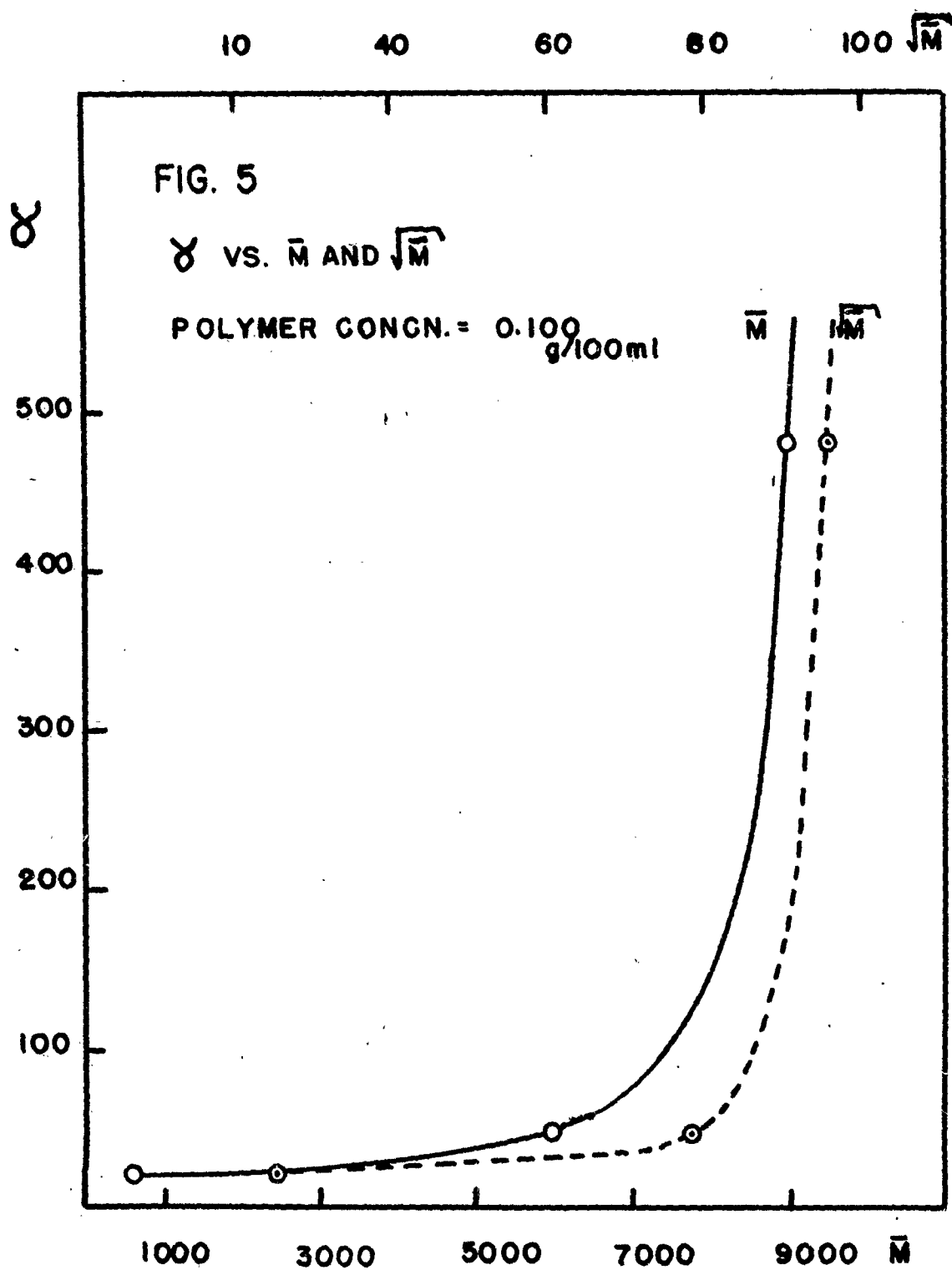
$\bar{M}$ AND $\sqrt{\bar{M}}$ vs. γ

CONCN. OF POLYMERS:

0.100 g/100 ml

$\bar{M}$	$\sqrt{\bar{M}}$	γ
600	24.5	18
6000	77.5	47
9000	94.8	480





CHAPTER V

DISCUSSION OF RESULTS

In Figure 4, there is drawn for comparison the four curves of the coagulation experiment which are plotted as coagulation values (ζ) vs. polymer concentration. The molecular weight of the polymers is the parameter of these curves. The blank is drawn in for comparison as a constant value and naturally does not contain any polymer addition. This average ζ for the blank was 10-15 which means that the concentration of KCl in millimoles per liter of sol was between 10 and 15.

The first question that is answered by these resulting curves is that non-ionic long-chain polymers definitely protect gold sol. In fact, the $\bar{M}$ -9000 protects extremely well in comparison to the other weight fractions. This signifies that there is, apparently, a critical molecular weight or chain length which yields protection. For this reason in Figure 5 a curve was drawn for comparison with dotted lines showing the ζ as a function of statistical chain length, $\bar{L}$. This $\bar{L}$ is proportional to the square root of the "stretched" chain length, $\bar{L}_0$, which is, in turn, proportional to the average molecular weight, $\bar{M}$.

Therefore: $L = k\sqrt{L_0} = K\sqrt{\bar{M}}$.

Thus, the dotted curve is drawn by using γ versus the square root of $\bar{M}$. Both of these curves are at a polymer concentration of 0.100 g/100 ml of sol. These two curves show the strong dependence of protective action on chain length. If the model for "steric effects" is used, one would expect a sharp increase in protection after some critical chain length had been reached. This critical value lies in between $\bar{M}$ -6000 and $\bar{M}$ -9000. Since there is the same weight of material on the particles in each case the protection in the higher molecular weight cannot merely be attributed to coverage as one might expect with starch or dextrin. This evidence supports the model of the long-chain polymers protecting by "steric effects." This difference in protection would be even greater if molar polymer concentrations were considered in place of weight concentrations.

The tendency for the protective action, indicated by in Figure 5, to level off at higher concentrations also supports the "steric" protection theory. It is also of practical importance since one would only be wasting polymer if he added more to a sol which had already been protected to the point where polymer addition only leads to a very small increase in protective action. This leveling off probably

indicates that two things are taking place: (1) Maximum protection has been reached as soon as enough polymer molecules are present to keep the gold particles from approaching each other close enough to coagulate. (2) Further addition of polymer does not help because the polymer molecules already on the particle prevent other polymer molecules from being adsorbed on the surface. Therefore, more than likely an adsorption study would show curves very similar to those in Figure 4. In his investigation, Tanaka showed such curves for polyethylene glycol on norit. These curves showed that at a concentration in excess of about 0.40 g/100 g of solution, there was not much additional adsorption.¹ The order of adsorption was in the same order of protection, that is, the highest molecular weight was adsorbed the most and also gave the best protection.

As expected with this "steric" type of protection there was no sensitization at low concentrations of polymer. Again, if this protection were just a case of enveloping the gold sol particle one would expect sensitization, excluding hydration of the polymer. As mentioned previously sensitization occurs with non-ionic protection because the unprotected sites on a particle are easily neutralized and the protected ones do not allow the repulsive force, due to the charge, to operate.

¹Tanaka, op. cit., p. 29.

CHAPTER VI

REFRACTIVE INDICES OF POLYMER SOLUTIONS

The refractive indices of polymer solutions are important in themselves besides being a valuable tool for investigations. For these reasons, the refractive indices of the entire series of polyethylene glycols are being presented here. See Chapter III B for $\bar{M}$ -600, $\bar{M}$ -6000 and $\bar{M}$ -9000 data and curves. The data of the other molecular weights and the curves are presented here along with a complete table and graph of molecular weight versus $\Delta n/c$. As also shown by Tanaka¹ and indicated preliminarily by the data of Buell,² $\Delta n/c$ increases as the molecular weight increases.

Both Tanaka and Buell obtained their concentrations by weighing the dried polymer for each concentration checked.^{3,4} In this investigation one low concentration stock solution was made and dilutions of it provided the lower concentrations. A low concentration was used for the stock solution in order to keep the additivity error at a minimum.

¹ Tanaka, op. cit., p. 47 and p. 50.

² Buell, op. cit., p. 12.

³ Tanaka, op. cit., p. 11.

⁴ Buell, op. cit., p. 14.

Naturally, the lower molecular weight fractions, which are more hygroscopic than the higher members, are subject to a larger additivity error. As one can see by the constancy of the $\Delta n/c$ values of a particular molecular weight fraction and relationship of the average values in this investigation to other independent sources, the volume error was minimal. The comparison to these other investigations was presented earlier in Table V. As mentioned before, Tanaka's data was in g/100 g of solution and the refractive index was measured using the Hg green line at 546 mu.

Tables XI-XIV give refractive index data which are plotted in Figures 6-10. In Table XV and XVI are the complete results of average $\Delta n/c$ values versus $\bar{M}$ for this investigation and those of Tanaka's. The results are plotted together in Figure 11. This plot shows that the refractive index of the polymer solutions approaches a constant value. Although the data are determined at two different wavelengths the similarity of shape and data shows that the polymer refractive index must not change very much with a change in wavelength.

REFRACTIVE INDEX vs. POLYMER CONCENTRATION

TABLE XII

$\bar{M}$ -300

Concn. g/100 ml	n_D 25.00°C	$\frac{\Delta n}{c}$
0.000	1.33252	
0.622	1.33327	.001205
1.778	1.33472	.001237
2.440	1.33553	.001234
3.485	1.33684	.001240
4.979	1.33876	.001243

Ave .001243

TABLE XIII

M-400

Concn. g/100 ml	n_D 25.00° C	$\frac{\Delta n}{c}$
0.000	1.33252	
0.542	1.33319	.001236
1.355	1.33419	.001232
2.033	1.33507	.001254
3.388	1.33678	.001257
4.744	1.33850	.001261

Ave .001248

TABLE XIV

$\bar{M}$ -1000

Concn.	n_D	$\frac{\Delta n}{c}$
0.000	1.33252	
0.554	1.33324	.001300
1.385	1.33433	.001307
2.308	1.33554	.001308
3.230	1.33678	.001319
4.615	1.33861	.001320

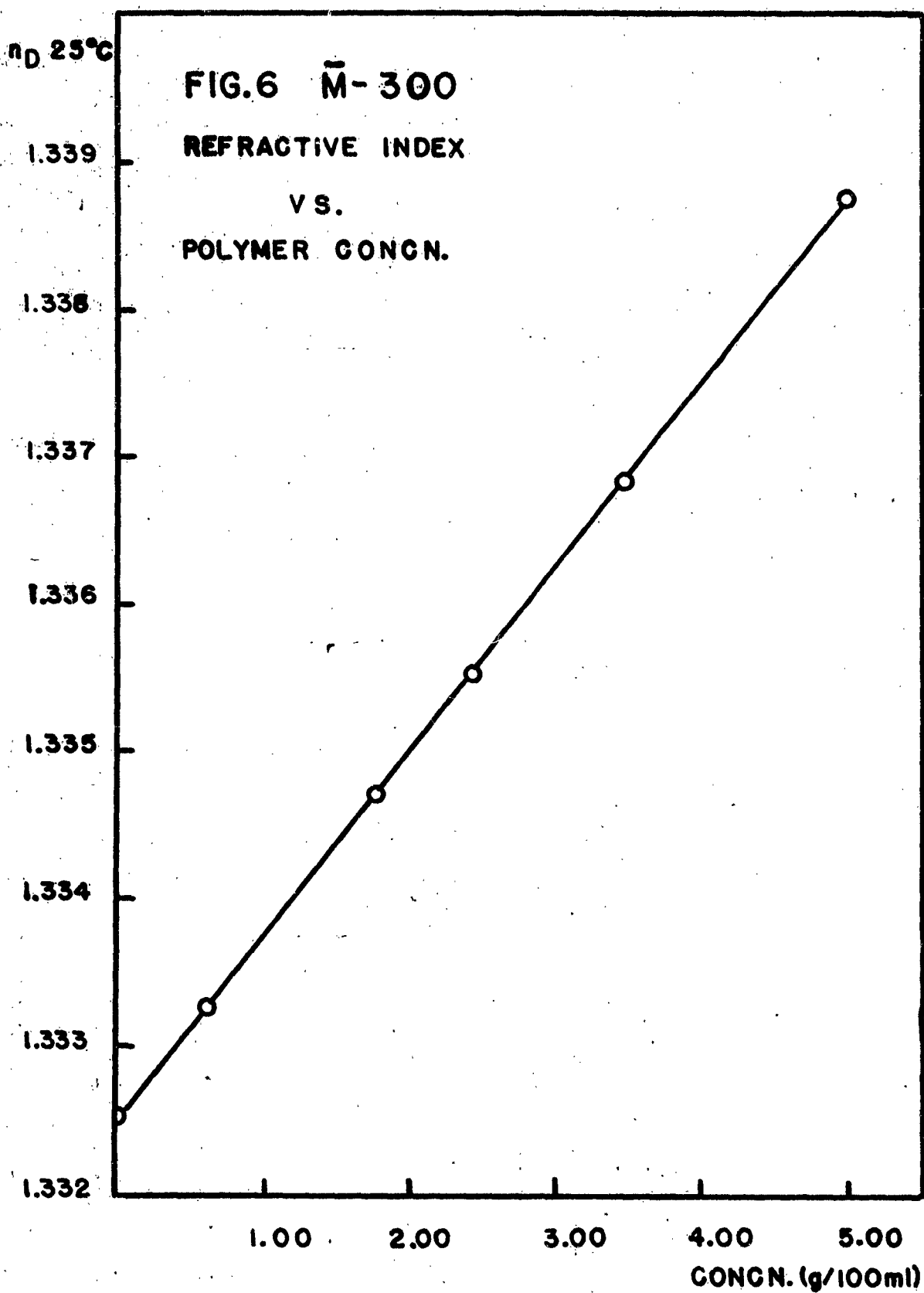
Ave .001311

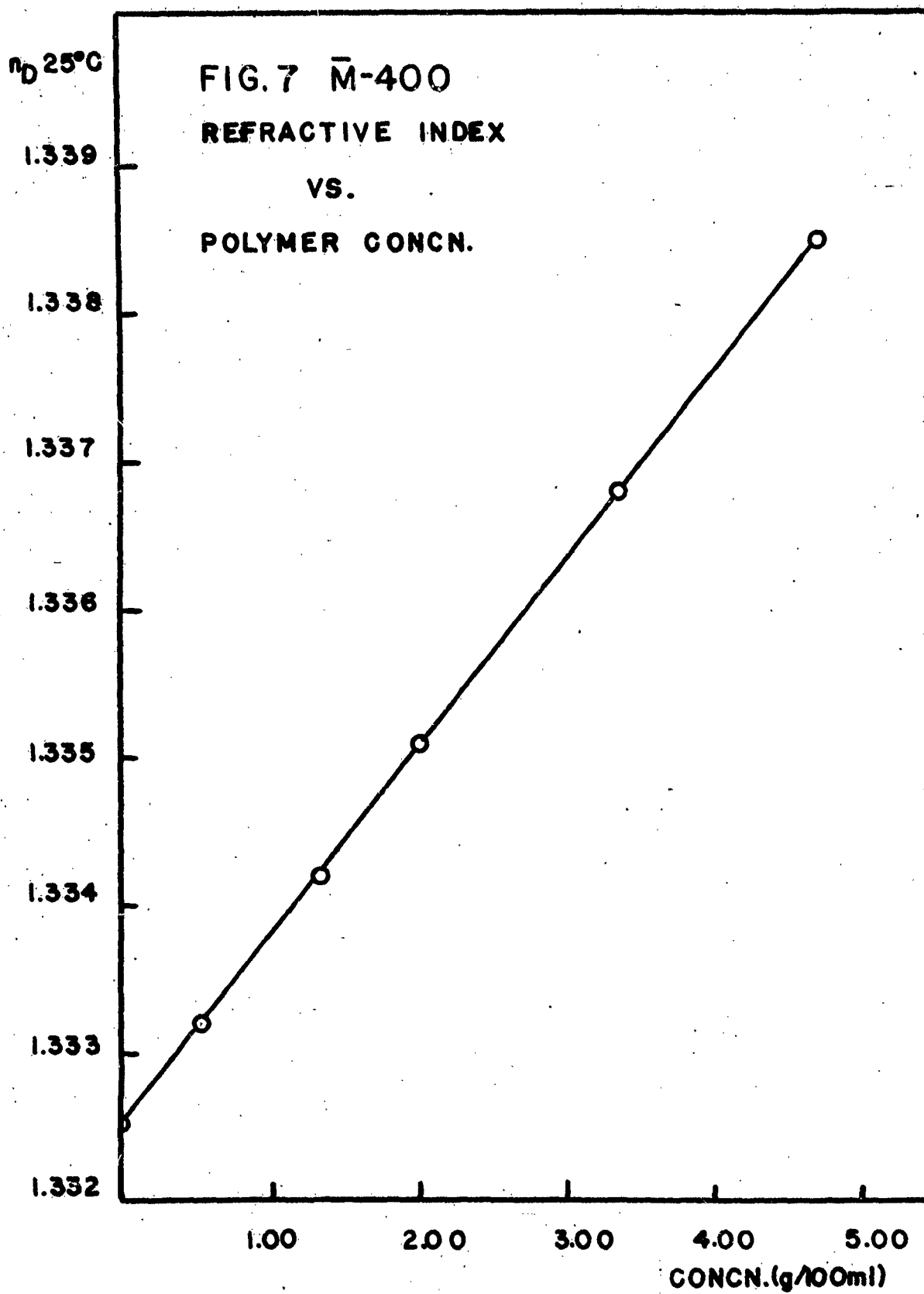
TABLE XV

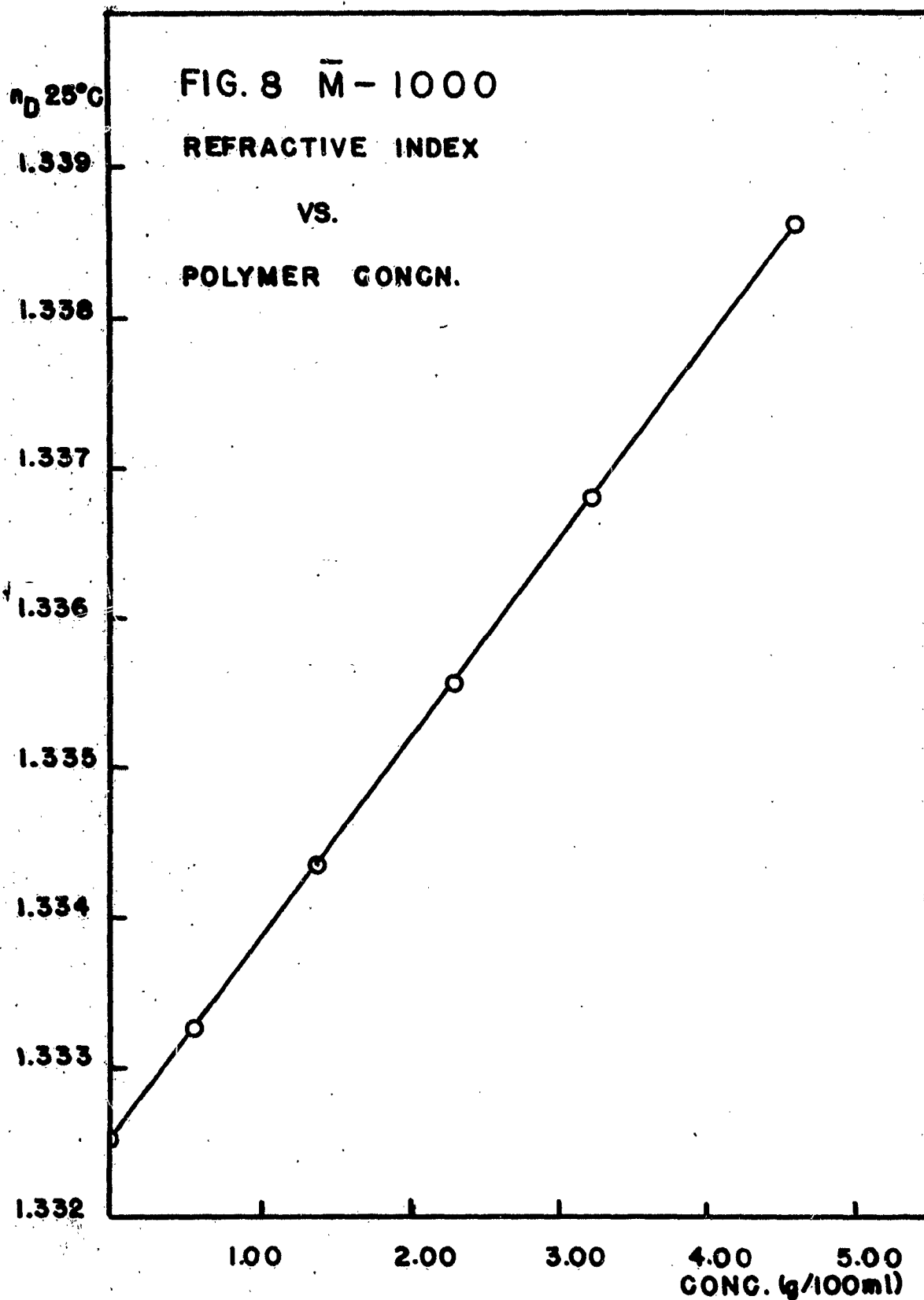
$\bar{M}$ -4000

Concn. g/100 ml	n_D 25.00°C	$\frac{\Delta n}{c}$
0.000	1.33252	
0.535	1.33323	.001327
1.605	1.33467	.001340
2.675	1.33610	.001338
4.280	1.33823	.001334
5.350	1.33969	.001340

Ave .001336







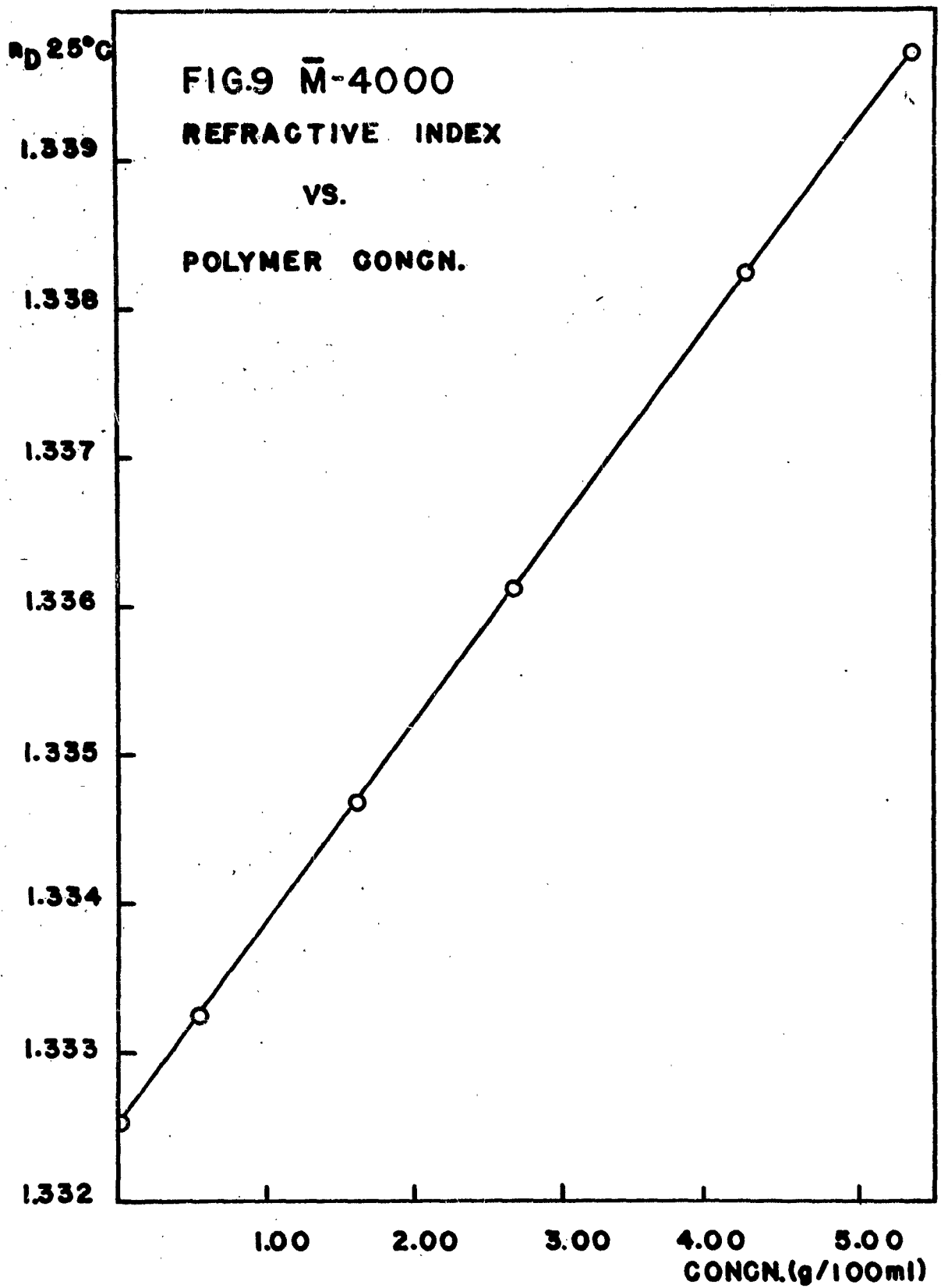


TABLE XVI

$\bar{M}$ vs. $\frac{\Delta n}{c}$

n_D 25.00°C, c = g/100 ml

Fraction	$\frac{\Delta n}{c}$
M-300	.001243
M-400	.001248
M-600	.001278
M-1000	.001311
M-4000	.001336
M-6000	.001342
M-9000	.001341

TABLE XVII

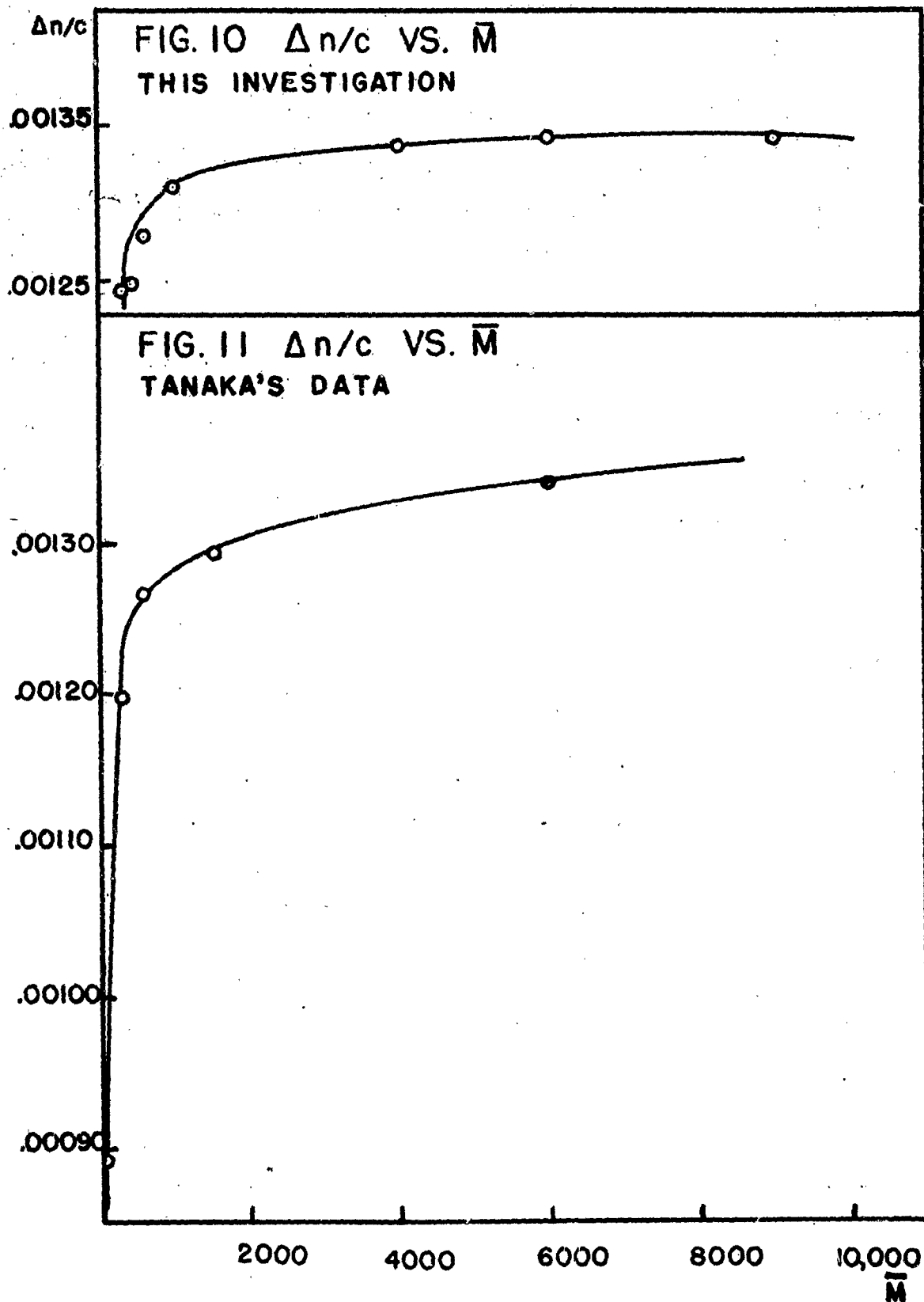
$\bar{M}$ vs. $\frac{\Delta n}{c}$

TANAKA'S DATA¹

$n_{5461 \text{ Å}}$ 25.00°C, c = g/100 g

Fraction	$\frac{\Delta n}{c}$
Monomer	0.000892
M-300	0.001197
M-600	0.001266
M-1540	0.001292
M-6000	0.001338

¹W. Tanaka, Thesis, Wayne Univ. 1951, p. 47 and p. 50.



CHAPTER VII

SUMMARY

1. It was shown that non-ionic polymers protected gold sol from coagulation.
2. The results tend to support the postulated "steric effects" model for long-chain polymers.
3. The protective action increases as a function of the molecular weight. This increase is not linear.
4. The non-linearity also supports the theory of protection due to "steric hindrance."
5. Parallelisms are shown between protective action and adsorption isotherms. The increase in protective action obtained beyond certain concentrations does not warrant additional polymer concentration after reaching these critical concentrations.
6. It is shown that there is an apparent critical chain length before protective action of any practical value is obtained.
7. No sensitization was noted at the lower concentrations according to expectations.
8. Refractive indices and $\Delta n/c$ values are given for the entire molecular weight series of polyethylene glycols.

9. It was shown, as noted previously by Tanaka,¹ that the $\Delta n/c$ values increase as a function of molecular weight. Their plot shows that the $\Delta n/c$ tends toward a constant value.

¹W. Tanaka, Thesis, Wayne Univ. 1951, p. 47 and p. 50.

BIBLIOGRAPHY

Buell, W. Thesis. Wayne Univ., 1949.

Chatterji, A. C. and Lodka, H. R. J. Indian Chem. Soc. 28
131-34 (1951).

Doscher, T. M., Meyers, G. E. and Atkins, Jr., D. C., J.
Colloid Sci., 6, 223-35 (1951).

Garrett, A. B. Ind. Eng. Chem., 25, 355 (1933).

Krulyt, H. R. and Horsting, C. W. Rec. trav. chim., 57,
737-40 (1938).

Mackor, E. L. J. Colloid Sci. 6, 492-95 (1951).

Mackor, E. L. and van der Waals, J. H. J. Colloid Sci. 7,
535-50 (1952).

Nazzaro, R. T. Paper Trade J. 121, No. 21, 90, 94 (1945).

Rinde, H. Inaugural Dissertation, Uppsala, 1928.

Shohei Uno and Naofji Ichiji, J. Chem. Soc. Japan, Pure Chem.
Section, 72, 607-10 (1951).

Stalzer, R. F., Dillon, E. S. and Vosburgh, W. C. Anal.
Chem., 22, 952-53 (1950).

Subramhanya, R., Doss, K. and Rao, B. Proc. Indian Acad.
Sci., 26A, 197-202 (1947).

Svedberg, T. Kolloider L6sungen. Dresden: Theodor Stein-
kopff, 1909.

Tanaka, W. Thesis, Wayne Univ., 1951

Tendeloo, H. J. C. Rec. trav. chim., 60, 347-48 (1941).

Titov, A. A. Kino. Fote-Khim. Prom., 1938, No. 9, 44-50;
Khim. Referat, Zhur., 2, No. 3, 129 (1939); Chem.
Abstr. 34, 921 (1940).

van der Waarden, M. J. Colloid Sci. 5, 317-25 (1950).

Distribution List--2

National Advisory Committee
for Aeronautics
1724 F Street, N. W.
Washington 25, D. C.

(1)

Chief, Bureau of Aeronautics
Department of the Navy
Washington 25, D. C.
Attn: Code AE-42

(1)

Chief, Bureau of Aeronautics
Department of the Navy
Washington 25, D. C.
Attn: Code AE-44

(1)

Chief, Bureau of Ordnance
Department of the Navy
Washington 25, D. C.
Attn: Code Rela

(1)

Chief, Bureau of Ordnance
Department of the Navy
Washington 25, D. C.
Attn: Code Re2d

(1)

Chief, Bureau of Ships
Department of the Navy
Washington 25, D. C.
Attn: Code 344

(1)

Chief, Bureau of Ships
Department of the Navy
Washington 25, D. C.
Attn: Code 346

(1)

Chief, Bureau of Ships
Department of the Navy
Washington 25, D. C.
Attn: Code 362

(1)

Chief, Bureau of Yards
and Docks
Department of the Navy
Washington 25, D. C.
Attn: Code P300

(1)

Commanding General
Wright-Air Development Center
Wright-Patterson Air Force Base
Dayton, Ohio
Attn: Materials Lab.

(1)

Office of Quartermaster General
Department of the Army
Washington 25, D. C.
Attn: Research & Development Div.
Chemicals & Plastics Branch

(1)

Commanding Officer
Signal Corps Engineering Lab.
Department of the Army
Fort Monmouth, New Jersey

(1)

Office of Chief of Engineers
Research and Development Div.
Department of the Army
Gravelly Point
Washington 25, D. C.

(1)

Engineers Research and Development
Laboratory
Ft. Belvoir, Virginia
Attn: Materials Branch
Mr. Mitton

(1)

Office of Chief of Ordnance
Department of the Army
Washington 25, D. C.
Attn: Code ORDTB

(1)

The Research & Development Board
Pentagon Building
Washington 25, D. C.
Attn: Committee on Materials

(1)

Commander
Mare Island Naval Shipyard
Rubber Laboratory
Vallejo, California

(1)

Dr. J. H. Faull, Jr.
72 Fresh Pond Lane
Cambridge 38, Massachusetts

(1)

Office of Ordnance Research
Box CM, Duke Station
Durham, North Carolina
Attn: Dr. A. Weissler

(1)

Dr. Richard S. Stein
Department of Chemistry and
Chemical Engineering
University of Massachusetts
Amherst, Massachusetts

(1)

DISTRIBUTION LIST

Technical and Summary Reports

Contract Nonr-736(00)

Project NR 330-027

Chief of Naval Research
Department of the Navy
Washington 25, D. C.
Attn: Code 424

(2)

Director
Office of Naval Research
Branch Office
346 Broadway
New York 13, New York

(1)

Director
Office of Naval Research
Branch Office
Tenth Floor
The John Crerar Library Bldg.
86 East Randolph Street
Chicago 1, Illinois

(1)

Director
Office of Naval Research
Branch Office
1030 E Green Street
Pasadena, California

(1)

Director
Office of Naval Research
Branch Office
1000 Geary Street
San Francisco 9, California

(1)

Officer-in-Charge
Office of Naval Research
Navy #100
Fleet Post Office
New York, New York

(2)

Director
Naval Research Laboratory
Washington 25, D. C.
Attn: Technical Information
Officer

(6)

Armed Services Technical
Information
Document Service Center
Knott Building
Dayton 2, Ohio

(5)

Office of Technical Services
Department of Commerce
Washington 25, D. C.

(1)

U. S. Department of Commerce
Office of Technical Services
Washington 25, D. C.

(3)

Armed Services Technical
Information Agency
Knotte Building
Dayton, Ohio

(3)

Naval Ordnance Laboratory
White Oak
Silver Spring, Maryland
Attn: Dr. Albert Lightbody

(1)

Applied Physics Laboratory
The Johns Hopkins University
8261 Georgia Avenue
Silver Spring, Maryland
Attn: Dr. Avery

(1)

Naval Ordnance Test Station
Inyokern
China Lake, California
Attn: Dr. Wiegand

(1)

Director
National Bureau of Standards
Washington 25, D. C.
Attn: Chief, Organic and
Fibrous Materials Div.

(1)