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# THE DISTRIBUTION OF MOLECULAR WEIGHT
## IN POLYSTYRENE

BY

GEORGE Y. S. LEI

A Thesis
Submitted to the Faculty of Graduate Studies through the
Department of Chemistry in Partial Fulfillment of
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of Science at the University of
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# ABSTRACT

Molecular weight distribution curves have been determined for two samples of polystyrene by fractionating them using a conventional single stage precipitation technique, followed by the measurement of the average molecular weights of the fractions by viscometry. The experimental results obtained were analysed by the usual method of plotting cumulative distribution curves. Subsequently the distribution curve for a mixture of aliquots of the two samples was obtained, and was found to agree with the expected curve which would be the sum of the curves for the two constituent samples. This finding confirms the internal self-consistency of this method for determining molecular weight distribution curves.

A comparison of the distribution curves of the individual samples with the curves predicted by postulated kinetic mechanisms of polymerization suggests that the growing radical chain is terminated by a process of combination of radicals, rather than by one of disproportionation.

# ACKNOWLEDGEMENTS

The author is greatly indebted to Dr. E. W. Channen, under whose direction and guidance the experiment was conducted, and to the National Research Council who provided financial support in the form of an operating grant.

Thank are also due to Mr. Charles Mellon and Mr. Wofgang Eberhart for their technical assistance in the design and construction of the fractionation vessel.

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# CHAPTER I

## INTRODUCTION

### General

Polymers are substances, the molecules of which consist of a large number of repeating units. Generally speaking, there are two kinds of polymer, natural polymers and synthetic polymers. The former are naturally occurring and the latter are the result of polymerization reactions. The natural polymers, such as cellulose and proteins are found in plants, etc., and are of great importance to us in food, clothing and so forth; synthetic polymers are obtained by the polymerization of a number of compounds, in which the molecules, i.e., the monomer, of one or several substances are linked together in the course of chemical reactions to form molecules with long chains of repeating units. Processes of polymerization reactions can be divided into condensation and addition polymerization.

Condensation polymerization occurs when condensation takes place between two polyfunctional molecules to produce a larger polyfunctional molecule, with the elimination of a small molecule. For example, the formation of a polyester and water, from a dibasic acid and dibasic alcohol:

$$HO(CH_2)_xOH + HO\overset{O}{\overset{\|}{C}}(CH_2)_y\overset{O}{\overset{\|}{C}}OH \longrightarrow HO(CH_2)_xO\overset{O}{\overset{\|}{C}}(CH_2)_y\overset{O}{\overset{\|}{C}}OH + H_2O$$

1

The reaction continues until one of the reagents is completely consumed.

Addition polymerization involves chain reactions in which the chain initiator may be an ion, a photon or a free radical. The free radical is usually formed by the decomposition of a relatively unstable material, such as benzoyl peroxide which easily decomposes as shown below.



initiator                          free radical
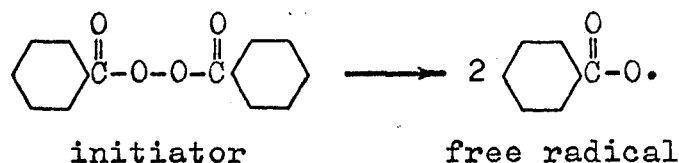
In this case, benzoyl peroxide is called an initiator. The free radical is capable of reacting to open the double bond of a vinyl monomer and add to it, with an electron remaining unpaired:



free            vinyl              growing polymer
radical         monomer                chain
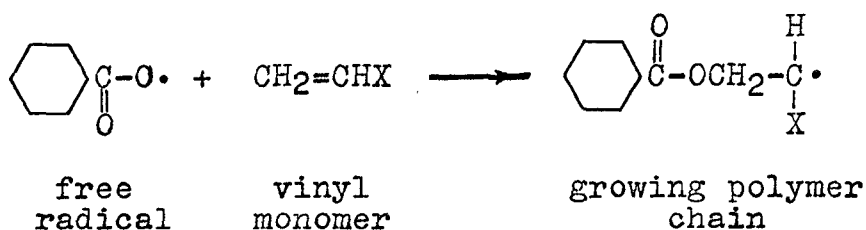
In a short time, usually much less than one second, many more monomers add successively to the growing chain. Finally, the growing chain is terminated and forms a stable polymer molecule by losing the free radical to another molecule, or by reaction between free radicals to annihilate each other's growing activity. For example:

$$\langle\bigcirc\rangle \overset{C-O(CH_2CHX)_x \cdot}{\underset{O}{\parallel}} + S \longrightarrow S \cdot + polymer$$

growing       solvent
radical       molecule

$$2 \langle\bigcirc\rangle \overset{C-O(CH_2CHX)_x \cdot}{\underset{O}{\parallel}} \longrightarrow inactive\ products$$
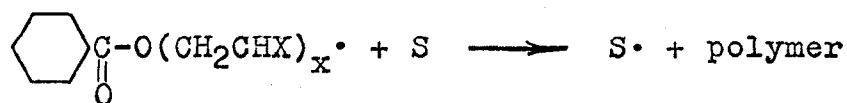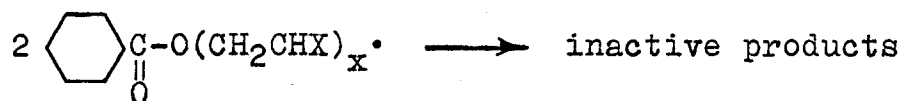
growing                                   polymer
chains

In either type of polymerization, the length
of a chain (a polymer molecule) is determined by purely
random events, and hence, the polymeric product will
contain many molecules having many different chain
lengths. The degree of polymerization, DP, is defined
as the number of monomers contained in a chain. The
resulting distribution of molecular weights can be roughly
determined experimentally.

General Kinetics of Free Radical Polymerization

There are at least three elementary reactions
involved in an addition polymerization, namely, initia-
tion, propagation and termination.

1. Initiation

In this step, the monomer is activated by the
initiator such as light (photon), Catalyst (free radical)
and thermal effect, for example,

a) by thermal effect

$$CHX=CH_2 + heat \longrightarrow \cdot CH_2-CH_2\cdot$$
$$\text{monomer} \qquad\qquad\qquad \text{diradical}$$

b) by light

$$CHX=CH_2 + photon \longrightarrow X\cdot + H_2C=CH\cdot$$
$$\text{radical}$$

and c) by catalyst

$$C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \longrightarrow 2C_6H_5-\overset{O}{\overset{\|}{C}}-O\cdot \longrightarrow 2C_6H_5\cdot + 2CO_2$$
$$\text{catalyst} \qquad\qquad \text{free radical}$$

$$CHX=CH_2 + C_6H_5\cdot \longrightarrow C_6H_5-CH_2\overset{\cdot}{C}HX$$
$$\text{monomer} \qquad\qquad\qquad \text{growing radical}$$
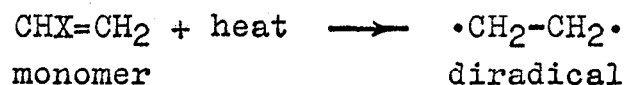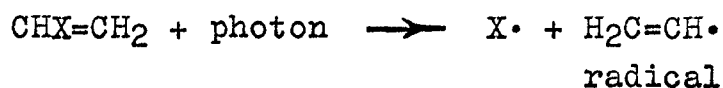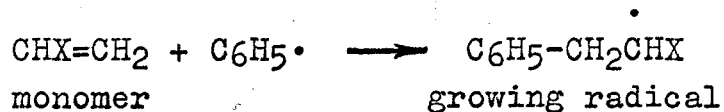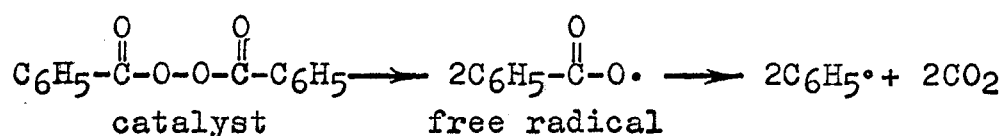
## 2. Propagation

The polymerizable monomer once activated to a free radical state can quite easily react with another monomer molecule to give a larger radical. Likewise more monomers may be added to form a long chain until it becomes terminated. For example,

$$\sim\!\sim\!\sim\!R\cdot + CHX=CH_2 \longrightarrow \sim\!\sim\!\sim\!R-\overset{\overset{H}{|}}{\underset{\underset{X}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}\circ$$

$$\text{growing chain} \qquad\qquad \text{growing chain}$$
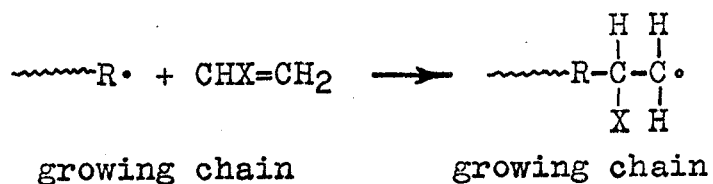
## 3. Termination

The cessation of the growth of a radical is known as termination, and hence the polymer molecule is

formed. This generally occurs by the interaction of two radicals either by combination or disproportion, or by chain transfer reaction:

a) by combination

$$R-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}\cdot + RCH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}\cdot \longrightarrow (R-CH_2-CHX)_2$$

b) by disproportionation

$$R-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}\cdot + R-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}\cdot \longrightarrow R-CH_2-CH_2X + R-CH=CHX$$
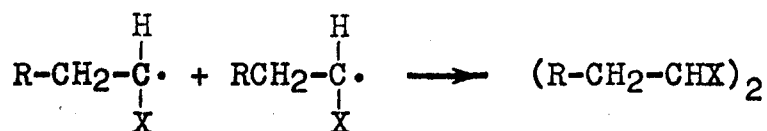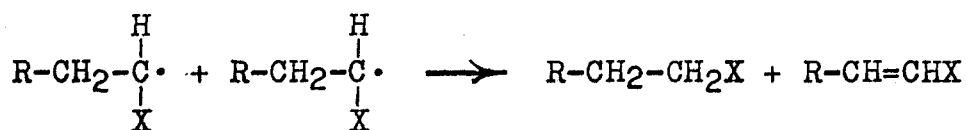
The above scheme, however, is not complete for those in which the chain transfer is involved. The following example shows how the "chain transfer reaction" can occur between the growing chain and a monomer molecule. It may occur also to the solvent, to the polymer or to any other foreign substances present. It should be noted that although the growing chain is terminated by this process, the molecule to which the radical is transferred can serve as the initiator for the start of a new chain.

$$C_6H_5(CH_2-CHX)_n-CH_2\overset{\bullet}{C}HX + CH_2=CHX$$

$$\longrightarrow C_6H_5(CH_2-CHX)_n-CH_2CH_2X + CH_2=\overset{\bullet}{C}X$$
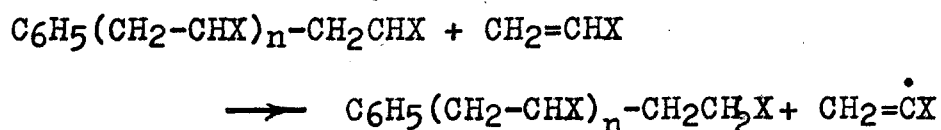
The overall reaction may be written in the simple form as in the following example. Consider a reaction in which the polymerization is determined only by the three elementary process, i.e., initiation, propagation and termination. The total reaction may be written

|  |  | Velocity constant |
|---|---|---|

Initiation $\quad\quad\quad\quad$ M $\longrightarrow$ M$_1^*$ $\quad\quad$ $k_i$

Propagation $\quad$ M$_1^*$ + M $\longrightarrow$ M$_2^*$ $\quad\quad$ $k_{p_1}$

$\quad\quad\quad\quad\quad\quad$ M$_2^*$ + M $\longrightarrow$ M$_3^*$ $\quad\quad$ $k_{p_2}$

$\quad\quad\quad\quad\quad\quad$ M$_{n-1}^*$ + M $\longrightarrow$ M$_n^*$ $\quad\quad$ $k_{p_n}$

Termination by combination

$$M_n^* + M_m^* \longrightarrow M_{n+m} \quad\quad k_c$$

Termination by disproportionation

$$M_n^* + M_m^* \longrightarrow M_n + M_m \quad\quad k_d$$
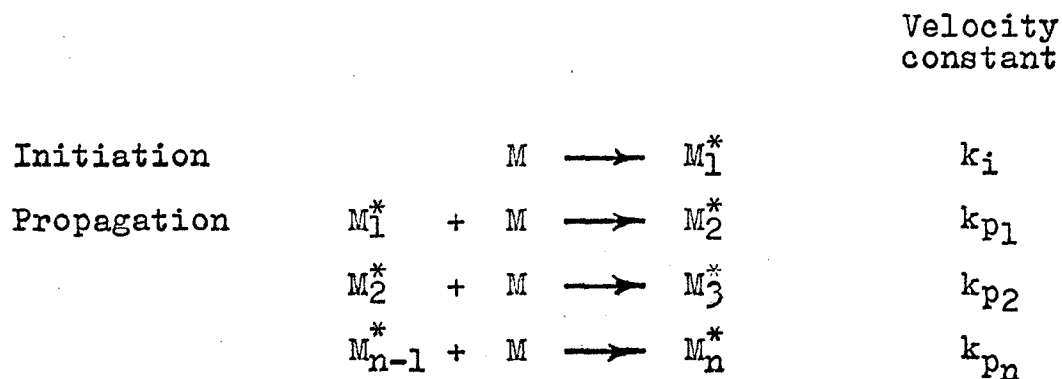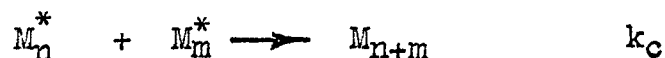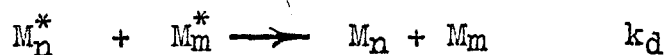
where  M  represents the monomer,  $M_n^*$  represents a grow-
ing radical chain with the degree of polymerization,  n.
In order to derive kinetic equations the first assumption
is made that all the rate constants involving growing
chains are independent of the radical size and the degree
of polymerization.  Therefore

$$k_{p_1} = k_{p_2} = \ldots\ldots = k_{p_{n-1}} = k_p$$

The second assumption is that the length of the
chain is great, and hence the velocity of propagation is
much greater than that of initiation and termination.
Since the propagation process involves only the addition
of monomer to the polymer radical, the velocity of pro-
pagation is, therefore,  $V_{prop} = k_p[M][C^*]$ , where  $[C^*]$
is the total concentration of polymer radicals.

The velocity of initiation is determined by its

nature. A few examples are illustrated in the following:

1. first order initiation (unimolecular)

$$V_{init} = k_i(M)$$

2. second order initiation (bimolecular)

$$V_{init} = k_i(M)^2$$

3. photon initiation

$$V_{init} = k(I)(M)$$

where   I = intensity of absorbed light

4. catalysed initiation

$$V_{init} = k_i(M)(Cat)$$

where   [Cat] = concentration of catalyst.

The velocity of termination, either by combination or dis-proportionation, is

$$V_{term} = k_t[C^*]^2$$

## Theoretical Calculation of Size Distribution

Polymer molecules produced during polymerization are not all of one size, a whole distribution of sizes is obtained. The average molecular weight of such a heterogeneous polymer is determined by the method of measurement. It varies from one method to another. For instance, the measurement of a colligative property of the polymer(i.e., by methods such as osmometry, cryoscopy and ebulliometry) gives the number average molecular weight while the light scattering method leads to the weight average. These two averages are not the same.

The latter gives a greater value than the former.

Based upon the kinetic scheme proposed in the previous section, methods are available to calculate the distribution of molecular size. Of course, different types of initiation and termination mechanisms lead to different forms of distribution curves. Therefore a comparison of the predicted with the experimental distribution curves can be used to check the theoretical kinetic relationships.

At the beginning, it is necessary to introduce a few terms which are useful in the future derivations. The number, weight, and viscosity average molecular weights ($M_n$, $M_w$, $M_v$) are defined as:

$$M_n = \frac{\sum_1^\infty n_p M_p}{\sum_1^\infty n_p} \quad \dots\dots\dots\dots\dots\dots\dots\dots(1)$$

$$M_w = \frac{\sum_1^\infty n_p M_p^2}{\sum_1^\infty n_p M_p} = \frac{\sum_1^\infty w_p M_p}{\sum_1^\infty w_p} \quad \dots\dots\dots\dots(2)$$

$$M_v = \left[\frac{\sum_1^\infty n_p M_p^{r+1}}{\sum_1^\infty n_p M_p}\right]^{1/r} = \left[\frac{\sum_1^\infty w_p M_p^r}{\sum_1^\infty w_p}\right]^{1/r} \quad \dots(3)$$

where for a particular polymer sample $n_p$ is the number of moles of molecules of length p ; $M_p$ is the molecular weight of the chain; $w_p$ is the weight of polymer of degree of polymerization p; and p is the degree of polymerization(or number of repeating units contained in a chain). In the definition of $M_v$, r is the constant in the Mark-Houwink equation relating the limiting viscosity number to the molecular weight of a monodisperse

sample (see equation 23 below). Notice that from the above definition

$$M_p = P \cdot M \quad \dots \dots \dots \dots \dots \dots (4)$$

$$w_p = n_p \cdot M_p \quad \dots \dots \dots \dots \dots \dots (5)$$

where M is the molecular weight of the monomer or repeating unit.

The details of the derivation of the distribution curve from the kinetic model of vinyl polymerization can be found elsewhere[1]. Of interest here are two special cases. In each, initiation is assumed to be bimolecular, as is presumably the case in spontaneous, uncatalysed thermal polymerization of bulk monomer. It is further assumed that the chain transfer reaction is negligible, and that termination is by the mutual reaction of growing radical chains. In the first case it is assumed that termination is by disproportionation, in the second by combination, of radicals.

In the former case(disproportionation) the distribution of the molecular weight in the initial polymer formed would be given by

$$w_p = BMP\epsilon^2 \left(\frac{1}{1+\epsilon}\right)^p \quad \dots \dots \dots \dots (6)$$

where $w_p$ is the weight of polymer of degree of polymerization equal to p, and $\epsilon$ is a constant, a combination of rate constants, and M is the molecular weight of a repeating unit, and B is a constant determining the weight of the sample. If, on the other hand, termination is by combination, then

$$w_p = (B'/2) \, M^2 P^2 \epsilon^3 \left(\frac{1}{1+\epsilon}\right)^p \quad \dots \dots (7)$$

---

1. Bawn, C. E. H., Chemistry of High Polymers (1948)

The frequency distributions, $n_p$, are obtained by dividing $w_p$ by $MP$. Thus, for disproportionation

$$n_p = B\epsilon^2 \left(\frac{1}{1+\epsilon}\right)^p \quad \dots\dots\dots\dots\dots\dots (8)$$

and for combination

$$n_p = \frac{B'}{2} MP\epsilon^3 \left(\frac{1}{1+\epsilon}\right)^p \quad \dots\dots\dots\dots\dots (9)$$

If the further substitution is made

$$\frac{1}{1+\epsilon} = e^{-b}$$

then, for disproportionation,

$$n_p = Ae^{-bp} \quad \dots\dots\dots\dots\dots\dots\dots (10)$$

$$w_p = MPAe^{-bp} \quad \dots\dots\dots\dots\dots\dots (11)$$

and for combination,

$$n_p = A'MPe^{-bp} \quad \dots\dots\dots\dots\dots\dots (12)$$

$$w_p = A'M^2p^2e^{-bp} \quad \dots\dots\dots\dots\dots (13)$$

Clearly in the above equations

$$A = B(e^{+b}-1)^2 \quad \dots\dots\dots\dots\dots\dots (14)$$

$$A' = \frac{B'}{2}(e^{+b}-1)^3 \quad \dots\dots\dots\dots\dots (15)$$

A study of the molecular weight distribution of

polymethylmethacrylate[2] showed that the theoretical distribution curve calculated from the kinetic model was compatible with the experimentally determined distribution, but the agreement was not as good as might be desired.

## The Experimental Determination of Molecular Weight Distribution Curves

The most frequently used method for the experimental determination of the distribution of molecular weight in a high polymer sample requires that the sample be fractionated into portions as nearly homogeneous as possible in molecular weight. Ideally the sample should be separated into completely homogeneous fractions from whose weights and molecular weights the distribution curves could be constructed. In practice it is impossible to achieve this degree of separation. As a result, it becomes necessary to reconstruct distribution curves from weights and average molecular weights of more-or-less homogeneous fractions.

To effect this reconstruction it is common practice to make use of the so-called "integral weight distribution curve". The frequency distribution curve as used above is a discontinuous function defined only for integral values of $p$. It can be written as a continuous function $n_p(p)$ if the average degree of polymerization is large. Under this condition $p$ is for practical purposes a continuous variable. If this is done, then $n_p(p)$ should be understood to mean the number of moles of polymer whose degree of polymerization lies between $p$ and $p+dp$. Thus

$$dn = n_p(p) \cdot dp \qquad \ldots \ldots \ldots \ldots \ldots \text{(16)}$$

---

2. Baxendale, J. H., Bywater, S., and Evans, M. B., Trans. Far. Soc., 42, 675 (1946).

A similar equation can be written for $w_p$. For this reason $n_p$ and $w_p$ are often called the differential frequency and weight distribution curves. Clearly, as before,

$$w_p(p) = M_p \cdot n_p(p) \quad \ldots\ldots\ldots\ldots \quad (17)$$

$$M_p = P \cdot M$$

If now one defines $\Omega(p)$ to be the "integral weight distribution curve"; that is to say, $\Omega(p)$ represents the total weight of polymer whose degree of polymerization is less than or equal to $p$, then clearly

$$\Omega(p) = \int_0^p w_p(t)\,dt$$

where $t$ is a dummy variable. $\Omega(p)$ and $w_p(p)$ are related by

$$\frac{d\,\Omega(p)}{dp} = w_p(p) \quad \ldots\ldots\ldots\ldots\ldots \quad (18)$$

Thus if $\Omega(p)$ were known as a function of $p$ then $w_p(p)$ and $n_p(p)$ could be determined from equations (17) and (18). Experimentally, the integral weight distribution curve is constructed by obtaining experimental data such as the weight and the molecular weight or chain length of the fractions which are separated from the heterogeneous polymer sample. Methods of separating the sample into fractions with regard to molecular weight or chain length are called fractionation. The molecular weight or chain length of each fraction may be determined by one of the methods described in the next section. Thus we can plot the weight(on an accumulative basis) of each fraction against its measured chain length.

For example, if the fractions were monodisperse, and if the weight of the fractions were $W_1$, $W_2$, $W_3$, .... .. $W_n$ and the measured corresponding chain length were $P_1$, $P_2$, $P_3$, .... $P_n$, then $W_1$ and $P_1$ would determine the first point in the "weight versus chain length" plot; $(W_1 + W_2)$ and $P_2$ would determine the second point; $(W_1 + W_2 + W_3 + .... + W_n)$ and $P_n$ will give the last point. In this way a stepwise curve could be drawn.

However, since the fractions can not be very sharply separated from the sample, therefore, each fraction is not really of one size but has a range of sizes, and hence the measured chain length of each fraction can only represent an average value within that range. Now the assumption is made that the distribution of sizes is symmetrical around the measured average chain length, and that the distribution of molecular weight within a fraction does not extend beyond the average molecular weight of its neighbouring fraction. Then the integral weight distribution curve may be established by drawing a smooth curve through the middle points of the vertical sections of the staircase curve. In other words, that the integral weight distribution curve may be constructed by plotting

$( \sum_{i=0}^{n} W_i + \tfrac{1}{2}W_{n+1} )$ against $P_{n+1}$ where $W_{n+1}$ and $P_{n+1}$ repre-

sent the measured weight and chain length of $(n+1)$th fraction (Fig. 6).

The assumptions made above regarding the symmetry and the sharpness of adjacent fractions are severe, and are probably not achieved in an ordinary single stage fractionation process as described below. It is possible to improve the sharpness of fractions by repeated fractionation either conventionally[3] or by chromatographic

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3. Cragg, L. H., and Hammerschlag, H., Chem. Revs., 39, 79 (1946).

techniques.[4] The latter procedure has achieved considerable favour in recent years but is limited by the small size of fractions it produces. It appears, moreover, that errors introduced by making the above assumptions tend to cancel out.[5] The research described herein was undertaken in part to check this point.

By applying equation (17) and (18), the differential weight and number distribution curves can be respectively constructed from the data obtained by graphical differentiation of the integral weight distribution curve and the corresponding chain length P.

## Measurement of Molecular Weight

The molecular weight of a polymer can be determined by measurement of its colligative properties, by light scattering or by viscosity. Since the heterogeneous polymer is composed of molecules with different chain length, any method of measurement can only give an average value. Different methods give different average values.

### 1. The Colligative Methods

The colligative property method is based on the measurement of vapor pressure lowering, boiling point elevation(ebulliometry), freezing point depression (cryoscopy), or the osmotic pressure(osmometry). From thermodynamic arguments the following relation can be derived for dilute solutions

$$\Delta Q = K \frac{C}{M} \quad \dots\dots\dots\dots\dots\dots\dots\dots (19)$$

---

4. Bannister, D. W., Phillips, C. S. G., and Williams, R. J. P., Anal. Chem., 26, 1451 (1954).

5. Booth, C., and Beason, L. R., J. Poly. Sci., 42, 81 (1960).

where $\Delta Q$ is the change in property measured, $C$ is the concentration of the solute, $M$ is the molecular weight and $K$ is a constant depending on the system concerned. For solutions at higher concentration equation (19) may be written in the general form:

$$\Delta Q/C = K/M + A_1 C + A_2 C^2 + A_3 C^3 + \ldots \quad (20)$$

If $\Delta Q$ is measured for various values of $C$, and the quantity $\Delta Q/C$ is plotted against $C$, the value of $K/M$ can be found by extrapolation of data to zero concentration, so that $M$ can be calculated.

Any of the colligative properties can be used to determine the number-average molecular weight of a polymer. But from the following comparison, it is obvious that the osmotic pressure is the easiest one to measure.

Comparison of Calculated Boiling Point, Elevation, Freezing Point and Vapor Pressure Lowering, and Osmotic Pressure for 1% Solution in Benzene.

| Molecular weight | Boiling point elevation ($^{o}$C.) | Freezing point depression ($^{o}$C.) | Vapor pressure lowering (mm. Hg) at 80$^{o}$C. | Osmotic pressure cm. benzene |
|---|---|---|---|---|
| 10,000 | 0.0031 | 0.0058 | 0.076 | 31 |
| 50,000 | 0.0006 | 0.0012 | 0.015 | 6 |
| 100,000 | 0.0003 | 0.0006 | 0.008 | 3 |

The use of osmotic measurement (osmometry) for determining molecular weight is very common and has been used for molecular weights up to $10^6$ and higher.

In this method, the polymer solution and the pure solvent are separated by a membrane which is permeable to the solvent molecules, but not to the polymer. Equilibrium is reached when the hydrostatic pressure difference across the membrane exactly compensates for the difference of chemical potential of the solvent arising from the presence of the polymer solute.

## 2. Light-scattering Measurement

It has been found that when a light beam passes through a non-absorbing liquid some light is scattered. If the solvent is made more inhomogeneous by the addition of solute molecules, the intensity of the scattered light is increased. The increase in scattering is related to the molecular weight of the dissolved solute. Thus, a measurement of this increase for a polymer solution can lead to the molecular weight of the polymer.

The scattered intensity for a monodisperse solute is given by (Debye equation)

$$H(\frac{C}{\tau}) \; = \; \frac{1}{M} + 2A_2C + \dots \qquad \qquad \dots \; (21)$$

where

$$H \; = \; \frac{32\pi^3}{3\,N_o} \cdot \frac{n^2}{\lambda^4}(\frac{\partial n}{\partial C})^2$$

The scattered light intensity is expressed in terms of the turbidity $\tau$ , defined as the fraction of the light scattered in all directions from the primary beam per centimeter of path. If a beam of intensity $I_o$ is reduced to intensity $I$ on passage through x cm, of the scattering medium, $I/I_o = e^{-\tau x}$. For typical polymer solutions $\tau = 10^{-3}$, n is the refractive index

of the system, $N_O$ is the Avogadro's number, $\lambda$ is the wave length of the incoming beam, and C is the concentration of the polymer solution.

The plot of $H(C/\gamma)$ against C will lead to the average molecular weight of the heterogeneous polymer. Light scattering measurement is one of the most important absolute methods.

## 3. Viscosity

Viscometry is the easiest and most rapid method for obtaining molecular weight, it is widely adopted for the routine determination of molecular weight.

In the measurement, the chief quantity of interest is the viscosity of a polymer solution relative to that of the pure solvent. From this, the molecular weight of the polymer solute can be calculated.

Huggins[6] found for a series of polymer fractions in the same solvent that the slopes of the linear portions of the plots of $\eta_{sp}/C$ against C were proportional to the square of the intercept and proposed the relation:

$$\frac{\eta_{sp}}{C} = [\eta] + K_1 [\eta]^2 C \quad \ldots\ldots\ldots\ldots (22)$$

where $\eta_{sp}$ is the specific viscosity which is equal to $(\eta - \eta_o)/\eta_o$, $\eta_o$ is the viscosity of the solvent, $\eta$ is the viscosity of the solution, $[\eta]$ is called limiting viscosity number and $K_1$ is a constant for a given polymer-solvent system. $[\eta]$ can be obtained by plotting $\eta_{sp}/C$ versus C.

It is usual to use the empirical equation (23) to calculate the molecular weight from the viscometric

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6. Huggins, M. ., JACS, 64, 2716 (1942).

results

$$[\eta] = KM^r \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (23)$$

where $[\eta]$ is the limiting viscosity number of a mono-
disperse sample of polymer of molecular weight M; K and
r are constants dependent on the polymer-solvent system
concerned. The molecular weight so obtained for a poly-
disperse sample is called "viscosity-average" molecular
weight. Equation (23) is usually associated with the
names Mark-Houwink.

# CHAPTER II

## APPARATUS AND PROCEDURE

### Apparatus

### 1. For Fractionation

The apparatus used for fractionation is shown schematically in Fig. 1. It is a double-walled glass vessel A, B, closed to the air by mercury seals D, E, and J. F is a rotating cup permitting the contents of the vessel to be stirred by rotation of the stainless steel stirrer C. An etched scale L on the side of the inner vessel permits the volume of liquid contained in it to be observed. Additions of reagents can be made to the vessel through port H. The temperature of the contents of the vessel can be controlled by circulating water from a thermostat through the jacket B. To the bottom of the inner vessel is connected a glass tube leading to a teflon-glass stopcock M to which may be attached glass receiver tube P. The receiver has a volume scale etched on it, and is connected at the bottom to a teflon stopcock Q which in turn is connected via a rubber tube R to a mercury reservoir T.

The overall length of the jacketed vessel is about 90 centimeters, and the capacity of the inner vessel is 5 liters. The receiver has a capacity of about 20 cubic centimeters, and the volume scale on its side is calibrated in 0.1 cubic centimeter division.

### 2. For Viscometry

Because of the simplicity and the convenience,

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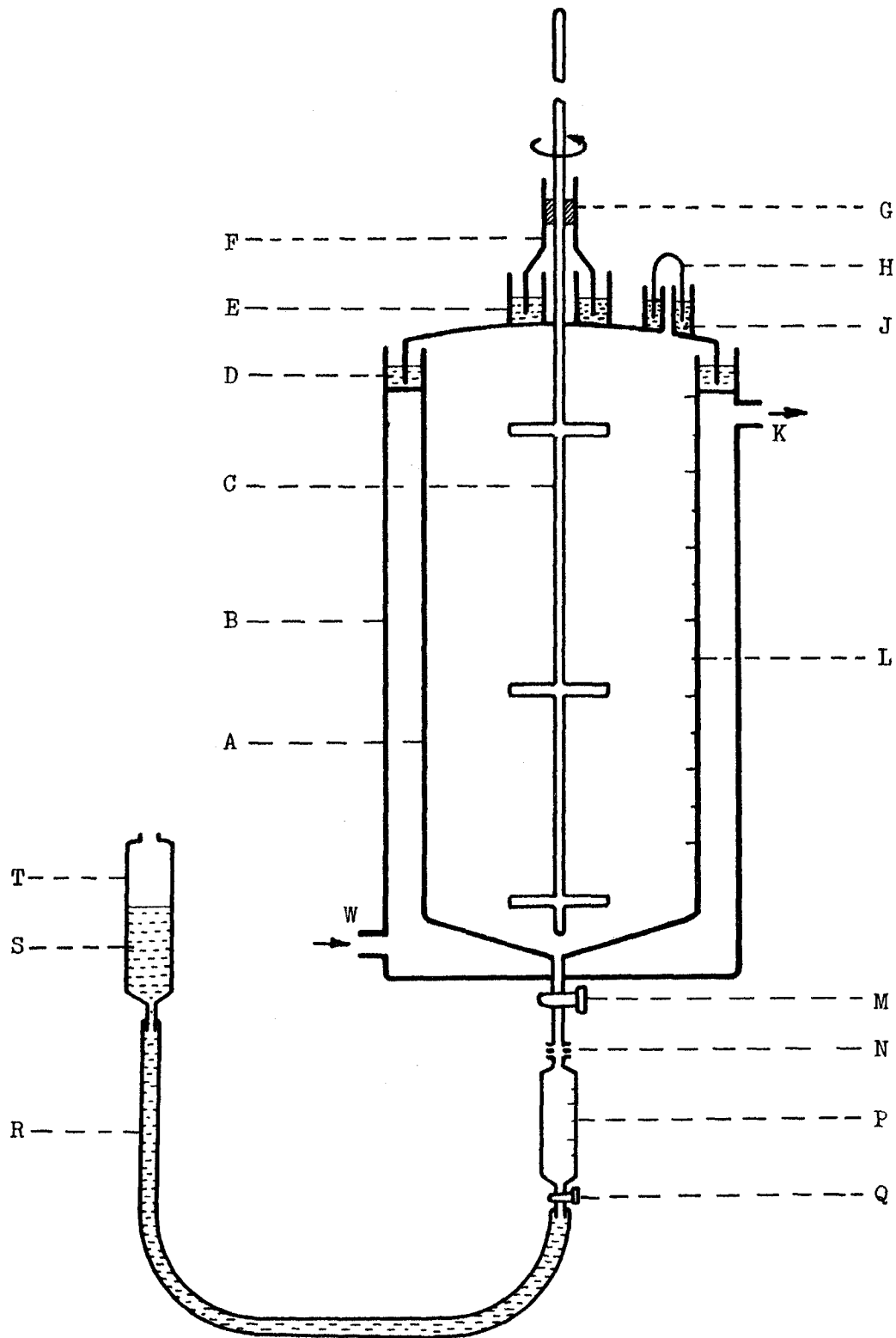
Fig. 1.    The fractionation vessel and the
reciever assembly.

A.   Fractionation vessel or inner vessel.
B.   Outer vessel for water circulation.
C.   Stainless steel stirrer.
D.   Mercury.
E.   Mercury cup with mercury.
F.   Rotating cup.
G.   Teflon ring.
H.   Cover for inlet of solution.
J.   Mercury.
K.   Outlet of water to water bath.
L.   Volumetric scale.
M.   Teflon stopcock.
N.   Connecting adaptor.
P.   Centrifuge tube.
Q.   Teflon stopcock.
R.   Flexible rubber tubing.
S.   Mercury.
T.   Container.
W.   Inlet of water from water bath.

among various types, the suspended-level or Ubbelohde dilution viscometer was chosen to measure the viscosity of the polymer solution. The essential features are shown in Fig. 2. The instrument is entirely made of glass. A, B, C, and D are bulbs. E is the capillary. The solution being measured is first introduced into the bulb A, then forced into the bulb C by pressure, and hence the flow time of the solution between the etched mark can be timed. Details of the operating procedure will be described in a later section.

## Chemicals

The principal chemicals used in this experiment were polystyrene, methyl ethyl ketone, methanol and toluene. Two different samples of polystyrene were used. They were different in average molecular weight as determined by viscosity measurement. One was about three times higher than the other. Both had been prepared previous to this work by Dr. E. W. Channen, using a standard method of bulk polymerization to low conversion(10%) in the presence of benzoyl peroxide as initiator. Nevertheless, the samples were repurified by precipitation from methyl ethyl ketone with aqueous methanol before being fractionated.

Methyl ethyl ketone, methanol and toluene were all obtained from Fisher Scientific Company, and certified by the manufacturer to meet the American Chemical Society specifications. They were used as supplied without further purification.

## Procedure

### 1. For Fractionation

Three polymer samples, 20g. each, were fractionated, one, sample-AB being a mixture of equal parts of sample-A and sample-B(i.e., 10g. each). Sample-B
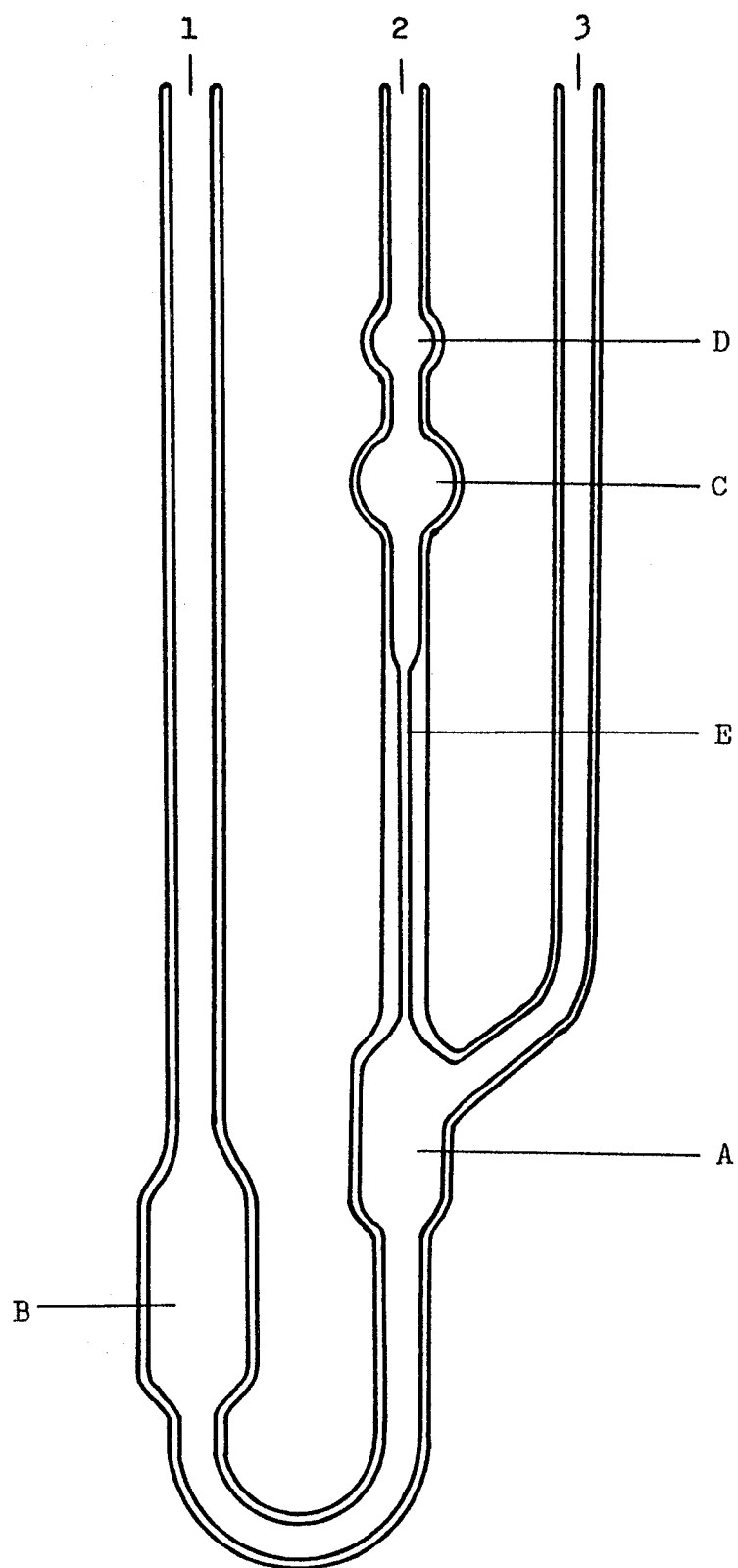
Fig. 2.    Ubbelohde dilution viscometor

was about three times higher in average molecular weight than sample-A, as measured by viscometry. Each sample was accurately weighed and a solution of about 1% in g./dl was made in methyl ethyl ketone (i.e., two liters of solution for each sample).

Before the solution was added into the inner vessel, the empty space above the mercury at D was filled with methyl ethyl ketone. The purpose of doing so was to minimize any condensation of the liquid vapor evaporated from the polymer solution during the long period of fractionation. Care was taken that the receiver assembly was securely connected to the column, and mercury was allowed to fill the receiver assembly to a level above stopcock M. The solution was then introduced.

After the temperature of the polymer solution in the vessel was brought up to 25°C by the circulating water from the water bath, the volume of the solution was recorded.

Under stirring, the precipitant, methanol, was slowly added into the solution through the feeding inlet at H until the solution appeared to be densely cloudy. This point was estimated by guess on the basis of a preliminary run. The volume of methanol added for each fraction was recorded. The temperature of the contents of the vessel was then raised to such a degree that the cloudiness of the solution disappeared. Normally, 10°C to 15°C above the bath temperature was sufficient. The solution was slowly cooled to 25 ± 0.01 °C, allowing the polymer to reprecipitate, the stirring was stopped and the reprecipitated polymer was allowed to settle over night. This heating and cooling cycle would take about eight hours.

The precipitate in this case was a moderately viscous solution that could be drained into the receiver

P as the stopcocks M and Q were opened and the mercury level in the container T was lowered. The stopcock M was closed after the last portion of the fraction had passed below the flanged connector to the receiver, preventing the supernatant liquid from draining through. The stopcock Q was closed after the mercury had come down to the beginning of the scale of the centrifuge tube so that the fraction could be measured. At this point the volumes of the fraction and the supernatant liquid were recorded and the receiving assembly was disconnected from the vessel.

The precipitate so obtained, containing some small mercury droplets, was redissolved in an excess amount of methyl ethyl ketone (about 10 times more than the volume of the precipitate) and the solution was filtered through a sintered filter of a medium porosity. The polymer was then reprecipitated under stirring by running the filtered solution slowly into methanol. The volume of the methanol was about three to four times as much as the filtered solution. The polymer was dried in an vaccum oven between 50-70°C over night. Finally, the polymer was weighed and its molecular weight was determined by viscosity measurement method. Except for the final fraction, this process of fractionation was repeated until all the polymer sample was entirely recovered. Usually 15 to 17 fractions were obtained. The final fraction was obtained from the residue resulting from the evaporation of all solution removed from the fractionation vessel. Failure was encountered in trying to precipitate the final portion through the regular means (i.e., by addition of precipitant) because at this stage, the solution has so low a molecular weight that further addition of precipitant would only result in a suspended solution with fine polymer particles which remained suspended even after several days and could not be filtered

with a medium porosity sintered filter.

## 2. For Viscometry

The apparatus employed in the viscosity measurement was the suspended-level or Ubbelohde dilution viscometor. Referring to Fig. 2, in operation, pressure was applied to the top of limb-1 while limb-3 was closed at the top by the operator's finger, thereby forcing liquid from bulb B into bulb A and C and finally into D. Then, releasing the pressure on limb-1, limb-3 was opened to let air into bulb A. This resulted in the formation of the suspended level at the lower end of the capillary. Since the suspended level was automatically fixed, it was unnecessary to charge the viscometor with the same volume of liquid each time, and it also permitted dilution of the solution while in the viscometer. Therefore the viscosity of solutions of different concentration could be measured with one filling of the viscometer.

Viscosity measurements were made using toluene as solvent. The additional apparatus required for the measurement were the water bath, the temperature of which was controlled to $25 \pm 0.2$ $^{\circ}$C and the stopwatch of capable to register to 0.1 second. The following general procedures were followed:

a. The capillary viscometer was thoroughly cleaned with warm chromic acid and the vertical alignment of the viscometer into the water bath was carefully checked.

b. Care was taken to prevent dust from entering the instrument.

c. Sufficient time was allowed for the viscometer and its contents to attain the bath temperature before measurements were made. This length of time was reduced by having the containers of solution and the diluting solvent stored in the same bath.

d. Raising the liquid level in the viscometer was

accomplished by applying a positive pressure of air to one limb.

    e. A fluorescent light under the water bath and a cathetometer facilitated accurate observation of the meniscus level.

    f. Using the stopwatch the reproducibility of the flow time was within $\pm 0.1\%$.

    The molecular weight of each fraction was then determined by equation (23).

$$[\eta] = KM^r$$

where in this case $K = 1.7 \times 10^{-4}$ and $r = 0.69$. Both of the constants were taken from the reference.[7] $[\eta]$ was the intercept of the extrapolation of the plot of $(\eta - \eta_o)/\eta_o C$ versus $C$. The unit of concentration, $C$ used was g./dl and the unit of $[\eta]$ would be dl/g..

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7.   Outer, Carr and Zimm, J. chem. Phys., 18, 830 (1950).

CHAPTER III


RESULTS, DISCUSSION AND CONCLUSION


Results

       The observations recorded during the fractiona-
tion step for the three different polymer samples are
shown in Table 1 to 3. The results show that the re-
covery of the starting material was 98.7%, 99.5%, and
99.3% respectively for the three runs. The losses pre-
sumably arose in handling, and were at a satisfactorily
low level.

       Typical observations obtained from the viscosity
measurements are shown in Table 4 to 6, and typical plots
of $\eta_{sp}/C$ versus C in Fig. 3 to 5. The viscosity re-
sults are summarized for the three samples studied in
Table 7 to 9, which include values of the molecular
weight, the degree of polymerization, and the cumulative
weight distribution function for each sample.

       The cumulative weight distribution functions
for samples A and B are shown in Fig. 6. The circles
and triangles represent the experimental points, and
curves representing the functions have been drawn through
them. Since sample AB is a 50:50 mixture of samples A
and B, its cumulative weight distribution curve ought to
be the mean of the curves of A and B. The dotted curve
drawn for sample AB in Fig. 6 was in fact constructed to
be the mean of the curves drawn for A and B, and the ex-
perimental points obtained for the sample were added
afterwards. As can be seen they agree quite well with
the expected curve.

       As described earlier, the differential weight
and frequency distribution curves can be obtained from

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## TABLE 1

Data Recorded on Fractionation of Polystyrene,
Sample A 20g. Used. Precipitated from Methyl Ethyl
Ketone with Aqueous Methanol.

| Fraction | Methanol added for each precipitation (ml.) | Volume of precipitate (ml.) | Volume of supernatant liquid (ml.) | Weight of precipitate (g.) |
|---|---|---|---|---|
| 1 | 534 | 4.2 | 2554 | 1.5479 |
| 2 | 37 | 5.15 | 2583 | 2.0485 |
| 3 | 22 | 3.0 | 2600 | 1.2648 |
| 4 | 21 | 2.4 | 2623 | 1.0540 |
| 5 | 22 | 2.0 | 2633 | 1.1043 |
| 6 | 24 | 2.2 | 2654 | 1.0247 |
| 7 | 28 | 2.1 | 2677 | 1.0258 |
| 8 | 27 | 1.75 | 2700 | 0.9294 |
| 9 | 22 | 1.2 | 2824 | 0.5821 |
| 10 | 47 | 2.4 | 2765 | 1.2357 |
| 11 | 28 | 1.4 | 2791 | 0.8209 |
| 12 | 66 | 2.1 | 2845 | 1.1606 |
| 13 | 97 | 1.7 | 2933 | 0.9999 |
| 14 | 104 | 1.3 | 3033 | 0.9333 |
| 15 | 267 | 1.7 | 3288 | 1.1417 |
| 16 | 2706 | * | ** | 2.8618 |
| Total | | | | 19.7354 |

* Only suspension was observed.
** Out of scale.

## TABLE 2

Data Recorded on Fractionation of Polystyrene,
Sample B 20g. Used. Precipitated from Methyl Ethyl
Ketone with Aqueous Methanol.

| Fraction | Methanol added for each precipitation ( ml.) | Volume of precipitate ( ml.) | Volume of supernatant liquid ( ml.) | Weight of precipitate ( g.) |
|---|---|---|---|---|
| 1 | 392 | 8.4 | 2433.6 | 1.9911 |
| 2 | 15 | 6.2 | 2438 | 1.5723 |
| 3 | 11 | 5.2 | 2441 | 1.3720 |
| 4 | 15 | 5.7 | 2450 | 1.5999 |
| 5 | 13 | 4.2 | 2455 | 1.2541 |
| 6 | 20 | 5.9 | 2463 | 1.8422 |
| 7 | 25 | 5.4 | 2483 | 1.8680 |
| 8 | 25 | 3.6 | 2507 | 1.3690 |
| 9 | 25 | 2.3 | 2516 | 0.9026 |
| 10 | 32 | 2.55 | 2553 | 1.0789 |
| 11 | 34 | 1.6 | 2588 | 0.7703 |
| 12 | 39 | 0.85 | 2621 | 0.6607 |
| 13 | 50 | 1.00 | 2658 | 0.5852 |
| 14 | 58 | 0.65 | 2710 | 0.4970 |
| 15 | -- | * | ** | 2.5233 |
| Total | | | | 19.8966 |

* Only suspension was observed.
** Out of scale.

TABLE 3

Data Recorded on Fractionation of Polystyrene,
Sample AB, a Mixture of Sample A and B, 10g. each.
Precipitated from Methyl Ethyl Ketone with
Aqueous Methanol.

| Fraction | Methanol added for each precipitation ( ml.) | Volume of precipitate ( ml.) | Volume of supernatant liquid ( ml.) | Weight of precipitate ( g.) |
|---|---|---|---|---|
| 1 | 426 | 6.0 | 2462 | 1.6319 |
| 2 | 25.5 | 5.0 | 2476 | 1.4848 |
| 3 | 27 | 5.0 | 2490 | 1.6487 |
| 4 | 22 | 3.8 | 2509 | 1.2952 |
| 5 | 24 | 3.15 | 2532 | 1.1962 |
| 6 | 22 | 2.6 | 2549 | 0.9937 |
| 7 | 22 | 2.1 | 2570 | 0.8780 |
| 8 | 21 | 1.8 | 2582 | 0.7768 |
| 9 | 24 | 1.85 | 2603 | 0.8250 |
| 10 | 28 | 2.0 | 2632 | 0.8911 |
| 11 | 27 | 1.45 | 2650 | 0.7679 |
| 12 | 36 | 1.6 | 2685 | 0.8254 |
| 13 | 38 | 1.2 | 2722 | 0.7105 |
| 14 | 60 | 1.2 | 2777 | 0.7979 |
| 15 | 154 | 2.25 | 2920 | 1.4146 |
| 16 | 446 | 1.1 | 3349 | 0.8799 |
| 17 | -- | * | ** | 2.8337 |
| Total | | | | 19.8513 |

* Only suspension was observed.
** Out of scale.

## TABLE 4

Typical Viscosity Data of Fraction 1, Sample A

Solvent: Toluene
Flow time of solvent at 25°C. : 128.15 sec.
Concentration of polymer stock solution: 0.9726 gm./dl.
Volume of polymer stock solution initially placed in
  viscometer: 5 ml.

| Total solvent added to viscometer ( ml.) | Concentration (gm./dl.) | Flow Time (sec.) Measured | Averaged | $\frac{\eta_{sp}}{C}$ |
|---|---|---|---|---|
| 0 | 0.9726 | 191.20 191.32 | 191.26 | 0.5063 |
| 1 | 0.8105 | 180.00 179.68 | 179.84 | 0.4977 |
| 3 | 0.6079 | 165.70 165.62 | 165.66 | 0.4815 |
| 8 | 0.3741 | 150.57 150.42 | 150.50 | 0.4662 |
| 13 | 0.2702 | 144.15 144.00 | 144.08 | 0.4601 |

Plot of $\frac{\eta_{sp}}{C}$ vs. C see Fig. 3.

TABLE 5

Typical Viscosity Data of Fraction 1, Sample B.

Solvent: toluene
Flow time of solvent at $25^\circ C$: 128.15 sec.
Concentration of polymer stock solution: 0.8176 gm./dl.
Volume of polymer stock solution initially placed in
    viscometer: 5 ml.

| Total solvent added to viscometer ( ml.) | Concentration (gm./dl.) | Flow Time (sec.) | | $\frac{\eta_{sp}}{C}$ |
|---|---|---|---|---|
| | | Measured | Averaged | |
| 0 | 0.8176 | 231.01 231.18 | 231.10 | 0.9826 |
| 1 | 0.6813 | 211.50 211.32 | 211.41 | 0.9536 |
| 3 | 0.5110 | 188.07 187.87 | 187.97 | 0.9135 |
| 8 | 0.3144 | 163.67 163.42 | 163.55 | 0.8786 |
| 13 | 0.2271 | 152.98 153.02 | 153.00 | 0.8539 |

Plot of $\frac{\eta_{sp}}{C}$ vs. C see Fig. 4.

TABLE 6

Typical Viscosity Data of Fraction 1, Sample AB.

Solvent: Toluene
Flow time of solvent at 25°C. : 128.15 sec.
Concentration of polymer stock solution: 0.8208 gm./dl.
Volume of polymer stock solution initially placed in
  viscometer: 5 ml.

| Total solvent added to viscometer (ml.) | Concentration (gm./dl.) | Flow Time (sec.) | | $\dfrac{\eta_{sp}}{C}$ |
|---|---|---|---|---|
| | | Measured | Averaged | |
| 0 | 0.8208 | 224.42 224.50 | 224.46 | 0.9156 |
| 1 | 0.6840 | 206.22 206.32 | 206.27 | 0.8912 |
| 3 | 0.5130 | 184.49 184.37 | 184.43 | 0.8561 |
| 8 | 0.3157 | 161.60 161.50 | 161.55 | 0.8274 |
| 13 | 0.2280 | 151.32 151.40 | 151.36 | 0.7944 |

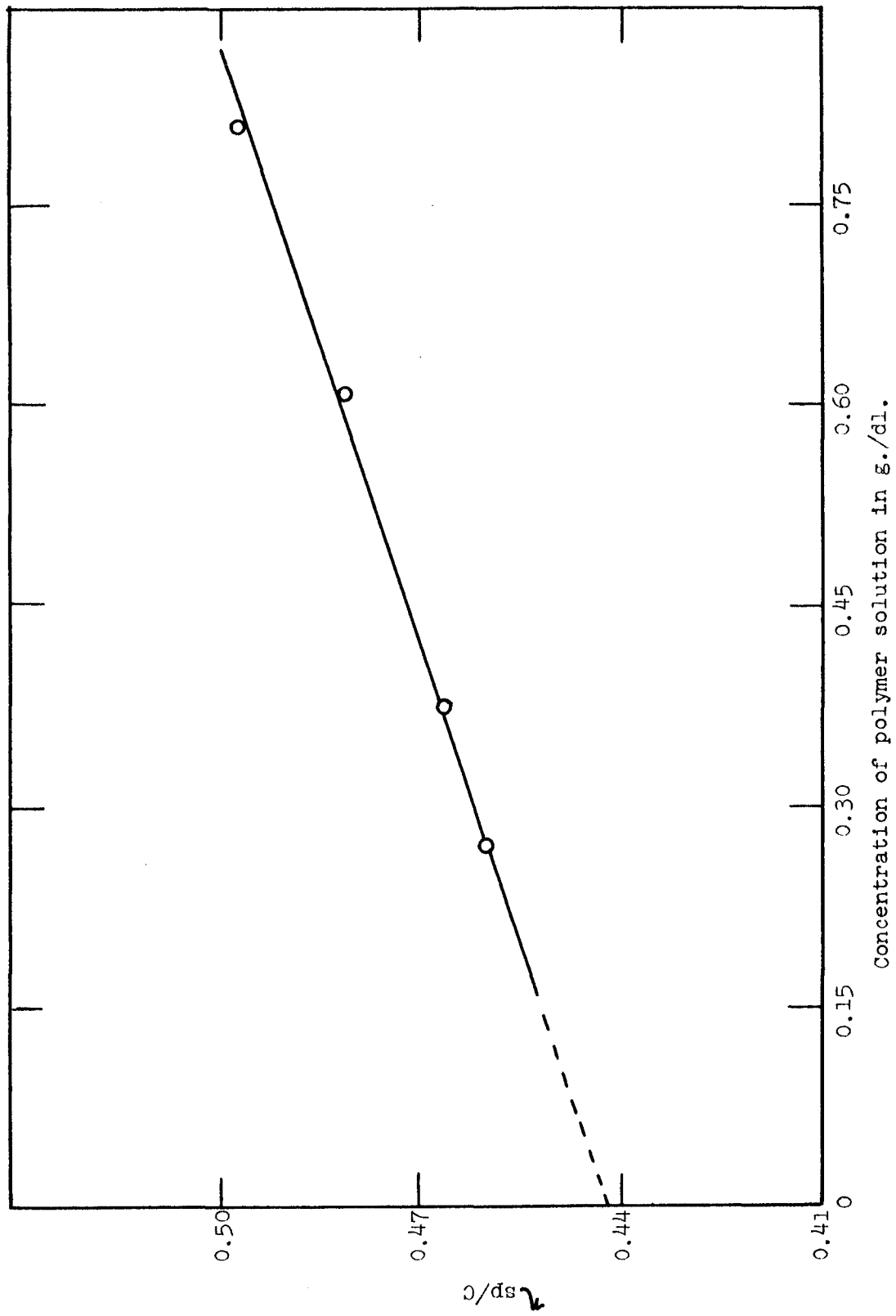Plot of $\dfrac{\eta_{sp}}{C}$ vs. C see Fig. 5.

Fig. 3.    Viscosity of polystyrene in toluene, fraction 1, Sample A.
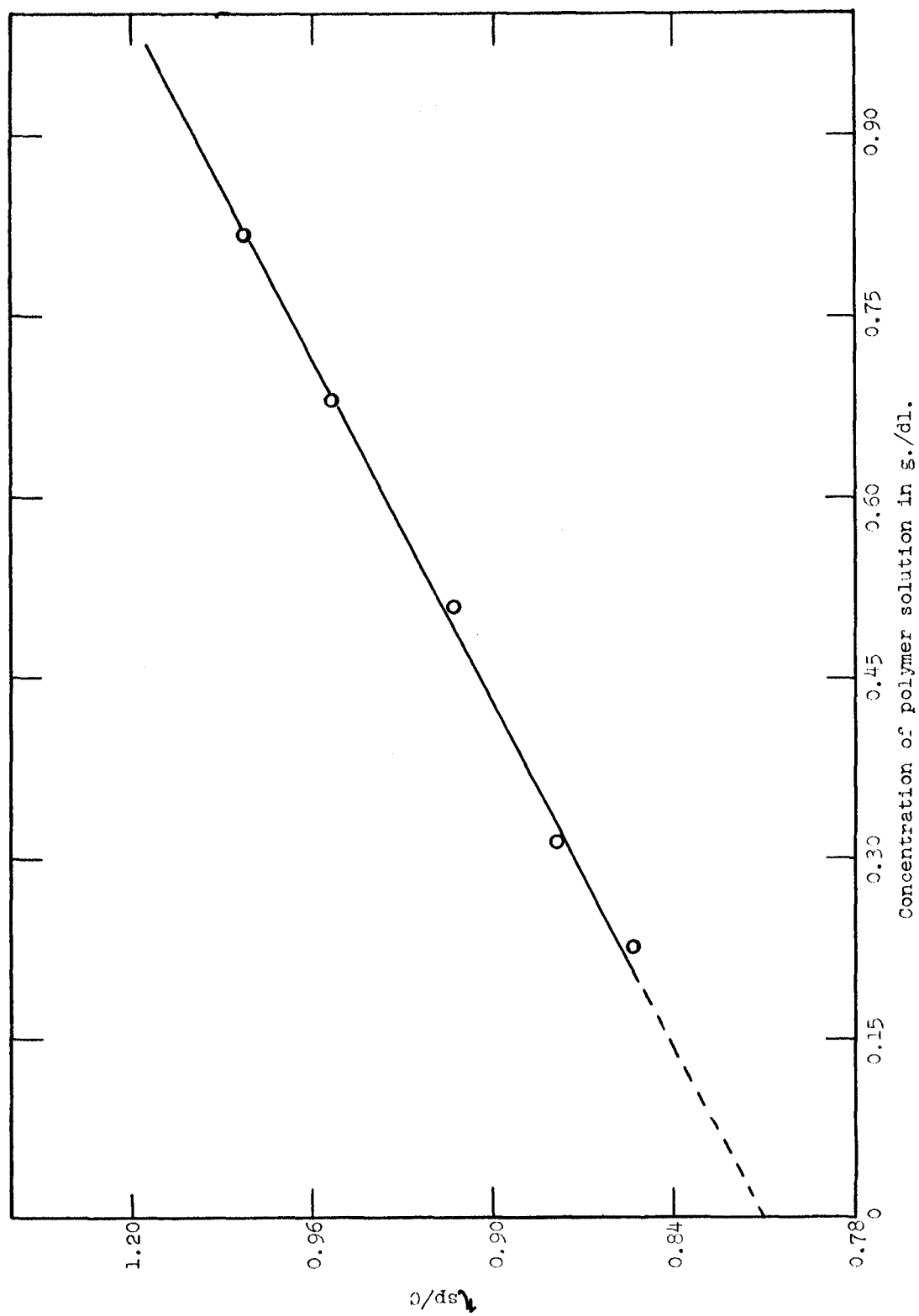
Fig. 4.   Viscosity of polystyrene in toluene, fraction 1, Sample B.
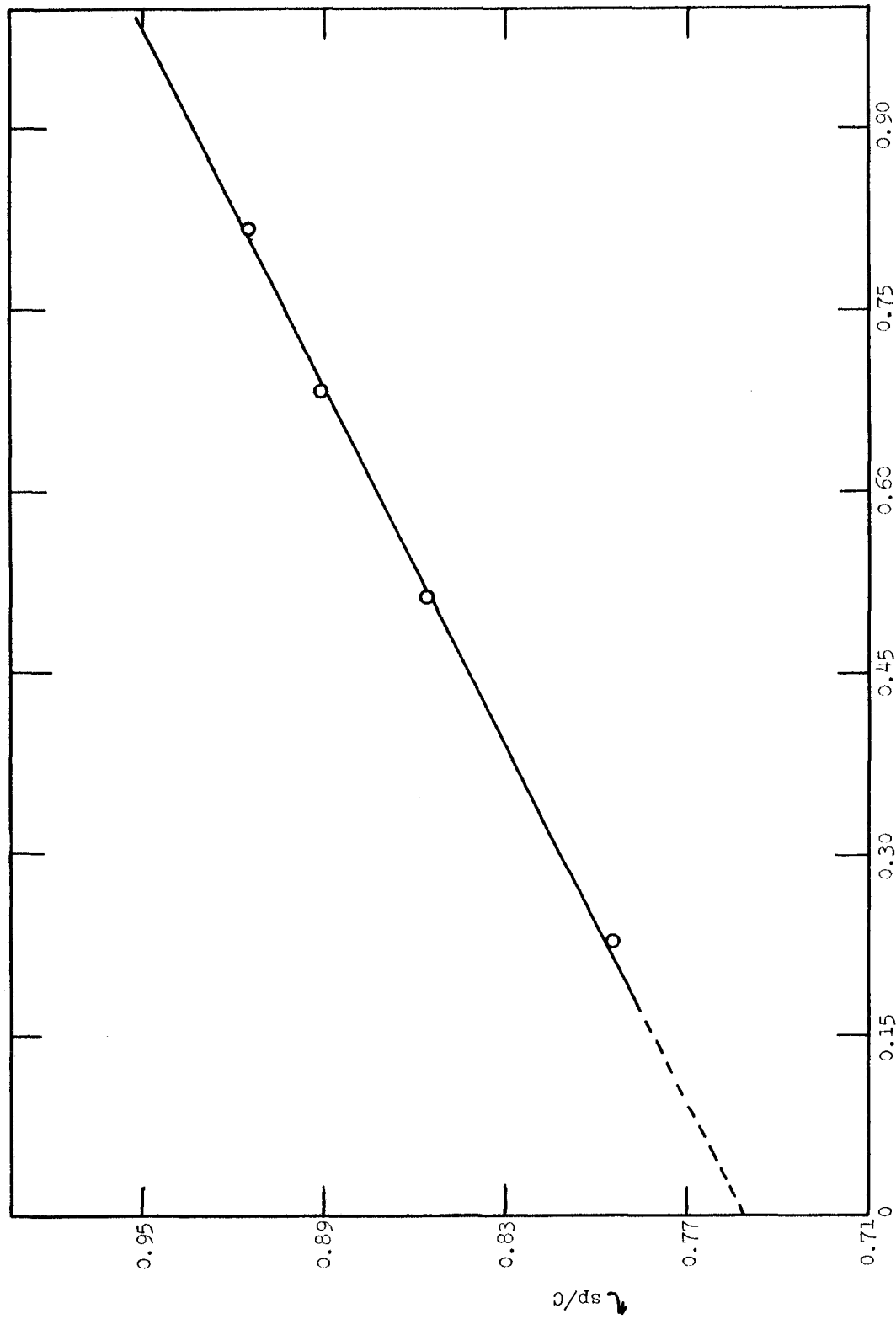
Fig. 5. Viscosity of polystyrene in toluene, fraction 1, Sample AE.

TABLE 7

Fractionation of Polystyrene, Sample A,
20g. Used. Precipitated from Methyl Ethyl Ketone
with Aqueous Methanol.

| Fraction | Actual weight (g.) | $[\eta]$ (dl./g.) | $\overline{M}_v$ ( x $10^{-4}$) | p ( x $10^{-2}$) | Wt. fraction up to p ($w_p$) |
|---|---|---|---|---|---|
| 1 | 1.548 | 0.442 | 8.90 | 8.54 | 0.987 |
| 2 | 2.049 | 0.336 | 5.99 | 5.75 | 0.909 |
| 3 | 1.265 | 0.297 | 5.03 | 4.83 | 0.807 |
| 4 | 1.054 | 0.286 | 4.72 | 4.54 | 0.744 |
| 5 | 1.104 | 0.263 | 4.20 | 4.04 | 0.691 |
| 6 | 1.025 | 0.256 | 4.03 | 3.87 | 0.636 |
| 7 | 1.026 | 0.224 | 3.33 | 3.19 | 0.585 |
| 8 | 0.929 | 0.219 | 3.21 | 3.08 | 0.533 |
| 9 | 0.582 | 0.207 | 2.95 | 2.84 | 0.487 |
| 10 | 1.236 | 0.201 | 2.85 | 2.74 | 0.458 |
| 11 | 0.821 | 0.195 | 2.71 | 2.60 | 0.396 |
| 12 | 1.161 | 0.175 | 2.33 | 2.23 | 0.355 |
| 13 | 1.000 | 0.166 | 2.14 | 2.06 | 0.297 |
| 14 | 0.933 | 0.138 | 1.64 | 1.58 | 0.247 |
| 15 | 1.142 | 0.133 | 1.55 | 1.49 | 0.200 |
| 16 | 2.862 | 0.098 | 1.01 | 0.97 | 0.143 |

where p represents chain length and $\overline{M}_v$ represents
viscosity-average molecular weight.

TABLE 8

Fractionation of Polystyrene, Sample B,
20g. Used. Precipitated from Methyl Ethyl Ketone
with Aqueous Methanol.

| Fraction | Actual weight (g.) | $[\eta]$ (dl./g.) | $\bar{M}_v$ ( x $10^{-4}$) | p ( x $10^{-3}$) | Wt. fraction up to p ($w_p$) |
|---|---|---|---|---|---|
| 1 | 1.991 | 0.810 | 2.14 | 2.05 | 0.995 |
| 2 | 1.572 | 0.715 | 1.79 | 1.71 | 0.895 |
| 3 | 1.372 | 0.645 | 1.54 | 1.48 | 0.816 |
| 4 | 1.600 | 0.597 | 1.38 | 1.32 | 0.748 |
| 5 | 1.254 | 0.565 | 1.27 | 1.22 | 0.668 |
| 6 | 1.842 | 0.495 | 1.04 | 1.00 | 0.608 |
| 7 | 1.868 | 0.466 | 0.96 | 0.92 | 0.513 |
| 8 | 1.369 | 0.429 | 0.85 | 0.82 | 0.419 |
| 9 | 0.903 | 0.404 | 0.78 | 0.75 | 0.351 |
| 10 | 1.079 | 0.363 | 0.67 | 0.64 | 0.306 |
| 11 | 0.770 | 0.333 | 0.59 | 0.57 | 0.252 |
| 12 | 0.661 | 0.312 | 0.54 | 0.52 | 0.213 |
| 13 | 0.585 | 0.278 | 0.46 | 0.44 | 0.180 |
| 14 | 0.497 | 0.249 | 0.39 | 0.37 | 0.151 |
| 15 | 2.523 | 0.193 | 0.27 | 0.25 | 0.126 |

where p represents chain length and $\bar{M}_v$ represents
viscosity-average molecular weight.

# TABLE 9

### Fractionation of Polystyrene, Sample AB,
### (a mixture of Sample A and B, 10g. each), 20g. Used.
### Precipitated from Methyl Ethyl Ketone with
### Aqueous Methanol.

| Fraction | Actual weight (g.) | $[\eta]$ (dl./g.) | $\overline{M}_V$ ( x $10^{-4}$) | p ( x $10^{-2}$) | Wt. fraction up to p ($w_p$) |
|---|---|---|---|---|---|
| 1 | 1.632 | 0.751 | 19.18 | 18.42 | 0.993 |
| 2 | 1.485 | 0.614 | 14.32 | 13.75 | 0.911 |
| 3 | 1.649 | 0.535 | 11.75 | 11.28 | 0.837 |
| 4 | 1.295 | 0.464 | 9.55 | 9.17 | 0.754 |
| 5 | 1.196 | 0.420 | 8.27 | 7.95 | 0.690 |
| 6 | 0.994 | 0.380 | 7.16 | 6.87 | 0.630 |
| 7 | 0.878 | 0.356 | 6.51 | 6.25 | 0.580 |
| 8 | 0.777 | 0.330 | 5.83 | 5.60 | 0.536 |
| 9 | 0.825 | 0.306 | 5.23 | 5.02 | 0.497 |
| 10 | 0.891 | 0.287 | 4.75 | 4.57 | 0.456 |
| 11 | 0.768 | 0.279 | 4.57 | 4.39 | 0.412 |
| 12 | 0.825 | 0.260 | 4.11 | 3.95 | 0.373 |
| 13 | 0.711 | 0.249 | 3.88 | 3.72 | 0.332 |
| 14 | 0.798 | 0.227 | 3.39 | 3.25 | 0.296 |
| 15 | 1.415 | 0.197 | 2.75 | 2.64 | 0.256 |
| 16 | 0.880 | 0.168 | 2.10 | 2.10 | 0.186 |
| 17 | 2.834 | 0.127 | 1.41 | 1.41 | 0.142 |

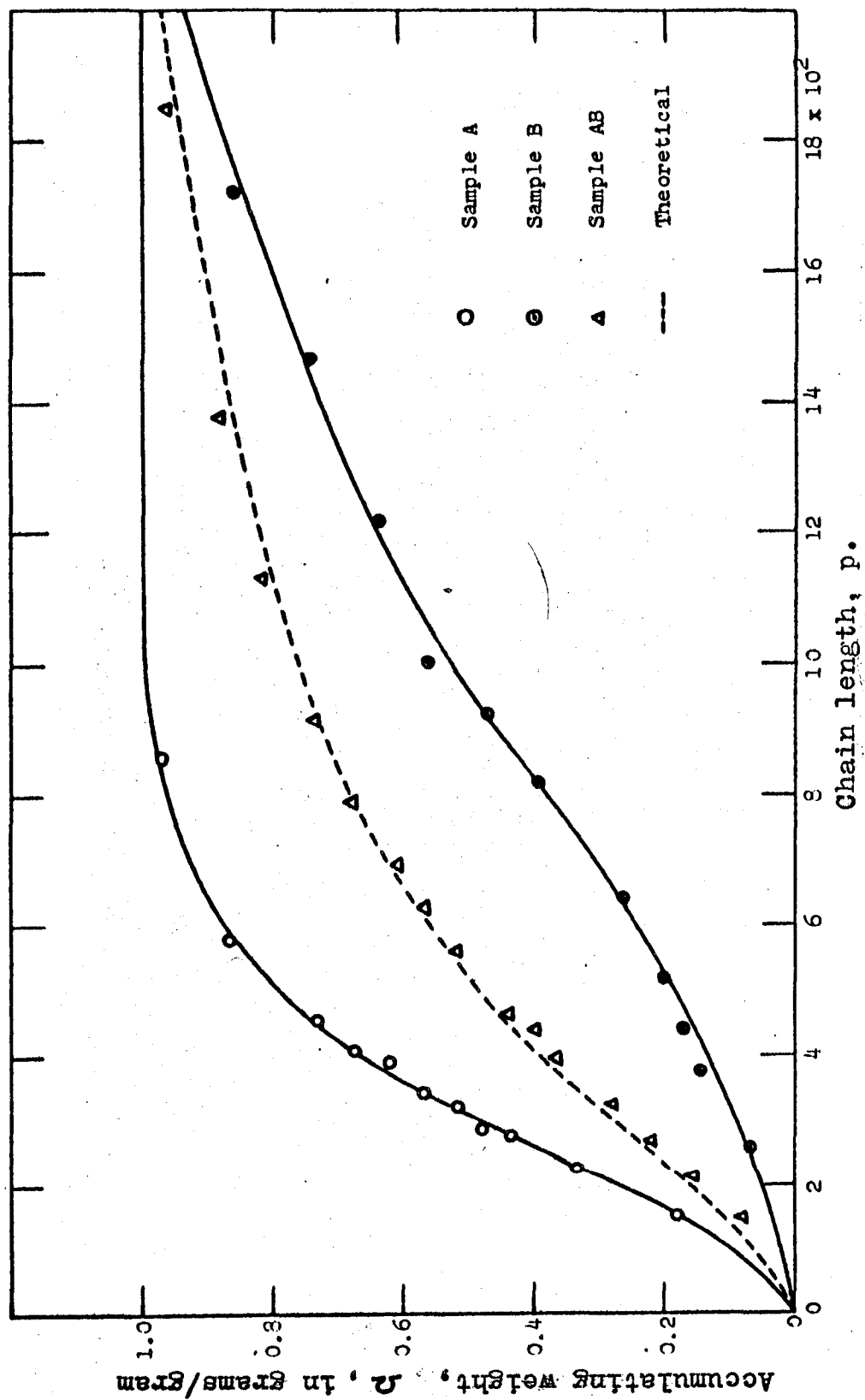where  p  represents chain length and  $\overline{M}_V$  represents viscosity-average molecular weight.

Fig. 6. Integral weight distribution curve of sample A, sample B and sample AB.

the cumulative curves. This was done, with the results shown in Fig. 7. Here the experimental points are obtained by taking slopes of the cumulative distribution curve, and do not correspond to individual fractions. As before, the curves for A and B are drawn through the plotted points for these samples. The dotted curve for AB is the mean of those for its progenitors, and the points for AB were obtained from the cumulative distribution for the mixed sample. Again the agreement is satisfactory. Fig. 7 shows the comparison for the differential weight distribution curves, Fig. 8 for the differential frequency curves.

As described on page 9 above, the differential weight distribution curve for a sample of polystyrene should be given either by

$$ w_p = MPAe^{-bp} \quad \dots\dots\dots\dots\dots \quad (11) $$

or

$$ w_p = M^2P^2A'e^{-bp} \quad \dots\dots\dots\dots \quad (13) $$

depending on whether termination is by desproportionation or by combination respectively. These equations may be cast into a linear form by using a logarithmic transformation

$$ \log_{10}\left(\frac{w_p}{p}\right) = \log_{10}(AM) - \frac{b}{2.303}p \quad \dots(11a) $$

$$ \log_{10}\left(\frac{w_p}{p^2}\right) = \log_{10}(A'M^2) - \frac{b}{2.303}p \quad \dots(13a) $$

The differential weight distribution curves were plotted in this way for samples A and B. The
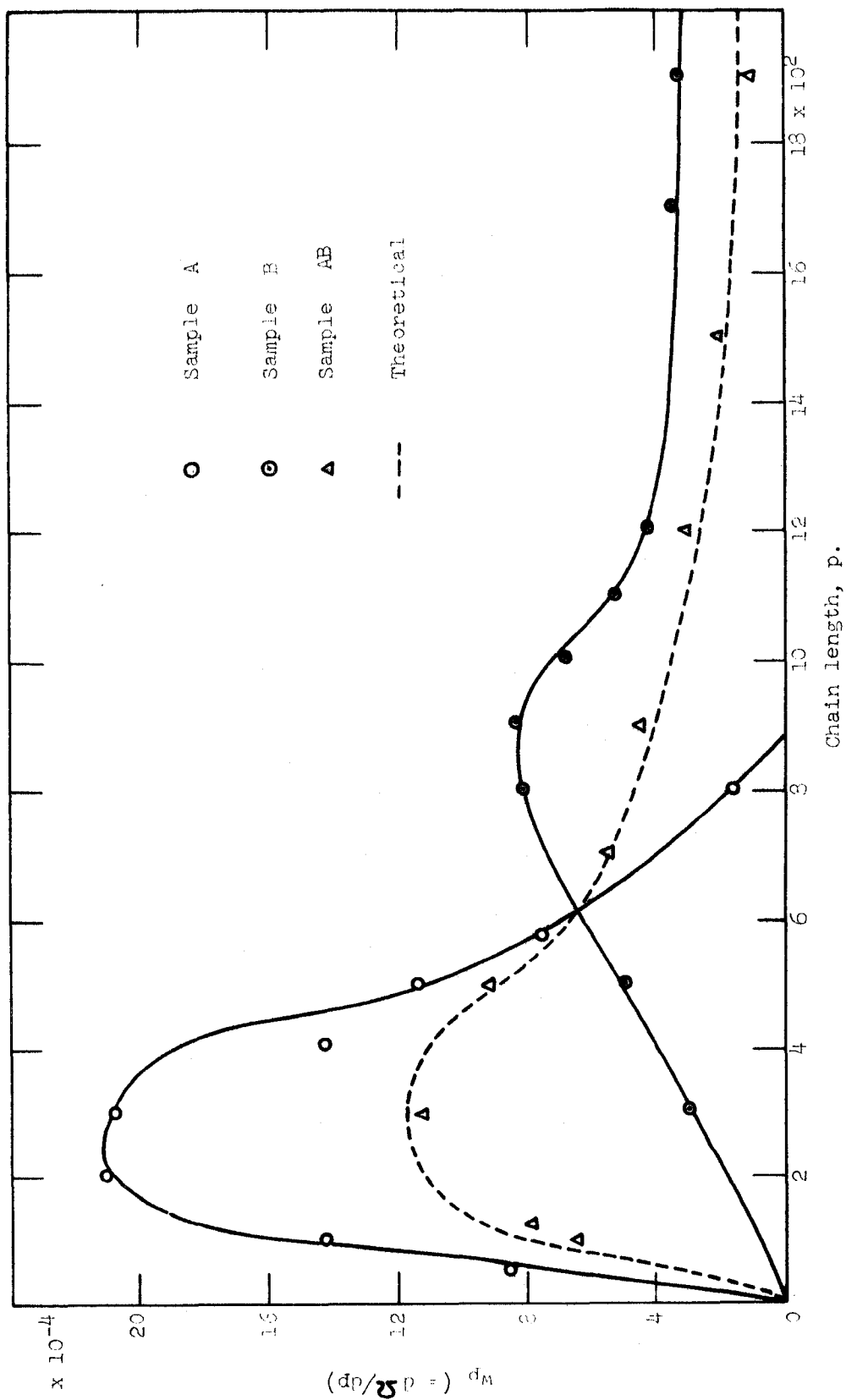
Fig. 7. The differential weight distribution curve of sample A, sample B and sample AB.
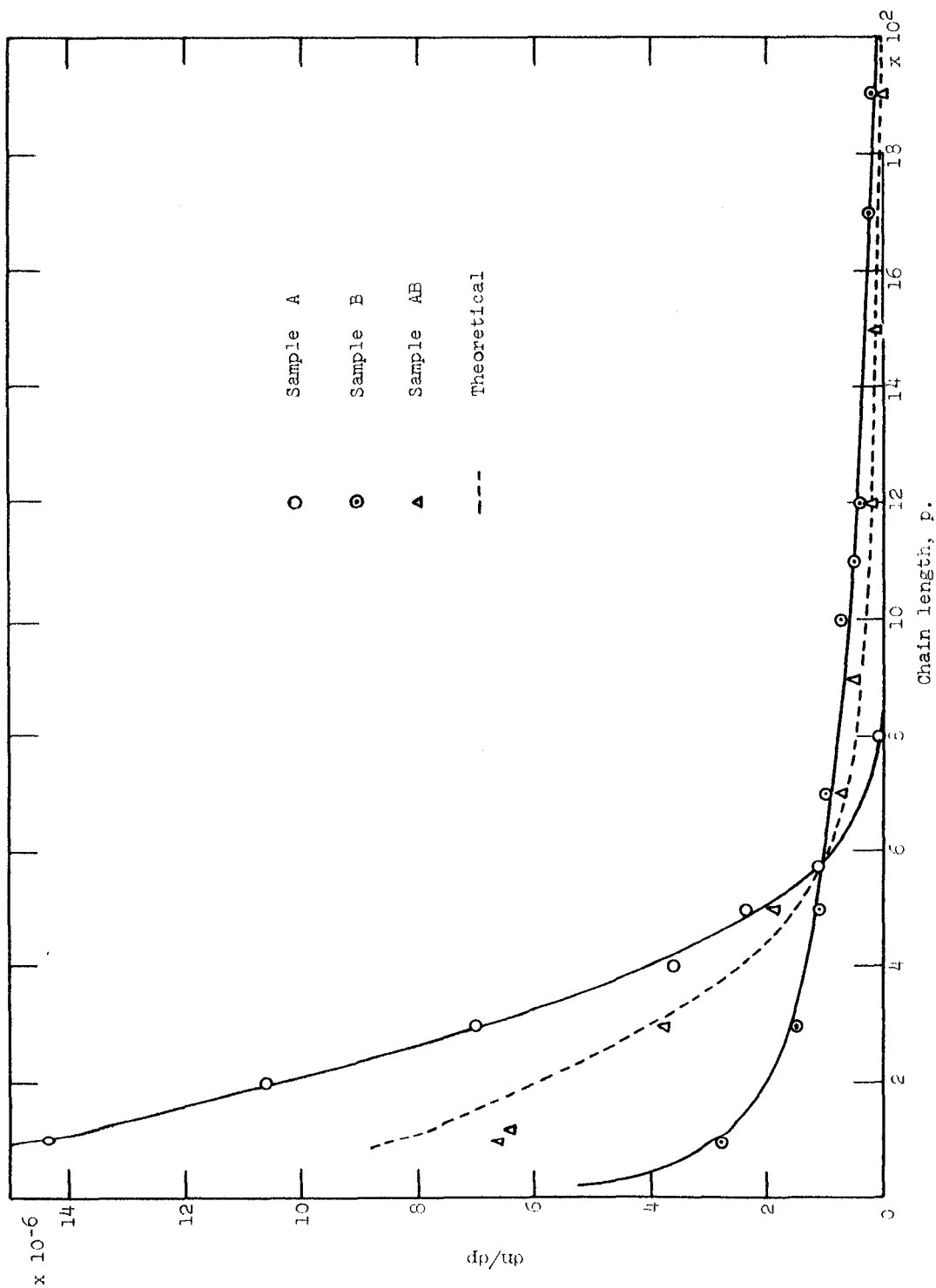
Fig. 8. The frequency distribution curve of sample A, sample B and sample AB.

results are shown in Fig. 9 to 12. Clearly the best
linear fit is obtained using the equation for termination
by combination. From the parameters of the best straight
lines in these plots it is possible to estimate values
for the parameters in equations (11) and (13) for each of
samples A and B. These functions can then be plotted on
the same graph as the experimental curves and a comparison
made. The results are seen in Fig. 13 and 14. Again
the better agreement with termination by combination is
observed.

## Discussion and Conclusions

The results presented in this thesis demonstrate
two points. First, it has been shown that the conventional
method of determining molecular weight distribution curves
from a single stage fractionation procedure is self-
consistent. By this it is meant that the distribution
curve for a mixture of samples is indeed the sum of the
curves for its components.

Secondly, it is shown that for two samples of
polystyrene prepared by benzoyl peroxide catalysed bulk
polymerization to low conversion, the distribution func-
tions are more closely represented by a kinetic model
postulating chain termination by combination, than by
one postulating termination by disproportionation. This
is in agreement with studies in which the number of
initiator fragments per molecule have been determined[8].
For polystyrene it appears that two fragments per molecule
are found, indicating termination by combination of
radicals.

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8. Baxendale, J. H., Bywater, S. and Evans, M. B.,
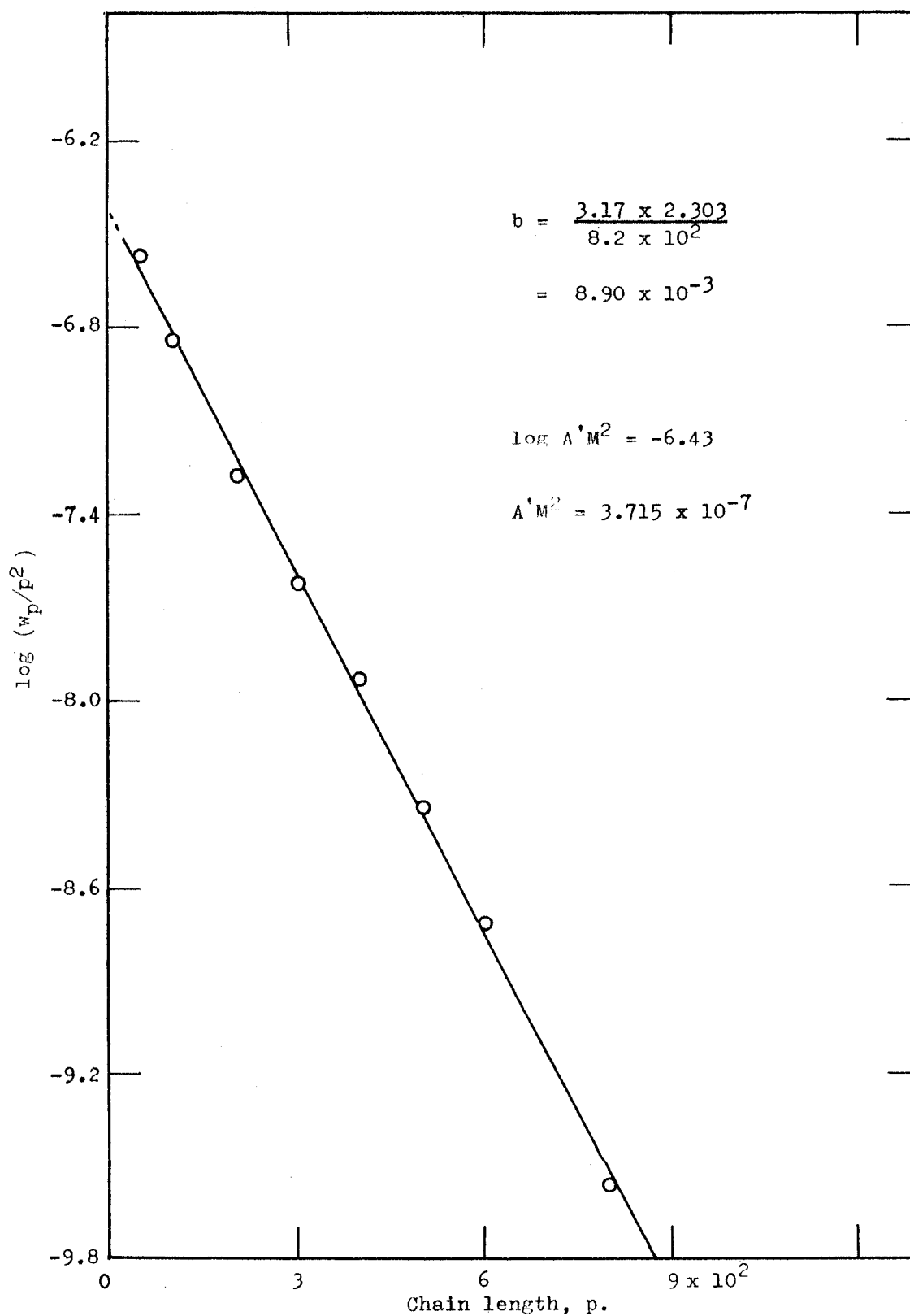Trans. Far. Soc., 42 675 (1946).

$$b = \frac{3.17 \times 2.303}{8.2 \times 10^2}$$

$$= 8.90 \times 10^{-3}$$

$$\log A'M^2 = -6.43$$

$$A'M^2 = 3.715 \times 10^{-7}$$

Fig. 9.    Termination by combination,
Sample **A**.

$$b = \frac{2.370 \times 2.303}{9.5 \times 10^2}$$

$$= 5.75 \times 10^{-3}$$

$$\log AM = -4.430 = \bar{5}.57$$

$$AM = 3.715 \times 10^{-5}$$
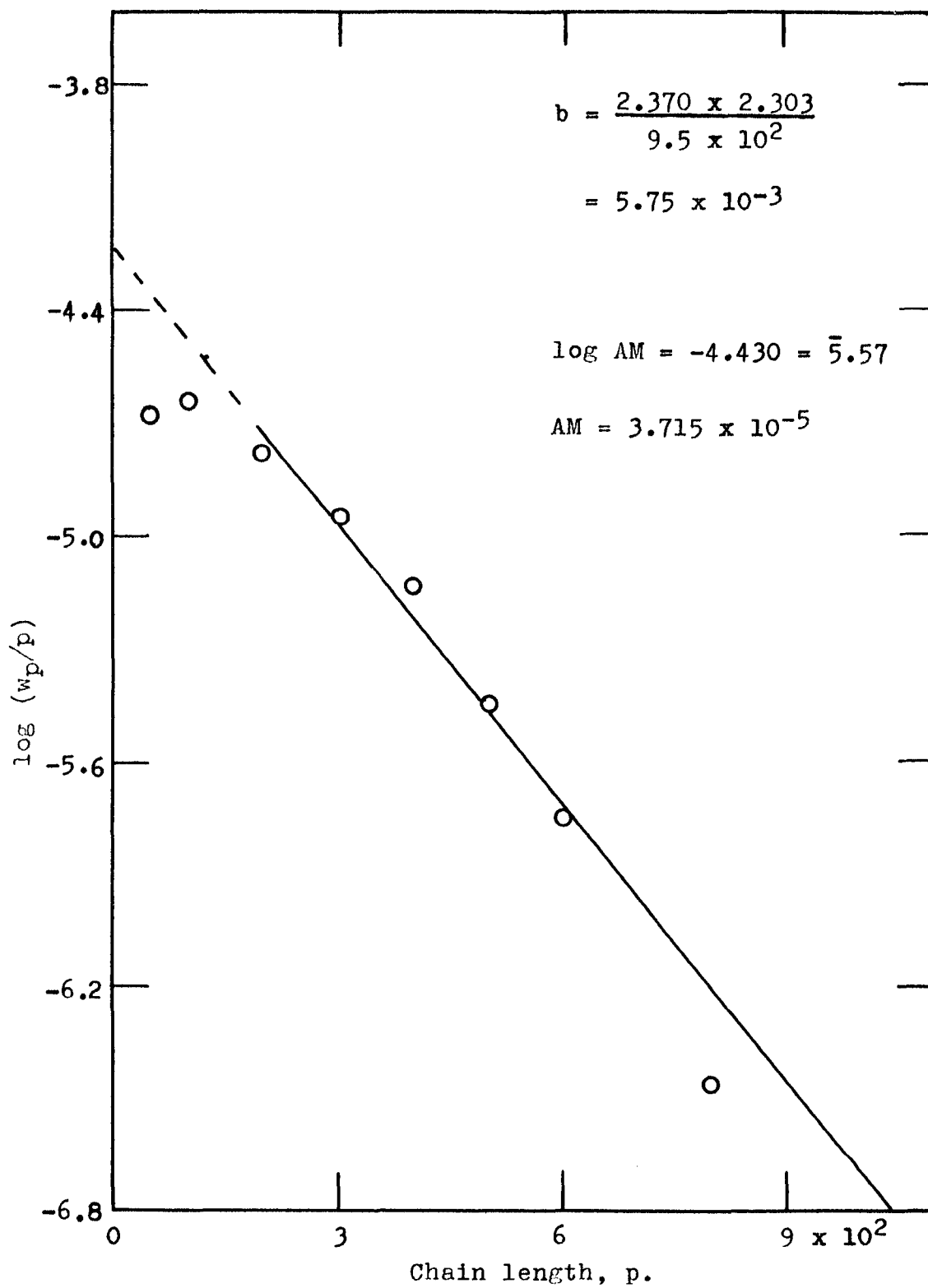
Fig. 10.    Termination by disproportionation,
Sample A.

$$b = \frac{1.9 \times 2.303}{1.67 \times 10^3}$$

$$= 2.63 \times 10^{-3}$$

$$\log A'M^2 = -8.1 = \bar{9}.90$$

$$A'M^2 = 9.542 \times 10^{-9}$$
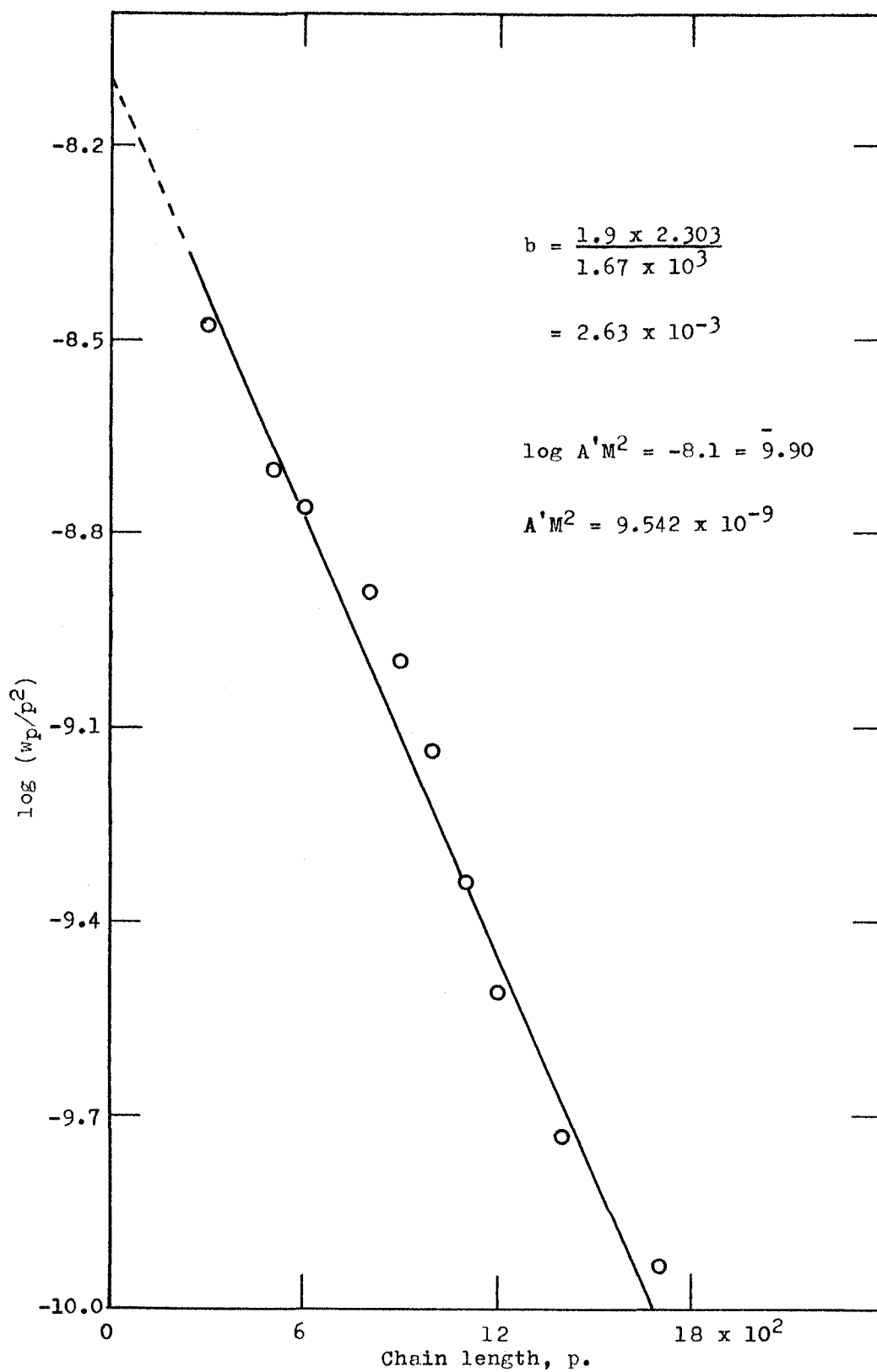
Fig. 11.    Termination by combination,
Sample B.

$$b = \frac{1.465 \times 2.303}{1.74 \times 10^3}$$

$$= 1.94 \times 10^{-3}$$
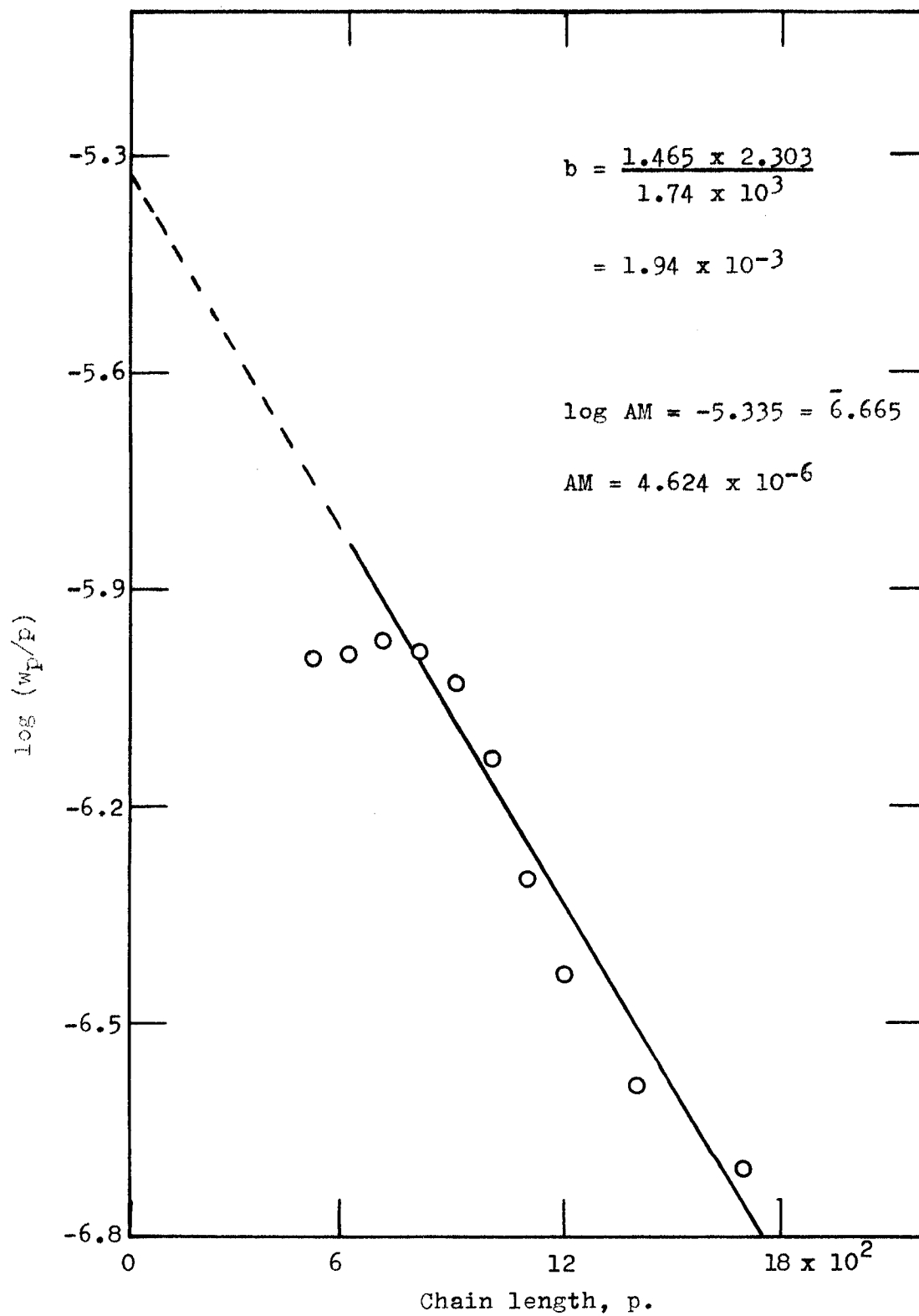
$$\log AM = -5.335 = \bar{6}.665$$

$$AM = 4.624 \times 10^{-6}$$

Fig. 12.    Termination by disproportionation,
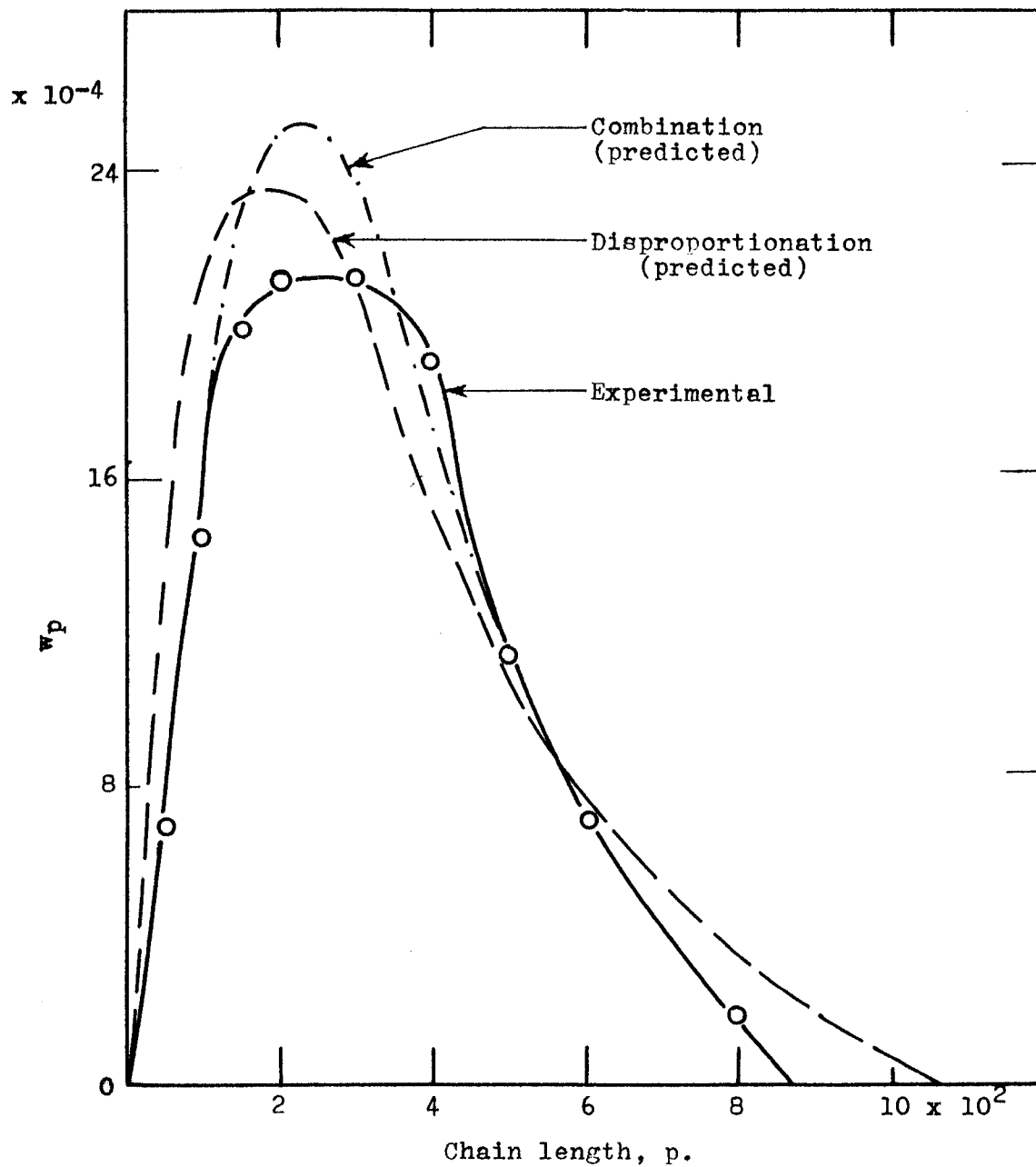Sample B.

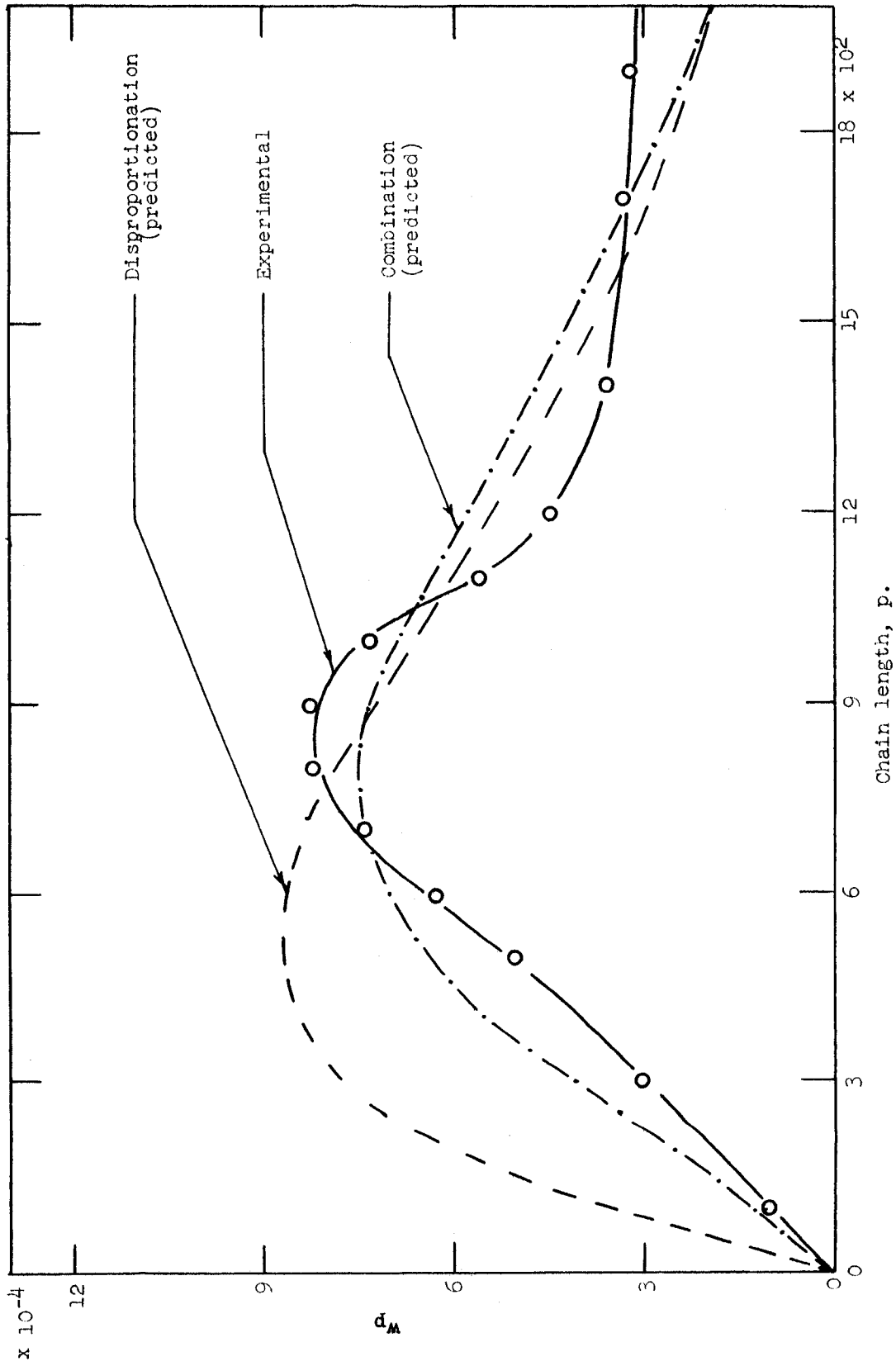Fig. 13. The experimental and predicted differential weight distribution curves, Sample A.

Fig. 14.  The experimental and predicted differential weight distribution curves, Sample B.

# BIBLIOGRAPHY

1. Bawn, C. E. H., *Chemistry of High Polymers*, New York, Interscience Publishers, (1948).

2. Baxendale, J. H., Bywater, S., and Evans, M. B., Trans. Far. Soc., 42, 675 (1946).

3. Cragg, L. H., and Hammerschlag, H., Chem. Revs., 39, 79 (1946).

4. Bannister, D. W., Phillips, C. S. G., and Williams, R. J. P., Anal. Chem., 26, 1451 (1954).

5. Booth, C., and Beason, L. R., J. Poly. Sci., 42, 81 (1960).

6. Huggins, M. L., J. Am. Chem. Soc., 64, 2716 (1942).

7. Outer, Carr, and Zimm, J. Chem. Phys., 18, 830 (1950).

8. Guzman, G. M., J. Poly. Sci., 19, 519 (1956).

9. Beall, G., J. Poly Sci., 4, 483 (1949).

10. Billmeyer, F. W., *Textbook of Polymer Science*, New York, Interscience Publishers (1962).

11. Jellinek, H. H. G., *Degradation of Vinyl Polymers*, New York, Academic Press Inc., (1955).

12. Channen, E. W., Revs. Pure and Appl. Chem., 9, 226 (1959).

13. Allen, P. W., *Techniques of Polymer Characterization*, London, Butterworths Scientific Publications (1959).

14. Tompa, H., *Polymer Solutions*, London, Butterworths Scientific Publications (1956).

15. Flory, P. J., *Principles of Polymer Chemistry*, Ithaca, Cornell University Press (1953).

16. Huggins, M. L., Physical Chemistry of High Polymers, New York, Wiley, (1958).

17. Burnett, G. M., Mechanism of Polymer Reaction, New York, Interscience Publishers, (1954).

18. Teach, W. C., Polystyrene, New York, Reinhold Pub. Corp., (1960).

19. Guzman, G. M., J. Poly. Sci., 19, 519 (1956).

20. Bamford, C. H., Barb, W. G., and Onyon, P. F., The Kinetics of Vinyl Polymerization by Radical Mechanisms, New York, Academic Press Inc., (1958).

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