

**A STUDY OF THE RELATION BETWEEN
" MOLECULAR WEIGHT DISTRIBUTION
AND MECHANICAL PROPERTIES OF
POLYVINYL ALCOHOL**

by

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**Thesis submitted to the Faculty of the
Virginia Polytechnic Institute
in Candidacy for the Degree of
DOCTOR OF PHILOSOPHY
in
CHEMISTRY**

APPROVED:

Chairman, Advisory Committee

August, 1953

Blacksburg, Virginia

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V. INTRODUCTION

The feature of high polymers which distinguishes them from other types of organic molecules is their mechanical properties - "their tensile strength, elasticity, deformability and hardness" (6). These properties are apparently closely connected with the structure, size and shape of the polymer molecule.

Polyvinyl alcohol, as is the case with other high polymers, does not consist of molecules of a single chain length, but rather is heterogeneous with respect to molecular weight. Thus a molecular weight (or degree of polymerization) determination on a given polymeric material gives only an average value. It has been noted by several investigators (13,14,23,34,43,44,46,52,55,64,72,76,77,80,82,86,89) that the mechanical properties of a polymer are dependent on the average degree of polymerization. In general it seems that there is a minimum value of polymerization degree below which no mechanical properties are shown, with a relatively rapid rise in properties above this value up to a limiting value above which there is little change in properties with increasing average degree of polymerization.

A number of investigators (11,14,17,34,42,43,44,45,65,66,76,77,86) have recognized that not only the degree

of polymerization but also the distribution of chain lengths has a role in determining the mechanical properties shown by samples of high polymers. Thus it is possible to prepare blends having the same degree of polymerization but considerably different properties, only the distribution of molecular sizes being different. In a few cases a moderately successful correlation between these mechanical properties and the chain length distribution curves has been obtained (14,44,66,76,77,86).

The purpose of the present investigation is to study the mechanical properties of polyvinyl alcohol films as a function of changing shape of the chain length distribution curves and to attempt to correlate these properties with the shapes of the distribution curves. Thus when sufficient data have been accumulated it may be possible at some time in the future to prepare polymers showing any desired properties from a knowledge of the effect of and how to control such factors as the composition and configuration of the monomer, the effect on the properties of the shape of the distribution curve, and how to control polymerization to obtain the desired distribution. Only the effect of the distribution on properties is to be studied in the present work.

In order to carry out this study it was necessary to separate commercial polyvinyl alcohol samples into a

series of fractions as nearly homogeneous with respect to degree of polymerization as may be obtained by the fractional precipitation method used. These homogeneous fractions were then blended to give samples varying in the shapes of their distribution curves. Two sets of blends were prepared with certain restrictions imposed upon them in terms of their differential distribution curves.

In the first set of blends the effect on mechanical properties of changing the height at the maximum of the differential distribution curve was studied. In this case the average degree of polymerization was held constant and the curves were all normal.¹

In the second set of blends the height at the maximum was held constant as well as the degree of polymerization at which the maximum occurred (P_M) and the effect of skew from the normal distribution was studied.

An attempt was then made to correlate the tensile strength of the blends as a function of the factors described above, i. e. height at maximum, P_M , and skewness. A further factor, namely, the effect of the amount of low degree of polymerization material was also noted, and an attempt was made to correlate the properties with percentage of material below D.P. = 1000.

¹ The term normal curve as used in this thesis refers to a differential distribution curve that is symmetrical.

VI. LITERATURE REVIEW

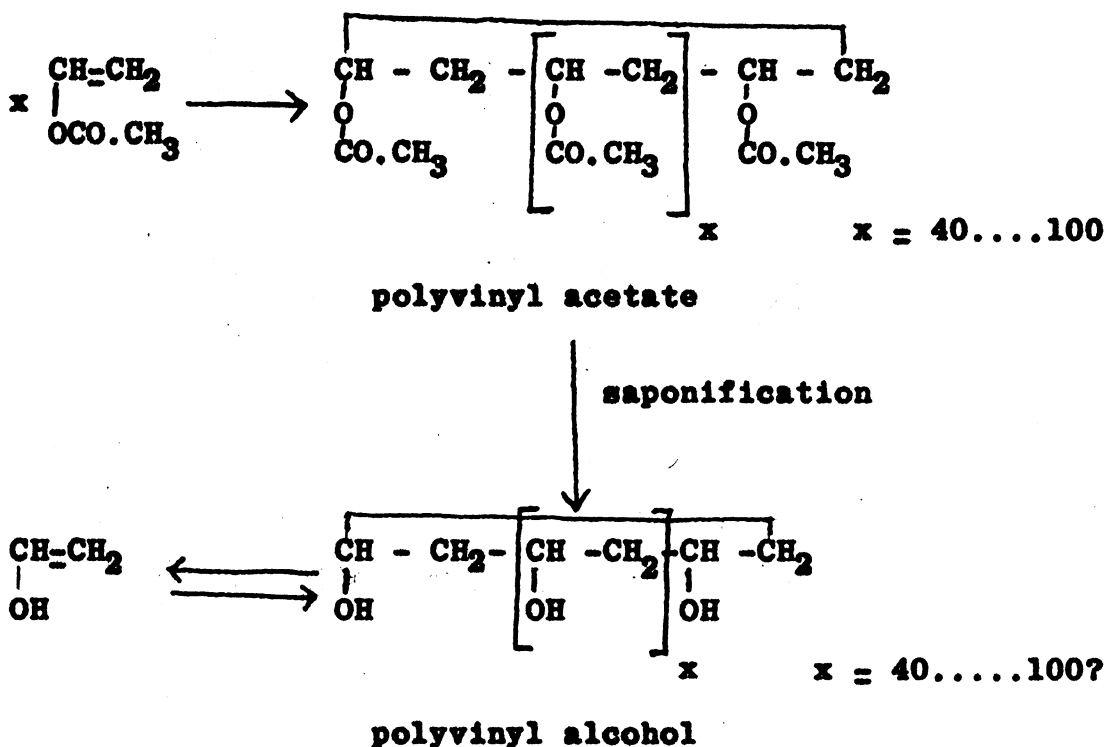
Historical

In 1838 Regnault (73) observed the formation of a white powder when sealed tubes of vinyl chloride were allowed to stand in sunlight. In 1872, Bauman (5) also polymerized vinyl halides. In 1912 Ostromislensky (21,71) produced rubberlike masses from polymerized vinyl halides. The intentional use of catalysts, such as benzoyl peroxide, to bring about polymerization was discovered by Klatte and Rollett in 1917 (48).

Aside from the polyvinyl halides nothing was known about other polyvinyl esters until the discovery of polyvinyl acetate by Klatte (47) in 1912. In 1927 Herrmann and Haehnel (36) showed that polyvinyl acetate reacts as a typical organic ester without losing its resinous nature. By hydrolysis with acids or alkalis they obtained polyvinyl alcohol, a water soluble polymer, which shows the reactions characteristic of a polyhydric alcohol.

Staudinger, Frey and Starck (85) also reported the preparation of polyvinyl alcohol in 1927. These investigators reached the conclusion that in polyvinyl polymers a large number of vinyl groups are combined, forming a saturated, unbranched carbon chain. This concept of

molecules of an organic compound combining by primary valence bonds into a macromolecule was revolutionary at that time but is now generally accepted. Their representation of the conversion of monomeric vinyl acetate to polyvinyl acetate and the formation of polyvinyl alcohol from polyvinyl acetate was as follows:



They also reported that the chemical behaviour of polyvinyl alcohol is that which would be expected of a poly-1,3-glycol.

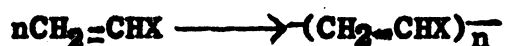
Classification of High Polymers

Polymers may be classified broadly into two types from the chemical point of view (6):

- (1) **Condensation Polymers**, where the monomers react by an elimination process involving the removal of simple molecules such as water, ammonia, HCl or NaCl. The structure of the monomer is such that the process can repeat itself in building up the polymer molecule. Since there is a loss of molecules the ultimate analysis of the polymer will differ from that of the monomer.
- (2) **Addition Polymers**, in which the monomers unite directly without formation of other products. The ultimate analysis of the polymer is identical with that of the monomer.

Polymerization of Vinyl Compounds

Vinyl polymers are classified as addition polymers. The total chemical change due to the polymerization reaction can be summarized as follows (56):



where X may be any substituent; in most cases it is Cl, OH, C₆H₅, CO.CH₃ or another well-known group of atoms. It is to be noted that in the above formulation no assumption is made regarding the nature of the groups at the end of the chain. The macromolecule represented on the right side of the above equation contains all the atoms of the n individual molecules linked together by primary valences.

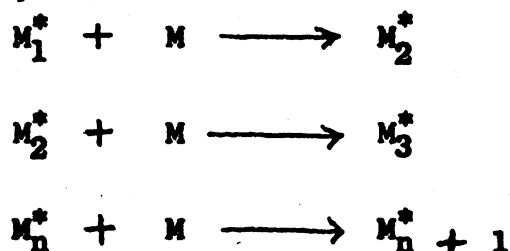
"Olefinic molecules such as styrene, some of its substituted derivatives and vinyl acetate polymerize slowly at ordinary temperatures when in the pure state. Most olefinic molecules which are polymerizable require, however, some form of activation, and this may be supplied by thermal or photo-chemical agencies or by the use of a suitable catalyst" (6). Starkweather and Taylor (83) proposed in 1930 that polymerization of vinyl acetate involves some kind of chain reaction. They found that benzoyl peroxide acts as a trigger catalyst in starting reaction chains and is itself destroyed in the process, since chemical tests showed its absence when the catalyzed reaction stopped. Curme and Douglas (19) pointed out that chain reactions in general are characterized by the existence of an induction period and by the fact that traces of impurities can have a decided inhibiting or accelerating effect, depending on whether the impurity tends to break or initiate chains. These characteristics are true of the polymerization of vinyl compounds and serve to establish this polymerization as a chain reaction.

Staudinger (84) first proposed that the chain initiator was a monomer molecule in which the double bond had been opened by a suitable activation.

A number of authors (1,12,19,37,41) have discussed the mechanisms of vinyl polymerizations. It is now generally agreed that the total polymerization reaction consists of a number of elementary processes such as activation, propagation, transfer, branching and termination (37).

Considering the initiation process, Abere and co-workers (1) proposed that activation occurs by collision of an unactivated monomer with another monomer, a solvent molecule, a polymer molecule or a catalyst. The most efficient catalysts are those substances which are known to be reactive toward double bonds (6). These substances can be classified into two groups: a) oxygen, peroxide compounds, ozonides, free radicals, etc. b) acids, BF_3 , SnCl_4 , TiCl_4 , AlCl_3 , etc.

The propagation process can be represented as follows (6):



The principal types of termination reactions are (6):

"a) reaction of the free radical end of one chain with a similar grouping in another chain

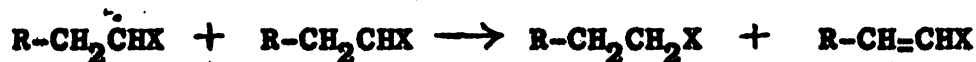
- b) addition of initiator (radical) to the active chain end
 c) termination by impurities such as oxygen, inhibitors, etc."

Probably the most general termination reaction is bimolecular and of type a. Two such types of bimolecular termination can occur:

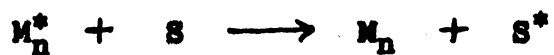
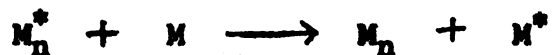
- 1) The union of radicals by a combination mechanism



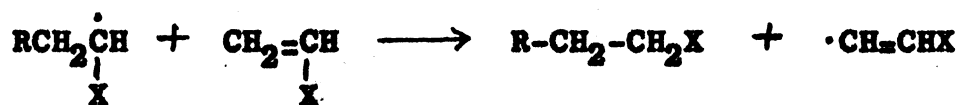
- 2) Disproportionation



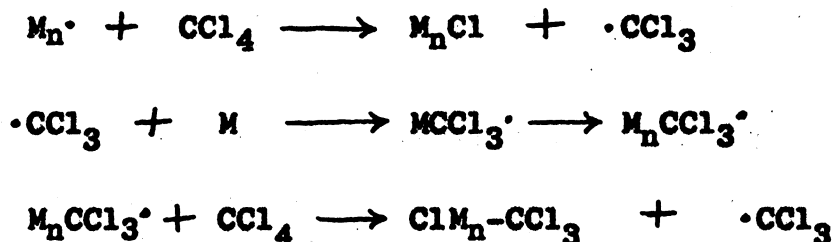
Besides the above processes in vinyl polymerization there is also the possibility of chain transfer (6), i. e. the activity may be transferred from the growing polymer to monomer (M) or solvent (S) molecules:



With the monomer:



With solvent (M is styrene) (11a):



Not only can a growing chain transfer its reactivity to a monomer or a solvent molecule but also to an inactive polymer molecule, at any position along the chain. The presence of an active center along the chain can give rise to branching and cross linking. Thus in vinyl polymers there may be a small number of branched or even cross linked chains (6). Bevington and Norrish (9,10) produced insoluble cross linked materials from solutions of various vinyl polymers by the action of metallic halides active in Friedel-Crafts reactions. Cross linking occurs by the elimination of a simple molecule HX between two polymer chains; X may be Cl or CH_3CO_2 .

Preparation of Polyvinyl Alcohol

Monomeric vinyl alcohol has never been isolated; it is known only in the form of polyvinyl alcohol (26,75). Fuson and coworkers (30,31,32) have isolated a very stable substituted vinyl alcohol, 1,2-dimesityl-1-buten-1-ol, which they found to be so stable that it could not be ketonized.

Polyvinyl alcohol must be prepared indirectly. This is usually done by the hydrolysis of polyvinyl acetate with either alkali or acid (26,36), for example by the use of hot alcoholic KOH or by passing HCl into a hot alcoholic solution of the ester (26,49). It is also possible to obtain polyvinyl alcohol by saponification of polyvinyl halides by alkaline reagents in the presence of catalysts (16). An example is the saponification of polyvinyl chloride with NaOH in the presence of light and a uranyl nitrate catalyst to give polyvinyl alcohol. It has also been reported (38,39) that polyvinyl chloroacetate or polyvinyl mixed esters such as polyvinyl acetate chloroacetate can be reacted with aqueous ammonium hydroxide to give polyvinyl alcohol.

By proper control of conditions it is possible to prepare polyvinyl alcohols of varying degrees of hydrolysis, ranging from very few OH groups in the polymer molecule up to 99-100% hydrolysis (25).

Copolymers of polyvinyl alcohol containing groups other than vinyl esters can be prepared by hydrolyzing a polymer such as a vinyl acetate - ethylene copolymer to the corresponding vinyl alcohol - ethylene copolymer (40).

Most investigators seem to agree that there is a decrease in degree of polymerization during the initial

hydrolysis of polyvinyl acetate to polyvinyl alcohol (24,60,67,74), but no appreciable change in degree of polymerization occurs on subsequent reacetylation and deacetylation. However, Korshak and Zamyatina (49) found no significant chain scission on the initial hydrolysis.

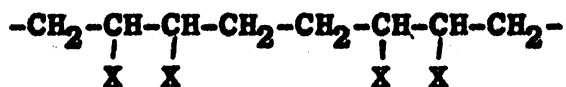
Structure of Polyvinyl Alcohol

In the case of a polymer such as polyvinyl acetate or polyvinyl alcohol there are three ways in which the monomers may be arranged (8,57). Illustrating with the formulation of Marvel (57):

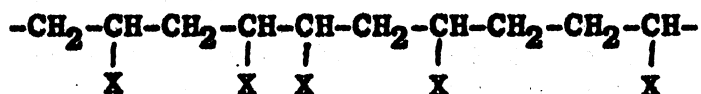
(1) Head-to-tail



(2) Head-to-head, tail-to-tail

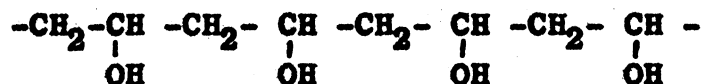


(3) Random



Actually it has been shown that the structural units of polyvinyl alcohol correspond to a 1,3-glycol

structure (head-to-tail) (57,58). Thus the presently accepted structure may be represented as follows:



According to Flory (28) the fact that the head-to-tail structure is preferred is explainable in terms of the free-radical mechanism of chain growth. The free-radical may add in either of the following two ways to the monomer:



If either step occurs to the virtual exclusion of the other a head-to-tail structure will result. "The free-radical produced in reaction (1) generally will be stabilized by the presence of the substituent on the free-radical carbon atom. No such stabilization occurs in the product of reaction (2)." Reaction (1) is concluded to occur preferentially.

It has been shown (29,61,69) that there are a small number of monomers combined head-to-head in polyvinyl alcohol. The number of such arrangements seems to depend on the temperature at which the vinyl acetate was

polymerized (29). Thus the mole percentages (based on the structural unit $-\text{CH}_2-\text{CHOH}-$) of 1,2-glycol structures vary from about 1.23% when the vinyl acetate from which the alcohol was made was polymerized at 25°C to 1.95% at 110°C .

Fractionation of High Polymers

The purpose of fractionation is to obtain some idea as to the heterogeneity of the molecular weight species present in the polymer sample. Fundamentally fractionation involves an attempt to separate the material into fractions which are completely homogeneous with respect to degree of polymerization. Actually such homogeneity is never realized. From a mathematical treatment (72,78) it has been concluded that there is not much hope of obtaining fractions sharper than about $\pm 5\%$ variation from the mean even by repeated fractionation by fractional precipitation or fractional solution.

Methods of Fractionation

A number of methods have been used for the fractionation of high polymers (18). These include: (1) fractional precipitation, (2) fractional solution, (3) distribution between two immiscible solvents, (4) diffusion, (5) ultracentrifuge, (6) chromatographic adsorption, (7) ultrafiltration, (8) molecular distillation.

The fractional precipitation method involves dissolving the heterogeneous polymer in a suitable solvent and then adding a nonsolvent. The precipitated phase, which contains the high molecular weight fraction, is separated from the supernatant solution by decantation (with or without centrifuging). More polymer is precipitated and the procedure is repeated. It has been pointed out a number of times (3,20,27) that the precipitation point of a polymer-solvent-precipitant system depends markedly on the temperature. Therefore it is necessary to control the temperature carefully during fractional precipitation. The actual fractionation may be carried out either isothermally or by lowering the temperature while keeping the composition constant, or frequently by a combination of the two. This fractional precipitation method is the most widely used method since it is easily carried out. It has been applied to a wide variety of polymers (18).

In the fractional solution method, the polymer is placed in a solvent-nonsolvent mixture and the system is allowed to come to equilibrium. The supernatant liquid is then decanted and the residue is treated with a new mixture, richer in solvent than the first, this process being repeated until all the polymer has dissolved. Thus the low-molecular fractions are extracted first. This method has been used rather frequently (18).

In the method involving distribution between two immiscible solvents a heterogeneous solvent system is used and the distribution of polymer molecules in the system depends on molecular weight. Schulz and Nordt (79) fractionated polyethylene oxide in this way using a water phase and a phase consisting of a solution of chloroform and benzene, the percentage of benzene being decreased stepwise in the separation of successive fractions. However, these authors believe that fractional precipitation is more efficient and should be used whenever possible. Lovell and Hibbert (53) also used this method for the fractionation of lignin.

In the diffusion method the separation according to molecular size is based on differences in the rate of solution or diffusion of the polymer molecules. Fractions are separated while they are still diffusing, before equilibrium is established. A large part of the diffusion fractionations have been carried out on natural rubber (18), although this method has been occasionally applied to synthetic polymers (18,88).

The ultracentrifuge method involves measurements of the rate of settling of a particle in a given centrifugal field. This method cannot be used to obtain usable fractions but is purely an analytical method giving both the average molecular weight and the distribution of

molecular weights (124). Kraemer and Lansing (50,51) discuss the advantages of the ultracentrifuge.

In the chromatographic adsorption method a solution containing the mixture to be separated is filtered through a column of an adsorbent. The principle of separation involves preferential adsorption. This method has been successfully used for cellulose acetate (56a) and for rubber (12a,79a).

The ultrafiltration method depends on filtering the polymeric molecules out by filters of varying pore size. This method is slow and probably unsatisfactory for linear molecules. It has been used for the fractionation of cellulose derivatives (18).

Molecular distillation is more useful for purification (removal of low degree of polymerization material) of high polymers than for the separation of high molecular weight fractions. "Molecular distillation is essentially a distillation at very low pressure, 10^{-3} or 10^{-6} mm of mercury. The distance between the distilling pan and the collecting plate is shorter than the mean free path of the evaporating molecules, so that they suffer (on the average) no collisions while in the vapor state. Under these conditions, even very slightly volatile substances can be distilled without decomposition. Moreover, the diffusion velocity of a molecule is inversely proportional

to the square root of the molecular weight, so that the lighter molecules distil off first, leaving the residue purified." (18).

Fractionation of Polyvinyl Alcohol

Several investigators (15,22,87) have fractionated polyvinyl alcohol by precipitation of the polymer fractions from water solution with acetone. Clarke and Blout (15) reported poor separation by this method. They also used a 1% solution of the polymer in ethylenediamine (98%) plus dioxane and benzene as the precipitant.

Flory and Leutner (29) carried out a careful fractionation of polyvinyl alcohol. They precipitated the polymer from water solution with dioxane at 60°C, dropped the temperature to 50°C and stirred for 16 hours. The precipitated polymer was removed by filtering without cooling.

Gavoret and Duclaux (33) found that coacervation took place when n-propanol was added to an aqueous solution of polyvinyl alcohol. They suggested that this would give a method of fractionation.

Of the methods of fractional precipitation found in the literature it was found that only the use of a n-propanol nonsolvent was readily applicable for the collection of the quantities of fractions that were needed in the present work.

Okajima and Takahashi (70) showed the possibility of fractional solution of polyvinyl alcohol by the temperature regulation of the extracting water.

Methods of Determining Molecular Weights of High Polymers

Several methods have found wide application in the determination of molecular weights of high polymers. These include: (1) osmotic pressure measurements, (2) end group determinations, (3) ultracentrifugation, (4) light scattering, and (5) viscosity measurements.

Viscosity and Molecular Weight

The simplest and most widely used method for molecular weight determinations of high polymers involves the measurement of the viscosity of a dilute solution of the polymer (6). This was the method used for molecular weight determinations in the present work.

"Although the theoretical and experimental basis of the law connecting viscosity with molecular weight has been widely discussed, the true form of the relationship still remains an unsettled question. The cause of the difficulty is the determination of the constants of proportionality in the equation originally proposed by Staudinger for linear molecules" (6). Staudinger's equation may be written:

$$\frac{\eta_{sp}}{c} = KM = K'P$$

where
$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1$$

η_{sp} is specific viscosity

η is viscosity of polymer solution

η_0 is viscosity of pure solvent

η_r is relative viscosity; $\eta_r = \frac{\eta}{\eta_0}$

K and K' are constants

M is molecular weight

P is degree of polymerization (D.P.)

c is the concentration of solution, usually expressed in grams per 100 ml.

A modification of the Staudinger equation which has found wide application is of the form (27,62,4,7,3):

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

where $[\eta]$ is the "intrinsic viscosity" (50) which is the limiting value of $\frac{\eta_{sp}}{c}$ at infinite dilution.

$$\lim_{c \rightarrow 0} \left(\frac{\eta_{sp}}{c} \right) = [\eta]$$

K and β are constants and M is molecular weight. The original Staudinger equation is seen to be the special case of $\beta = 1$ in the modified equation. "The exact meaning of the arbitrary constants K and β and their variation with structure and other factors is far from clear" (6).

This latter equation, rather than the original Staudinger equation, seems to be more applicable in relating molecular weight (or D.P.) of polyvinyl alcohol to viscosity, since various investigators have found that β is not equal to 1 for polyvinyl alcohol (29,35, 50,68).

In evaluating K and β independent determinations of molecular weights must be made by some other method such as the ultracentrifuge.

Distribution Curves

As was pointed out earlier, by a process of fractionation it is possible to separate a given polymeric material into a series of fractions differing in the average degree of polymerization. From a knowledge of the percentage of the original material which each fraction comprises and from a knowledge of the degrees of polymerization of the individual fractions it is possible to construct an integral distribution curve. This may be done by plotting $100 - A$, where A is the accumulative percent starting with the fraction of highest degree of polymerization, against the average degree of polymerization of the fraction.

By differentiation of the integral distribution curve the differential distribution curve is obtained.

This may be done mathematically if the equation for the integral distribution curve is known or it may be done graphically by taking slopes of various points on the integral distribution curve and plotting them against the corresponding degrees of polymerization.

It is of interest to note that in almost every case reported in the literature there is only one maximum in the differential distribution curve. In at least two cases recently differential distribution curves of synthetic polymers showing two maxima have been reported (59,63). One of these is a polyvinyl alcohol (59).

Factors Affecting Mechanical Properties of High Polymers

This subject has been rather thoroughly reviewed by a number of authors (2,34,55,72). It appears that for the most part complete quantitative information is lacking as to the effect of the various factors on the mechanical properties and, in particular, as to the interrelationships between the factors.

It is necessary to consider several factors in studying the way in which the mechanical properties of high polymers are connected with their fundamental architecture. There is the average degree of polymerization. There is the chemical nature of the monomer and, related to this, the intermolecular forces between chains

and the flexibility of the chains. Finally there is the effect of the molecular weight distribution.

The effect of average degree of polymerization on mechanical properties has been the subject of a considerable amount of study (13,14,17,19,23,34,42,43, 44,46,52,55,64,72,76,77,80,81,82,86,89,90). In general, it appears that to obtain any mechanical strength the average degree of polymerization (D.P.) must be above a certain minimum value. Above this D.P. the strength increases rapidly with increasing D.P. up to a certain point above which the curve (property versus D.P.) flattens out and there is little further change in mechanical properties with increasing D.P. above this point. The slope of such a curve seems to depend not only on the nature of the high polymer but also on the type of spinning or casting used to prepare the sample. If crystallization and orientation are favored during formation of the test specimen a higher level of mechanical strength is reached sooner than if the conditions are such that the material is left in a more disordered state (55).

Considering a property such as tensile strength, the magnitude of forces between the chains, the flexibility of the chains and the way in which the attraction centers are distributed along the chains are all important in

determining this property. At first glance it would seem that the magnitude of the attractive forces would be the most important factor by far. However, this may not be true when the chains are especially bulky and inflexible. In such cases, even very strong forces may be counteracted by the difficulty of fitting the molecules into a regular pattern (72).

"The intermolecular forces in polymers arise in the same way as those in liquids; by dipole or induced dipole attractions or by electronic interaction. The magnitude of these forces on any one monomer unit in a polymer will be expected to be about the same as in the liquid monomer, but with necessary modifications due to rigidities and orienting effects introduced by the chain structure" (34).

In the case of a polymer such as polyethylene the forces between hydrocarbon molecules are very small but due to the possibility of close packing the properties are closer to those of a plastic than those of a rubber. On the other hand, in cases such as styrene-butadiene copolymers, the irregularities along the chain work against close packing and the properties of rubbers are exhibited by these copolymers. In cases of relatively weak intermolecular attractions the entropy terms apparently play an important role (72).

In the case of strong intermolecular forces such as in cellulose or in polyvinyl alcohol these forces determine mechanical behaviour to a large extent. Even here, however, the chain flexibility affects the properties considerably as may be seen by comparison of cellulose and polyvinyl alcohol. When bone-dry both show fiber properties, with high strength and low elongation. If wetted, cellulose, having inflexible chains, does not show a large change in properties, whereas polyvinyl alcohol, having very flexible chains, shows decidedly rubber-like properties.

Turning to the effect of D.P. heterogeneity on the mechanical properties of high polymers, it seems to be impossible at the present time to make any sweeping generalizations as to the nature and magnitude of this effect although considerable work has been done on the subject (11,14,17,34,42,43,44,45,65,66,76,77,86). Some workers (45,54) have found that material of high D.P. heterogeneity (blended) was superior in mechanical properties to that of low heterogeneity (unblended), while others have observed the reverse to be true (66,76,77). Douglas and Stoops (23) found blends of vinyl chloride-acetate copolymer to be inferior in fatigue resistance and approximately equal in strength to fractions of the corresponding D.P. It seems at least conceivable that each of these differing viewpoints may

be essentially correct for the case studied, inasmuch as in the present work some indication was found that it may not be the heterogeneity or lack of the same which is of fundamental importance but rather the amounts of a certain range of relatively low D.P. material which are present. This point will be discussed in considerable detail later.

Scherer and his coworkers (14,44,76,77,86) have devised empirical equations which give a fair correlation between the mechanical properties of several high polymers and the shapes of their D.P. distribution curves.

VII. EXPERIMENTAL

Materials Used

The polyvinyl alcohol, Grade 71-24, completely hydrolyzed, medium viscosity, was obtained from Delkote, Inc., Wilmington, Delaware.

The n-propyl alcohol, technical grade, was obtained from Stoney-Mueller, Inc., Lyndhurst, New Jersey.

Small Scale Fractionation of Polyvinyl Alcohol

In order to obtain polyvinyl alcohol fractions which were as homogeneous as possible with respect to D.P. a method of fractionation was used which combined the use of a nonsolvent with a temperature decrease.

Various nonsolvent systems were investigated in order to fractionally precipitate the polyvinyl alcohol from water solution. These included:

- (1) acetone
- (2) acetone-water 1:1, 3:1, and 3:2 by volume
- (3) ethyl alcohol
- (4) acetone-ethyl alcohol
- (5) methyl alcohol
- (6) isopropyl alcohol
- (7) n-propyl alcohol and n-propyl alcohol-water
- (8) dioxane.

The only practical fractionation was obtained with n-propyl alcohol and n-propyl alcohol-water mixtures as nonsolvents. In the case of acetone, acetone-ethyl alcohol, and acetone-water (3:2) local precipitation which would not readily go back into solution made the systems impractical. In the other cases a gel which could be decanted was not formed within 72 hours at 15°C.

The procedure which was developed for the fractionation of polyvinyl alcohol from water solution using n-propyl alcohol as precipitant was as follows: 2.000 grams of polyvinyl alcohol and 98.0 grams of distilled water in a 250 ml. Erlenmeyer flask were heated on a water bath at 80-90°C until solution was apparently complete. The solution was cooled to 25°C and the weight of solution adjusted to 100.0 grams by addition of water. After standing overnight the solution was placed under a 3 foot long water condenser and heated to approximately 60°C on the water bath. 75 ml. of n-propyl alcohol were added. Sufficient 4:1 (by volume) n-propyl alcohol-water was then added to precipitate the desired fraction. The use of water with n-propyl alcohol as the precipitant was necessary in order to lower the nonsolvent power of the precipitant sufficiently so that fractionation could be controlled. If water were not

used very small changes in the amount of precipitant added would give relatively large changes in amount of material precipitated and satisfactory duplication between runs could not be obtained. After addition of the nonsolvent the system was brought to 25°C and then allowed to stand at 15°C for 24 hours. At the end of this period the supernatant liquid was decanted. This liquid was then heated to 60°C and the next portion of 4:1 n-propyl alcohol-water was added, after which the treatment was the same as for Fraction 1. After about 70% of the material had been separated, n-propyl alcohol was used alone as the nonsolvent in order to keep the total volume as small as practicable.

The gel after decantation was dissolved in a small amount of hot water, the resulting solution was poured into a tared evaporating dish and dried to constant weight at $75 \pm 10^\circ\text{C}$. This was Fraction 1. Subsequent fractions were treated in an exactly similar manner.

Determination of D.P. values of the fractions for several small scale fractionations indicated that there was inversion in the fractions of highest D.P., that is, the first fraction had a lower D.P. than the second but subsequent fractions behaved normally. It was found that this inversion could be removed either by bringing down 20-25% of the material in the first fraction and then

refractionating this fraction, or by precipitating a small purification fraction which was discarded.

Data for a fractionation are given in Table 1 and the corresponding precipitation curve is shown in Figure 1. Table 2 gives data for the D.P. values of fractions obtained after precipitation of a purification fraction as indicated above. These results showed that the fractionation method used led to the separation of fractions of successively lower D.P. which was the only purpose of carrying out the small scale work.

Large Scale Fractionation of Polyvinyl Alcohol

In order to obtain sufficient amounts of the fractions for the planned investigation the small scale fractionation was modified so as to accumulate the fractions in considerable quantity. The large scale procedure adopted was as follows: 40.0 grams of the polymer and 1960 grams of distilled water were placed in a 6 liter Erlenmeyer flask and the solution was heated on a water bath at 80-90°C until solution was apparently complete. The solution was cooled to 25°C and the weight was adjusted to 2000 grams by the addition of water. The solution was then heated under a 3 foot water condenser to 85°C and 1170 grams of n-propyl alcohol and 80.0 grams of 3.2:1 by weight n-propyl alcohol-water were added with vigorous stirring. The system was cooled to 25°C and

Table 1Small Scale Fractionation of 2% Solution of Polyvinyl Alcohol in Water. Precipitation Data

100 grams of polyvinyl alcohol solution used. Initially added 75 ml. n-propyl alcohol.

<u>Fraction Number</u>	<u>Accumulative Amount Nonsolvent Added</u>	<u>% Original in Fraction</u>	<u>Accumulative %</u>
1	4 ml 4:1 PrOH-H ₂ O	21.7	21.7
2	7 ml "	15.3	37.0
3	10 ml "	10.4	47.4
4	14 ml "	9.3	56.7
5	18 ml "	6.0	62.7
6	24 ml "	6.3	69.0
7	5 ml PrOH	4.3	73.3
8	13 ml "	4.5	77.8
9	23 ml "	2.9	80.7
10	43 ml "	3.2	83.9

Figure 1Precipitation Curve for Fractionation
of Polyvinyl Alcohol

Data from Table 1

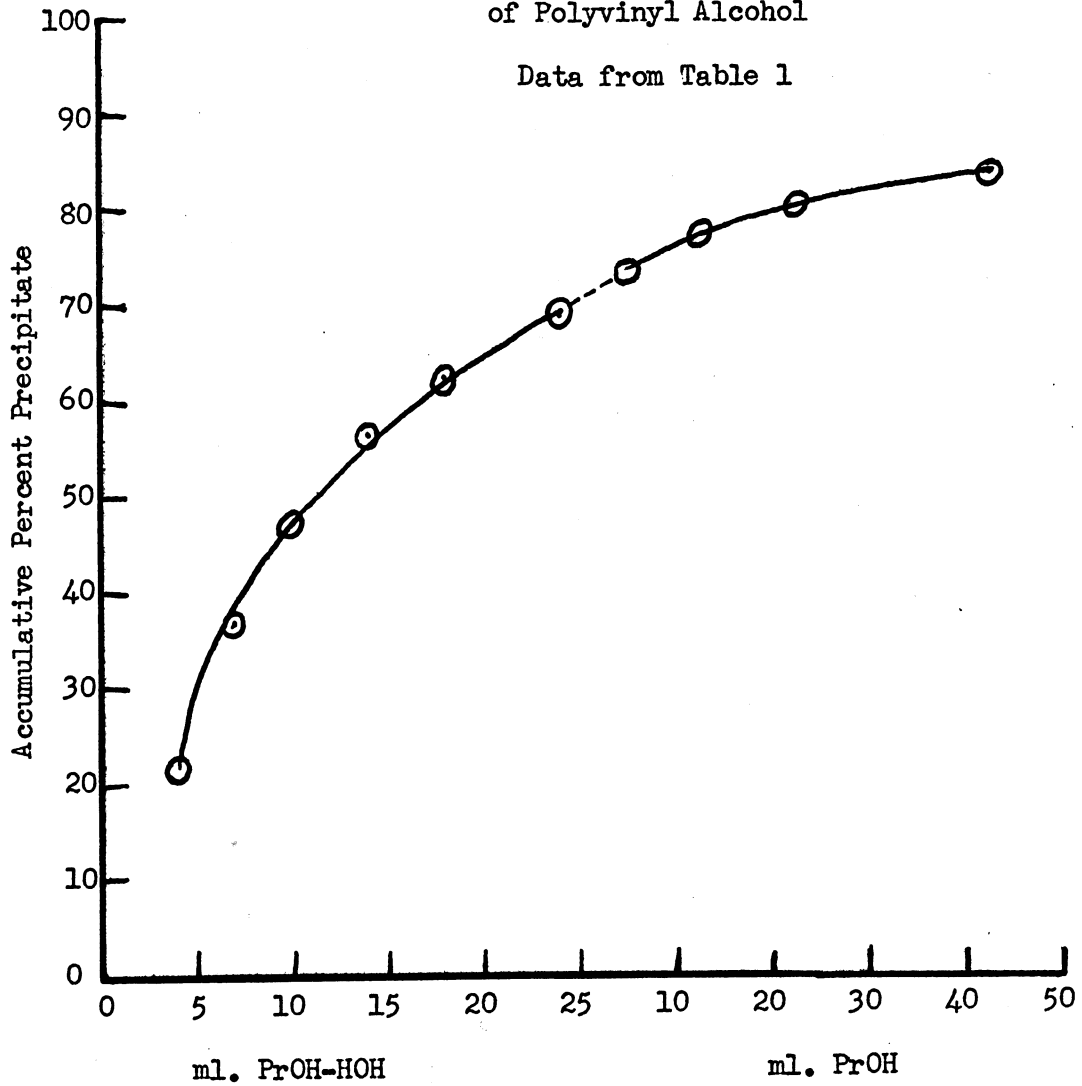


Table 2D.P. Data for Small Scale Fractionation

Fraction Number	% Original in Fraction	D.P. of Fraction
1	7.8	1850
2	13.5	1804
3	9.7	1696
4	11.3	1567
5	10.2	1343
6	11.9	1173
7	10.4	970
8	10.6	712

then allowed to stand for 24 hours at 15°C. At the end of this time the supernatant liquid was decanted. This liquid was heated under a condenser to 65-70°C and the next portion of nonsolvent was added, after which the treatment was the same as for Fraction 1.

The gel was dissolved in a small amount of hot distilled water, poured into a flat-bottom pyrex dish and dried at $75 \pm 10^\circ\text{C}$. The resultant film in the dish was wet with cold water, stripped from the dish, and dried to constant weight at $75 \pm 10^\circ\text{C}$. This was Fraction 1. Subsequent fractions were treated similarly.

By using the above procedure nine fractions were obtained from each sample fractionated. The large scale fractionation process was repeated 33 times so as to obtain a sufficient amount of each fraction. The results of the fractionation of two typical samples are given in Table 3.

The Refractionation of the Original Fractions of Polyvinyl Alcohol

After the accumulation of the nine original fractions was complete, it was necessary to refractionate in order to obtain fractions that were as homogeneous as possible with respect to D.P. In order to do this two 40 gram batches of each of the original fractions were fractionated by exactly the same procedure as was

Table 3Large Scale Fractionation of Polyvinyl Alcohol

Fraction Number	Nonsolvent Added	% Original in Fraction		Accumulative	
		I	II	I	II
1	80.0 g. PrOH-HOH	25.0	26.0	25.0	26.0
2	26.0 g. "	8.5	7.8	33.5	33.8
3	34.0 g. "	8.8	9.0	42.3	42.8
4	45.0 g. "	8.0	7.5	50.3	50.3
5	70.0 g. "	9.5	9.3	59.8	59.6
6	80.0 g. "	7.0	6.8	66.8	66.4
7	150.0 g. "	7.5	7.8	74.3	74.2
8	150 g. PrOH	7.5	7.5	81.8	81.7
9	800 g. "	7.3	7.0	89.1	88.7

used in the original fractionation. D.P. values were then determined for each subfraction and all subfractions differing in D.P. by approximately 50 units or less were combined. These were then fractionated again and the process was repeated until further refractionation gave no significant change in D.P. The results of the refractionation are summarized in Table 4 and the D.P. and weight accumulated of the final homogeneous fractions are given in Table 5.

Determination of Degree of Polymerization

Values of the constants K and β for the equation $[\eta] = KP^\beta$ were obtained from the literature (68). The values of these constants given for polyvinyl alcohol dissolved in water at 30°C are $K = 7.50 \times 10^{-3}$ and $\beta = 0.64$. Using these values and the data which were experimentally obtained and are recorded in Table 6 and Figure 2, the value of K in the equation $\frac{\eta_{sp}}{c} = KP$ was found to be 6.41×10^{-4} .

In carrying out the viscosity measurements a sample of polyvinyl alcohol of slightly over 0.1 gram was roughly weighed out and dried in an oven at $75 \pm 10^\circ\text{C}$. The sample was cooled and weighed accurately by difference. The weighed sample was placed in a pyrex test tube and 50 ml. of distilled water were added from a pipette. The mixture was heated under a water con-

Table 4

Refractionation of Polyvinyl Alcohol

Original Fraction	Sub Fraction	D.P.	Amt. (%)	Fract. Comb.	Sub Fract.	D.P.	Sub Fract.	D.P.
1	1A	2354	14.9		Ia	2423	1a	2499
	1B	2330	26.5					
	1C	2173	18.0	1A;1B	lb	--	1b	--
	1D	1920	10.4					
	1E	1750	6.9	1C	IIa	2265	2a	2245
	1F	1410	7.2					
	1G	1365	5.5		IIb	--	2b	--
	1H	913	2.7					
	2	2A	2013	59.0		IIIa	2103	3a
2B		1807	11.8	1D;2A	IIIb	--	3b	--
2C		1660	11.5	3A;2B	IVa	1926	4a	1930
2D		1373	4.5					
2E		1019	7.5	1E	IVb	--	4b	--
3	3A	1865	55.9	4A;4B	Va	1730	5a	1751
	3B	1654	18.4	2C;3B	Vb	--	5b	--
	3C	1230	20.9					
4	4A	1661	39.6					
	4B	1669	28.8		VIa	1597		
	4C	1420	11.3	5A				
	4D	1031	11.9		VIb	--		
5	5A	1560	40.0	5B;4C	VIIa	1496		
	5B	1485	32.6	1F				
	5C	1268	15.1		VIIb	--		
	5D	924	5.3					
6	6A	1377	32.0	6A;2D	VIIIa	1394		
	6B	1269	46.0					
	6C	1094	11.3	1G				
	6D	894	5.6		VIIIb	--		
7	7A	1228	15.3	6B;5C	IXa	1288		
	7B	1158	57.4	3C;7A				
	7C	1040	16.3		IXb	--		
	7D	846	7.0					
8	8A	949	44.0	7B;6C	Xa	1102		
	8B	949	34.3	7C;4D				
	8C	786	16.3	2E	Xb	--		
9	9A	778	56.0	8A;8B	XIa	974		
	9B	747	19.3	5D;1H				
	9C	663	14.1		XIb	--		
				6D;7D	XIIa	829		
				XIIb	--			
			8C;9A	XIIIa	765			
			9B	XIIIb	--			
			9C	XIVa	652			
				XIVb	--			

Note: Last two columns represent small scale sample refractionation to verify homogeneity of the total fraction.

Table 5**Weight and D. P. of Polyvinyl Alcohol Fractions**

Fraction Number	Weight of Fraction Accumulated (grams)	D. P.
1	28	2423
2	13	2265
3	48	2103
4	53	1926
5	70	1730
6	28	1597
7	40	1496
8	33	1394
9	77	1288
10	83	1102
11	68	974
12	10	829
13	73	765
14	10	652

denser at 80-90°C until solution was complete, cooled to room temperature, and filtered by gravity through a coarse sintered glass funnel. The solution was then placed in a 30°C water bath and viscosity determinations were made at this temperature on 5 ml. samples in an Ostwald Viscometer. Independent determinations were made on three solutions for each D.P. value recorded. The tolerated deviations were approximately 3% of the D.P. of the sample.

By assuming that the densities of the solvent and the solution are very nearly the same for the very dilute solutions used the specific viscosity was calculated as follows:

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1$$

where η = time of efflux of solution
 η_0 = time of efflux of solvent

$$\eta_r = \frac{\eta}{\eta_0}$$

The average D.P. was then calculated by:

$$\frac{\eta_{sp}}{c} = 6.41 \times 10^{-4} p$$

where c is concentration in grams per 100 ml.

P is the D.P.

Table 6Data for Calculation of K of Polyvinyl Alcohol in Water
at 30°C

The polyvinyl alcohol used was the original material.

Sample Number	Specific Viscosity	c (g./100 ml.)	$\frac{\eta_{sp}}{c}$
1	0.473	0.5170	0.913
2	0.118	0.1546	0.763
3	0.078	0.1016	0.768
4	0.106	0.1392	0.762
5	0.176	0.2192	0.803
6	0.060	0.0810	0.741
7	0.094	0.1272	0.739
8	0.102	0.1362	0.749

Calculations:

$$\text{From Figure 2: } [\eta] = \lim_{c \rightarrow 0} \left(\frac{\eta_{sp}}{c} \right) = 0.71$$

$$\log 0.71 = \log 0.0075 \quad 0.64 \log P$$

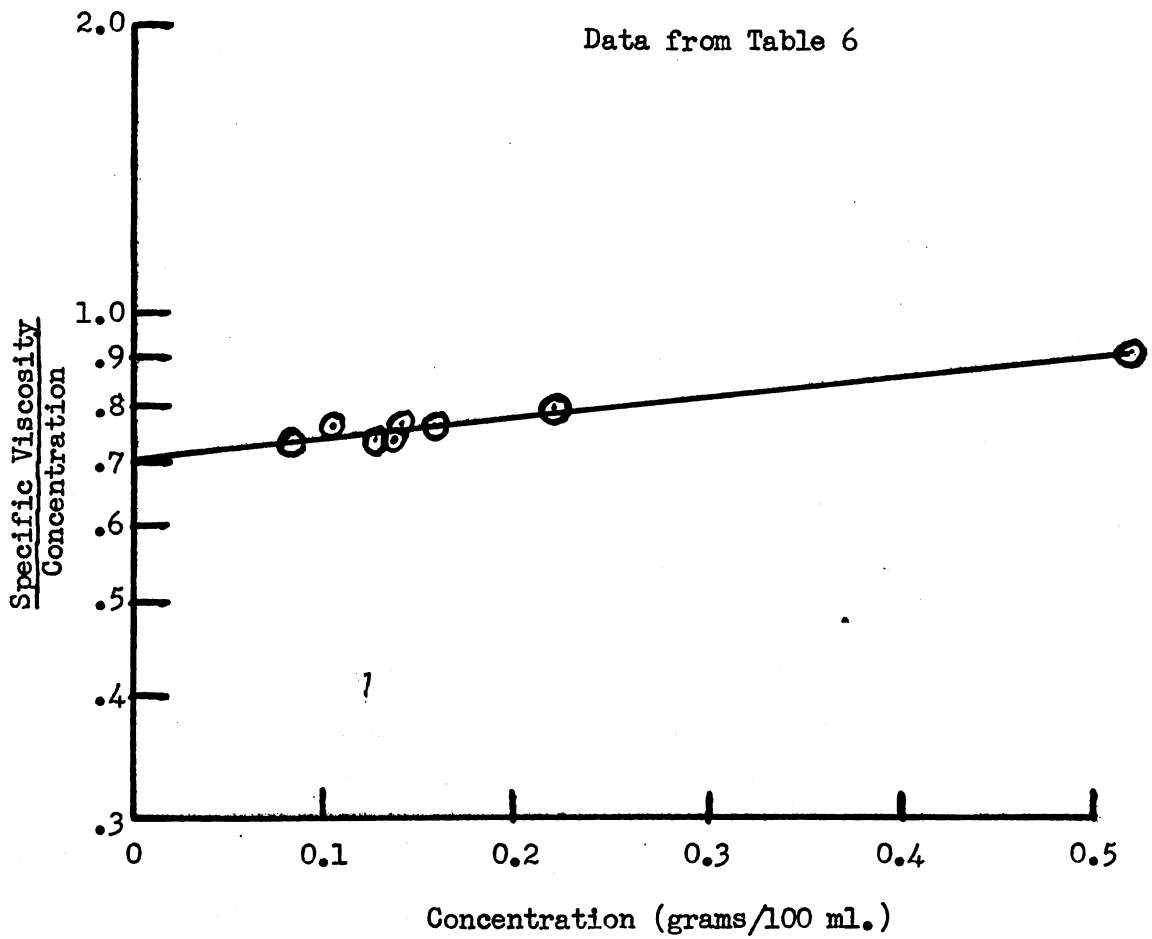
$$P = 1224$$

$$\text{From Figure 2 at 0.200 g/100 ml } \frac{\eta_{sp}}{c} = 0.785$$

$$K = \frac{0.785}{1224} = 6.41 \times 10^{-4}$$

Figure 2

Log $\frac{\text{Specific Viscosity}}{\text{Concentration}}$ versus Concentration



The Preparation of Films

A procedure was developed which was satisfactory for casting polyvinyl alcohol films 0.001 inch thick. This involved preparing an approximately 8% solution of the polymer in water by heating to 80-90°C, filtering the resultant solution through glass wool, cooling to room temperature, and then pouring the solution on a glass plate and adjusting the thickness by pulling a film spreader slowly over the solution on the plate. This latter operation was carried out in an oven which opened on top. After the solution was spread the top was closed and the wet film was dried for 40 minutes at $65 \pm 5^\circ\text{C}$. The plate was then removed from the oven and allowed to stand at room conditions for several hours, after which the film was stripped from the plate and placed in the conditioning room. This was the procedure for film casting used throughout the investigation.

Mechanical Testing of the Films

Testing Room Conditions. The specifications set forth in the Tentative Method of Conditioning Paper and Paper Products for Testing (A.S.T.M. Designation: D685) of the American Society for Testing Materials call for a temperature of $77 \pm 1.8^\circ\text{F}$ and $50 \pm 2\%$ relative humidity. The data given in Table 7 and Figure 3 show that in the case of polyvinyl alcohol films even small changes in

relative humidity affect the tensile strength markedly. Due to this fact the tests on properties of the films were performed only if the relative humidity was averaging 50%, with variation above and below this value not exceeding about 1% during the 48 hours preceding testing. The temperature was held at $77 \pm 1.8^{\circ}\text{F}$. The temperature and relative humidity were recorded by a Brown Recorder, Model 6882-601, manufactured by Brown Instrument Company, Philadelphia, Pennsylvania.

Thickness of Film. The thickness of the conditioned film was obtained by measuring 5 specimens, cut to the specified dimensions for the test, with a dead weight micrometer. The average thickness was taken as the thickness of each individual film strip.

Tensile Strength and Elongation. The tensile strength and elongation were determined using a Schopper Type Tensile Strength and Elongation Tester. Test specimens 0.5 inch in width and at least 5 inches long were cut from the films in each of the principal directions. The specimens were designated as "with" or "cross" depending on whether the length of the strip was parallel to or perpendicular to the pull of the spreader. At least 5 specimens from each of 3 films were cut for each of the directions in obtaining a value for a fraction or blend. The tests were made according to the Tentative

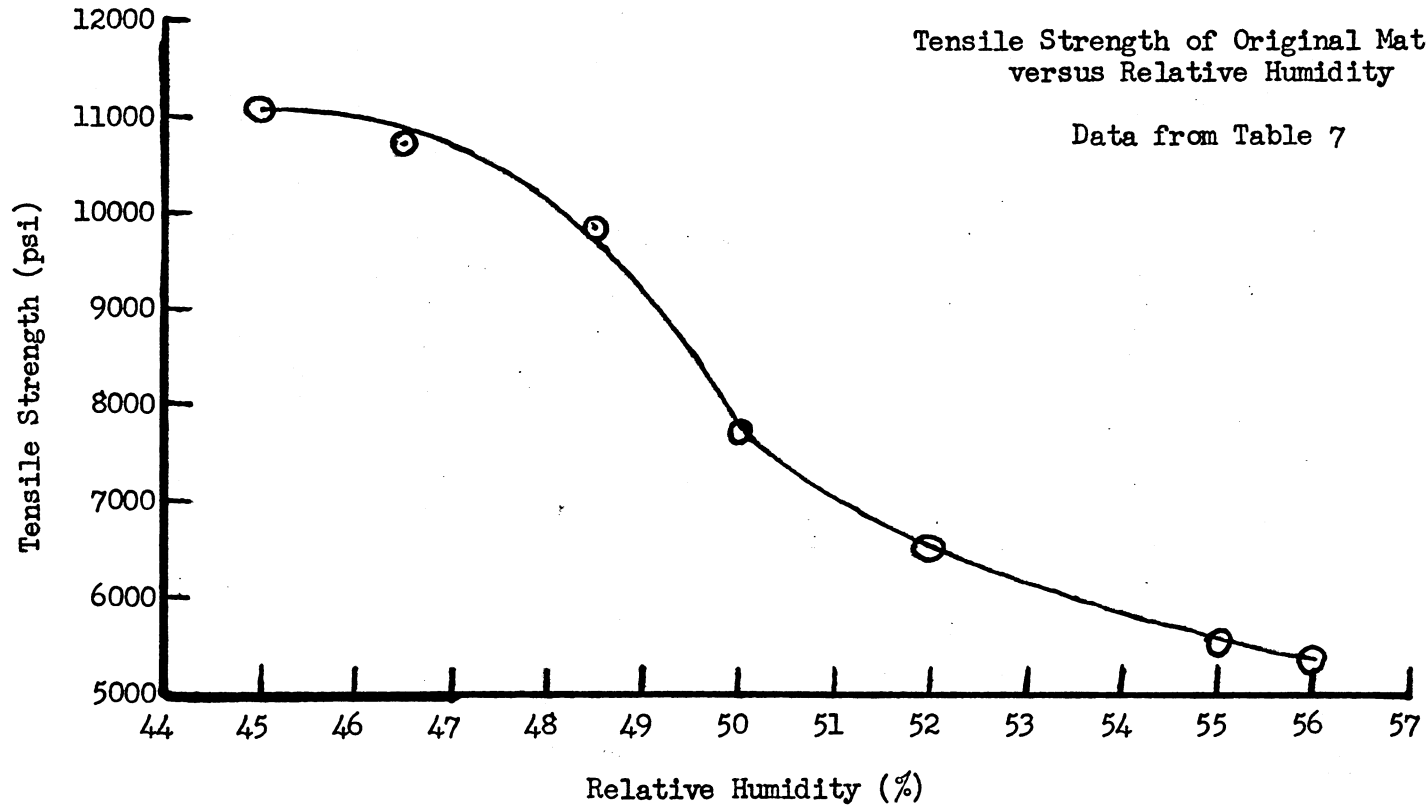
Table 7Effect of Changing Relative Humidity on Tensile Strength
of Original Polyvinyl Alcohol

Expt.	Direction	Avg. T.S. (psi)	Max. T.S. (psi)	Min. T.S. (psi)	Avg. Dev. (psi)	No. of Samples	Avg. Rel. Hum. (%)
1	cross	6840	8330	5450	660	10	52
	with	6180	8400	4600	800	10	
	average	6510				20	
2	cross	5590	8630	3630	770	10	56
	with	5180	8000	3440	1160	10	
	average	5390				20	
3	cross	5320	7130	3880	1100	10	55
	with	5760	8110	3560	860	10	
	average	5540				20	
4	cross	7250	8890	4750	1390	10	50
	with	8180	8890	6670	370	10	
	average	7720				20	
5	cross	10150	11000	8220	550	10	48.5
	with	9510	10890	7440	550	10	
	average	9830				20	
6	cross	10510	12400	8880	850	10	46.5
	with	10920	12330	9560	660	10	
	average	10720				20	
7	cross	11580	13670	9730	920	10	45
	with	10580	12780	8780	1040	10	
	average	11080				20	

Figure 3

Tensile Strength of Original Material
versus Relative Humidity

Data from Table 7



Method of Test for Tensile Properties of Thin Plastic Films (A.S.T.M. Designation D: 882) of the American Society for Testing Materials, except that gage marks were not used, the elongation being obtained directly from the scale reading of the tester.

The results of the tensile strength tests on the fractions are given in Table 8 and tensile strength is plotted against D.P. in Figure 4. The corresponding values for elongation are given in Table 9. Since there was no significant difference in properties in the "with" and "cross" directions, the average of the values for the two directions was taken as the property of the fraction.

Bursting Strength. A bursting strength of the films was determined on the Mullen Tester, manufactured by B. F. Perkins and Son, Inc., Eolyoke, Massachusetts. The test specimens were cut 2.5 x 2.5 inches. The test was made by visually observing the point at which the film burst and recording the scale reading at that point as bursting strength. Data for the tests of burst strength of the fractions are given in Table 10 and burst strength of the fractions is plotted against D.P. in Figure 5.

Since the burst strength being measured was not obtained by a conventional method, a study was made of

the effect on the property of changing the membrane on the testing machine. A thinner membrane was used. Results of the tests on the fractions are given in Table 11 and burst strength is plotted against D.P. in Figure 6. It was noted that the same type of relationship was obtained as with the original membrane, although the numerical values were lower. Only nine tests were obtained on Fraction 13 since on the tenth test the membrane burst.

From Figures 5 and 6 it was noted that the values for burst strength tended to increase slightly as the D.P. became lower. It was suspected that the fact that the line was not horizontal was due to the effect of average film thickness on the burst strength. A plot of burst strength against average thickness suggested a linear relation as shown in Figure 7. On the basis of this apparent relation the values could be corrected to account for average film thickness by the following empirical equation:

$$C = R + (20,000)(0.0010 - A)$$

where C is the corrected average burst strength

R is the observed average burst strength

A is the average thickness of the film.

Table 8Tensile Strengths of Polyvinyl Alcohol Fractions

Fraction	Direction	Avg. T.S. (psi)	Max. T.S. (psi)	Min. T.S. (psi)	Avg. Dev. (psi)	Number of Samples
1	cross	8900	9860	8000	490	11
	with	8480	9570	7000	550	12
	average	8690				23
3	cross	8270	9750	7000	620	10
	with	8160	9750	7250	500	12
	average	8220				22
4	cross	7350	8380	6380	470	14
	with	8000	9000	6880	590	11
	average	7680				25
5	cross	8260	9500	7330	650	11
	with	7890	9220	7110	540	13
	average	8080				24
6	cross	7790	9220	7000	370	12
	with	8630	9220	7560	390	10
	average	8210				22
7	cross	8620	9200	7700	340	10
	with	8400	9560	7220	630	12
	average	8510				22
8	cross	8600	9560	7900	500	10
	with	8530	9330	7000	690	11
	average	8570				21
9	cross	7720	8400	7110	300	10
	with	8510	9330	7900	400	13
	average	8120				23
10	cross	8660	9640	7640	490	13
	with	8560	9910	7700	380	13
	average	8610				26
11	cross	8000	10920	5580	1400	12
	with	8020	9640	6360	640	10
	average	8010				22
13	cross	7040	8700	5270	950	11
	with	6080	7670	5130	500	10
	average	6560				21

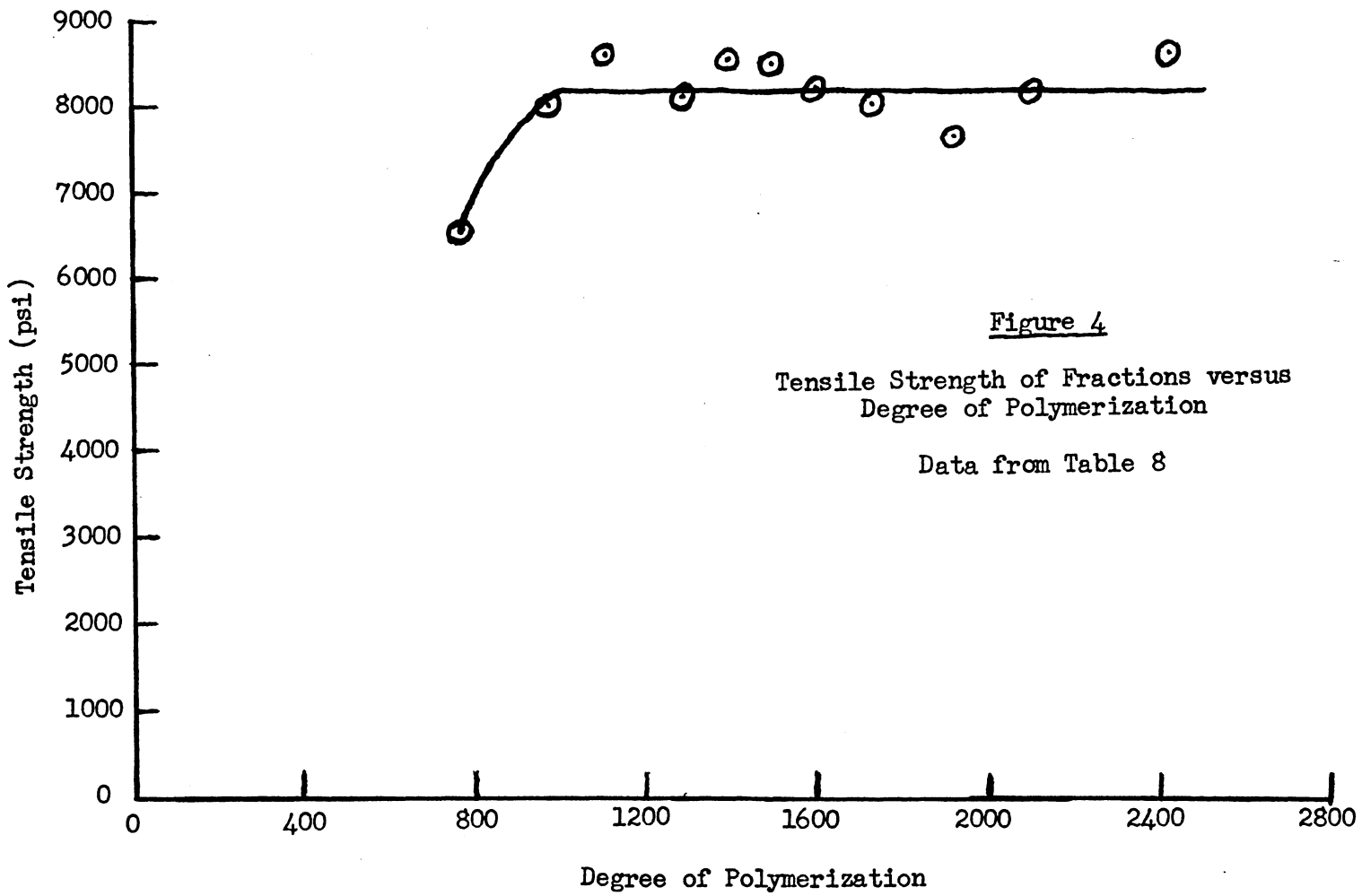


Figure 4
Tensile Strength of Fractions versus
Degree of Polymerization
Data from Table 8

Table 9Ultimate Elongation of Polyvinyl Alcohol Fractions

Fraction	Direction	Avg. Elong. (%)	Max. Elong. (%)	Min. Elong. (%)	Avg. Dev. (%)	Number of Samples
1	cross	126	172	104	15	11
	with	104	173	32	32	12
	average	115				23
3	cross	103	160	24	40	10
	with	113	176	48	33	12
	average	108				22
4	cross	100	182	26	41	14
	with	101	168	30	30	11
	average	101				25
5	cross	148	186	104	29	11
	with	123	181	51	34	13
	average	136				24
6	cross	88	157	36	24	12
	with	111	154	19	34	10
	average	100				22
7	cross	67	153	19	34	10
	with	64	164	14	43	12
	average	66				22
8	cross	108	166	33	45	10
	with	121	182	41	36	11
	average	115				21
9	cross	103	169	37	38	10
	with	103	172	28	31	13
	average	103				23
10	cross	124	184	33	42	13
	with	109	181	44	33	13
	average	117				26
11	cross	141	180	37	38	12
	with	82	180	4	42	10
	average	112				22
13	cross	92	136	47	26	11
	with	58	77	42	9	10
	average	75				21

Table 10Burst Strengths of Polyvinyl Alcohol Fractions

Fraction	Avg. B.S. (psi)	Max. B.S. (psi)	Min. B.S. (psi)	Avg. Dev. (psi)	Number of Samples
1	46	51	37	3	14
3	49	56	40	3	11
4	52	54	48	2	12
5	51	57	43	4	15
6	54	62	44	4	15
7	53	59	45	4	13
8	52	59	43	3	14
9	51	58	45	4	13
10	53	64	47	4	12
11	54	64	41	5	17
13	55	60	46	4	11

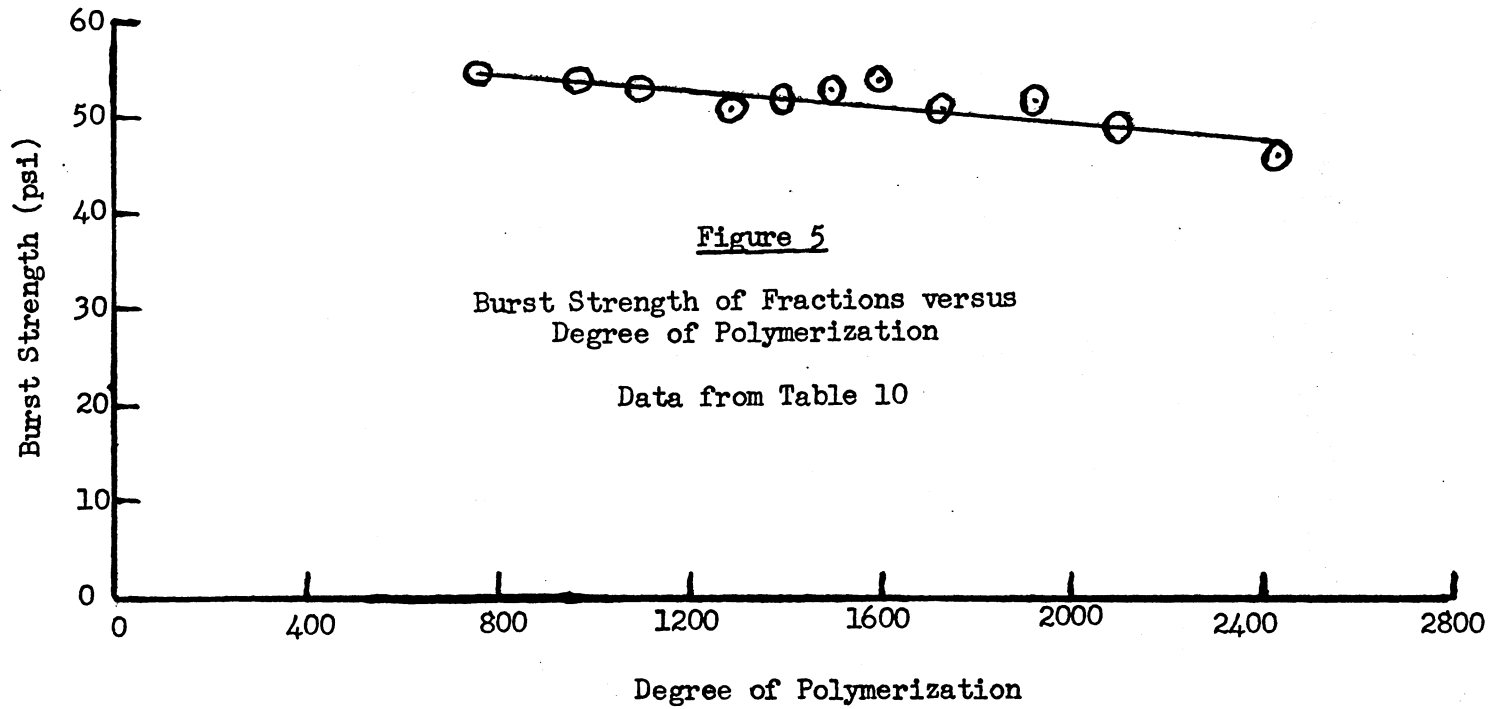


Figure 5

Burst Strength of Fractions versus
Degree of Polymerization

Data from Table 10

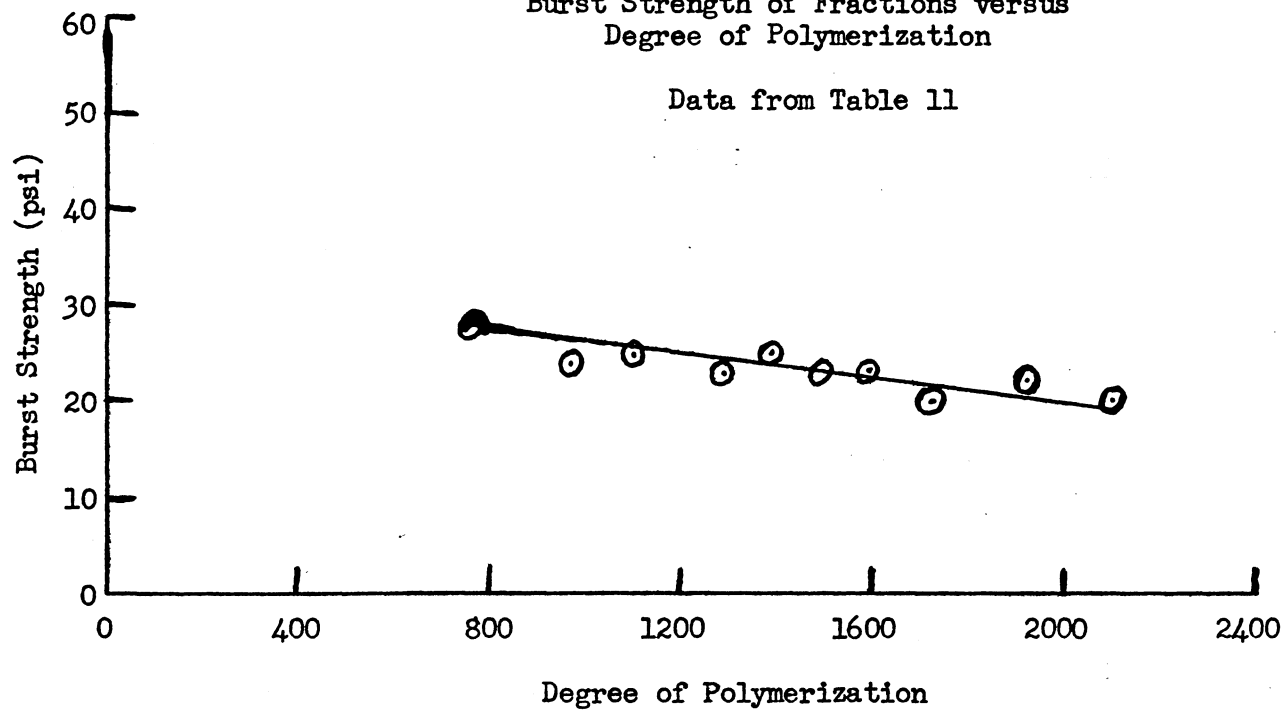
Table 11Burst Strengths of Polyvinyl Alcohol Fractions. Thin Membrane Used

Fraction	Avg. B.S. (psi)	Max. B.S. (psi)	Min. B.S. (psi)	Avg. Dev. (psi)	Number of Samples
3	20	24	19	1	12
4	22	26	19	2	12
5	20	25	14	3	12
6	23	27	20	2	12
7	23	26	19	2	12
8	25	29	20	2	12
9	23	26	20	1	12
10	25	27	23	1	12
11	24	30	18	3	12
13	28	31	22	2	9

Figure 6

Burst Strength of Fractions versus
Degree of Polymerization

Data from Table 11



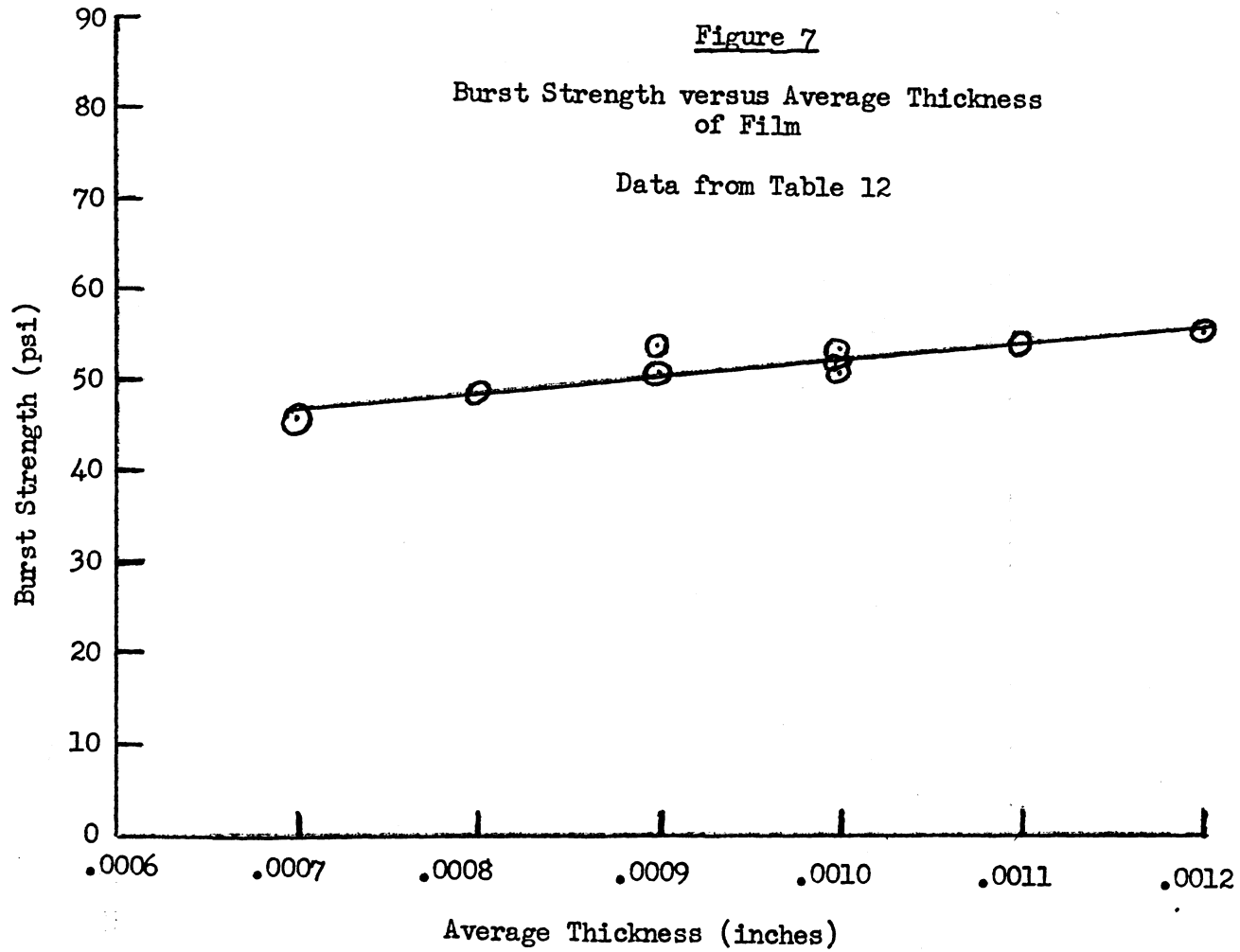


Table 12Data for Correction of Burst Strengths of
Polyvinyl Alcohol Fractions

Fraction	Avg. Thickness of Film Square (in.)	Observed B.S. (psi)	Corrected B.S. (psi)
1	0.0007	46	52
3	0.0008	49	53
4	0.0010	52	52
5	0.0009	51	53
6	0.0009	54	56
7	0.0010	53	53
8	0.0010	52	52
9	0.0010	51	51
10	0.0010	53	53
11	0.0011	54	52
13	0.0012	55	51

Figure 8

Corrected Burst Strength of Fractions
versus Degree of Polymerization

Data from Table 12

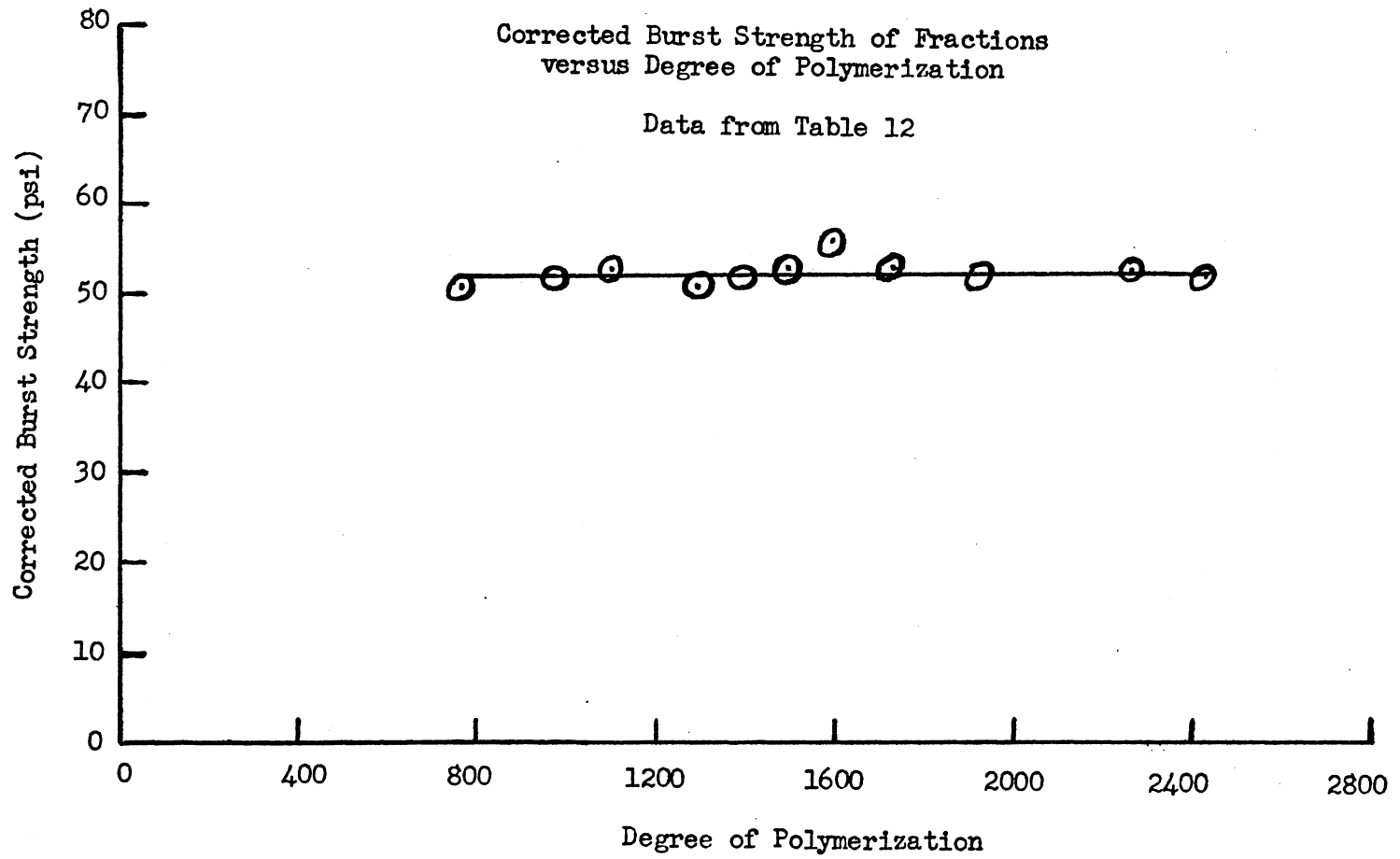
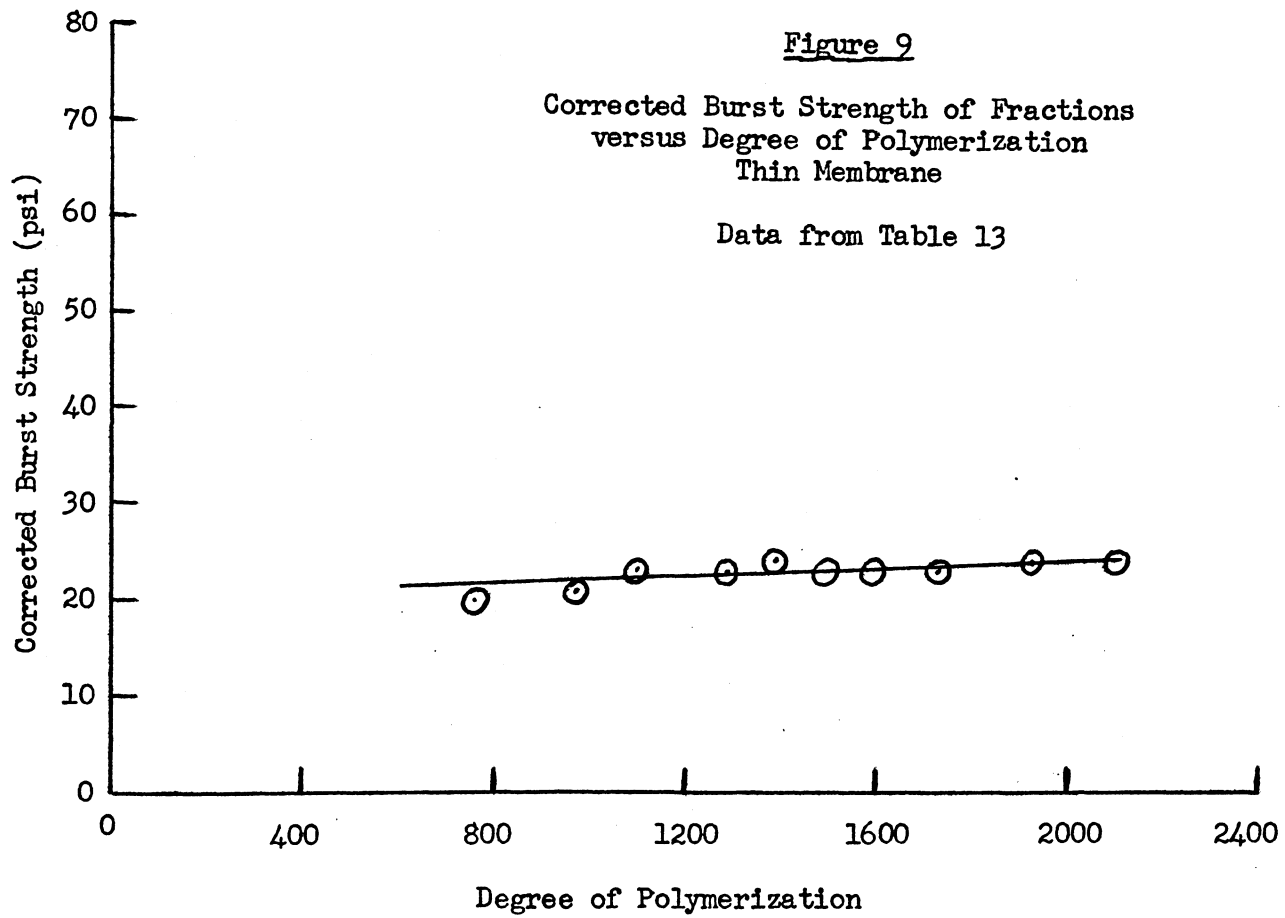


Table 13Data for Correction of Burst Strengths of Polyvinyl
Alcohol Fractions. Thin Membrane

Fraction	Avg. Thickness of Film Square (in.)	Observed B.S. (psi)	Corrected B.S. (psi)
3	0.0008	20	24
4	0.0009	22	24
5	0.00085	20	23
6	0.0010	23	23
7	0.0010	23	23
8	0.00105	25	24
9	0.0010	23	23
10	0.0011	25	23
11	0.00115	24	21
13	0.0014	28	20



Using this equation and the data in Tables 12 and 13, burst strengths corrected for average thickness of film were calculated. A plot of these corrected values against D.P. of the fractions gave the horizontal lines shown in Figures 8 and 9.

The Preparation, Analysis and Testing of the Blends

In the first set of blends 1B, 2B and 3B, the properties were studied as a function of the height of the maximum (H) of the differential distribution curve, the D.P. at the maximum (P_m) being held constant and all the curves being normal.

Normalized differential distribution curves which met these requirements were arbitrarily constructed (Tables 14, 15, and 16) and are shown in Figures 10, 11 and 12. By using these curves the blends were made by mixing the prescribed quantities of homogeneous fractions.

The actual distribution was checked by carrying out a routine fractionation of the three blends. The results are given in Tables 17, 18 and 19. The corresponding theoretical data for the fractions put in the blends are given in Tables 20, 21 and 22. As shown in Figures 13, 14 and 15 the agreement between the calculated values based on the fractions used and the analysis values is reasonably good. For this reason analyses on the later blends were not carried out.

In the second set of blends, 1R, 2R, 3R, 1L, 2L, 3L (R designates skew to right, L skew to left), the height at the maximum and P_m were held constant and the blends were skewed to the right or left, in order to study the mechanical properties as a function of the skewness. The data given in Tables 23 through 28 were used in the construction of the arbitrary differential distribution curves shown in Figures 16 through 21. The data for the corresponding integral distribution curves are given in Tables 29 through 34 and the curves are plotted in Figures 22 through 27.

The two groups of blends were tested for mechanical properties in the same manner as that described for the homogeneous fractions. Tables 35, 36 and 37 give the mechanical property data of the blends. Table 38 gives the characterization of the blends.

Table 14**Data for Normalized Differential Distribution Curve of Blend 1B**

D. P.	Normalized Percent
100	0.000
300	0.003
500	0.012
700	0.063
900	0.107
1100	0.135
1300	0.107
1500	0.063
1700	0.012
1900	0.003
2100	0.000

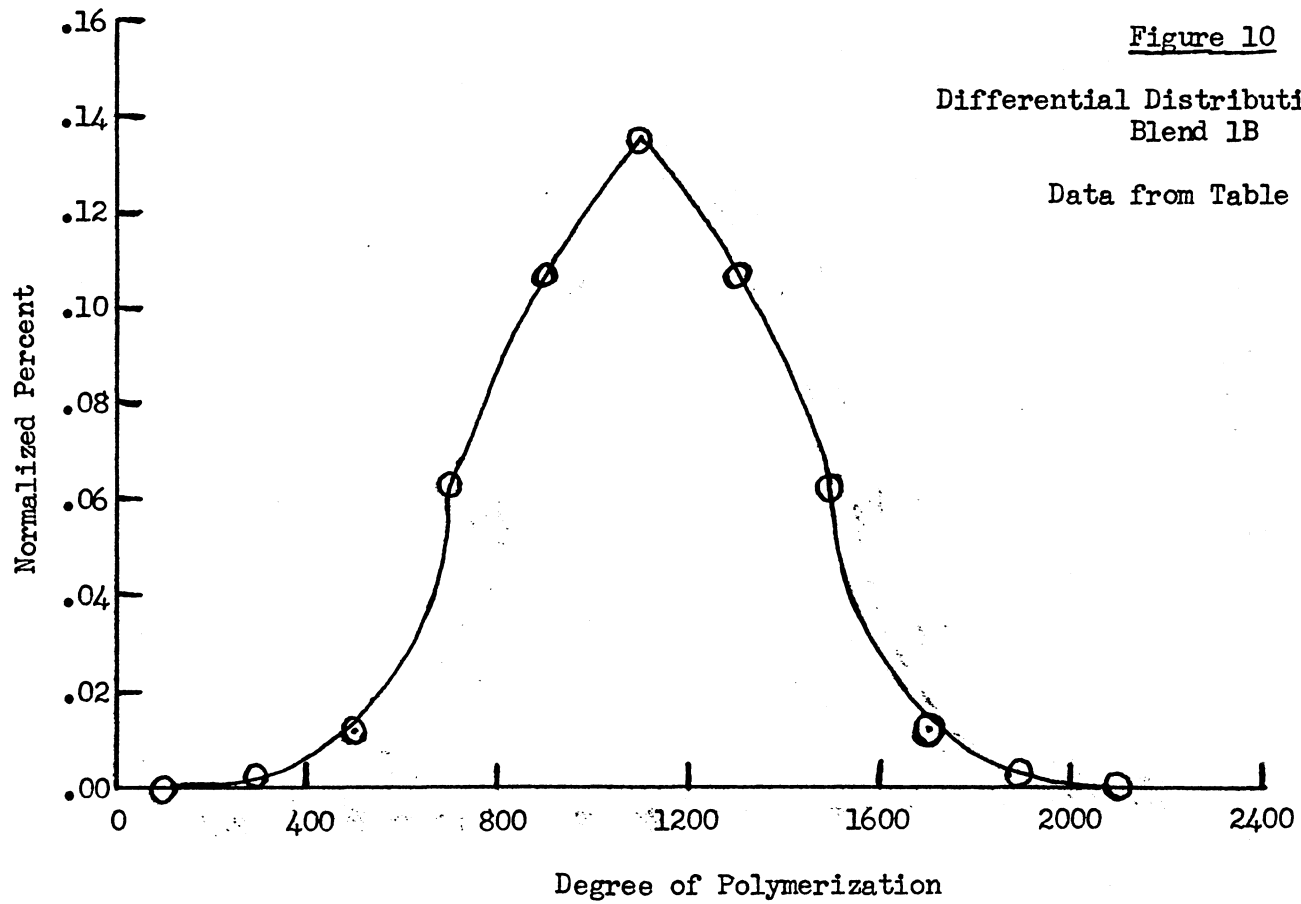


Table 15Data for Normalized Differential Distribution Curve of
Blend 2B

<u>D. P.</u>	<u>Normalized Percent</u>
100	0.001
300	0.005
500	0.016
700	0.043
900	0.106
1100	0.158
1300	0.106
1500	0.043
1700	0.016
1900	0.005
2100	0.001

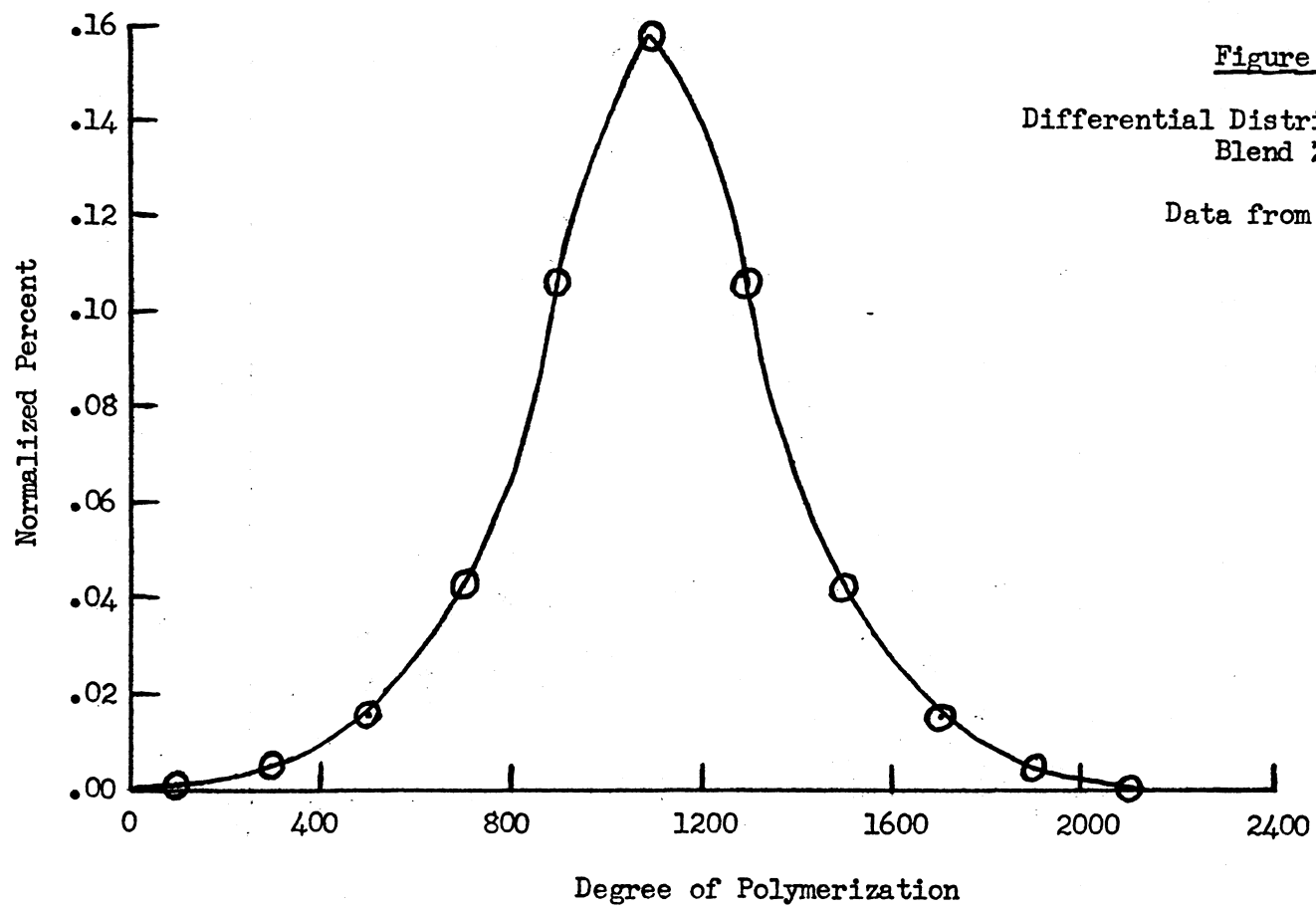


Figure 11
Differential Distribution Curve
Blend 2B
Data from Table 15

Table 16Data for Normalized Differential Distribution Curve of
Blend 3B

D. P.	Normalized Percent
100	0.000
300	0.001
500	0.007
700	0.029
900	0.122
1100	0.183
1300	0.122
1500	0.029
1700	0.007
1900	0.001
2100	0.000

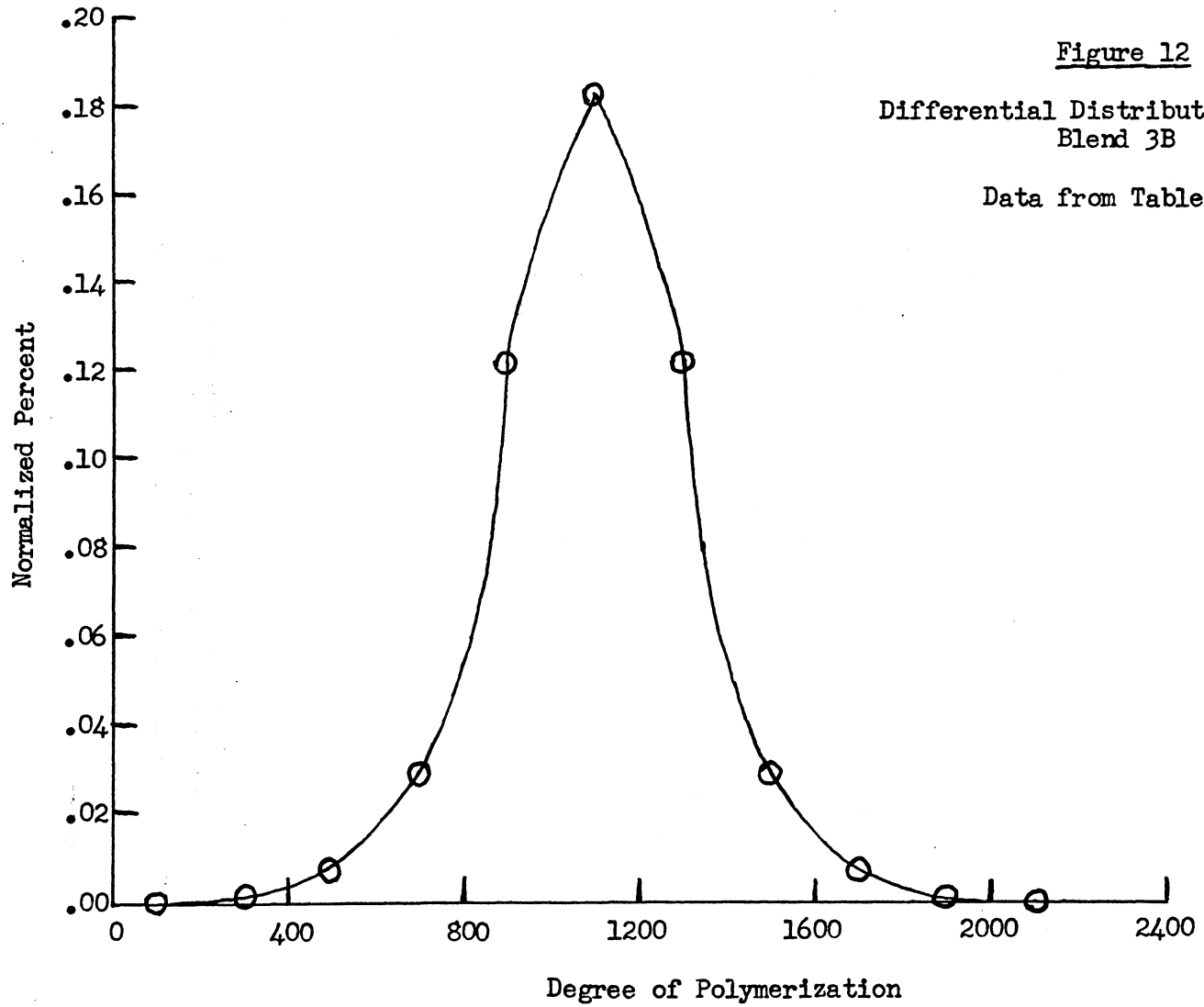


Figure 12
Differential Distribution Curve
Blend 3B
Data from Table 16

Table 17Experimental Analysis of Blend 1B

Average D.P. of Blend = 1101

Fraction Number	D. P.	Accumulative % = A	100 - A
1	1408	6.3	93.7
2	1367	28.8	71.2
3	1337	32.8	67.2
4	1295	44.6	55.4
5	1176	54.8	45.2
6	1105	62.5	37.5
7	1024	68.8	31.2
8	942	77.8	22.2
9	753	89.7	10.3

Note: An initial large fraction was precipitated, re-fractionated, and the precipitated material was taken as Fraction 1. The supernatant liquid was combined with the original solution and fractionation was carried out normally from this point.

Table 18Experimental Analysis of Blend 2B

Average D.P. of Blend = 1098

Fraction Number	D. P.	Accumulative % = A	100 - A
1	1390	23.0	77.0
2	1335	27.3	72.7
3	1289	40.2	59.8
4	1153	51.1	48.9
5	1075	59.9	40.1
6	1019	68.6	31.4
7	953	79.0	21.0
8	742	90.4	9.6

Note: From an initial large fraction a small (less than 2%) purification fraction was precipitated, the solutions were recombined and fractionated as usual.

Table 19Experimental Analysis of Blend 3B

Average D.P. of Blend = 1084

<u>Fraction Number</u>	<u>D. P.</u>	<u>Accumulative % = A</u>	<u>100 - A</u>
1	1302	22.1	77.9
2	1309	27.5	72.5
3	1233	41.9	58.1
4	1146	53.9	46.1
5	1082	62.9	37.1
6	1017	70.8	29.2
7	988	80.7	19.3
8	764	89.9	10.1

Note: A purification fraction was precipitated, the procedure being the same as for Blend 2B.

Table 20Theoretical Analysis of Blend 1B

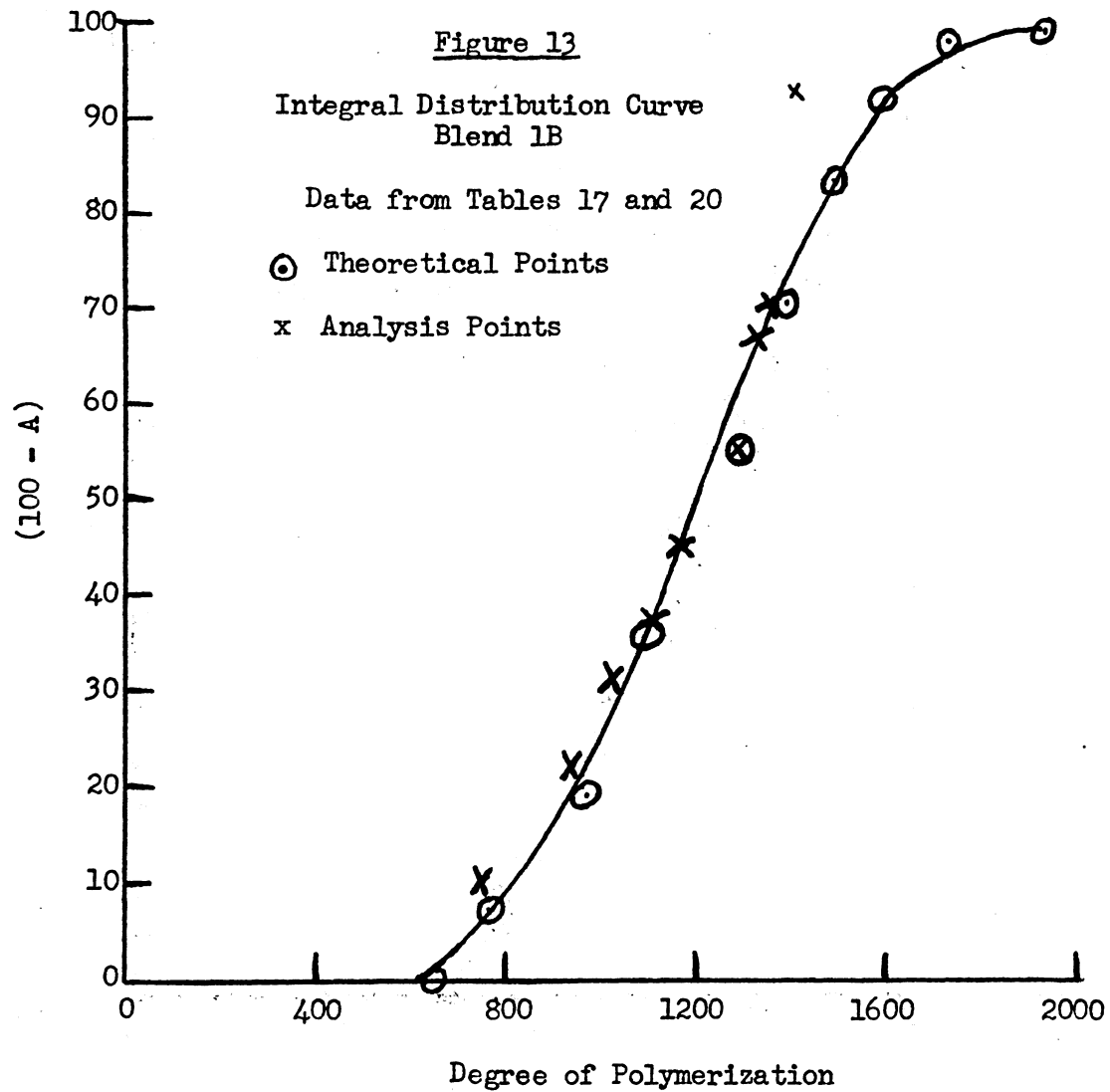
Homogeneous Fraction Number	D. P.	Percentage in Blend	Accumulative % = A	100 - A
4	1926	0.4	0.4	99.6
5	1730	1.2	1.6	98.4
6	1597	6.0	7.6	92.4
7	1496	8.8	16.4	83.6
8	1394	12.8	29.2	70.8
9	1288	15.2	44.4	55.6
10	1102	19.2	63.6	36.4
11	974	17.2	80.8	19.2
13	765	11.6	92.4	7.6
14	652	7.6	100.0	0.0

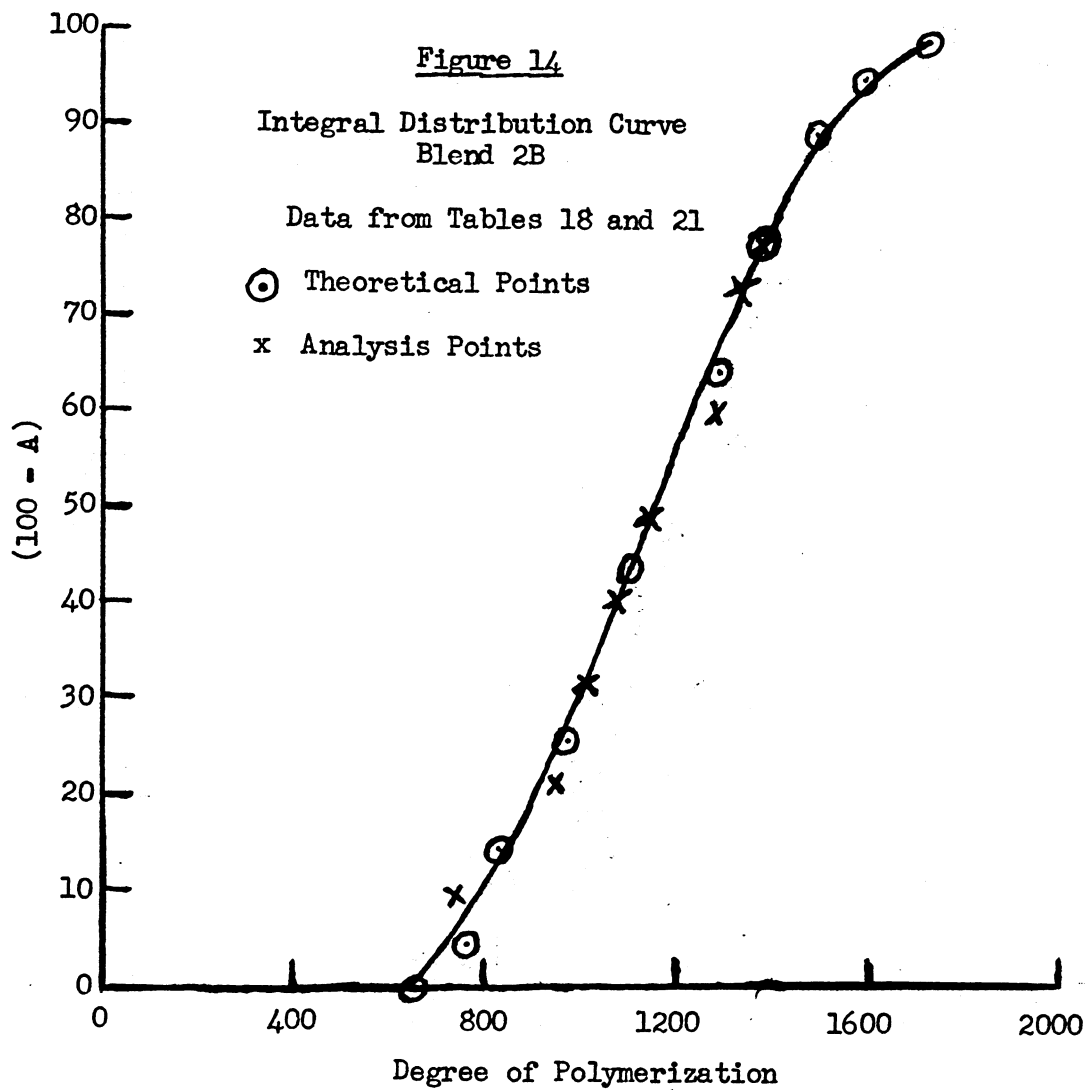
Table 21Theoretical Analysis of Blend 2B

Homogeneous Fraction Number	D. P.	Percentage in Blend	Accumulative % = A	100 - A
5	1730	1.6	1.6	98.4
6	1597	4.0	5.6	94.4
7	1496	5.6	11.2	88.8
8	1394	11.2	22.4	77.6
9	1288	13.9	36.3	63.7
10	1102	20.7	57.0	43.0
11	974	17.5	74.5	25.5
12	829	11.2	85.7	14.3
13	765	9.6	95.3	4.7
14	652	4.8	100.1	0.0

Table 22Theoretical Analysis of Blend 3B

Homogeneous Fraction Number	D. P.	Percentage in Blend	Accumulative % = A	100 - A
5	1730	0.8	0.8	99.2
7	1496	4.8	5.6	94.4
8	1394	9.6	15.2	84.8
9	1288	19.2	34.4	65.6
10	1102	28.8	63.2	36.8
11	974	25.6	88.8	11.2
13	765	7.6	96.4	3.6
14	652	3.6	100.0	0.0





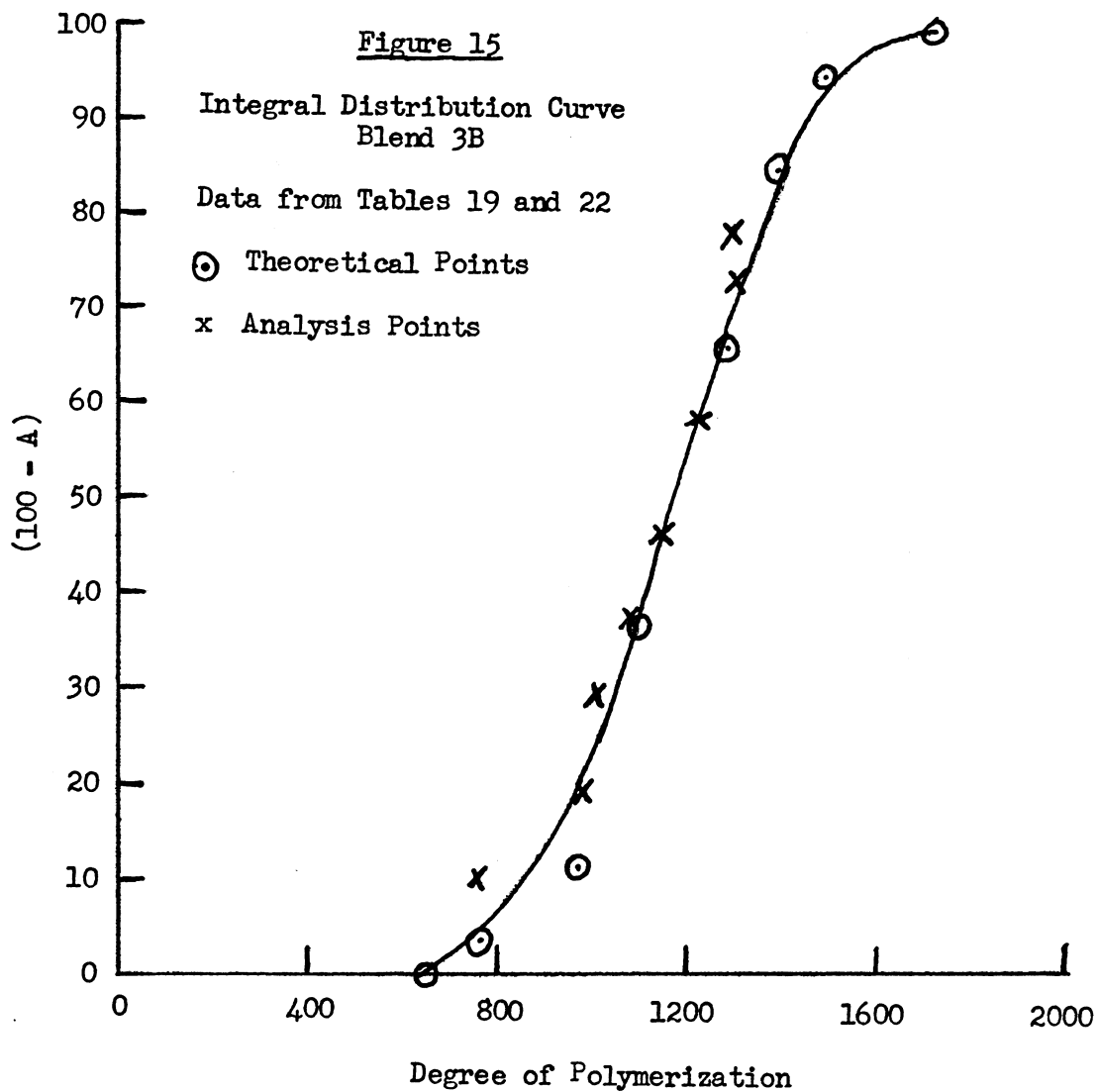


Table 23**Data for Normalized Differential Distribution Curve of
Blend IR**

D. P.	Normalized Percent
700	0.004
900	0.018
1100	0.036
1300	0.059
1500	0.085
1700	0.079
1900	0.072
2100	0.063
2300	0.053
2500	0.033

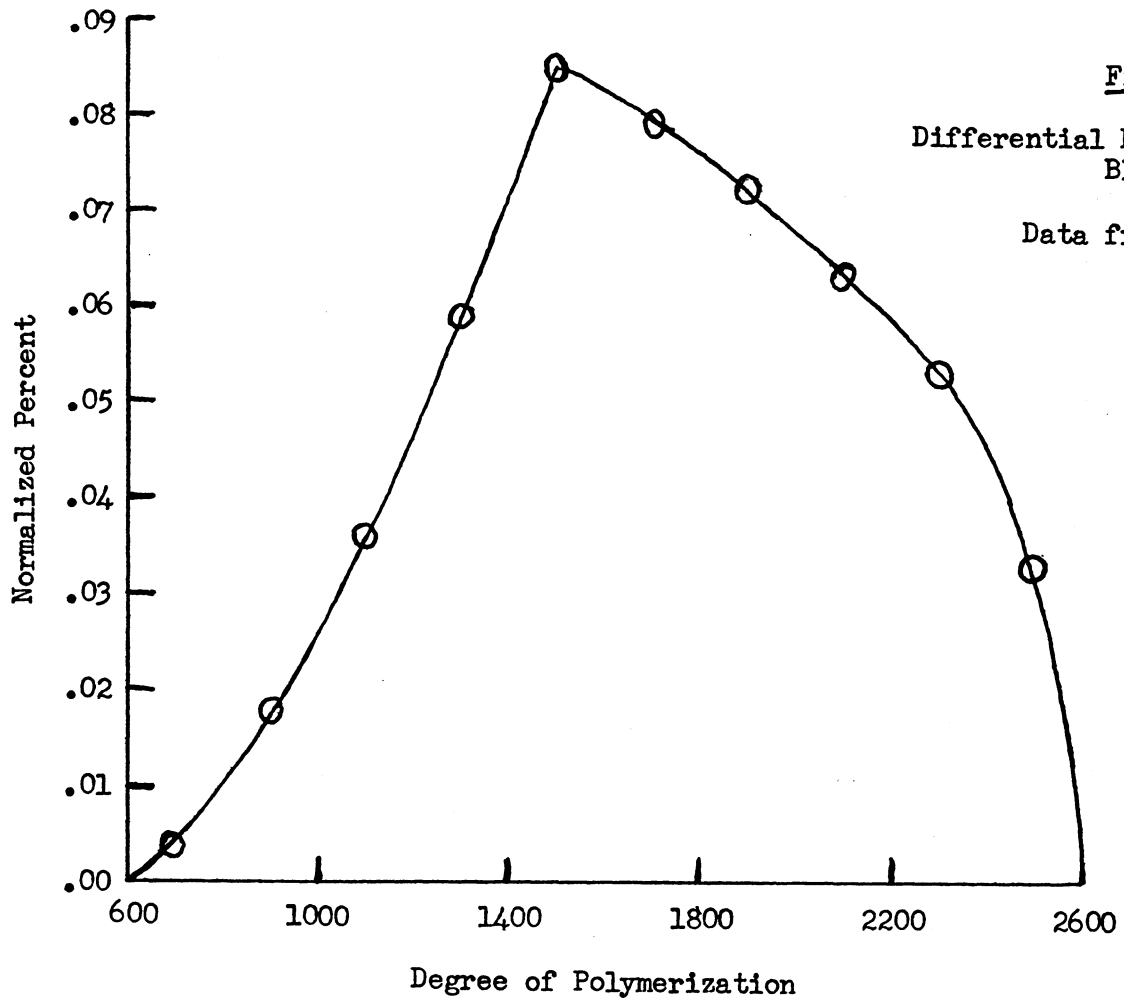


Figure 16

Differential Distribution Curve
Blend IR

Data from Table 23

Table 24**Data for Normalized Differential Distribution Curve of
Blend 2R**

D. P.	Normalized Percent
700	0.012
900	0.034
1100	0.054
1300	0.071
1500	0.085
1700	0.075
1900	0.065
2100	0.053
2300	0.038
2500	0.020

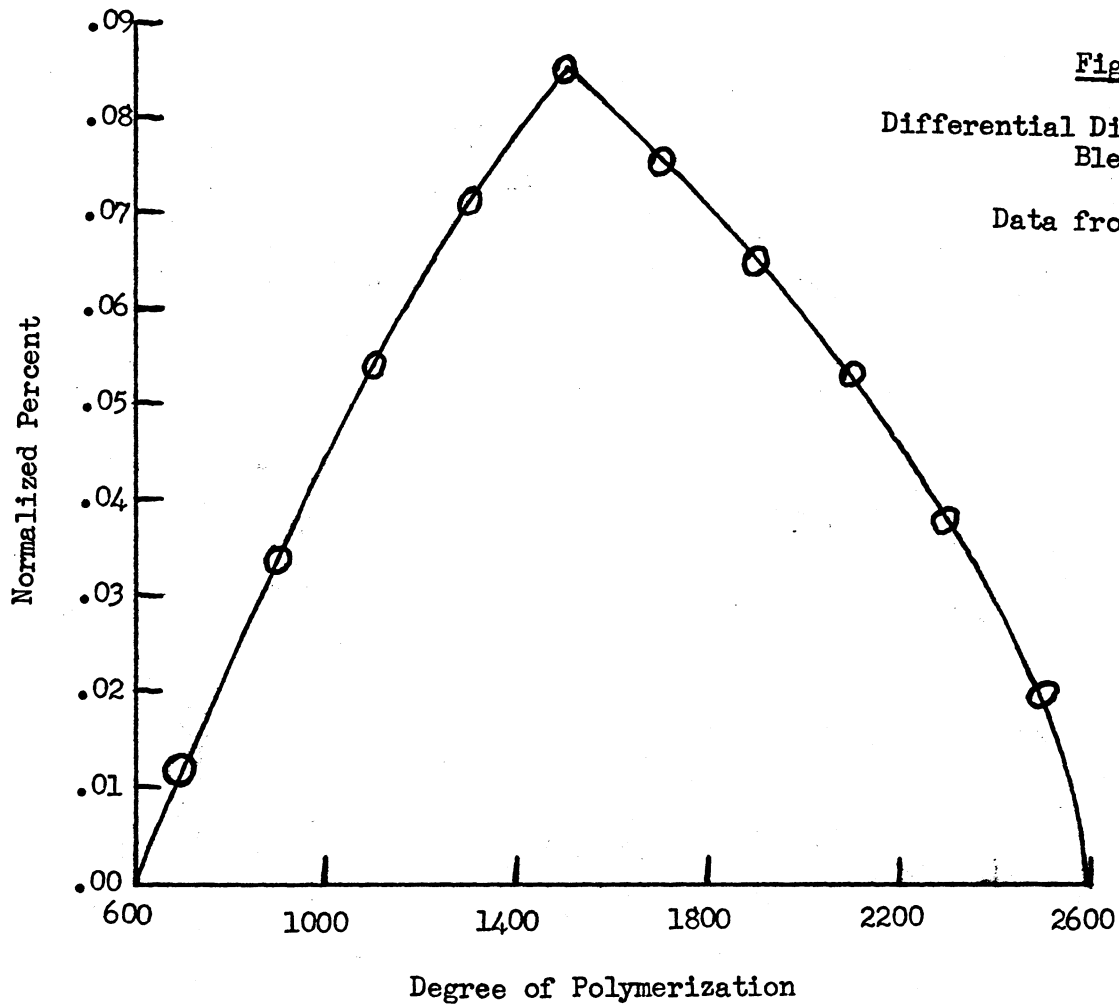


Figure 17
Differential Distribution Curve
Blend 2R
Data from Table 24

Table 25Data for Normalized Differential Distribution Curve of
Blend 3R

<u>D. P.</u>	<u>Normalized Percent</u>
700	0.018
900	0.041
1100	0.058
1300	0.073
1500	0.085
1700	0.074
1900	0.060
2100	0.047
2300	0.033
2500	0.016

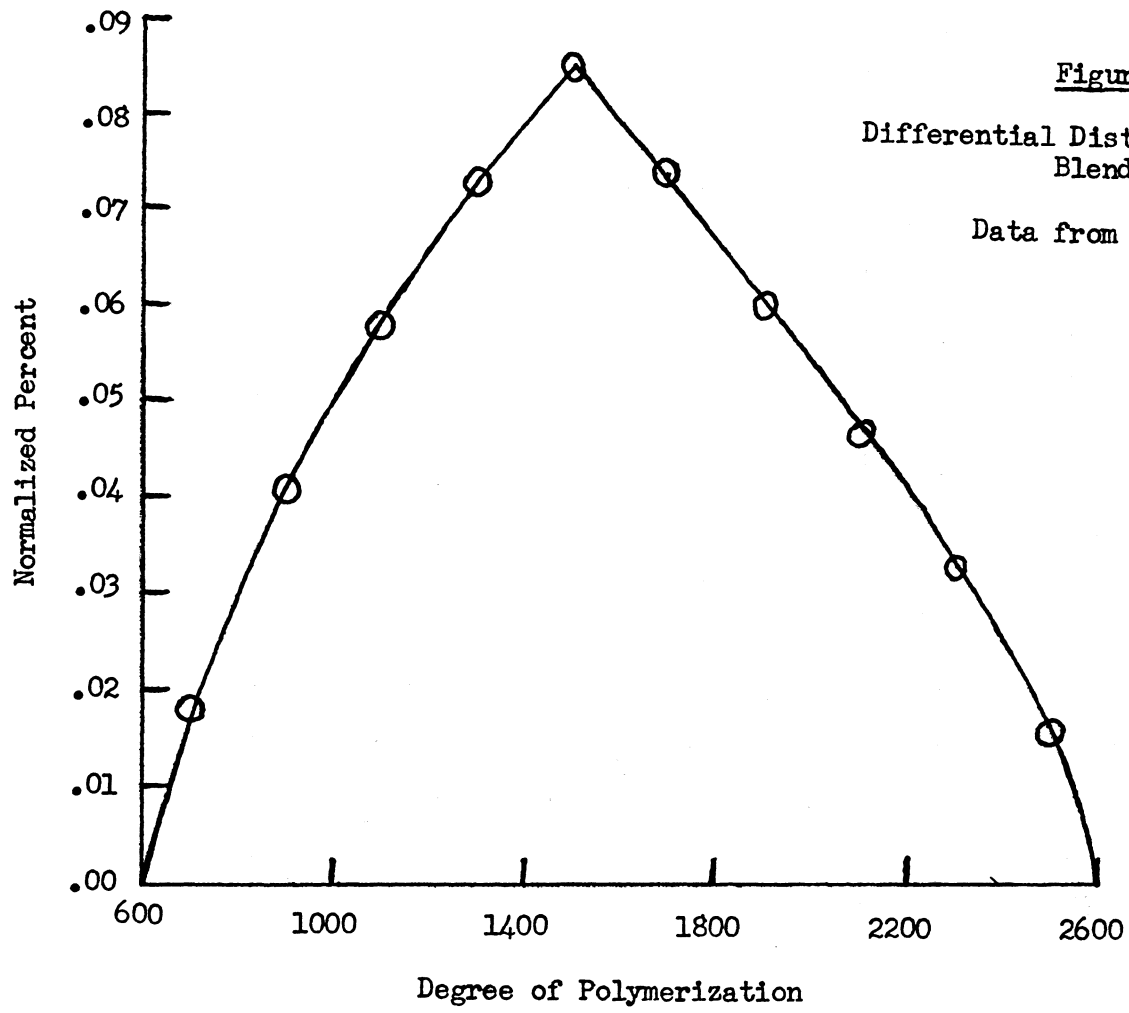


Figure 18
Differential Distribution Curve
Blend 3R
Data from Table 25

Table 26Data for Normalized Differential Distribution Curve of
Blend 1L

<u>D. P.</u>	<u>Normalized Percent</u>
700	0.044
900	0.067
1100	0.075
1300	0.081
1500	0.085
1700	0.063
1900	0.044
2100	0.025
2300	0.008

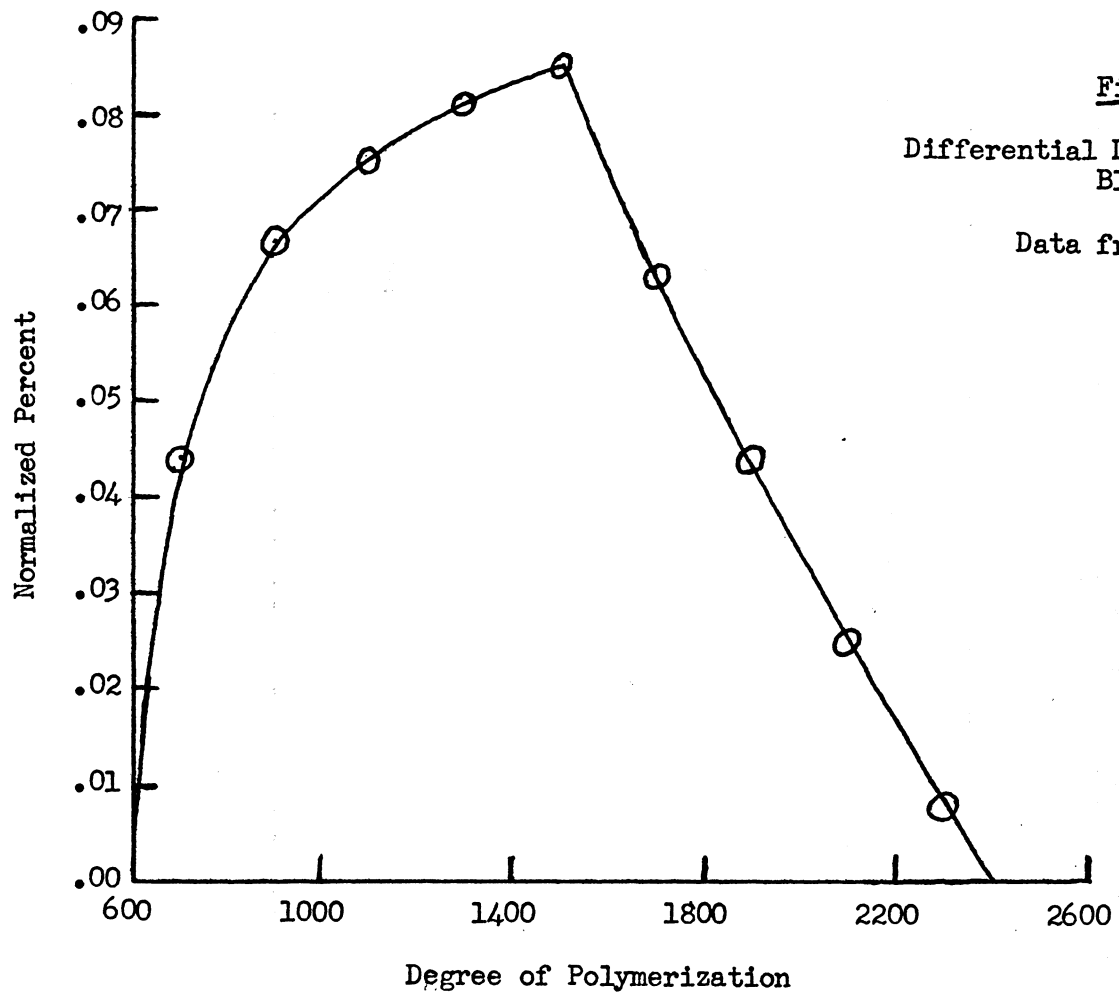


Figure 19
Differential Distribution Curve
Blend 1L

Data from Table 26

Table 27Data for Normalized Differential Distribution Curve of
Blend 2L

<u>D. P.</u>	<u>Normalized Percent</u>
700	0.037
900	0.062
1100	0.072
1300	0.080
1500	0.085
1700	0.071
1900	0.053
2100	0.033
2300	0.012

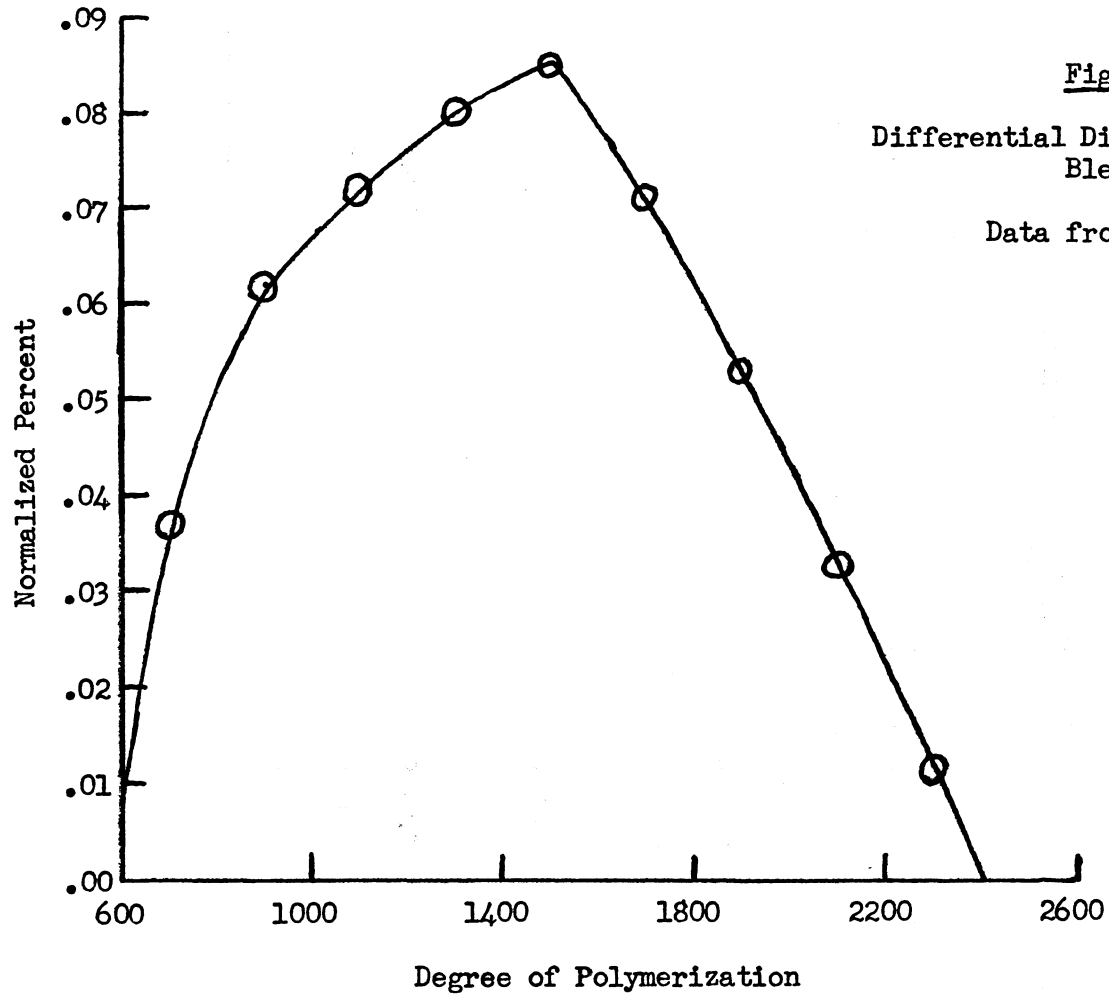


Figure 20
Differential Distribution Curve
Blend 2L
Data from Table 27

Table 28**Data for Normalized Differential Distribution Curve of
Blend 3L**

D. P.	Normalized Percent
700	0.023
900	0.054
1100	0.070
1300	0.079
1500	0.085
1700	0.076
1900	0.061
2100	0.042
2300	0.017

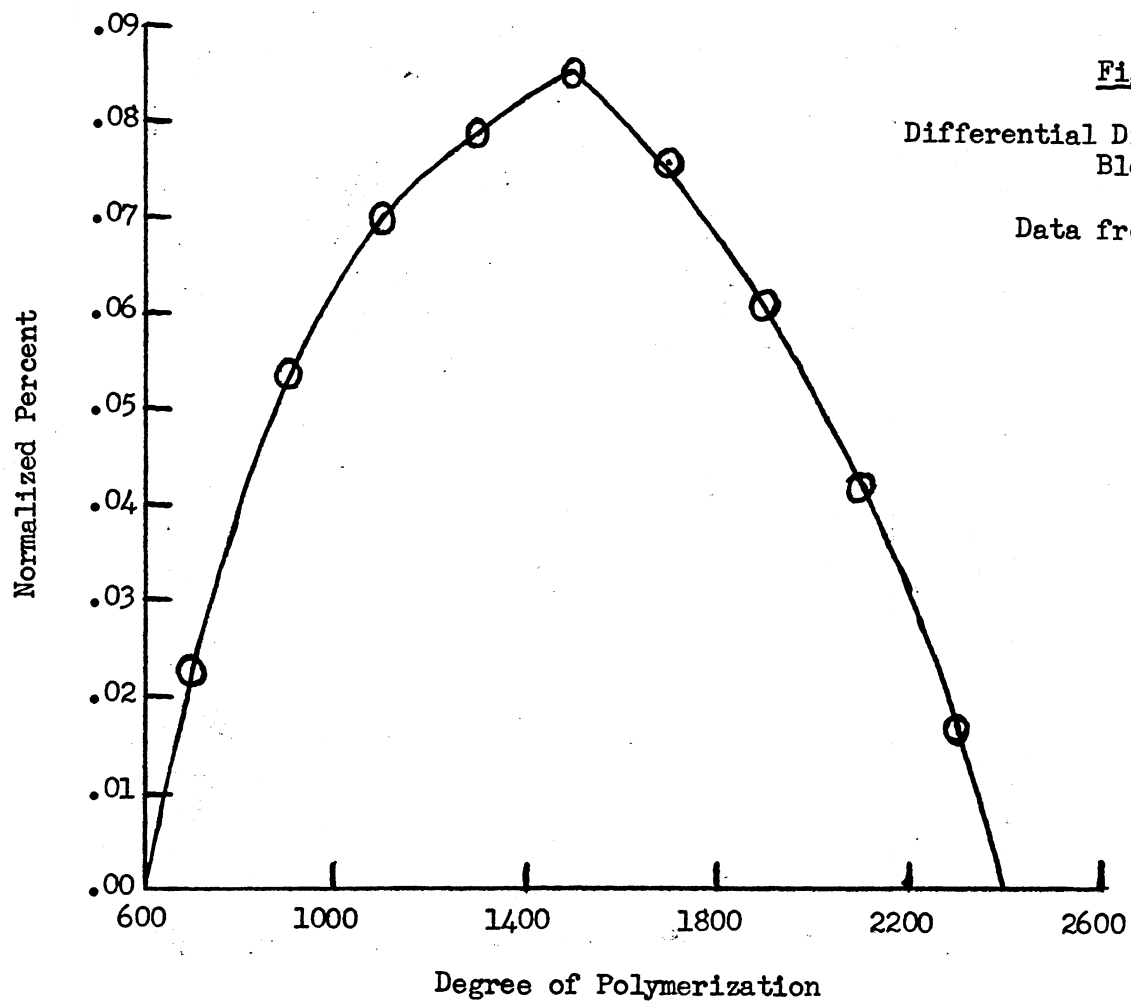


Figure 21
Differential Distribution Curve
Blend 3L
Data from Table 28

Table 29Theoretical Analysis of Blend 1R

Experimental Average D. P. of Blend = 1625

Homogeneous Fraction Number	D. P.	Percentage in Blend	Accumulative % = A	100 - A
1	2423	6.2	6.2	93.8
2	2265	8.0	14.2	85.8
3	2103	9.2	23.4	76.6
4	1926	10.3	33.7	66.3
5	1730	11.4	45.1	54.9
6	1597	12.0	57.1	42.9
7	1496	12.4	69.5	30.5
8	1394	10.3	79.8	20.2
9	1288	8.4	88.2	11.8
10	1102	5.3	93.5	6.5
11	974	3.4	96.9	3.1
12	829	1.8	98.7	1.2
13	765	1.2	99.9	0.1
14	652	0.3	100.2	0.0

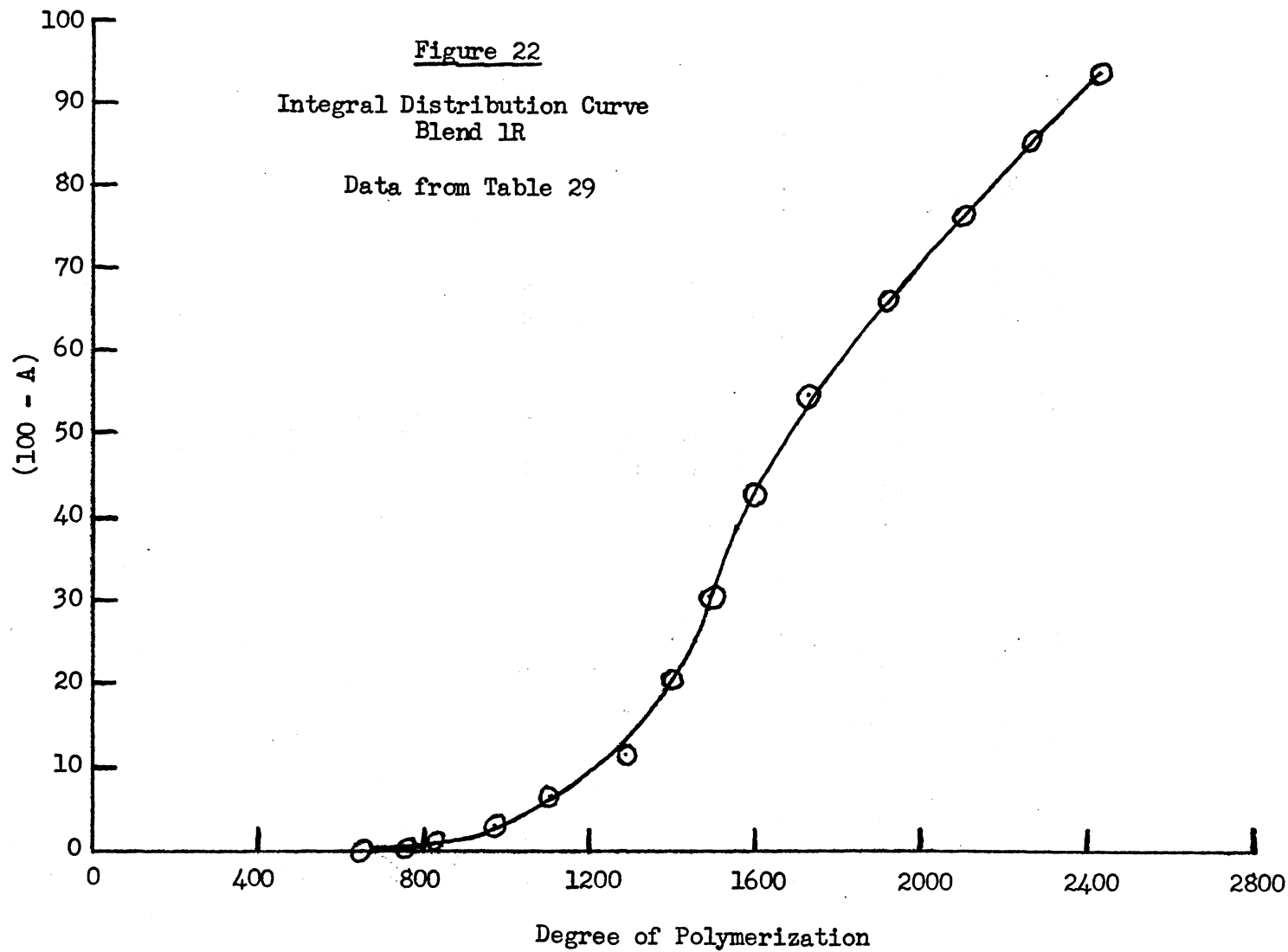


Table 30Theoretical Analysis of Blend 2R

Experimental Average D.P. of Blend = 1536

Homogeneous Fraction Number	D. P.	Percentage in Blend	Accumulative % = A	100 - A
1	2423	3.8	3.8	96.2
2	2265	5.7	9.5	90.5
3	2103	7.3	16.8	83.2
4	1926	8.8	25.6	74.4
5	1730	10.3	35.9	64.1
6	1597	11.2	47.1	52.9
7	1496	11.9	59.0	41.0
8	1394	11.0	70.0	30.0
9	1288	9.8	79.8	20.2
10	1102	7.5	87.3	12.7
11	974	5.7	93.0	7.0
12	829	3.6	96.6	3.4
13	765	2.7	99.3	0.7
14	652	0.8	100.1	0.0

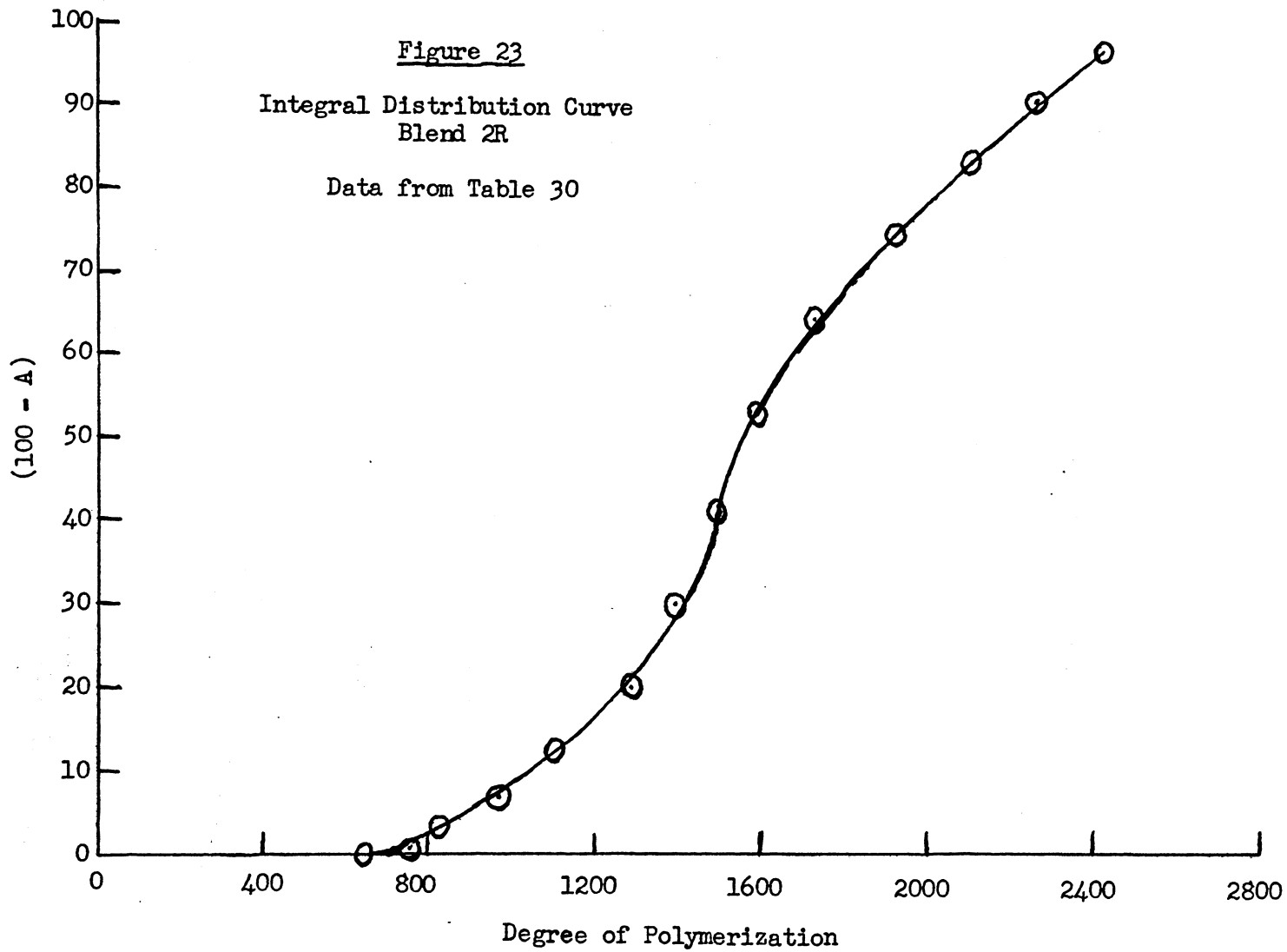


Table 31Theoretical Analysis of Blend 3R

Experimental Average D.P. of Blend = 1440

Homogeneous Fraction Number	D. P.	Percentage in Blend	Accumulative % = A	100 - A
1	2423	3.1	3.1	96.9
2	2265	4.8	7.9	92.1
3	2103	6.5	14.4	85.6
4	1926	8.1	22.5	77.5
5	1730	9.9	32.4	67.6
6	1597	11.0	43.4	56.6
7	1496	11.7	55.1	44.9
8	1394	10.9	66.0	34.0
9	1288	10.0	76.0	24.0
10	1102	8.0	84.0	16.0
11	974	6.6	90.6	9.4
12	829	4.6	95.2	4.8
13	765	3.5	98.7	1.3
14	652	1.4	100.1	0.0

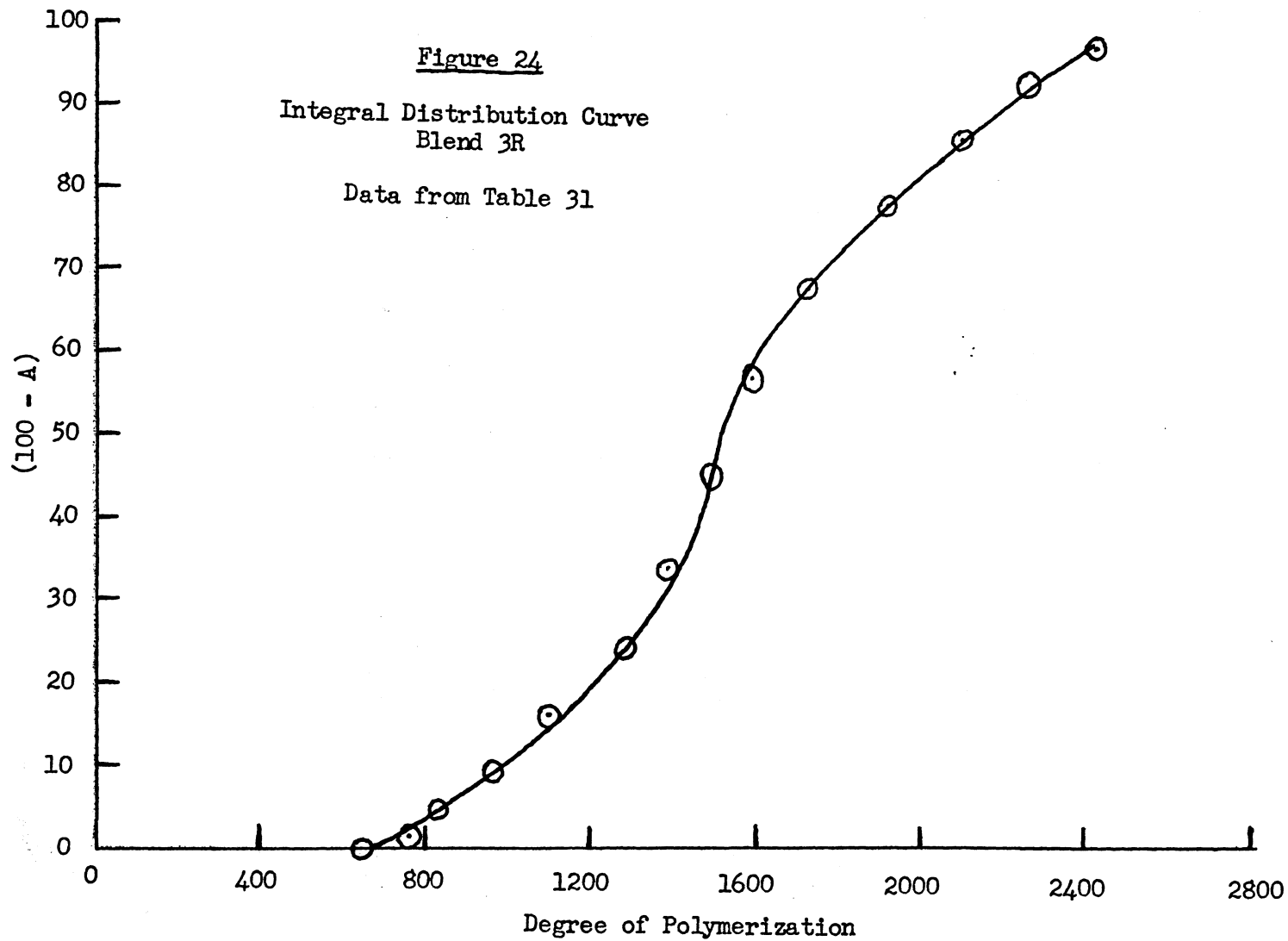


Table 32Theoretical Analysis of Blend 1L

Experimental Average D.P. of Blend = 1312

Homogeneous Fraction Number	D. P.	Percentage in Blend	Accumulative % = A	100 - A
2	2265	1.6	1.6	98.4
3	2103	3.6	5.2	94.8
4	1926	6.0	11.2	88.8
5	1730	8.7	19.9	80.1
6	1597	10.7	30.6	69.4
7	1496	12.3	42.9	57.1
8	1394	12.0	54.9	45.1
9	1288	11.7	66.6	33.4
10	1102	10.9	77.5	22.5
11	974	10.2	87.7	12.3
13	765	7.9	95.6	4.4
14	652	4.4	100.0	0.0

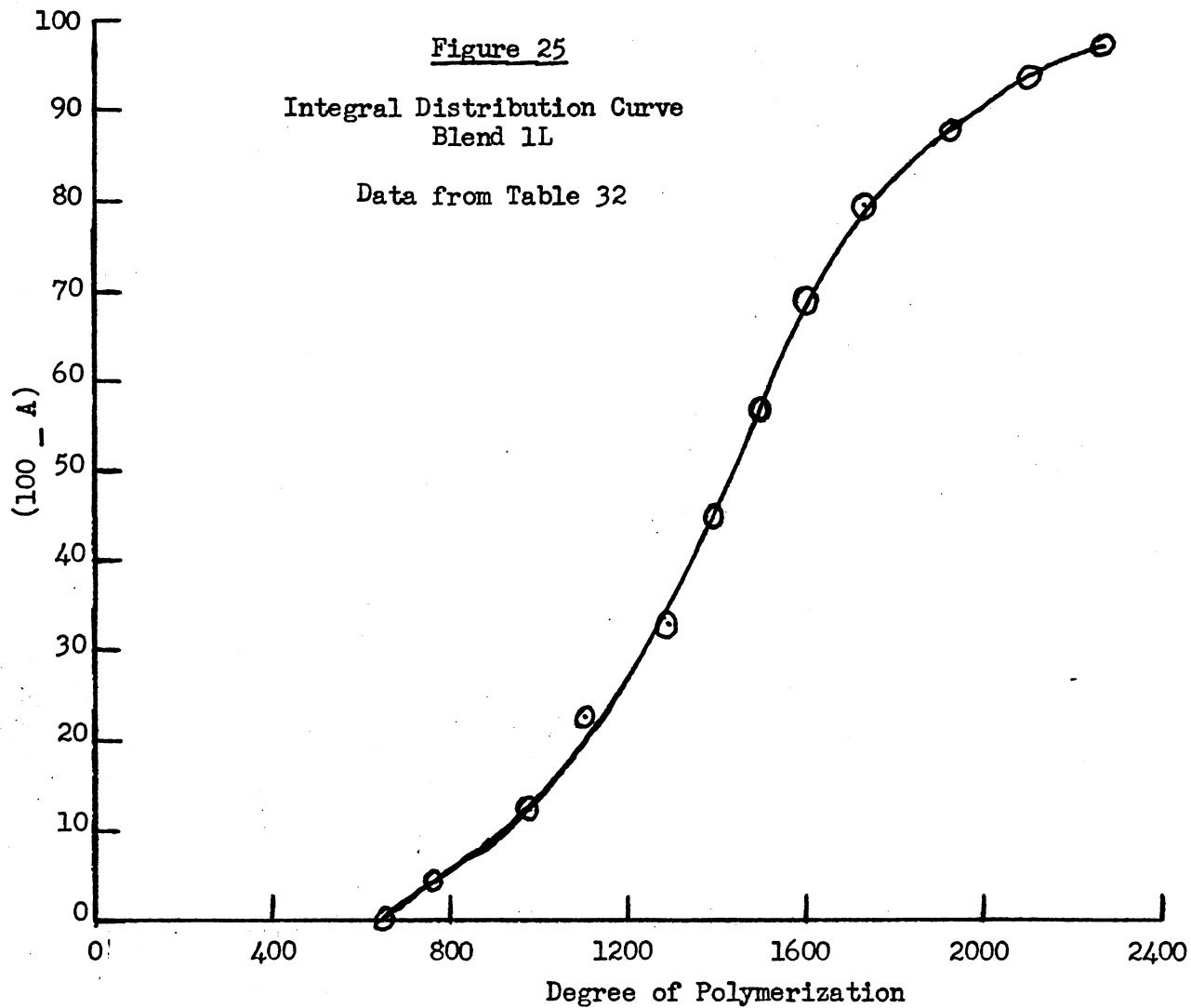


Table 33Theoretical Analysis of Blend 2L

Experimental Average D.P. of Blend = 1354

Homogeneous Fraction Number	D. P.	Percentage in Blend	Accumulative % = A	100 - A
2	2265	2.2	2.2	97.8
3	2103	4.7	6.9	93.1
4	1926	7.2	14.1	85.9
5	1730	9.8	23.9	76.1
6	1597	11.3	35.2	64.8
7	1496	12.1	47.3	52.7
8	1394	11.8	59.1	40.9
9	1288	11.3	70.4	29.6
10	1102	10.3	80.7	19.3
11	974	9.4	90.1	9.9
13	765	6.6	96.7	3.3
14	652	3.4	100.1	0.0

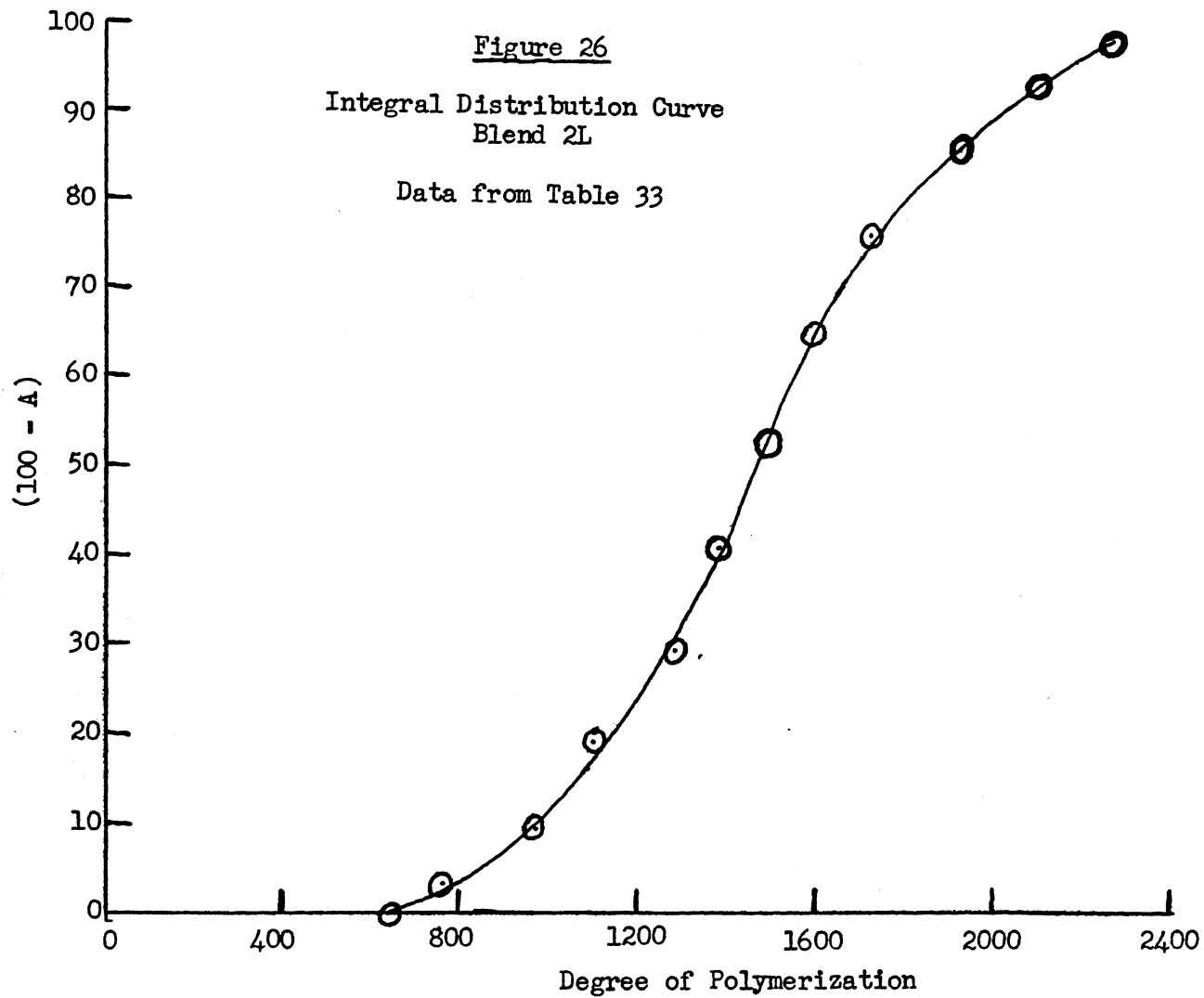


Table 34Theoretical Analysis of Blend 3L

Experimental Average D.P. of Blend = 1446

Homogeneous Fraction Number	D. P.	Percentage in Blend	Accumulative % = A	100 - A
2	2265	3.1	3.1	96.9
3	2103	5.9	9.0	91.0
4	1926	8.4	17.4	82.6
5	1730	10.5	27.9	72.1
6	1597	11.6	39.5	60.5
7	1496	12.1	51.6	48.4
8	1394	11.7	63.3	36.7
9	1288	11.1	74.4	25.6
10	1102	10.0	84.4	15.6
11	974	8.8	93.2	6.8
13	765	4.9	98.1	1.9
14	652	2.0	100.1	0.0

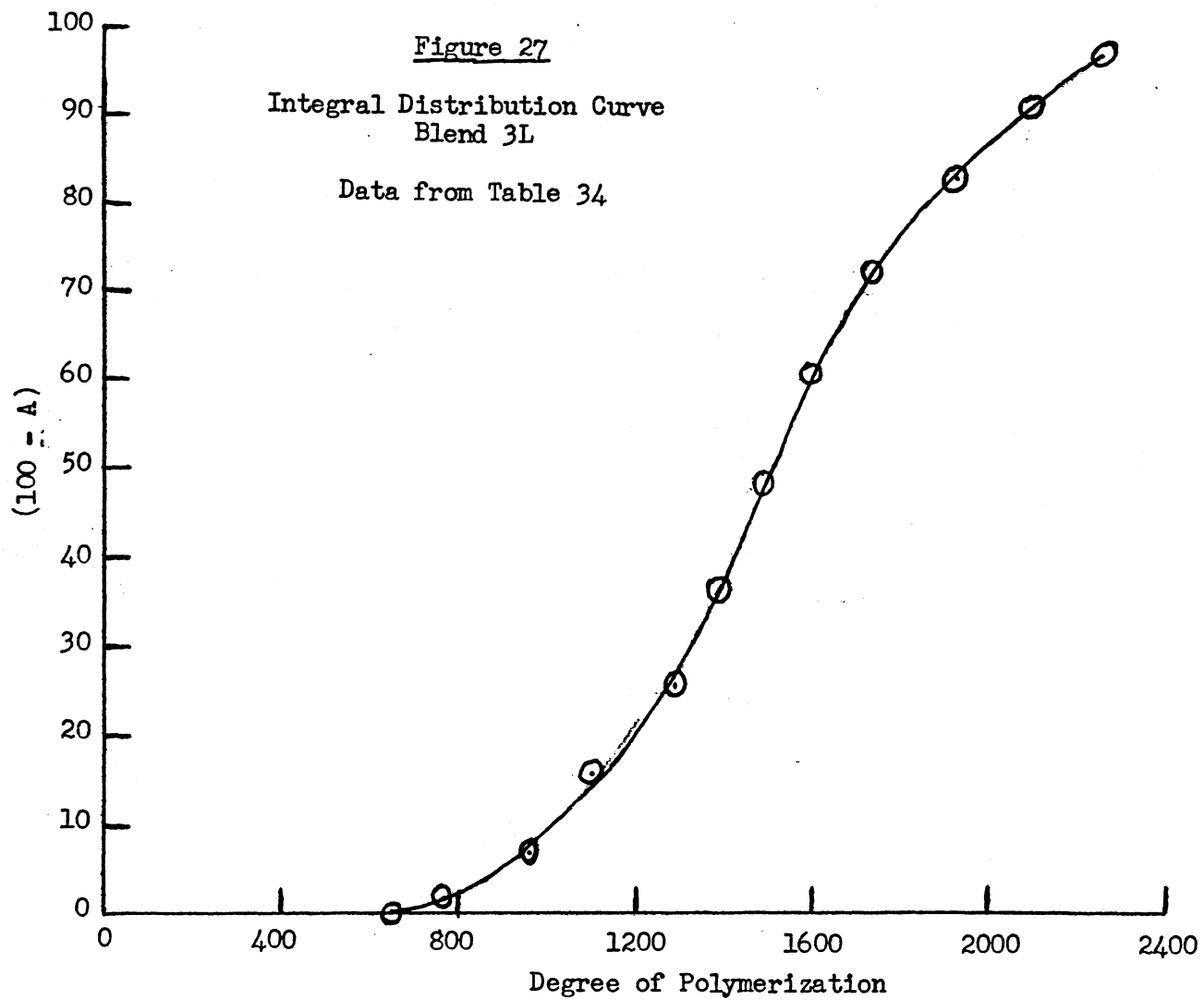


Table 35Tensile Strengths of Polyvinyl Alcohol Blends

Blend Number	Direction	Avg. T.S. (psi)	Max. T.S. (psi)	Min. T.S. (psi)	Avg. Dev. (psi)	Number of Samples
1B	cross	7220	8000	6500	390	11
	with	7520	8400	6900	460	10
	average	7370				21
2B	cross	7440	8110	6300	670	11
	with	7680	8360	6560	410	12
	average	7560				23
3B	cross	8030	9000	6900	530	10
	with	7990	8900	6670	510	11
	average	8010				21
1R	cross	8300	9200	7750	360	10
	with	8140	9330	6890	790	12
	average	8220				22
2R	cross	8620	9500	7100	470	12
	with	8210	9380	7400	500	13
	average	8420				25
3R	cross	8720	10110	7220	540	10
	with	9050	9670	8110	440	12
	average	8890				22
1L	cross	8800	9780	8000	380	10
	with	8690	9780	7440	570	11
	average	8750				21
2L	cross	9220	10130	8600	370	11
	with	9120	9900	7440	530	12
	average	9170				23
3L	cross	8380	8780	8000	260	10
	with	8500	9440	7780	510	11
	average	8440				21

Table 36Ultimate Elongation of Polyvinyl Alcohol Blends

Blend Number	Direction	Avg. Elon. (%)	Max. Elon. (%)	Min. Elon. (%)	Avg. Dev. (%)	Number of Samples
1B	cross	85	165	36	34	11
	with	117	172	53	35	10
	average	101				21
2B	cross	86	123	26	22	11
	with	108	155	70	23	12
	average	97				23
3B	cross	128	163	89	27	10
	with	124	173	75	27	11
	average	126				21
1R	cross	70	161	21	36	10
	with	87	159	32	27	12
	average	79				22
2R	cross	99	182	20	40	12
	with	107	151	26	33	13
	average	103				25
3R	cross	105	135	66	23	10
	with	93	158	17	45	12
	average	99				22
1L	cross	92	163	11	41	10
	with	70	169	15	37	11
	average	81				21
2L	cross	44	136	3	25	11
	with	55	104	9	20	12
	average	50				23
3L	cross	77	117	45	14	10
	with	65	121	21	20	11
	average	71				21

Table 37Burst Strengths of Polyvinyl Alcohol Blends

Blend Number	Avg. B.S. (psi)	Max. B.S. (psi)	Min. B.S. (psi)	Avg. Dev. (psi)	Number of Samples
1B	52	59	41	4	18
2B	53	58	48	4	12
3B	55	61	45	4	12
1R	50	54	45	2	12
2R	52	61	46	3	11
3R	52	61	44	4	14
1L	55	63	45	3	14
2L	51	57	45	3	13
3L	49	54	42	4	12

Table 38Characterization of Blends

Blend Number	Exptl. Average D.P.	D.P. at Max. (P_m)	Max. Ht. (%) (H)	Bowley's Skew	Area Skew
1B	1101	1102	0.135	0	0
2B	1098	1102	0.158	0	0
3B	1084	1102	0.183	0	0
1R	1625	1496	0.085	0.267	36.7
2R	1536	1496	0.085	0.180	15.9
3R	1440	1496	0.085	0.119	8.1
1L	1312	1496	0.085	-0.160	-26.1
2L	1354	1496	0.085	-0.059	-16.2
3L	1446	1496	0.085	0.077	- 6.2

VIII. CORRELATION OF THE DATA

Earlier work on other polymers (14,44,86) has shown that a reasonably good correlation of the shape of the distribution curve with mechanical properties may be obtained by considering three factors as defining the shape of the distribution curve. These factors are: (1) The D.P. at the maximum of the differential distribution curve (P_m), (2) the height of this maximum (H), and (3) the skew (B) of the distribution from the normal distribution.

Following this earlier work, the first attempt at correlation in the present investigation was in terms of these factors. From the data recorded in Tables 9 and 36 it was noted that the ultimate elongation values varied too widely for any practical correlation to be expected. As shown in the tables and curves recording the data for burst strengths, this test, as performed, was apparently not sensitive enough to show any appreciable variations in any of the fractions or blends. Thus the attempt at correlation was limited to the relation between tensile strength and the shape of the distribution curve.

In the case of the homogeneous fractions it would appear to be a valid assumption that the distributions

are very narrow, normal, and that the heights at the maxima are essentially the same. Then for these fractions H and B should be constant and the plot of D.P. against tensile strength should represent only the effect of varying P_m on the property. Analyzing the curve of Figure 4 mathematically it was found that the tensile strength is related to the D.P. at the maximum as follows:

$$T = 8200 - 10^{6.87-0.00476P_m}$$

where T is tensile strength

P_m is D.P. of fraction

Turning to a consideration of the normal blends with P_m constant and only H varying, it was noted (Table 39) that the calculated values on the basis of P_m alone were low by a different increment in each case. This increment is plotted against H in Figure 28. Mathematically the relation is:

$$T_H = 2.786 \times 10^6 H^{4.767} - 1000$$

Then for calculating tensile strength (T') considering P_m and H the equation is:

$$T' = (8200 - 10^{6.87-0.00476P_m}) + (2.786 \times 10^6 H^{4.767} - 1000)$$

Where for values of H above about 0.190 the height effect apparently does not reduce the tensile strength and the second term in brackets is dropped.

As shown in Table 39, the values calculated for the skewed blends by the above method are considerably lower than the experimental values. The increments are plotted against area skew (B) in Figure 29. Area skew consists of the difference in the area on the right and left side of the differential distribution curve. The least squares straight line was drawn in Figure 29 as a first approximation. The equation for this line is:

$$T_B = 1450 - 10.4B$$

And the final equation for relating tensile strength to the shape of the distribution curve becomes:

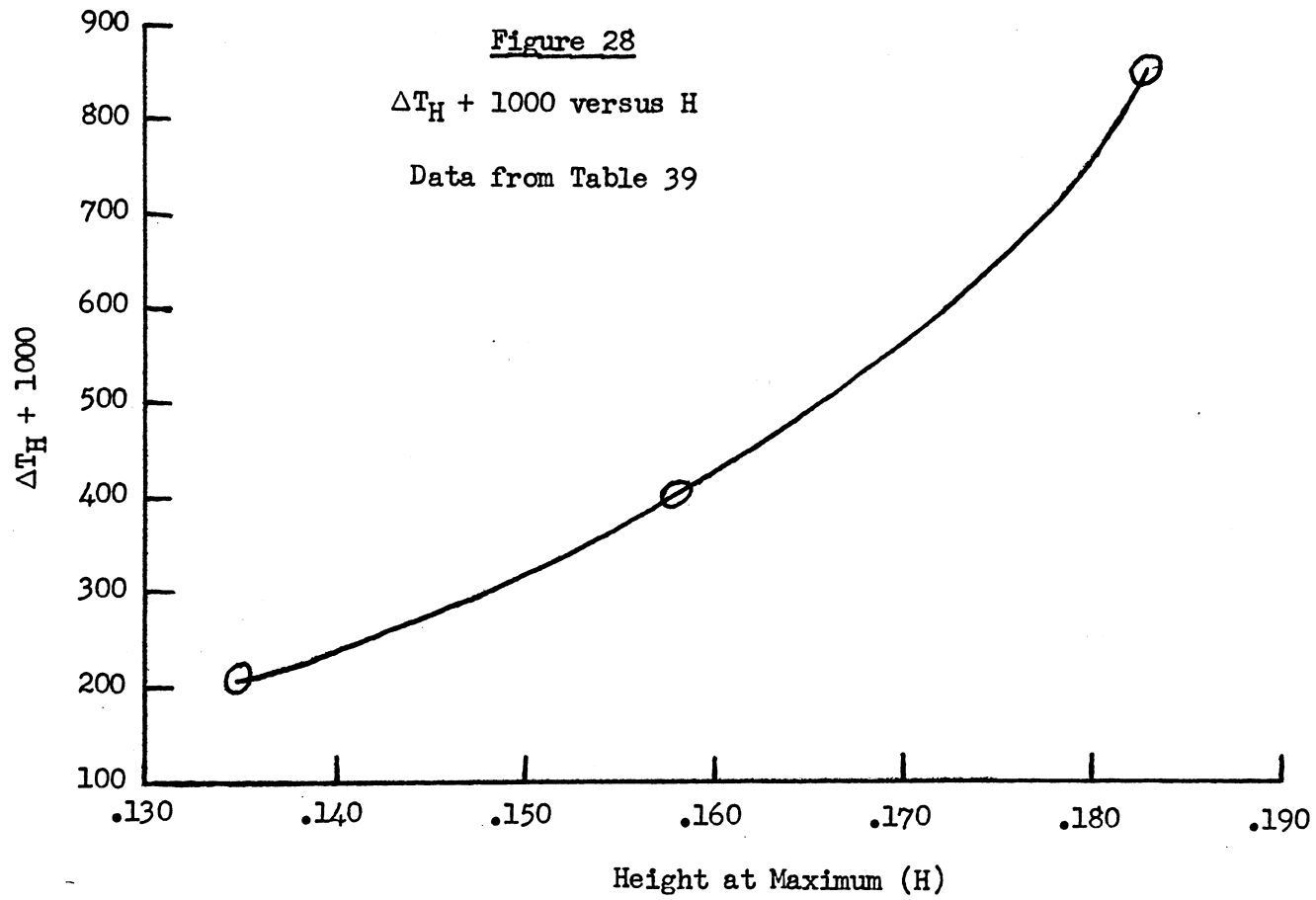
$$T = (8200 - 10^{6.87 - 0.0476P_m}) + (2.786 \times 10^6 H^{4.767} - 1000) \\ + (1450 - 10.4B)$$

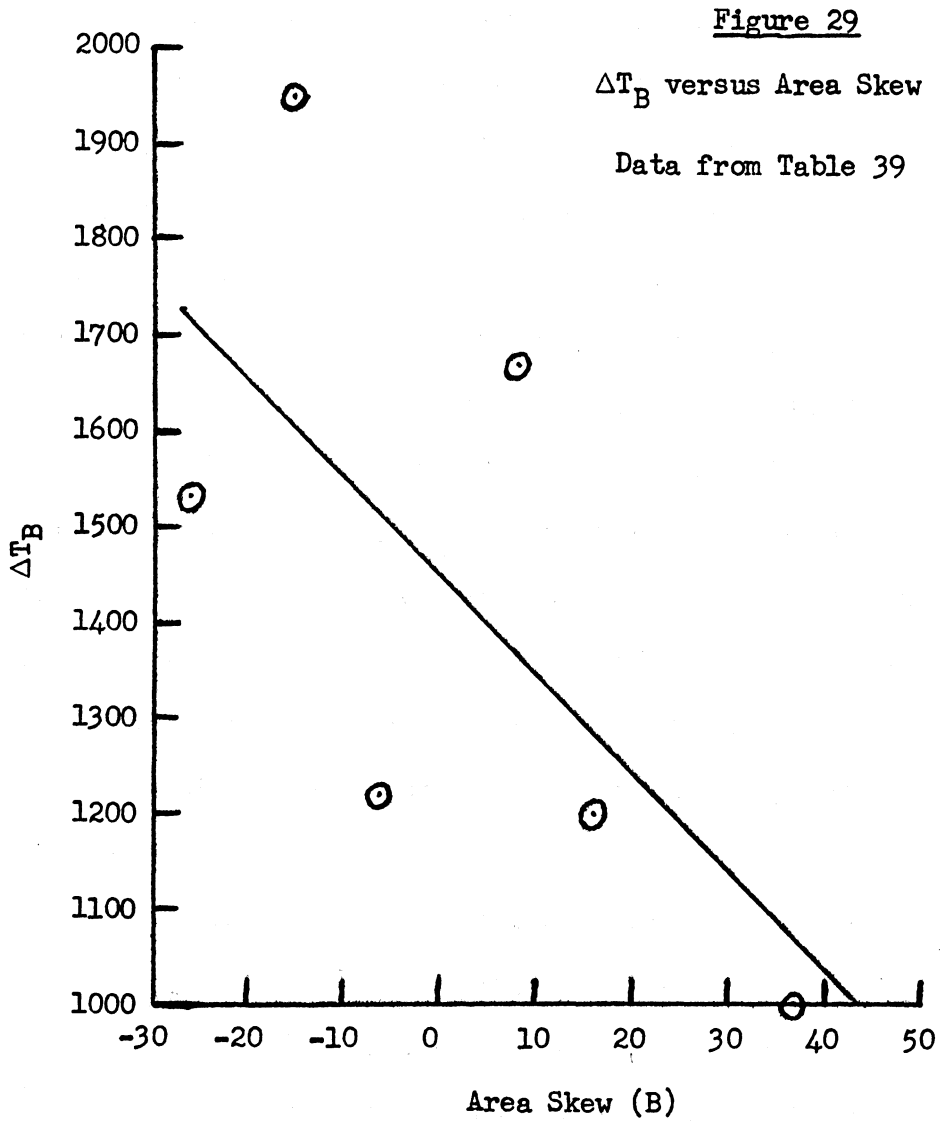
Where the second term in brackets is dropped when H is greater than 0.190 and the entire last term is dropped when B = 0. The values of tensile strength calculated by this equation are shown in Table 39.

Besides being troublesome to handle and having the non-mathematical qualifications in its use that are indicated above, this equation has the disadvantage that

Table 39Curve Characteristics and Tensile Strengths of Blends

Blend	P_m	H	B	T.S. (Exptl)	ΔT_H^+ 1000	T'	ΔT_B^- T - T' (calc.)	T.S.
1B	1102	0.135	0	7370	210	7360	10	7360
2B	1102	0.158	0	7560	400	7580	-20	7580
3B	1102	0.183	0	8010	850	8010	0	8010
1R	1496	0.085	36.7	8220		7220	1000	8290
2R	1496	0.085	15.9	8420		7220	1200	8510
3R	1496	0.085	8.1	8890		7220	1670	8590
1L	1496	0.085	-26.1	8750		7220	1530	8940
2L	1496	0.085	-16.2	9170		7220	1950	8840
3L	1496	0.085	- 6.2	8440		7220	1220	8730





it gives only a rough correlation for the skew blends and does not seem to reflect the trend clearly for these blends. For this reason a further examination of the data seemed in order.

It has been postulated recently (86) that the reason that, in the plot of mechanical properties versus D.P., the points at the leveling off position of the curve generally are high is due to an optimum plasticization by the low D.P. material which is present. If this assumption is accepted it is immediately noted that the presence of low D.P. material leads to two opposing effects on the mechanical properties. In the first place the plasticizing action tends to increase the properties. On the other hand the lowering of D.P. tends to decrease the properties. In any case it would seem reasonable that the difference in properties of two blends of the same D.P. would be dependent on the differing amounts of low D.P. material present.

The next point to consider is what constitutes the low D.P. material, that is, the material which shows this plasticizing action. The most obvious assumption would be that all material below the leveling point of the curve mentioned above is of this nature.

Further reflection indicates that the quantity of this low D.P. material might be related to the factors

used in the calculation of the so-called Shape Factor. Skewness to the left or right will obviously be reflected by the percentage of low D.P. material present. The height of the maximum (H) of the normalized differential distribution curve will also be reflected by this quantity since a higher height will correspond to a pulling in of the sides, in order to maintain an area of 100% under the curve. The position of P_m in the normalized differential distribution curve may also be assumed to be reflected by the percentage of this low D.P. material. The fact that this may be so may be most easily seen by comparing normal curves of constant height with P_m at different positions. Obviously the one with P_m at a higher value will have less material of low D.P.

In order to test the above postulate for polyvinyl alcohol the necessary data are shown in Table 40 and tensile strength is plotted against total percentage below D.P. = 1000 in Figure 30. With the exception of one wild point, a good graphical correlation is obtained.

Further tests were carried out using the data of other investigators. Thus for cellulose nitrate (44) the data are shown in Table 41 and the plots in Figures 31, 32, and 33. For cellulose acetate (86) the data are given in Table 42 and plots are given in Figures 34 and 35. For polyvinyl acetate (14) the data

are shown in Table 43 and plotted in Figures 36 and 37. In general, it seems that this much simpler method of correlation gives results comparable to those obtained by the use of the much more complicated Shape Factor.

It must be noted that, although the correlation seems promising by this new method, it is actually purely empirical. It does seem to have some support, however, in some recent work on polystyrene (63a,64a). This work has indicated that optimum properties were obtained provided the number average molecular weight was above a certain limiting value and the low molecular weight species do control this number average molecular weight.

Table 40

Tensile Strength and Total Percentage Below D.P. = 1000.
Data for Polyvinyl Alcohol Blends

Blend	Total % Below D.P. = 1000	Experimental T.S. (psi)
1B	22.5	7370
2B	28.0	7560
3B	22.0	8010
1R	3.5	8220
2R	8.5	8420
3R	10.5	8890
1L	15.0	8750
2L	13.0	9170
3L	9.0	8440

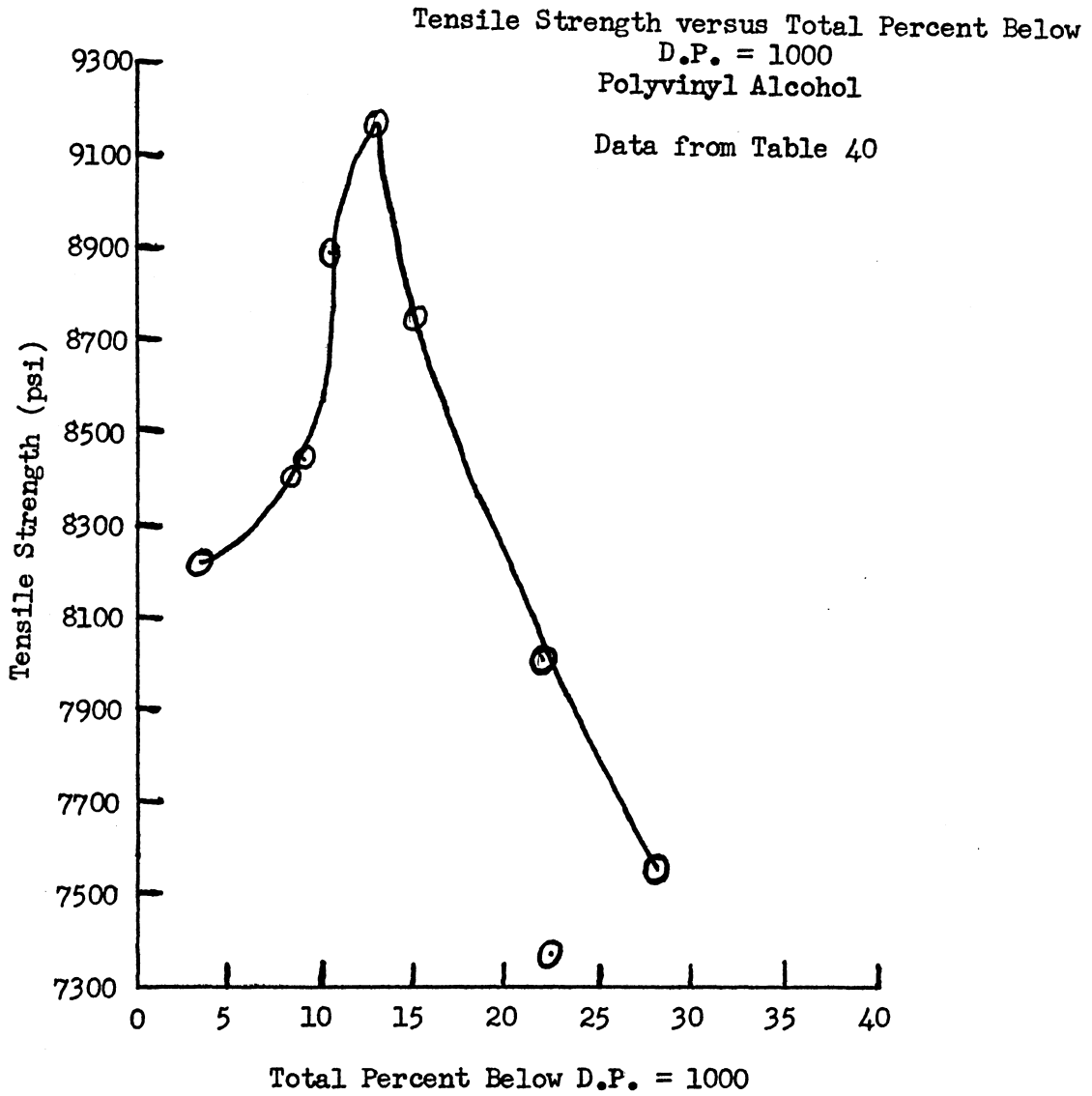
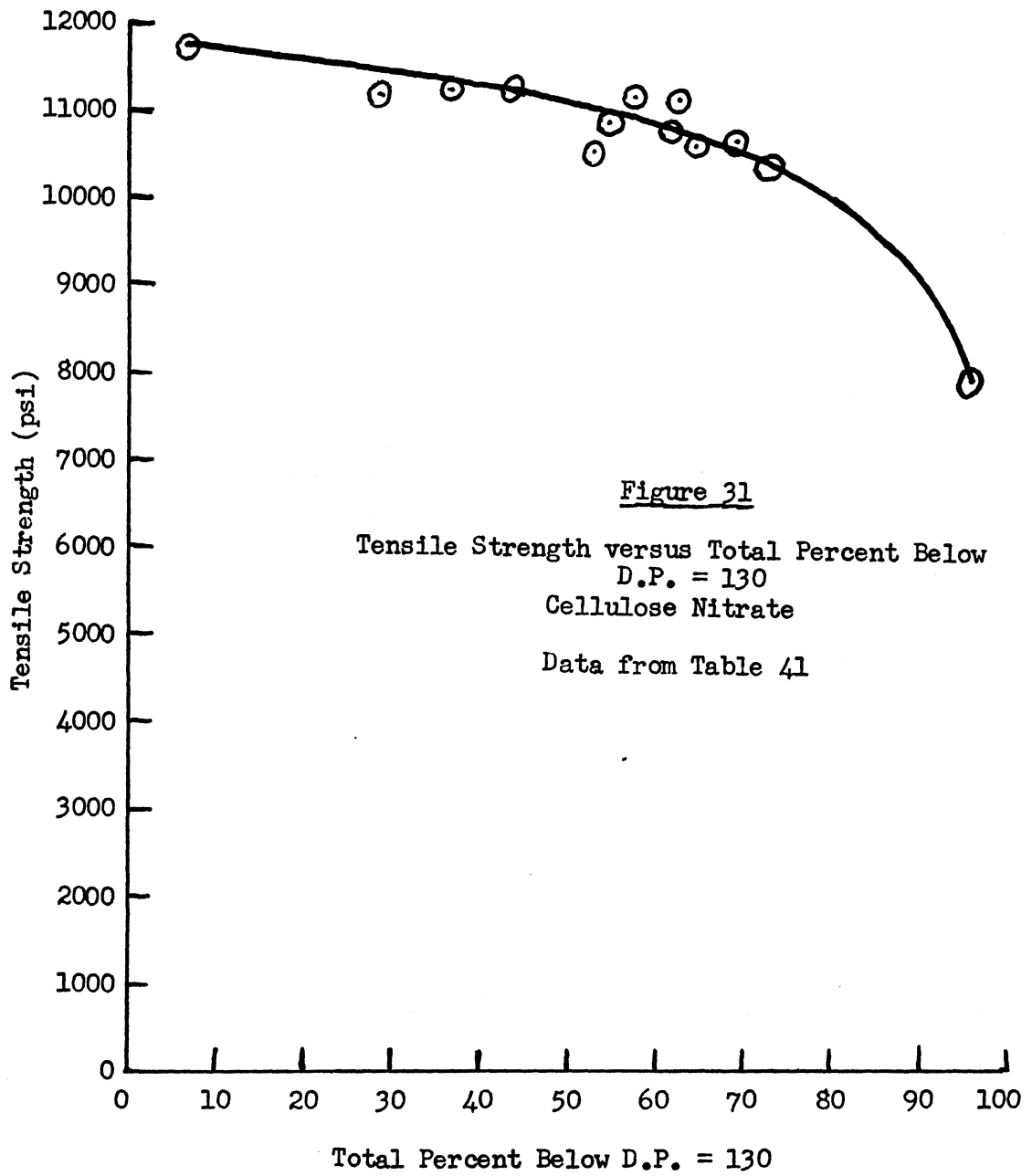
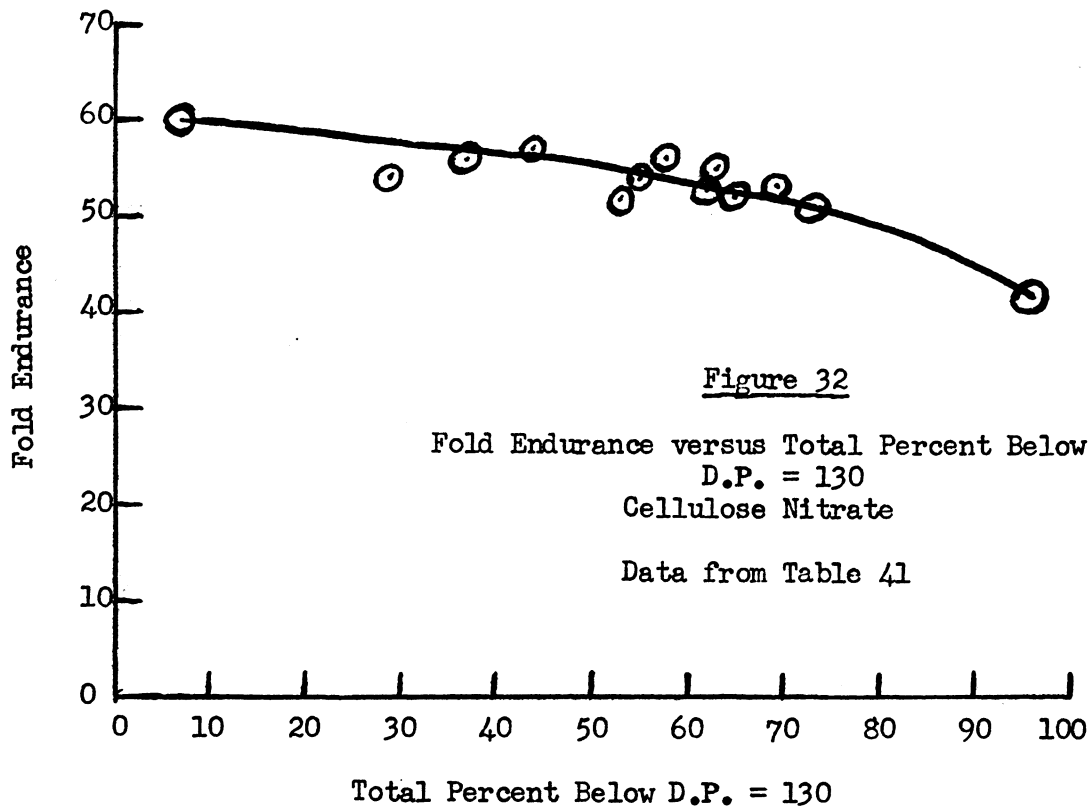
Figure 30

Table 41Mechanical Properties and Total Percentage Below D.P. = 130.
Data for Cellulose Nitrate Blends.

Data from the Thesis of Johnson (44).

Blend	Total % Below D.P. = 130	T. S. (psi)	Fold End.	B. S. (psi)
1A	53	10,520	52	72
2A	55	10,880	54	73
3A	58	11,160	56	75
4A	63	11,120	55	76
1B	96	7920	42	59
3B	7	11,720	60	78
1L	62	10,760	53	73
2L	65	10,600	52	73
3L	73	10,360	51	71
4L	69.5	10,600	53	72
1R	37	11,240	56	76
2R	29	11,200	54	75
3R	44	11,280	57	76





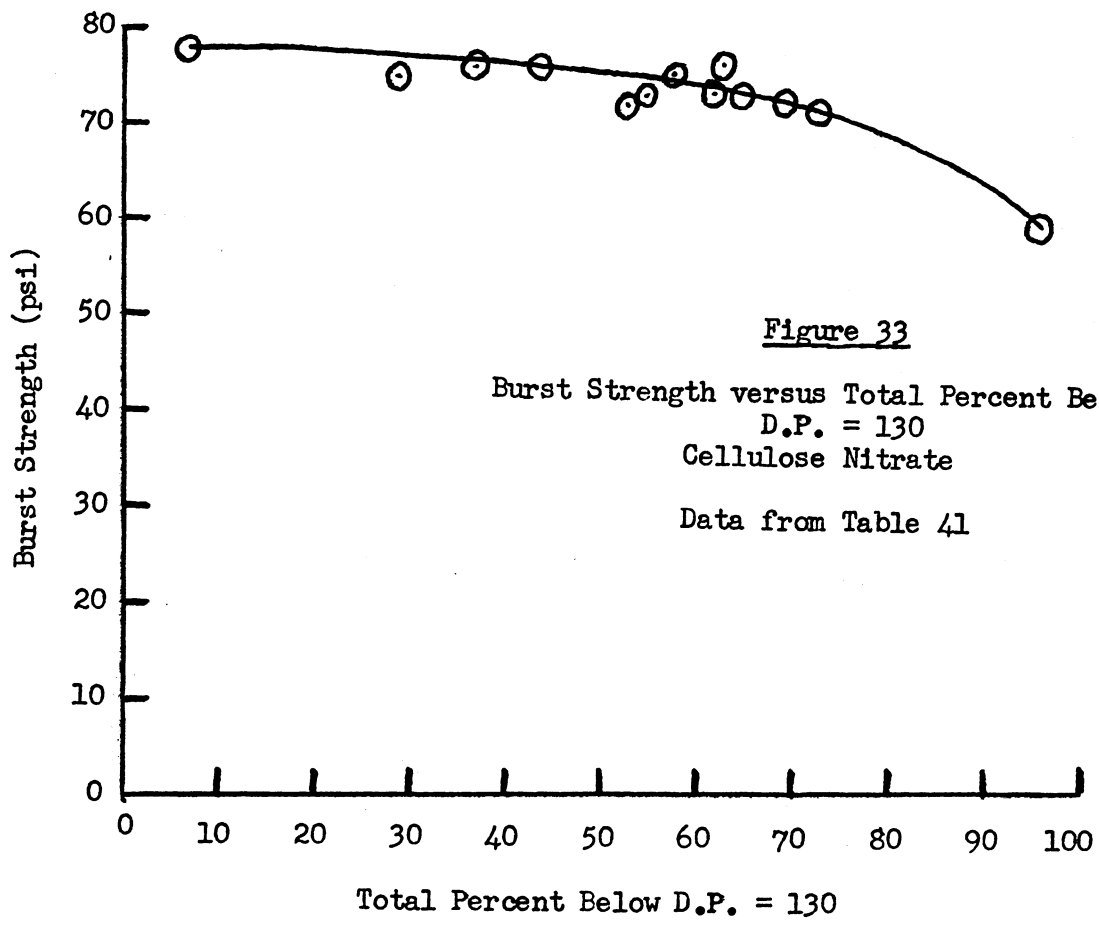


Figure 33

Burst Strength versus Total Percent Below
 D.P. = 130
 Cellulose Nitrate

Data from Table 41

Table 42Mechanical Properties and Total Percentage Below D.P. = 110.
Data for Cellulose Acetate Blends.

Data from the Thesis of Thompson (86).

Blend	Total % Below D.P. = 110	B. S. (psi)	Fold End.
1	65	55	51
2	8	73	91
3	1.5	81	91
4	9	74	93
5	8	77	91
6	33.5	64	61
7	26	81	69
8	16	69	78
9	4.5	76	84
10	18	70	78

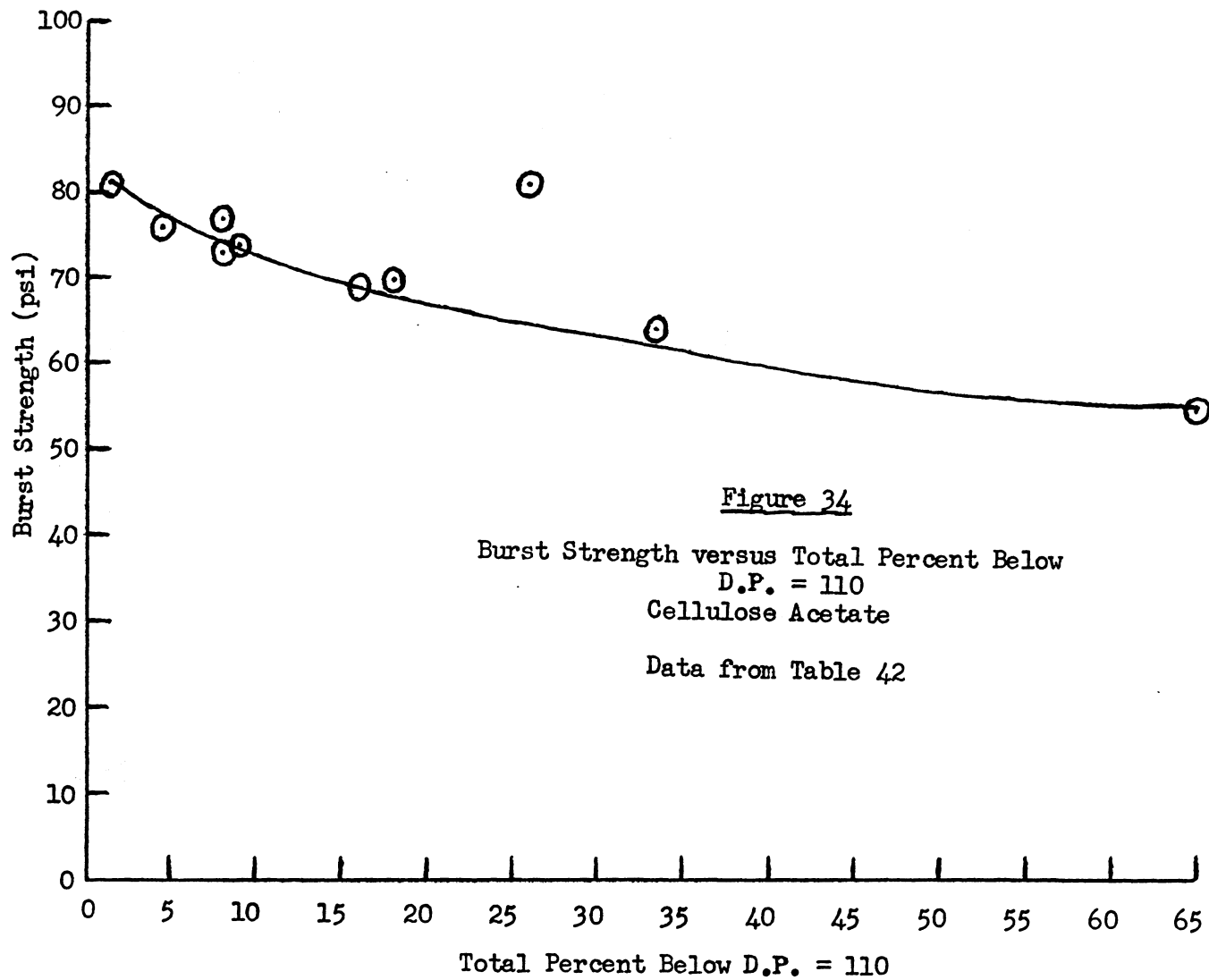


Figure 34

Burst Strength versus Total Percent Below

D.P. = 110

Cellulose Acetate

Data from Table 42

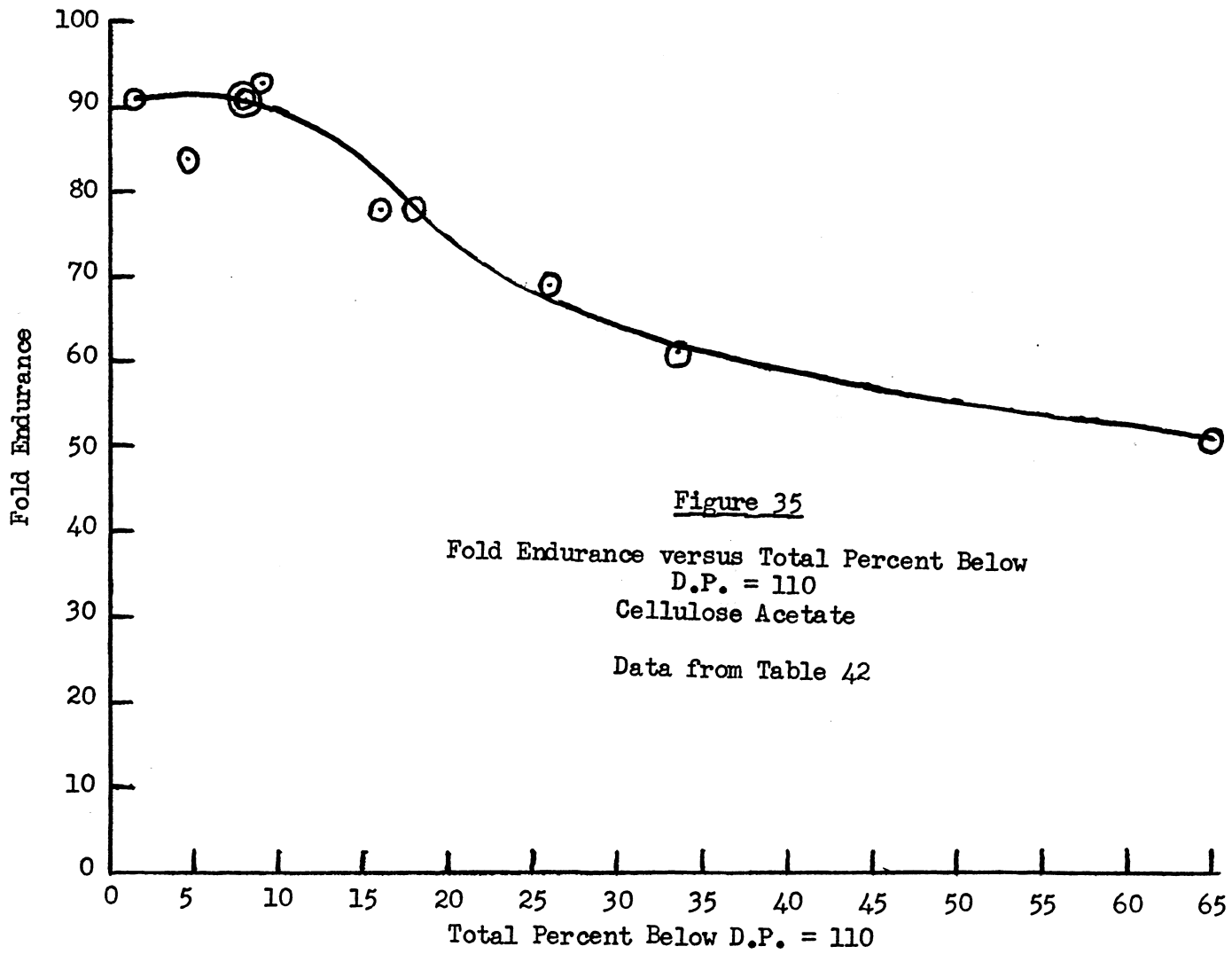


Table 43Mechanical Properties and Total Percentage Below D.P. = 1000.
Data for Polyvinyl Acetate Blends.

Data from Thesis of Chinai (14).

Blend	Total % Below D.P. = 1000	T. S. (psi)	Fold End.
B1	34	6100	142
B2	33	6115	152
B3	29.5	6080	155
B4	30	6240	172
B5	20	6365	184
1R	16	6183	233
2R	9.5	6800	249
3R	8	6838	269
1L	34	6078	140
2L	35	6002	108
3L	42	6176	83

Figure 36

Fold Endurance versus Total Percent Below
D.P. = 1000
Polyvinyl Acetate

Data from Table 43

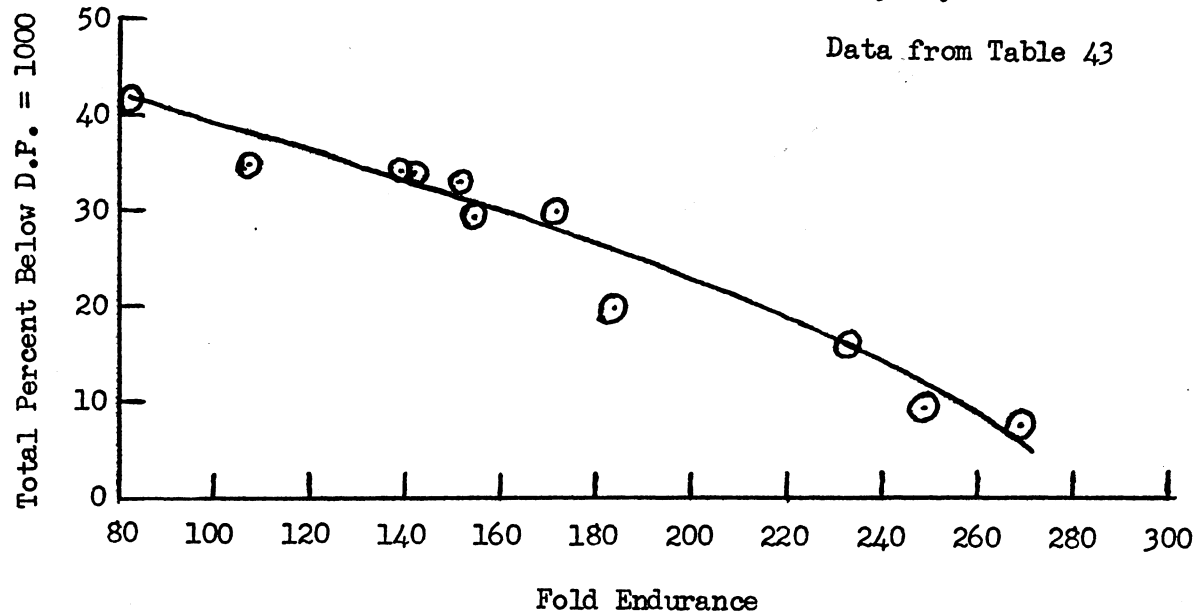
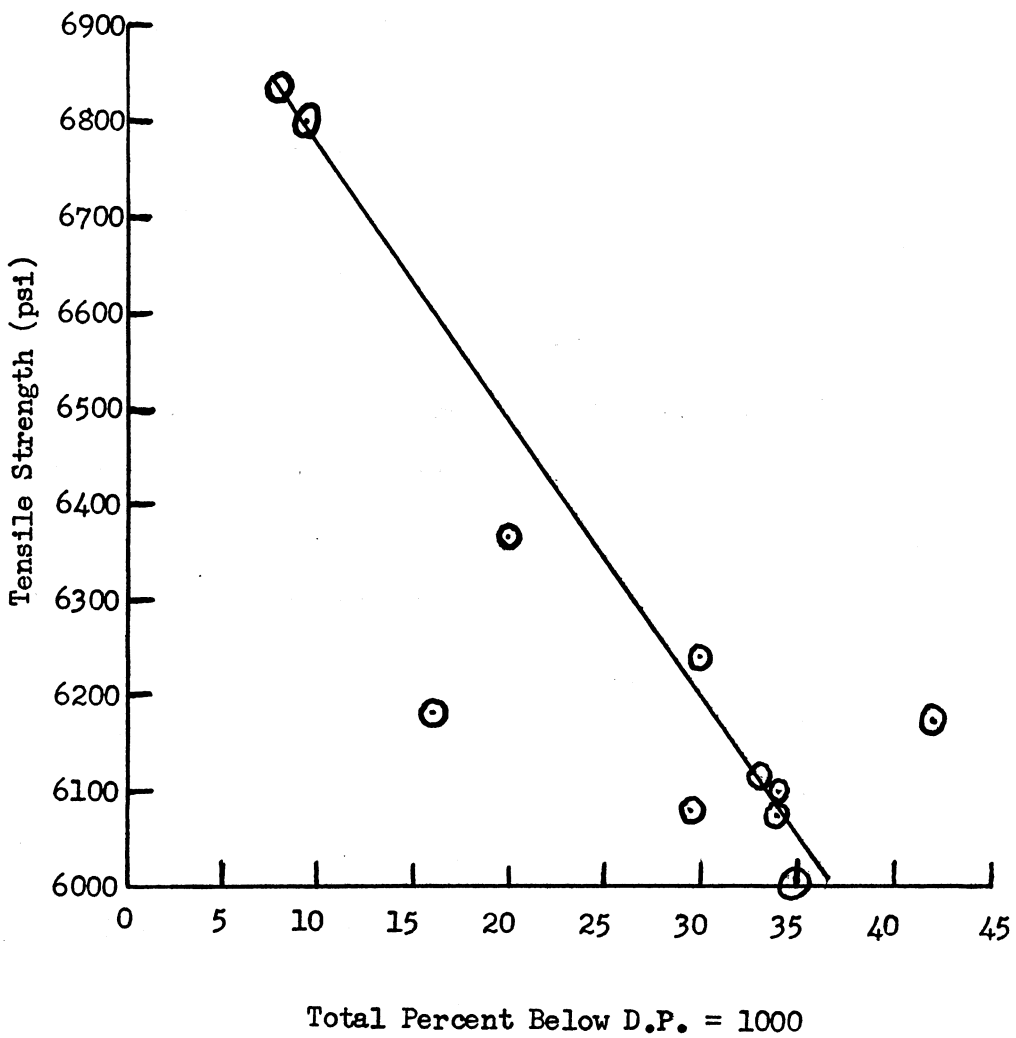


Figure 37

Tensile Strength versus Total Percent Below
D.P. = 1000
Polyvinyl Acetate

Data from Table 43



IX. DISCUSSION OF RESULTS

A fractionation procedure for polyvinyl alcohol using water as solvent and n-propyl alcohol as nonsolvent was found to be satisfactorily reproducible and was adapted so as to obtain fractions in sufficient quantity for testing mechanical performance. By appropriate refractionation, fractions were obtained which were as homogeneous as possible by this method.

The viscosity chain length determinations reported in this work led to relative values for chain lengths but probably did not give exact values for D.P.

A satisfactory procedure for casting 0.001 inch thick films of polyvinyl alcohol was devised during the course of the work. These films were tested for tensile strength, elongation and burst strength. The results of elongation tests, both for fractions and blends, were so variable that no definite conclusions could be drawn from tests of this property. When the wide variations of elongation even within the same film are considered, it appears that the machine and/or conditions of performing tests of this property were unsatisfactory for polyvinyl alcohol. Burst strengths were virtually constant for all films tested, probably due to a lack

of sensitivity in the method of testing. The tests of tensile strength of the homogeneous fractions showed the same general relation between D.P. and tensile strength that has been found for a number of other polymers.

In the case of blends having a normal distribution, and constant D.P. at the maximum, but variable height at the maximum, it was found that the tensile strengths were lower than those of the homogeneous fractions but that the tensile strengths increased with increasing height at the maximum and finally approached those of the fractions. In the light of the correlation with low D.P. material (Figure 30) it appears possible that the lower properties of these blends may have been due to the fact that they all contained more than 20% of material of D.P. below 1000.

The skewed blends, in general, showed tensile strengths somewhat higher than the homogeneous fractions. In terms of the correlation shown in Figure 30 this could be explained by the fact that these blends contained the proper proportion of low D.P. material to show optimum properties.

This investigation has shown that the tensile strengths of polyvinyl alcohol films are not a simple function of average D.P. alone. It has further been shown that a rough correlation of tensile strength with

the shape of the differential distribution curve as defined by the D.P. at the maximum, height at the maximum and the skew from the normal distribution can be obtained, but that this correlation is not too satisfactory, in particular with respect to skew.

A graphical correlation of mechanical properties with total percentage of material below the value of D.P. at which the D.P. versus proper curve begins to level off has been presented for polyvinyl alcohol, and also (using the data obtained by other investigators) for cellulose nitrate, cellulose acetate and polyvinyl acetate blends. This method has the advantages of being very simple to use and of appearing to generally give results comparable to the correlation by consideration of P_m , H and B.

On the other hand it is not clear why only the total percentage below a certain D.P. will correlate with properties. It would be expected that very low D.P. material would tend to exert a decidedly greater plasticizing and, of course, D.P. lowering than material in the upper region of D.P. of the percentage taken. A number of possibilities such as the use of the percentages at particular D.P. values have been tried, but the results were negative. The entire method is empirical.

This latter method of correlation suggests a number of further experiments. Investigation of how the addition of varying amounts of a low D.P. fraction to a high D.P. fraction affects properties should throw some light on the method. Another interesting possibility is a study of how fixed amounts of low D.P. fractions of varying D.P. affect the properties of a high D.P. fraction. A further suggested study would involve the use of a fixed high:low D.P. ratio, the low D.P. portion being made up by various combinations of low D.P. fractions, in order to determine how the different combinations affect the mechanical properties.

X. CONCLUSIONS

1. A fair correlation of tensile strength of polyvinyl alcohol with the shape of the differential distribution curve was obtained by assuming that the shape of the distribution curve was defined by the D.P. at the maximum (P_m), the height at this maximum (H) and the skew from the normal distribution (B).
2. A new correlation is proposed which relates mechanical properties to the total percentage of low D.P. material. From the data available results seem to be good for polyvinyl alcohol, cellulose nitrate, cellulose acetate, and polyvinyl acetate.

XI. SUMMARY

The procedure followed in the investigation may be summarized as follows:

1. Polyvinyl alcohol was fractionated on a small scale by precipitation from 2% water solution with n-propyl alcohol. This procedure was then converted to a larger scale in order to accumulate sufficient amounts of fractions for mechanical testing and for preparing blends. Refractionation was carried out until the fractions were as homogeneous as possible.
2. Films of polyvinyl alcohol fractions 0.001 inch thick were cast from water solution and their mechanical properties were determined.
3. A set of blends were prepared having normal differential distribution curves, constant D.P. at the maxima and varying heights at the maxima and their mechanical properties were determined.
4. A second set of blends with constant D.P. at the maxima and constant height at the maxima but with variable skew were prepared and their mechanical properties were determined.
5. By assuming that the shape of the distribution curve was described by the D.P. at the maximum (P_m) of the

differential distribution curve, the height (H) at this maximum and the skew (B) from the normal distribution, an empirical equation was deduced which related tensile strength to these factors. This equation was of the form:

$$T = (8200 - 10^{6.87 - .00476B}) + (2.786 \times 10^6 H^{4.767} - 1000) \\ + (1450 - 10.4B)$$

Where the second term in brackets is dropped when H is greater than 0.190 and the entire last term is dropped when B = 0. This equation gave a fair correlation.

6. A graphical correlation of total percentage of low D.P. material with mechanical properties is given. This method gives results comparable to those obtained by use of the shape factor. Besides polyvinyl alcohol, data obtained by other investigators on cellulose nitrate, cellulose acetate and polyvinyl acetate were correlated in this manner.

XII. ACKNOWLEDGEMENTS

The author wishes to express his deep appreciation to Dr. Philip C. Scherer for his direction, advice and interest in this investigation.

Thanks are extended to Army Ordnance Research for the grant in support of this work.

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A STUDY OF THE RELATION BETWEEN MOLECULAR
WEIGHT DISTRIBUTION AND MECHANICAL PROPERTIES
OF POLYVINYL ALCOHOL

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Abstract of a Thesis Submitted to the Faculty
of the Virginia Polytechnic Institute
in Candidacy for the Degree of

DOCTOR OF PHILOSOPHY
in
CHEMISTRY

August, 1953
Blacksburg, Virginia

A STUDY OF THE RELATION BETWEEN MOLECULAR
WEIGHT DISTRIBUTION AND MECHANICAL PROPERTIES
OF POLYVINYL ALCOHOL

A study of the relation between mechanical properties and molecular weight distribution of polyvinyl alcohol was carried out.

The polyvinyl alcohol was fractionated with respect to degree of polymerization (D.P.) by precipitation of the fractions from 2% solution in water with a n-propyl alcohol-water nonsolvent. The initial small scale procedure was modified so as to accumulate fractions in sufficient quantity for the testing of mechanical properties and for the preparation of blends. The fractions were refractionated until further refractionation gave no further change in D.P.

The homogeneous fractions were cast into films using water as the solvent. These films were then used in determining mechanical properties.

A series of three blends, all with normal distributions and the same D.P. at the maximum of the differential distribution curve but with variable heights at the maximum D.P., were prepared and the mechanical properties were determined.

A second series of six blends, all with constant height and constant D.P. at the maximum, but all being skewed from the normal distribution, were prepared and their mechanical properties were determined.

A correlation of tensile strength with the shape of the distribution curve was found to have the form:

$$T = (8200 - 10^{6.87 - .00476P_m}) + (2.786 \times 10^6 H^{4.767 - 1000}) \\ + (1450 - 10.4B)$$

Where T is tensile strength

P_m is D.P. at maximum of the differential distribution curve

H is height at the maximum

B is area skew

The second term in brackets is dropped when H is greater than 0.190 and the entire last term is dropped when

$B = 0$.

A graphical correlation of mechanical properties with total percentage of low D.P. material gives fairly good results for polyvinyl alcohol and, using the data of other investigators, for cellulose nitrate, cellulose acetate, and polyvinyl acetate.