

THE CORRELATION OF MECHANICAL PROPERTIES OF ETHYL
CELLULOSE FILMS WITH SHAPE OF DISTRIBUTION CURVES

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INTRODUCTION

Commercial production of ethyl cellulose in the form of sheets and powders was started in this country in 1936. During the last decade the use of ethyl cellulose in sheeting, films, adhesives, and molding powders has increased tremendously. This phenomenal growth is due to the flexibility of ethyl cellulose at low temperatures, to its excellent electrical insulating qualities, to its toughness, and to its compatibility with many other substances.

Some of these properties are due to the chemical nature of ethyl cellulose and its parent substance, cellulose, while other properties find their origin in the physical composition of the ethyl cellulose. Of these, the mechanical properties are largely a result of the polymeric structure of cellulose. As with all cellulosic substances, ethyl cellulose is a heterogeneous mixture of low molecular weight molecules and high molecular weight ones. It is now generally accepted that the cellulose molecule is a long randomly kinked chain of beta-anhydro-glucose units and the longer the chain the higher the molecular weight.

As will be explained in a later section, there is a close relationship between physical properties and degree of polymerization. Some investigators (2, 10, 48, 50, 51) have been able to show how the tensile strength and elongation vary with the

chain length. To do this they either tested commercial products having different average molecular weights, or they fractionated the original material to obtain samples having different degrees of polymerization.

STATEMENT OF PROBLEM

It is the purpose of this investigation to determine the relationship between mechanical properties such as tensile strength, elongation, folding endurance, bursting strength and internal tear resistance, and the degree of heterogeneity of chain lengths within the sample, that is, the molecular weight distribution. This requires a satisfactory isolation of homogeneous groups of chain lengths by a practical fractionation procedure (40). The mechanical properties of films cast from these fractions and from blends of fractions and the distribution of chain lengths within the blends and fractions are to be experimentally determined. The results of these tests may show whether it is possible for a uniform or a heterogeneous product to have properties impossible to realize with the other extreme or whether the relationship between the mechanical properties and the degree of polymolecularity can be shown graphically.

LITERATURE REVIEW

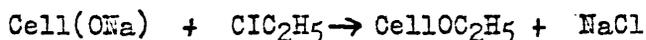
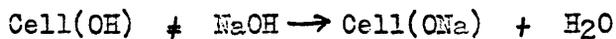
STRUCTURE OF ETHYL CELLULOSE

Cellulose is a generic name given to a series of homologous compounds produced by plants which have the same chemical properties but whose physical properties depend upon the length of the chain. Almost without exception present day cellulose chemists accept the Haworth (18) structural formula for cellulose as the best possible representation of a single chain. Evidence for and against this theory of cellulosic structure is discussed rather completely in any of the standard works on cellulose (24, 35, 45) and so need not be considered here. It is sufficient to state that a cellulose chain is composed of beta-anhydro-glucose units joined by oxygen bridges at the number 1 and 4 carbon atoms of succeeding glucose units. Every other one of these glucose units is inverted so that all of the units lie in the same plane.

The cellulose chains are held together by secondary valences which are hydrogen bondings between the chains. However, the chains are not all perfectly aligned as there are alternating crystalline and amorphous regions within the fibrils (30, 32). The estimates of crystalline portions of the fibers indicate multiples of a crystal unit with axes $a = 8.35 \text{ \AA}$, $b = 10.3 \text{ \AA}$, $c = 7.9 \text{ \AA}$, and the angle between a and c equal to 84° (38).

Ethyl cellulose may be prepared by first treating the cellulose

with 18% NaOH solution to form the so called soda cellulose (9, 23) then with diethyl sulfate (12, 29) or with ethyl chloride (28). The latter is the etherifying agent used commercially today. The principal reactions may be shown as



In this way the ethoxy content may go as high as 50% although the average commercial ethyl cellulose has between 43.5 and 50% ethoxy content (19). Except for the tri-ethyl ether of cellulose substitution does not occur in a uniform manner since the ethyl groups are distributed among the available (OH) positions in a purely random manner. Any uniformity along the chain is probably due to all hydroxyls being equally available (31). The lower the degree of substitution the more evident the non-uniformity becomes, and it has been possible to separate some cellulose ethers into fractions having different alkoxy content (24a). However, Okamura (44) working with commercial ethyl cellulose of 49.4% ethoxy content and McNeer (40) using 48.7% ethoxy content obtained fractions varying in the molecular weight, but not in ethoxy content. The degree of substitution of ethyl cellulose is therefore the average of substitution on all the cellulose chains present.

THEORIES OF SOLUBILITY AND OF FRACTIONAL PRECIPITATION

Solvation occurs with some cellulose derivatives between the polar groups on the derivative and the polar

constituents of the solvent and similarly between the two sets of non-polar groups, but in the case of cellulose ethers evidence does not support the theory of solvation of the alkoxy group. It seems more important to have the same internal pressure in the solvent and cellulose derivative (25). By internal pressure is meant the difference in the free energy necessary to separate solute molecules from their neighbors and solvent molecules from their neighbors and the free energy gained when solute molecules come in contact with solvent molecules (39).

Three theories as to the state of cellulose derivatives in solution have been presented and discussed in the literature. Hess (22) claimed that the cellulose derivatives of high molecular weight were actually complexes of low molecular weight molecules held together by some force peculiar to lyophilic colloids. The second theory according to Meyer and Mark (37) assumed that the cellulose chains were grouped in bundles or micelles. The theory which is now generally accepted is that of Staudinger (52) who maintained that each molecule is individually dispersed and that any occasional association of two or more molecules is soon broken up by thermal agitation. A more detailed discussion of these theories would be too lengthy to be undertaken here.

A very good review of the theories and methods of fractionation of high polymers has been published by Cragg and Hammerschlag (8) so that only those which directly pertain to this investigation

will be considered. The lower molecular-weight particles, or the shorter chains of heterogeneous polymers, are more soluble in a given liquid than are those of higher molecular weight. The solvent power of a liquid mixture of solvent and non-solvent depends upon the ratio of the two components. These two facts are the basis of the fractional precipitation by non-solvent in which the heterogeneous polymer is dissolved in a suitable liquid and then partially precipitated by the addition of some non-solvent. After the precipitate has settled, the supernatant liquid is decanted and more of the non-solvent added which causes more precipitate to form. Sometimes it is possible to cause fractional precipitation by lowering the temperature of the solution. In this investigation a combination of the two methods was used.

Morey and Tamblyn (42) give a very good theoretical discussion of the theories explaining the selective precipitation of molecules having different molecular weight. They state that in the initial coalescence only a few cross links are necessary to form an embryo aggregate and that the probability of establishing these first links is related to the chain length, but the number of links required for coalescence is practically independent of the chain length. It is evident that low molecular weight molecules may start coagulating and forming a precipitate before the high molecular weight ones if the concentration of the former is much greater than that of the latter. Therefore, the heterogeneity or

homogeneity of the precipitate is determined in part by the distribution of the various molecular weight particles in the original sample. As these aggregates of "small" molecules increase in size larger molecules are able to form aggregates which actually make up the final precipitate.

Since the time required for the precipitate to settle depends upon the relative density of the aggregates and the body of the solution, any method which would increase the relative density of the aggregates would greatly reduce the settling time. The centrifuge offers a convenient means of increasing the relative density of the aggregates since the effective gravitational pull on the particle is increased. The heavier (larger) particles are the first to settle so that the length of time in the centrifugal field also affects the amount of precipitate formed.

VISCOSITY-MOLECULAR WEIGHT RELATIONSHIPS

A measurement of viscosity is actually a measurement of the resistance of one portion of a liquid to another portion moving over it; thus the increased viscosity of a dilute solution over that of the pure solvent is due to the resistance to flow offered by the solute particles. A study of the effect of the shape of the solute molecule upon the viscosity revealed that if the solute molecules are larger than those of the solvent and if the Brownian motion has a greater effect on the distribution of solute molecule orientation than does the velocity gradient, the ratio of

specific viscosity to concentration is a constant for spherical solute molecules, is proportional to the square of the number of rod-like solute molecules, and is proportional to the number of randomly kinked solute molecules (26). The only theoretical equation which seems applicable to solutions of natural or synthetic polymers has been derived on the assumption that the molecules of these substances in solution are chain-like and kinked in a random manner (26). This equation is much like Staudinger's (52) empirical relationship

$$\frac{\eta_{sp}}{C} = KM$$

in which C is the concentration of solute in grams per liter, M is the molecular^w weight of the solute particle, K is the constant of proportionality and

$$\eta_{sp} = \frac{\eta_{\text{solution}} - \eta_{\text{solvent}}}{\eta_{\text{solvent}}}$$

In addition to the two assumptions of Staudinger already mentioned, i.e., that in solutions the molecules of cellulose and of cellulose derivatives are separated and that the cellulose chains are randomly kinked it was assumed that the solvent and the phenomena of solvation do not affect the viscosity measurements. All of these assumptions have been challenged; but when the ultracentrifuge and osmotic pressure methods were applied to high molecular-weight polymers, the validity of the equation was established for some cellulose derivatives (26a).

Various types and modifications of viscometers have been used (46). The short-tube efflux type is used principally in the petroleum industry; the rotational types do not give accurate results when the viscosity is below 100 centipoises; the falling-ball method is used for liquids of high viscosity; while the capillary-tube method has been used more often for viscosity measurements of high-molecular weight polymers. The best known of these is the Ostwald viscometer, which consists of a capillary discharging into a wide U-tube. By adding the same amount of material each time the effect of the liquid level in the wide tube is made negligible.

At the very dilute concentration used for molecular weight determinations the density of the solution is scarcely different from that of the solvent so the density terms may be neglected in

$$\eta/\eta_1 = DT/D_1T_1$$

in which η and η_1 are the viscosities of solvent and solution respectively, D and D_1 are the respective densities, and T and T_1 are the respective times of efflux. Thus a measure of the time of efflux is effectively a measure of the viscosity and as such is used in Staudinger's equation.

Viscosity and centrifuge methods of determining average molecular weights depend upon the weight of the particles thus giving more importance to the high molecular weight particles. Cryoscopic

and osmotic methods depend upon the number of particles present, and from them the number-average molecular weight is determined. Flory (14) has shown that the ratio of weight average to the number average is practically constant at two when there is a "normal" distribution of molecular weights within the sample.

DISTRIBUTION CURVES

The curve showing the molecular weight distribution in the ethyl cellulose as obtained from the manufacturer has already been determined (40), but similar curves are to be determined as these fractions are blended during the course of this investigation. If it were possible to reach into a solution of ethyl cellulose and pick out all of the longest chains and lay them out, then the next longest chains and so on, a smooth curved line could be drawn through the ends of the chains. Any point on this curve would give the number of chains which have as a minimum that degree of polymerization. This would be the integral distribution curve for that sample.

Differentiation of this integral distribution curve may be done mathematically when the equation of the curve is known or may be done mechanically by drawing the tangent to the various points along the curve if the equation is unknown. Plotting the slopes of these tangent lines against the degree of polymerization gives the differential distribution curve so that any point on

this curve gives the percentage of the sample having that degree of polymerization.

FILM CASTING

Industrially films are usually cast from a melt or from a solution, and the patent files are full of patents covering both methods and nearly every conceivable modification of these methods. Whether cast from a melt or from solution, most films are given their uniform thickness by means of rollers set at a finite distance apart. Some of these methods are also applicable to laboratory production of films, and small size machines have been developed for laboratory and pilot plant use.

While numerous references are found in the literature to films produced in the laboratory, rarely do the authors describe the method used to produce the films. For small scale laboratory production films may be cast more readily from a solution than from a melt as no elaborate heating apparatus to insure uniform melt or rollers to insure uniform thickness are needed. Bass and Kauppi (2) cast films of uniform thickness from a 15% solution of a cellulose derivative in a suitable mixture of low-boiling point solvents on a clean piece of plate glass by using a leveling device which had runners of the same height on either side. Thus uniform thickness of the film upon evaporation of the solvent was assured. The film was allowed to dry overnight, stripped from the glass plate, heated for an hour at 70°C, and then conditioned at

20° C and 50% RH for 48 hours before being tested. As no special equipment is needed, a similar procedure was followed by other writers. Gloor (16) cast films 0.0035 inches thick on glass. It has been found that a bead of water at the interface of film and glass will make the stripping of the film much easier and since less force is required, the films are not stretched during the stripping (5).

Bass and Kauppi (2) used a 80-20 toluene-ethanol by volume mixture as solvent for the ethyl cellulose, and they later reported that ethyl cellulose films of maximum tensile strength and elongation are formed when the alcohol-hydrocarbon solvents are formulated so that the last solvent to evaporate from the film consists almost entirely of the hydrocarbon. If the rates of evaporation of both components are approximately the same, the solvent mixture producing the least viscous solution also produces the best films. They found that aromatic hydrocarbons, hydrogenated naphthas, or high-solvency naphthas can be used with the alcohols. Ternary mixtures of hydrocarbons, alcohols, and ketones or esters which give solutions of low viscosity also produce good films. Ushakov and his collaborators (54) studied the rates of evaporation of some solvent mixtures and found that the following are the best solvents for making ethyl cellulose films: benzene; 90-10 mixture of benzene and ethanol; 50-40-10 mixture of benzene, ethyl acetate, and ethanol; 40-40-20 mixture of benzene, toluene,

and ethanol; and 80-20 mixture of toluene and ethanol. A more general discussion of the effects of solvent composition on film properties is given by one of the large producers of ethyl cellulose (19). Flexible films of maximum tensile strength are obtained when the major portions of the solvent at the moment that gelation occurs is a non-polar solvent which has little or no affinity for water. Such solvents might be toluene, xylene, butyl acetate or methyl isobutyl ketone. When polar solvents which are miscible with water constitute the major portion of the solvent at moment of gelation, the films are more brittle and have poorer tensile strength. The water may have been in the solvent, as in acetone or alcohol, or may be introduced by condensation into the solution just before gelation due to the rapid rate of cooling. It is recommended that for ordinary atmospheric drying the solvent mixture should not contain more than 30-40% of the low boiling water miscible solvent and that the remainder should be a highly non-polar solvent.

Any mention of plasticizers has so far been avoided as it is not the purpose of this investigation to study the effect of these high-boiling solvents which are mixed with a high polymer to give a softer, more flexible product that will not become sticky at high temperatures. Many investigations along this line have been carried out and reported in the literature. Manufacturer's pamphlets (20, 27) are very good sources of information.

concerning the effect of various plasticizers on the physical properties of ethyl cellulose in lacquers, films, and plastic sheets.

FILM STRUCTURE

After the film has been stripped from the forming surface, the next question is one of orientation of the cellulose molecules or chains. It is remembered that Staudinger (52) assumed the cellulose chains to be dispersed into single molecules and that these chains were randomly kinked and not rod-like, and that these assumptions have been found basically sound by later investigators (26). Therefore, a brush pile type of arrangement of the cellulose chains would be expected in the film.

Frey-Wyssling and Muhlethaler (15) studied cellulose films produced by Bacterium Xylinoids Henneberg under an electron microscope and found that the visible cellulose threads are ribbon-like, have a cross section of 100 to 200 Å , and are at least 40 microns long. It seems that these molecular cellulose films are not stable, but exhibit a tendency to crystallize into threads. Probably the thin films are characterized by a random orientation of the cellulose molecules and slow parallelizing hindered by the length of the molecules causes the crystallization. The slow parallelizing referred to may be explained as resulting from the mutual attraction of hydroxyl groups along two overlapping chains gradually pulling the chains into a more or less parallel position.

Sheppard and Newsome (49) report that generally equal tension during the drying of a film of a cellulose derivative produced an uniaxial film. Plate coated films cured on a support are uniaxial or weakly biaxial and become biaxial when stretched with the second axis in the direction of the pull. One patent (27) claims that the stress developed in the films by uneven drying of the films can be removed by heating the film.

Several methods are available for determining the complete or partial orientation of films (1). The X-ray pattern of the unstretched state of a polymer shows either a number of sharp rings caused by a large number of very small micelles, bundles or chains, randomly arranged or a few diffuse halos produced by a liquid-like structure. If the sample is stretched, the halos separate into two segments arranged symmetrically on both sides of the incident beam. Optical birefringence of oriented films allows a relative determination of the extent of orientation since the larger refractive index exists parallel to the direction of stress applied to the film. Another good method for determining the orientation of disordered films is to study the way in which they swell. Randomly arranged chains when swollen will give an isotropic volume increase; but if the molecules have been somewhat parallelized by a stress, then the greatest swelling occurs at right angles to the axis of orientation. Still another method might be a study of the difference in physical properties of films cut parallel to and perpendicular to the axis of orientation.

CELLULOSIC STRUCTURE AND MECHANICAL BEHAVIOR

For a better understanding of the mechanical properties exhibited by cellulose and its derivatives, it is necessary to see what relationship there is between the structural factors and such properties. Meyer and Lotmar (36) have calculated the elastic modulus of cellulose to be between 7900 and 12300 kg per square millimeter which agrees rather closely with experimental results. If the modulus of elasticity is due to the van der Waals' forces, theoretically it would be much less than the observed value (33). This is more evidence supporting the primary valence theory of cellulose structure. A very high modulus of elasticity and rigid structure can be explained by assuming the chains have been drawn parallel to one another and packed tightly together.

With cellulose chains so arranged it is conceivable that rupture of a film, or filament, might occur because of a break in the chains themselves or because of a slipping of the chains along each other. The weakest points in the cellulose chain are the -C-O-C- linkages between the glucose units, and about 90 kg calories per mole is required to break such bonds. From this the strength of a single cellulose chain may be calculated to be 2.4×10^{-4} dynes or 60 grams per denier tensile strength, but such a theoretical value is about eight times that of the maximum observed with well oriented natural and synthetic fibers (33). Thus this is not the true explanation of the observed tensile strength

of cellulose.

Three arrangements of parallel chains within a chain bundle are possible. There can be random overlapping of the chain ends with long chains and short chains indiscriminately arranged along the axis of the chain bundle. Second, there can be no overlapping of the chain ends so that only chains of the same length lie side by side. Third, there can be a regular overlapping of the chain ends which means that short and long chains would have to be regularly arranged within the chain bundle. If the ternary valence forces between the ends of the chains are considered as the source of tenacity, the minimum value of such tenacity would be found when there is no overlapping of the chain ends. This has been theoretically calculated to equal 2 grams per denier which is approximately the tensile strength of very dry and poorly oriented viscose or acetate rayon filaments. However, the usual fiber strength is about 6-7 grams per denier and it is assumed (33) that such fibers are better oriented than rayon fibers and that more of their chains are parallel to the axis of the filament. This lessens the probability of any cross section being composed of only chain ends and an uneven or ragged cross-sectional area results. Therefore, not only must the van der Waals' forces between the ends of the chains be overcome before a rupture can occur, but also the chains must tear loose and slip along each other.

For one chain to slip along another after they have been

parallelized, it is only necessary to supply energy enough to rupture one of the bonds between attracting groups as the others are immediately reunited with a new partner. As the slipping continues, more and more of these bonds are broken, but effectively only one at a time. This slipping force has been calculated to equal about 8 grams per denier. If slippage were the only factor affecting tensile strength, the tenacity of fibers composed of short and those made up of long chains would be the same. This concept also excludes the possibility of regular overlapping of short and long chains. Therefore, in order to explain the observed tensile strength of cellulosic fibers it is necessary to assume that the rupture starts at the weakest point and gradually progresses to the stronger portions. A combination of all the above possibilities with each supplying a different portion of the total is as reasonable an explanation as any at the present time.

There is practically no quantitative material published which would indicate the effect of the chemical nature of the different parts of the cellulose derivative chain on the mechanical behavior of that derivative. This scarcity of information is found also when considering the type of attractive group, hydroxyl, acetyl, or ethyl, and the distribution of the groups along the chain. About all that can be done is to classify the material according to the flexing properties of their chains. It has been

found that partially esterified, or etherified cellulose does not pack as tightly as the original cellulose and so cannot be as well oriented. This may be due to a lack of uniformity in the substitution along the chain as the forces of attraction between a hydroxyl and an ethoxyl group would not be as great as that between two hydroxyls or between two ethoxyl groups.

All of the mechanical strength tests applied to the ethyl cellulose films during this investigation measure in one form or another the tensile strength and the degree of bonding between the molecules whether parallelized or in a brush pile structure. It is this complicated nature of tensile strength which has prevented the establishment of reliable quantitative relationships between structure and tensile strength (33).

LOAD-ELONGATION OR STRESS-STRAIN CURVES

Any rupture in a plastic material may be caused by various combinations of stresses, but so far little has been done to evaluate these stresses except by the use of notched specimens which have been used in empirical studies rather than in any detailed study of the stresses. Some work has been done in studying the load-elongation curves of polymers.

It has been found by Haward (17) that light loads are sustained much longer before rupture than are heavy loads. For example, a stress of 37.5 kg per square centimeter broke a sample of cellulose acetate after about 50 minutes while a similar sample

broke in 10 minutes when a load of 53.9 kg per sq. cm. was applied. Busse and his co-workers (4) found that fatigue in a fiber resulted in irreversible changes, that is, the total test life was about constant regardless of how rest periods interrupted the tests.

Haward also found that heating a test sample to 65°C for 10 minutes and then reapplying the test did not lengthen the test life. He also set up an empirical relationship by assuming that the original sample has the strength P_0 , and that

$$dP/dt = -(1/K)S_m$$

in which the change in strength with time is proportional to the negative of the average stress applied. However, this can be definitely proved only by means of sequences of different stresses.

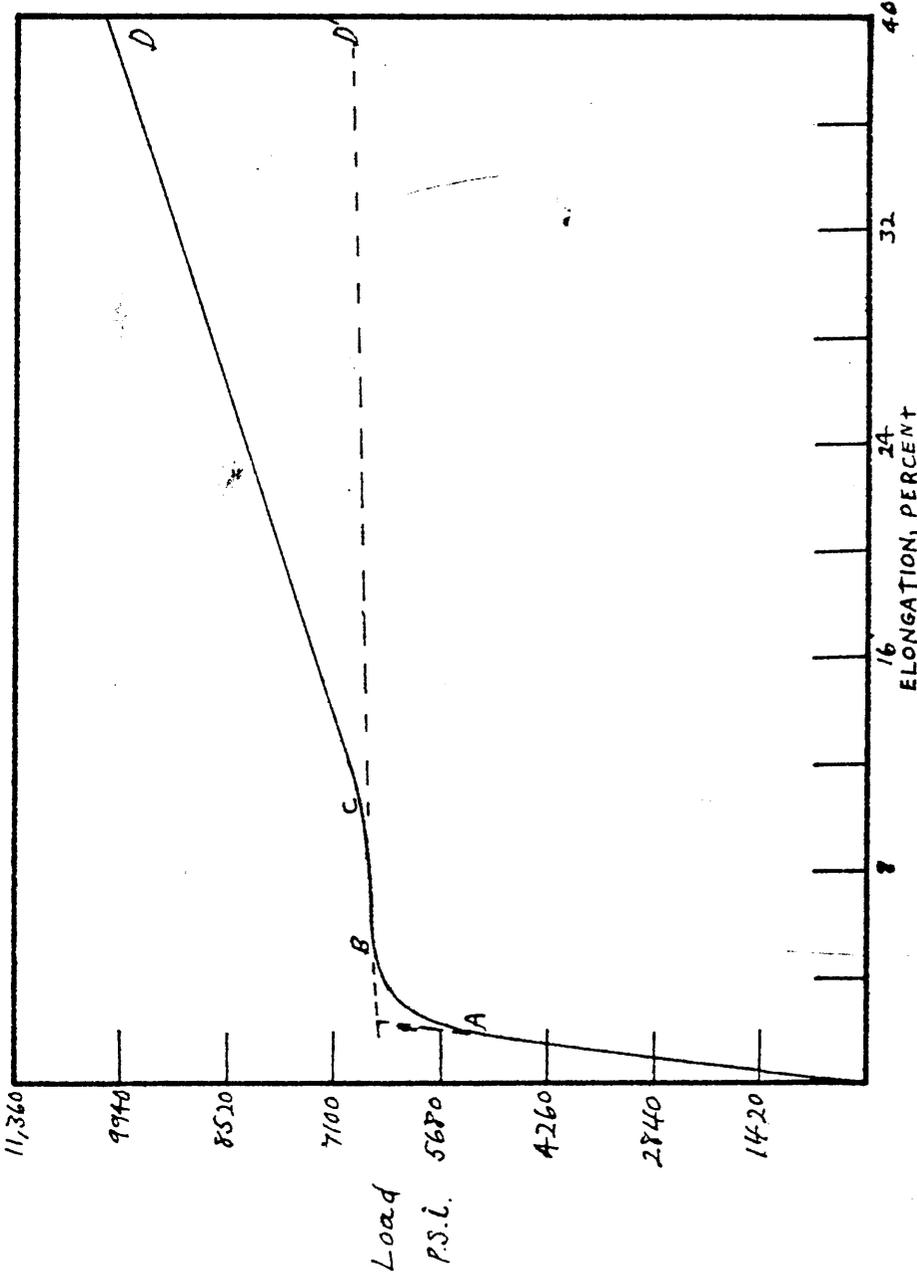
Much more work has been done and more useful information has been obtained from the stress-strain or load-elongation curves. Since this investigation is concerned primarily with ethyl cellulose, a curve which has been drawn from experimental data obtained from that material is given in Figure 1 rather than a more theoretical one such as Carswell and Nason developed (6).

According to Bass and Kauppi (2) this curve represents physical changes within the ethyl cellulose films as follows:

OA -- region of purely elastic behavior

AB -- the type of deformation changes from that of purely elastic body to permanent deformation of plastic body.

Figure I



Load-Elongation Curve
for Ethyl Cellulose (13)

- B -- lower point of plasticity, load at this point is called "yield point".
- BC -- realignment of the cellulose derivative from a random arrangement to one of partial orientation in direction of applied force.
- CD -- increased resistance to deformation due to forces of molecular cohesion being brought more strongly into play.
- D -- breaking point, coordinates give tensile strength and elongation, cohesion and slippage ability of chains are exceeded.

They also point out that the point of breakage depends upon the viscosity, degree of substitution, and conditions of manufacture of the ethyl cellulose. The above curve indicates the ability of ethyl cellulose to undergo a large amount of plastic deformation and to increase its resistance to deforming forces which characterize a very tough material. Toughness of a material is best measured by the total work required to break the film, which is given by the area under the curve. When a film is stretched repeatedly beyond its yield point, it will become more and more brittle and finally break with little elongation. This ultimate elongation when defined as ability to undergo deformation may be considered as a measure of flexibility. When the deforming load is light, hardness may be measured by the resistance offered to deformation.

$$\text{Hardness} = K \frac{\text{Load}}{\text{Deformation}}$$

Another relationship, $\text{Hardness} = K(\text{Yield Point})$, is true at greater deforming loads since the yield point is the load at which a section of the material begins to undergo permanent deformation most rapidly. This is thought to measure actual hardness as it is not complicated by toughness of the film or by hardness of a substrate.

Carswell and Nason (6) point out that the stress-strain curve of most plastic materials can be represented by some part of a similar curve if "(a) the curve is obtained by a constant-rate-of-straining type of test, and, (b) the point of rupture of the test specimen may occur at any point on the curve". The slope of the first part of the curve is a measure of the stiffness of the material and the ratio of stress to strain along this part of the curve is the modulus of elasticity. They also state that the area under the curve, the work required to rupture the sample, is a measure of toughness of the sample. They have classified plastic materials as:

- "Soft, weak materials show low modulus, low yield point, low elongation at rupture.
- Hard, brittle materials show high modulus, no well-defined yield point, and low elongation at break.
- Soft, tough materials show low modulus, low yield point, and high elongation and high stress at break.
- Hard, strong materials show high modulus, high yield point, and moderate elongation.
- Hard, tough materials show high modulus, high yield point, high elongation and high breaking stress."

Blom (3) identified similar portions in the stress-strain curve, and he found that when samples of cellulose nitrate were

of higher and higher viscosity types the point of rupture moved from the AB region of the curve through BC to the CD region.

Thus it would be possible by proper interpretation of the stress-strain curve of a substance to determine several of its mechanical properties.

POLYMOLECULARITY AND MECHANICAL PROPERTIES

A search of the literature failed to give a single reference to a study of polymolecularity of ethyl cellulose and its mechanical properties. Bass and Kauppi (2) did measure the tensile strength and elongation of ethyl cellulose of different viscosities, but no tests were run on specimens made from fractions of the original material. They found that as the viscosity of the ethyl cellulose samples increased from low to high the tensile strength increased from 450 to 700 kg per sq. cm. and the elongation increased from 10 to 14%. This led them to the conclusion that the tensile strength of a cellulose derivative is determined by its ability to stretch. A greater ability to stretch is a property of materials of higher viscosity (longer chains) which also develop a higher degree of orientation and greater tensile strength. Their findings confirm predictions based upon the preceding theoretical discussions.

More experimental investigations have been made on other cellulose derivatives and high polymers which will be briefly reviewed because the similarity of the substances should permit

predictions of the outcome of this investigation. Should the results of this investigation not bear out predictions then some indication of the effect of other substituents upon the properties of cellulose derivatives will have been determined.

Some of the first studies made on the effect of blending high and low molecular weight materials on tensile strength and elongation of the samples indicated that blends were superior to uniform fractions having the same viscosity (21, 34). Both Ohl (43) who tested cellulose acetate filaments and Rocha (46) who tested cellulose acetate films reported the tensile strength of blends superior to fractions of corresponding D. P. (degree of polymerization).

More recent work, which will be discussed later, indicates that the uniform fractions have the better mechanical properties. Two reasons for this difference of opinion may be given. The first and the more plausible is that the early investigators used poorly fractionated material and did not run enough experiments. The other is that in some methods of preparing films from blends the long chain molecules being the least soluble may be precipitated out first either on the surface or as a network throughout the film. In this case a blend of short and long chains would exhibit the superior mechanical properties.

Spurlin (51) reported that when films 0.003 inches thick were cast from half-second cellulose nitrate the fractions of higher viscosity were superior in folding endurance tests, but

the superiority of fractions over the unfractionated was not so great in the quarter-and half-second regions. The fractions of highest viscosity gave Schopper Fold Test results similar to the unfractionated material which he attributed to the ash and haze content of the fraction. Blends of low and high viscosity material were definitely inferior when approximately equal quantities of each were blended. However, those blends were not made from fractions but from the commercial products. Since low viscosity materials were used, it is highly probable that in the blends there was actually a preponderance of very short chains and only a few of the long chains. If very long and very short chains were blended so that two peaks appeared in the distribution curve, only about half of the expected number of Schopper folds were obtained which is another indication of the large number of short chains in the blend.

Rogovin and Glazman (48) reported little difference between fractions and blends when the tensile strength and ultimate elongation of cellulose nitrate films were studied. Gloor (16) studied the effect of degree of substitution on low viscosity cellulose nitrate and found that when the viscosity dropped below 39 centipoises good flexible films were not obtained. The higher the nitrogen content of cellulose nitrate of higher viscosity the better the tensile strength and elongation so that the degree of substitution does have some effect on the properties of the

cellulose derivative.

Sookne and Harrie (50) fractionated cellulose acetate and studied the change in properties from fraction to fraction. They found that a coherent film could not be formed if the D. P. was 30 or below, but above that there was a rapid improvement of mechanical properties up to about a D. P. of 150. Beyond this the improvement was slight over the narrow D. P. range used. It was found that folding endurance and ultimate elongation were sensitive to changes in D. P. and also to heterogeneity with respect to D. P. Investigation of these properties as a function of both weight-average D. P. and number-average D. P. indicated that at any given weight-average D. P. the fractions are superior to the blends and that the blends containing fractions of low D. P. are inferior to those containing none of the low D. P. material. However, at any given number-average D. P. within the range studied, the properties of fractions and all of the blends are approximately equal. This number-average depends upon the number of molecules present regardless of the uniformity so that for equal number-average molecular weights the same number of molecules per unit volume would be present.

It has been found that a blend of 75% by weight of ethyl cellulose (D. P. 1000) with 25% by weight of partially ethylated glucose forms good films (55). Theoretically this is impossible because the number-average D. P. is about 4. In this case the

monomer acts as a plasticizer with the low-molecular-weight portions of the blend probably serving to fill up the voids in the films left by the immobilization of the longer chains with respect to one another (33a).

Douglas and Stoops (10) fractionated vinyl chloride-acetate copolymers and then blended the fractions. They found that the calculated and experimental values for blends usually agreed to within 5% with the greatest difference occurring when the molecular weights of the two fractions were very different (6000 and 17,000). Although two peaks in the distribution curve would be expected, they tend to converge which is explained by the slight difference of solubility between consecutive chain lengths. When the mechanical properties were tested, it was found that the tensile strength, impact strength, fatigue resistance, and modulus of elasticity increased rapidly between molecular weights of 5000 to 8000 followed by a much more gradual increase above 8000. The blends were inferior in fatigue resistance and approximately equal in strength to a fraction of corresponding D. P.

Mark (33a) concludes that the present information shows that the best mechanical properties may be obtained by increasing the average degree of polymerization regardless of the heterogeneity within the polymer. Alfrey (1a) concludes that short chains affect a decrease in mechanical properties far out of proportion to their weight proportion in the sample. With the information

now available it seems that the strength properties of films cast so that the chains had little opportunity to align themselves. are largely controlled by the gross features of the molecular-weight distribution curve rather than by the fine details such as smoothness or general contour.

MATERIALS USED

The ethyl cellulose used throughout this investigation was a commercial grade type W200 with 48.7% ethoxy content and with a viscosity of 169 centipoises in 5% solution obtained from Hercules Powder Company of Wilmington, Delaware.

The acetone, C.P., ethyl acetate, commercial grade, and n-butyl acetate, reagent grade, were obtained from Commercial Solvents Corporation of Baltimore, Maryland.

The benzene, 99-100% purified, was obtained from Baker and Adamson, Marcus Hook, Pennsylvania.

TESTING EQUIPMENT USED

The constant temperature water bath used for the viscosity measurements was a Fisher Unitized Bath obtained from the Fisher Scientific Company, Pittsburg, Pennsylvania. A mixture of acetone and ethyl ether was used in the gas bulb of the mercury thermostat.

The all glass apparatus used in the ethoxy determination was similar to that designed by Clark (7) and was fabricated by the Otto R. Greiner Co., Newark, New Jersey, from Drawing No. 11690-W of the Hercules Powder Company.

The Schopper Type Folding Endurance Tester, Motor Driven, the Elmendorf Tearing Tester, the Schopper Type Tensile Strength and Elongation Tester, and paper thickness micrometer were obtained from the Testing Machine, Inc., New York.

The Mullen Tester was obtained from B. F. Perkins and Sons, Inc., Holyoke, Massachusetts.

EXPERIMENTAL

Before the distribution of chain lengths within a given sample of ethyl cellulose can be changed it is necessary to determine its original distribution. At the present time this can best be done by some means of separating the chains into nearly homogeneous groups according to chain length followed by a determination of the average chain length within each fraction. Several methods of fractional precipitation were tried and discarded before successful separation of the fractions of ethyl cellulose according to degree of polymerization (D. P.) was accomplished (40).

METHOD OF FRACTIONATION

This method was developed using 3% solutions of ethyl cellulose in 80-20 acetone-ethyl acetate mixture in 900 gram batches. The size of the batches was later increased twelve-fold in order to stock pile a usable quantity of the fractions within a reasonably short time.

Three hundred twenty-four grams of dried ethyl cellulose were dissolved in 2095.2 grams of ethyl acetate and the solution maintained at 25°C. for 18 to 20 hours to assure homogeneity. 8380.8 grams of acetone were added to dissolve the gel, and the solution was maintained at 25°C. for two hours before the non-solvent, 75;25 water-acetone, was added. The localized precipitate formed by this addition was dissolved by shaking the flask, and the flask was

maintained at 25°C. for another hour before being cooled at 15°C. for 18 hours. The supernatant liquid was decanted and warmed to 25°C. for 5 hours before more non-solvent was added and the process repeated for all fractions through the seventh. The eighth fraction, the residue, was obtained by boiling off the acetone and ethyl acetate under reduced pressure. This evaporation to dryness was necessary because an excess of water would not precipitate all of the ethyl cellulose from the acetone-ethyl acetate mixture.

In order to recover the ethyl cellulose the precipitates from each fractionation except the eighth were redissolved in a minimum amount of acetone. An excess of acetone was carefully avoided since such a solution when poured into water would form a colloidal suspension of ethyl cellulose in water which required a long time to filter. A fibrous form of the precipitate was desired and could be obtained when the volume of acetone solution was a minimum. After the ethyl cellulose was precipitated in water, it was filtered, dried, and weighed.

Experience had shown that it was possible to increase the average degree of polymerization of the first fraction by refractionation. From the weight of the first fraction, the weight of ethyl acetate and acetone was calculated to give a 80-20 mixture as used in the original fractionation. The same control of temperatures and time was used as previously described. Distilled water was added as non-solvent until there were visible signs of

precipitation within ten minutes at 25°C. The precipitate and solution were then cooled to 15°C. for 18 hours and decanted. The supernatant liquid was saved and added to that of the seventh fraction and evaporated. The precipitate, slightly grey in color due to impurities, was handled as previously described.

The results obtained from three runs are listed in Table I and are shown graphically in Graph I.

Eleven such batches were fractionated by this same method.

Then to insure complete homogeneity within the same fraction all of the fractions of the same D. P. were dissolved in acetone and precipitated by adding to an excess of water, filtered, and dried. That is, all of the first fractions were dissolved in one batch and precipitated, then all of the second fractions, and so on through all eight of the fractions. The average D. P. of each composite was experimentally determined and is the value used throughout this investigation.

TABLE I

FRACTIONATION OF ETHYL CELLULOSE FROM A
ACETONE-ETHYL ACETATE SOLUTION*

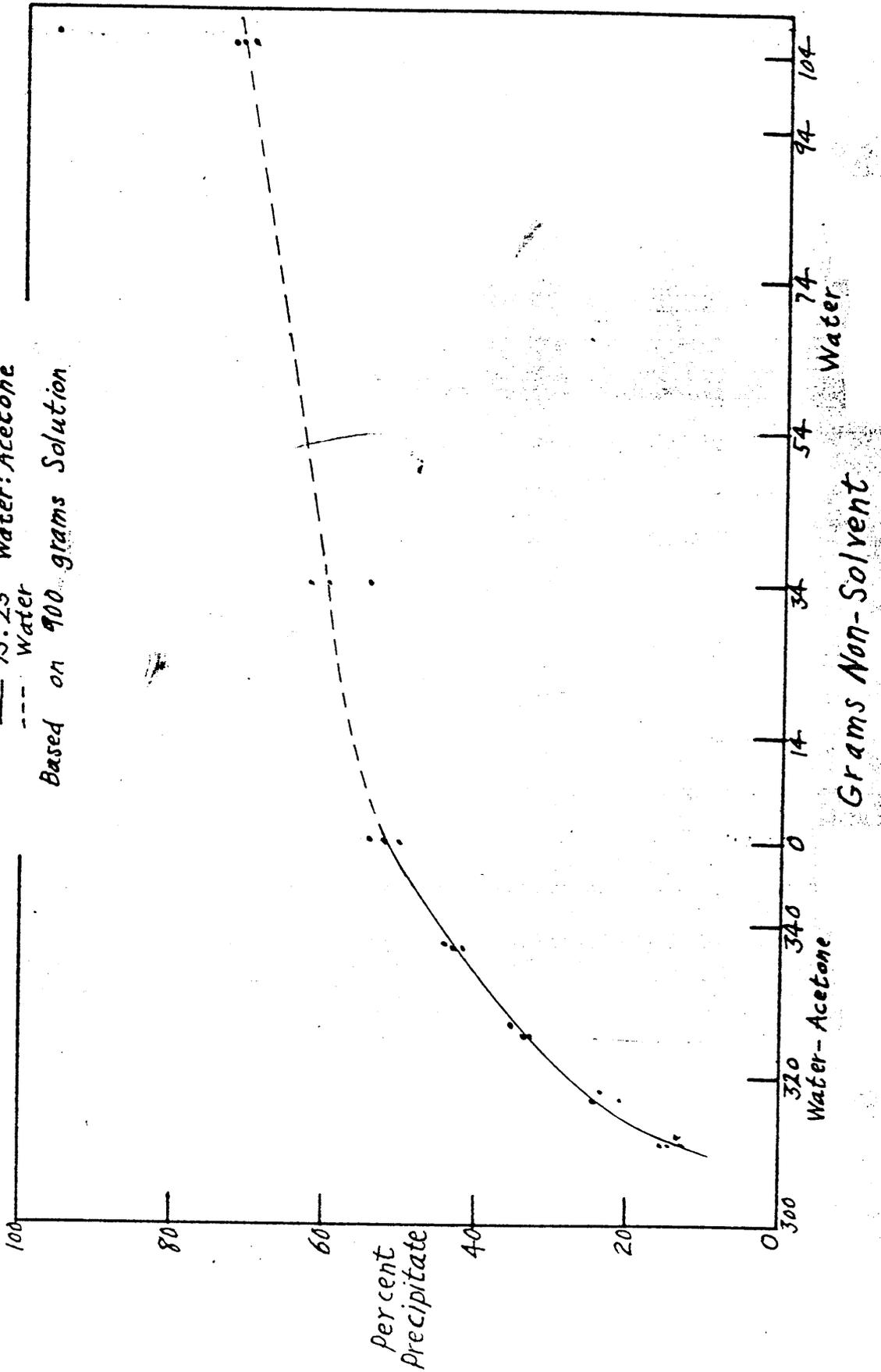
Frac- tion	Weight Solution	Wt. non- solvent added per 900 gm. solution	Precipitate Avg. %	Degree of Polymerization
1 A	10800	311	Not Isolated	---
B	10800	311	" "	---
C	10800	312	" "	---
1aA**	2612	---	15.8	---
B	2809	---	12.4	---
C	2499	---	13.5	13.9 356
2 A	13920	6	8.5	---
B	13720	6	8.6	---
C	14050	6	10.0	9.0 302
3 A	13790	8.6	9.0	---
B	13590	8.6	11.8	---
C	13860	8.8	11.9	10.9 273
4 A	13700	11.3	9.9	---
B	13450	11.3	9.1	---
C	13750	11.2	9.2	9.4 218
5 A	13680	14.2	9.3	---
B	13420	14.2	9.2	---
C	13720	14.1	9.6	9.4 188
6 A	13710	34 H ₂ O	10.3	---
B	13460	34 "	3.3	---
C	13750	34 "	5.8	7.1 126
7 A	14090	71 "	7.5	---
B	13890	71 "	18.4	---
C	14150	71 "	13.5	13.1 119
8 A	Evaporated		28.3	---
B	"		21.2	---
C	"		24.6	24.7 60
Total			97.5	

* 75% Water-25% acetone used as non-solvent for fractions 1 through 5, distilled water used as non-solvent for fractions 6 and 7, fraction 8, the residue, recovered by evaporation.

** Refractionation of the first fraction. Water added until first signs of permanent precipitate appeared.

GRAPH I

Fractionation of Ethyl Cellulose
From Ethyl Acetate-Acetone Solution by
75:25 Water: Acetone
--- Water
Based on 900 grams Solution



DEGREE OF POLYMERIZATION AND SUBSTITUTION

In order to show that the ethyl cellulose had actually been separated into groups according to chain length, viscosity measurements were made. The data so obtained was substituted into Staudinger's equation, and the degree of polymerization was calculated.

Staudinger and Reinecke (53) had used butyl acetate as the solvent and had also reported the η_{sp}/c and degree of polymerization obtained from the study of ethyl cellulose at 20, 40, and 60°C. From this the constant of proportionality, K_p , for ethyl cellulose dissolved in butyl acetate at 40°C. was calculated as 10.57×10^{-4} .

The viscosity determinations were made in Ostwald viscometers, size 80-100 seconds, by measuring the time for 2 ml. of solution to flow through the capillary. Calculation of the average D. P. of the original ethyl cellulose shows how these values were substituted in Staudinger's equation. The time of efflux of the solvent was 62.9 seconds, and the efflux time of the solution was 72.7 seconds when 0.0404 grams of ethyl cellulose were dissolved in 50 ml of n-butyl acetate.

$$D. P. = \frac{\eta_{sp}}{K_p \times C} = \frac{\frac{72.7 - 1}{62.9} - 1}{10.57 \times 10^{-4} \times 0.0404 \times 20} = 181$$

The 20 appears in the denominator in order to convert the concentration to grams per liter.

When fractionating a heterogeneous polymer such as ethyl

cellulose, there is always the possibility that the precipitation might be due to a difference in the degree of substitution rather than to a difference in chain length. Therefore, the ethoxy content of the fractions was determined (40). The method used was similar to that originated by Zeisel (57), and was the procedure developed in the laboratories of the Hercules Powder Company (56) Method E-80, Analysis of Ethyl Cellulose, 6-26-36, Rev. 8-2-38. This test showed that the ethoxy content of the fractions was nearly the same (greatest deviation from the mean was 0.5%).

Throughout this investigation the degree of polymerization has been used rather than the molecular weight because the D. P. is more descriptive of the chain length. The average molecular weight may be calculated from the average D. P. by multiplying the latter by 236.4 which is the average molecular weight of an anhydro-B-glucose unit with a 48.7% ethoxyl content or a degree of substitution of 2.67.

A check on the average D. P. of the original ethyl cellulose made a year after that calculated above gave a value of 183 which means that the ethyl cellulose is very stable with regard to chain length and degree of substitution. Any change in ethoxy content would likely affect the viscosity of the solution due to a change in the nature of the solvated film.

DISTRIBUTION CURVES

When the average values of Table I are plotted as accumulative

percentage versus degree of polymerization Graph IIa, Integral Distribution Curve, results. The curve itself is drawn from values previously obtained from six small batches (40) which because of more accurate weighings of solutions may be considered a more accurate representation than if based solely upon values on Table I. However, for sake of comparison these values are shown on the graph.

Graph IIb, Differential Distribution Curve, was obtained by plotting the slope of the tangents to the curve of Graph II versus the degree of polymerization. A tangentometer was used to measure the slopes and so the numbers assigned to the ordinate axis in all of the differential distribution curves are the values read from the scale of the tangentometer. This curve may be converted to the percentage curve by estimating the area under the differential distribution curve according to Simpson's Rule (58) and then dividing the area of the increments by the total area. These values when plotted against the degree of polymerization will give a normalized curve from which the percentage of each D. P. present may be read directly from the ordinate.

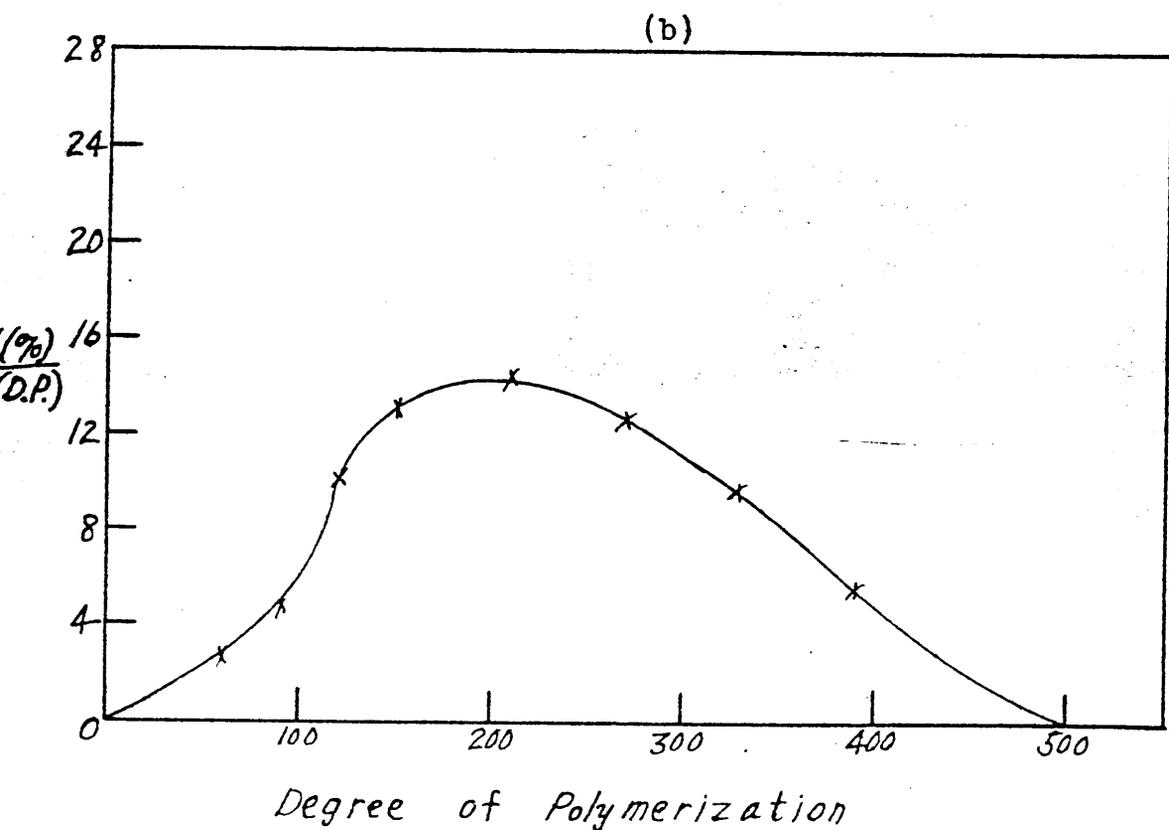
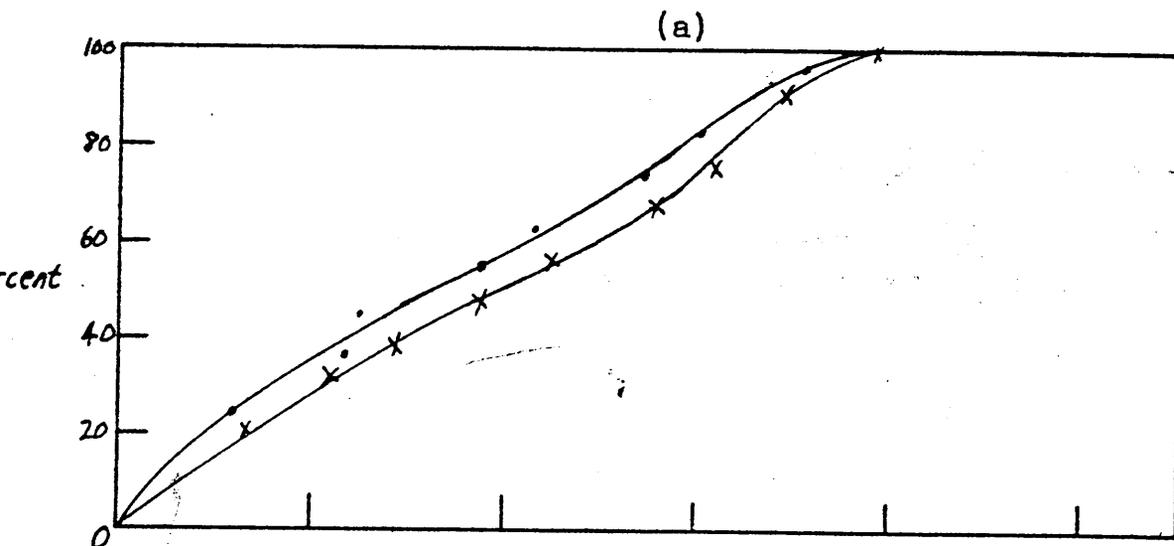
PREPARATION OF FILMS

Two references in the literature (19, 54) indicated that good films of ethyl cellulose could be cast from a benzene solution, and some preliminary work proved this was correct. Bass and Kauppi (2) and Gloor (16) had cast films of uniform thickness on plate glass

GRAPH II

Original Ethyl Cellulose
(a) Integral Distribution
(b) Differential Distribution

x x Average of six batches
. . Large batch



by use of a leveling device. It was decided to use this same method in this investigation so a single wire loop was prepared for each end of a piece of straight glass tubing, two centimeters in diameter, to make the leveling device. It was soon found that wire of differing diameters was needed as it was not always practical to use the same concentration for all casting solutions due to the differing viscosities of the solutions. The relationship between wet thickness or the diameter of the wire used to make the loops and the concentration of the solution is given in Table II. Gloor (16) had cast films of 0.0035 inches thick and Spurlin (51) tested films 0.003 inches thick so when it was found that films 0.003 inches thick could be conveniently prepared this thickness was used throughout this study.

TABLE II

<u>Wet Thickness Required to Give 0.003 inch Films</u>			
<u>Fraction</u>	<u>Average D. P.</u>	<u>Conc. of Solution</u>	<u>Inches Wet Thickness</u>
1	349	5%	0.106
2	274	9%	0.063
3	248	9%	0.063
4	212	9%	0.063
5	186*	10%	0.051
6	130	10%	0.051
7	109	10%	0.063
8	64	15%	0.051

* Approximate average D. P. for all blends and unfractionated material which were cast with the same wet thickness.

Films were cast from the solutions when they were visibly free of air bubbles. A portion of the solution was poured across one end of the piece of plate glass, 15 by 20 inches, and then spread by moving the glass tube supported on each end by the proper size of wire over this layer of solution with a slow and steady pull. Uniform thickness could be maintained only when the glass tube and wire runners were firmly held against the glass plate.

The glass plate with the wet film was then placed in a 30-40°C. drying oven for 45 minutes. It was found that the films were easier to strip from the plates when a few milliliters of water were placed around the outer edge of the films before loosening the outer edge with a knife blade. All films were stripped from the plates in the same direction in which they were leveled. A steady pull on this loosened edge would remove the film from the plate if the bead of water was maintained at the stripping edge. However, the films formed from Fraction 8 could not be pulled from the plates because of breaking and cracking so these were allowed to soak free by running the knife blade around the entire perimeter of the film and maintaining a bead of water all along this stripping edge.

The films were then conditioned for at least 40 hours in the constant temperature, constant humidity room set at $50 \pm 2\%$ relative humidity and $77 \pm 1.8^\circ$ Fahrenheit as recorded by an automatic temperature and humidity recorder. These are the atmospheric

requirements of a standard testing room as set forth in ASTM D 618-46T.

MECHANICAL TESTS APPLIED TO FILMS

The Schopper Type Tensile Strength and Elongation Tester, the Schopper Type Folding Endurance Tester, the Elmendorf Tearing Tester, and the Mullen Tester used for measuring some of the mechanical properties of the ethyl cellulose films fulfilled the respective ASTM requirements for such machines. All specimens tested were visibly free of foreign particles and blemishes.

As recommended in ASTM 882-46T for determining the tensile strength and percentage elongation, the test specimens were cut 0.5 inches wide and 6 inches long. Ten or more specimens parallel with and a like number normal to the direction of leveling and stripping were cut from at least three films cast from each fraction or blend. These directions are hereafter called "With" and "Cross" directions. The values obtained from each direction were arithmetically averaged separately and then these two values were again averaged to give the final value for the test. The fifteen pound weight was used on the weight arm for the tests. Tensile strength in pounds per square inch was calculated from the cross sectional area of the specimen and the breaking load in pounds,

$$\frac{1}{0.003 \text{ in.} \times 0.5 \text{ in.}} \times 11.6 \text{ p} = 7737 \text{ psi.}$$

Percentage elongation was calculated by dividing the average

inches elongated by 4 inches which was the actual distance between the jaws.

Test specimens for the Schopper Type Folding Endurance Test were cut 15 ± 0.25 mm by 4 inches in accordance with ASTM D 634-43. Again three films were used as source of ten or more "with" and "cross" specimens. The number of double folds required to sever the specimens as recorded on the automatic counter were averaged as previously described and reported as such.

It was necessary to tear 16 sheets together in order for the scale reading to be between 20 and 60 as required by ASTM D 687-44, Internal Tearing Resistance of Paper. These specimens were cut 3 inches by exactly 63 mm; the knife cut a 20 mm slit in the sheets which left 43 mm to be torn during the test as required in the above ASTM. Enough sheets to give at least 5 tests of 16 sheets each for the two directions were cut from five or more films. Since 16 sheets were required, the scale readings gave the force in grams required to tear the specimens. These values were averaged as previously described and reported to the nearest 0.5 gram as the force required to tear one specimen.

ASTM D 774-46 sets forth the conditions for determining the bursting strength of paper as the hydrostatic pressure required to produce a rupture in a circular area of the material 1.2 inches in diameter. A total of ten specimens 2.5 by 2.5 inches were cut from three or more films and the maximum pressures indicated by

the gage were averaged and reported as pounds per square inch.

The results of these tests are reported as specified in the ASTM procedures, i.e., the high and low scale readings are listed as well as the number of specimens tested, the average deviation of the readings from the arithmetic mean regardless of the sign, and the mean values themselves are recorded in Table III. In Table IV the average values for tensile strength and percent elongation have been converted from the scale readings to pounds per square inch and percentage respectively and the average values of the other mechanical properties, Schopper Folds, Internal Tear Resistance, and Bursting Strength, have been summarized for ready reference.

TABLE IIIa

MECHANICAL PROPERTIES OF ETHYL CELLULOSE FILMS

Sample	Tensile Strength (pounds breaking load)*										
	With					Cross					
	High	Low	No. Spec.	Avg. Devi.	Mean	High	Low	No. Spec.	Avg. Devi.	Average	
F 1**	14.20	12.35	10	0.53	13.16	14.80	10.35	10	1.29	12.57	12.87
F 2	14.00	11.15	14	0.66	12.57	15.10	11.00	13	0.87	13.08	12.83
F 3	14.10	10.60	11	1.35	11.82	12.50	9.27	12	0.65	11.48	11.65
F 4	11.50	10.25	10	0.54	11.08	12.90	11.25	10	0.51	12.05	11.57
F 5	13.55	9.20	13	1.15	11.54	13.80	9.70	13	0.99	11.47	11.51
F 6	12.35	9.75	10	0.81	11.17	12.20	9.30	10	0.97	10.90	11.04
F 7	10.85	9.20	10	0.68	10.08	12.40	9.85	13	0.90	11.00	10.54
F 8	10.45	8.75	12	0.55	9.86	9.65	7.80	11	0.45	8.83	9.35
Original	10.90	8.75	14	0.44	10.07	10.05	8.05	15	0.50	9.25	9.66
B 1	10.37	8.15	14	0.87	9.95	9.50	8.05	14	0.33	8.59	9.27
B 2	10.50	8.45	13	0.56	9.30	9.70	7.60	12	0.58	8.73	9.02
B 3	12.95	10.00	13	0.85	11.60	14.10	10.90	12	0.60	11.60	11.60
B 4	11.05	9.20	14	0.36	10.34	12.90	10.50	12	0.64	11.74	11.02
B 5	11.45	9.35	15	0.55	10.62	11.60	9.40	15	0.69	10.47	10.55
B 6	10.10	8.40	15	0.37	9.03	10.55	7.90	16	0.51	9.07	9.05
B 7	12.50	9.90	15	0.62	11.11	11.55	9.70	15	0.68	10.81	10.96
B 8	12.70	9.00	15	0.69	10.31	14.90	10.05	15	1.23	12.08	11.20
B 9	13.45	11.10	15	0.69	12.61	14.35	10.75	15	0.80	12.00	12.31
B10	13.75	10.65	15	0.71	12.15	14.75	11.40	15	0.73	13.14	12.65

* Multiply values by 667 to get results in pounds per square inch.

** F 1 etc. means Fraction 1; B 1 means Blend 1.

TABLE IIIb

Inches Elongation per 4 inch Strip*

Sample	With				Cross				Average	
	High	Low	No. Spec.	Avg. Devi.	High	Low	No. Spec.	Avg. Devi.		
F 1**	1.15	0.86	10	0.12	1.19	0.74	10	0.09	0.97	0.94
F 2	1.40	0.73	14	0.15	1.10	0.72	13	0.12	0.91	0.95
F 3	1.02	0.52	11	0.15	0.94	0.62	12	0.08	0.77	0.79
F 4	1.05	0.62	10	0.12	1.10	0.77	10	0.08	0.95	0.93
F 5	1.10	0.49	13	0.12	1.02	0.66	13	0.11	0.86	0.79
F 6	0.91	0.25	10	0.18	0.84	0.31	10	0.11	0.56	0.59
F 7	0.65	0.31	10	0.09	0.88	0.32	11	0.10	0.68	0.56
F 8	0.44	0.15	12	0.05	0.27	0.13	11	0.02	0.17	0.20
Original	1.07	0.31	14	0.17	0.83	0.39	15	0.10	0.65	0.70
B 1	0.77	0.42	14	0.11	0.63	0.22	14	0.12	0.41	0.51
B 2	0.78	0.26	13	0.11	0.77	0.21	12	0.14	0.43	0.49
B 3	0.98	0.59	13	0.08	0.98	0.74	12	0.05	0.86	0.83
B 4	0.95	0.55	14	0.11	1.03	0.60	12	0.09	0.83	0.79
B 5	0.92	0.53	15	0.12	0.88	0.30	15	0.13	0.65	0.70
B 6	0.86	0.31	15	0.14	0.53	0.31	16	0.08	0.42	0.44
B 7	1.02	0.65	15	0.10	1.10	0.62	15	0.14	0.32	0.84
B 8	0.95	0.56	15	0.08	1.11	0.55	15	0.13	0.85	0.79
B 9	1.09	0.70	15	0.08	1.00	0.72	15	0.09	0.87	0.89
B 10	1.07	0.53	15	0.08	1.21	0.80	15	0.07	0.93	0.89

* Divide the values by 0.04 to get the percent elongation.

** F 1 means Fraction 1; B 1 means Blend 1.

TABLE IIIc

Number of Double Schopper Folds

Sample	With				Cross				Average		
	High	Low	No. Spec.	Avg. Devi.	Mean	High	Low	No. Spec.		Avg. Devi.	
F 1*	380	154	10	55	247	288	163	11	30	205	226
F 2	314	187	11	37	251	460	166	14	92	292	272
F 3	386	208	14	54	286	341	166	11	51	246	266
F 4	350	176	10	50	261	355	117	10	39	196	229
F 5	386	146	16	65	248	370	127	17	57	210	229
F 6	149	66	16	20	104	139	65	20	19	92	98
F 7	140	72	12	19	101	114	63	13	14	83	92
F 8	22	9	14	2	17	25	17	14	1	20	19
Original	265	106	25	36	172	276	105	21	32	153	163
B 1	111	50	16	11	78	178	53	16	31	107	93
B 2	101	61	16	12	83	110	53	18	17	83	83
B 3	242	121	15	28	177	201	104	16	31	151	164
B 4	275	112	15	37	181	244	85	17	40	151	166
B 5	215	105	15	28	148	198	90	15	23	136	142
B 6	106	57	15	15	84	113	55	15	14	79	82
B 7	293	156	15	33	225	288	120	15	53	185	205
B 8	287	120	15	39	172	213	100	15	31	153	163
B 9	196	78	15	35	145	196	74	15	28	138	142
B 10	192	90	15	27	138	191	99	15	25	142	140

* F 1 means Fraction 1; B 1 means Blend 1, etc.

TABLE IIIId

Internal Tear Resistance*

Sample	With				Cross				Average		
	High	Low	No. Spec.	Avg. Devi.	Mean	High	Low	No. Spec.		Avg. Devi.	
F 1**	27	24	6	0.8	25.8	31	25	6	1.8	28.3	27.0
F 2	34	27	6	2.9	30.5	38	28	6	3.3	32.6	31.5
F 3	38	32	5	1.8	35.2	30	27	5	1.4	28.2	31.0
F 4	34	27	6	1.8	29.1	34	27	6	1.7	29.3	29.0
F 5	40	28	6	3.0	32.0	37	28	6	2.3	33.0	32.5
F 6	35	31	6	0.8	32.6	27	20	6	1.7	24.0	28.5
F 7	32	24	6	1.7	27.0	31	24	6	2.7	26.0	26.5
F 8	21	15	6	1.0	18.0	21	16	6	1.3	18.0	18.0
Original	27	24	6	1.0	25.3	28	24	6	1.1	25.8	25.5
B 1	20	19	6	0.5	19.5	21	19	6	0.7	19.7	19.5
B 2	21	19	6	0.8	20.3	21	18	6	0.8	19.5	20.0
B 3	22	20	6	0.5	20.8	19	16	6	0.7	17.7	19.5
B 4	29	26	6	0.7	27.3	31	27	6	1.0	28.7	28.0
B 5	24	22	5	0.5	22.8	27	21	6	1.3	24.0	23.5
B 6	23	18	6	1.1	19.8	22	18	6	1.0	19.6	20.0
B 7	25	23	6	0.7	23.5	28	25	6	0.8	26.5	25.0
B 8	27	23	6	1.3	24.0	28	22	6	1.5	24.5	24.5
B 9	29	25	6	1.1	26.5	27	23	6	1.0	25.5	26.0
B 10	26	22	6	1.1	23.5	26	23	6	1.1	24.5	24.0

* Scale Readings when 16 sheets were torn or grams required to tear one sheet.

** F 1 means Fraction 1; B 1 means Blend 1.

TABLE IIIe

Bursting Strength (pounds per square inch)

<u>Sample</u>	<u>High</u>	<u>Low</u>	<u>No.</u> <u>Spec.</u>	<u>Avg.</u> <u>Devi.</u>	<u>Average</u>
F 1*	91	77	10	4.1	84.5
F 2	104	68	11	10.8	82.5
F 3	94	77	10	5.7	75.6
F 4	88	70	10	5.3	79.2
F 5	85	63	10	4.8	75.7
F 6	81	65	11	4.4	75.6
F 7	69	44	11	7.4	56.4
F 8	43	27	13	4.7	35.7
Original	73	49	13	5.4	61.7
B 1	61	37	14	6.0	52.0
B 2	66	46	13	6.0	57.6
B 3	81	42	14	11.0	62.6
B 4	83	61	11	7.4	70.9
B 5	65	53	12	3.6	60.1
B 6	63	48	12	4.0	55.1
B 7	81	59	12	5.3	68.1
B 8	82	55	11	6.0	71.7
B 9	87	60	10	7.6	74.2
B 10	80	59	11	6.2	69.1

* F 1 means Fraction 1; B 1 means Blend 1.

TABLE IV

MECHANICAL PROPERTIES OF 0.003 INCH ETHYL CELLULOSE FILMS SUMMARIZED

Sample	Avg. D.P.		Tensile-Strength (p.s.i.)		Percent Elongation		No. Schopper Folds		Internal Tear Resistance (grams)		Bursting Strength			
	D.P.	Avg.	With	Cross Avg.	With	Cross Avg.	With	Cross Avg.	With	Cross Avg.	P.s.i.			
F 1	249	8370	8780	8580	22.6	24.3	23.5	247	205	226	25.8	28.3	27.0	84.5
F 2	274	8420	8720	8570	22.6	24.8	23.7	251	292	272	30.5	32.6	31.5	82.5
F 3	248	7880	7660	7720	19.9	19.2	19.5	286	246	266	35.2	28.2	31.0	75.6
F 4	212	7390	8030	7710	22.6	23.7	23.2	261	196	229	29.1	29.3	29.0	79.2
F 5	186	7700	7650	7670	17.6	21.5	19.5	248	210	229	32.0	33.0	32.5	75.7
F 6	130	7450	7270	7360	15.2	14.0	14.6	104	92	98	32.6	24.0	28.5	75.6
F 7	109	6730	7340	6530	11.0	17.0	14.0	101	83	92	27.0	26.0	26.5	56.4
F 8	64	6580	5890	6230	5.6	4.2	4.9	17	20	19	18.0	18.0	18.0	35.7
Original	183	6720	6170	6440	18.2	16.2	17.2	172	153	163	25.3	25.8	25.5	61.7
B 1	194	6640	5730	6180	15.0	10.2	12.6	78	107	93	19.5	19.7	19.5	52.0
B 2	186	6200	5820	6020	13.7	10.7	12.2	83	83	83	20.3	19.5	20.0	57.6
B 3	184	7740	7740	7740	19.8	21.5	20.6	177	151	164	20.8	17.7	19.5	62.6
B 4	190	6900	7830	7360	18.7	20.7	19.7	181	151	166	27.3	28.7	28.0	70.9
B 5	190	7080	6980	7040	18.5	16.3	17.4	148	136	142	22.8	24.0	23.5	60.1
B 6	187	6020	6060	6040	11.5	10.5	11.0	84	79	82	19.7	19.6	20.0	55.1
B 7	175	7410	7210	7310	21.2	20.5	20.8	225	185	205	23.5	26.5	25.0	68.1
B 8	190	6880	8060	7470	18.2	21.2	19.7	172	153	163	24.0	24.5	24.5	71.7
B 9	190	8400	8000	8200	22.5	21.7	22.1	145	138	142	26.5	25.5	26.0	74.2
B 10	153	8100	8760	8430	21.0	23.3	22.2	138	142	140	23.5	24.5	24.0	69.1

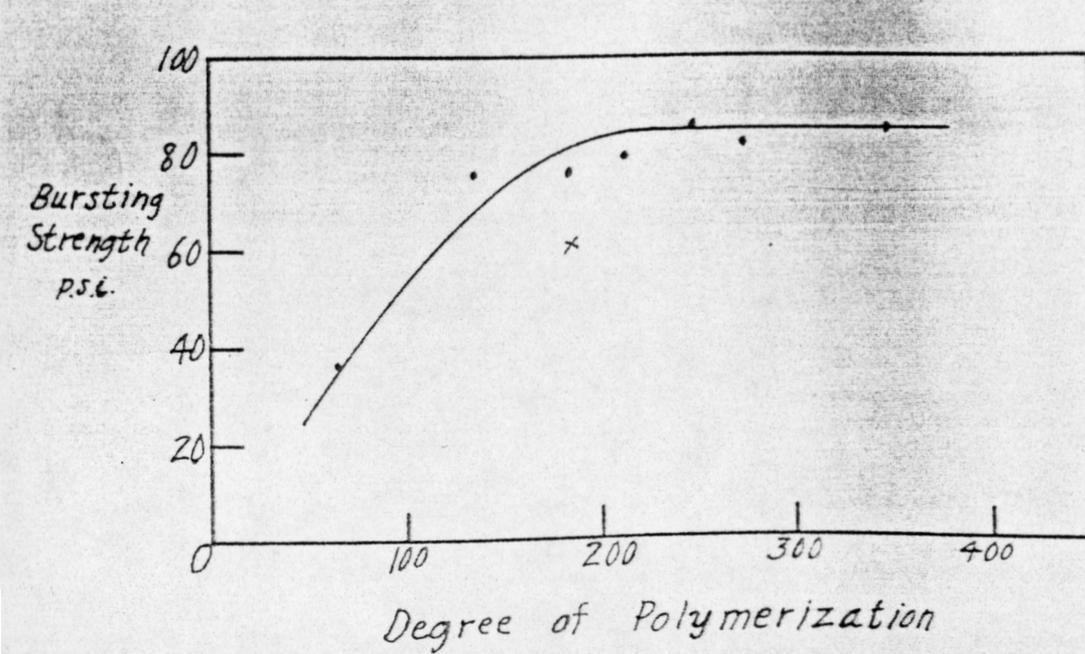
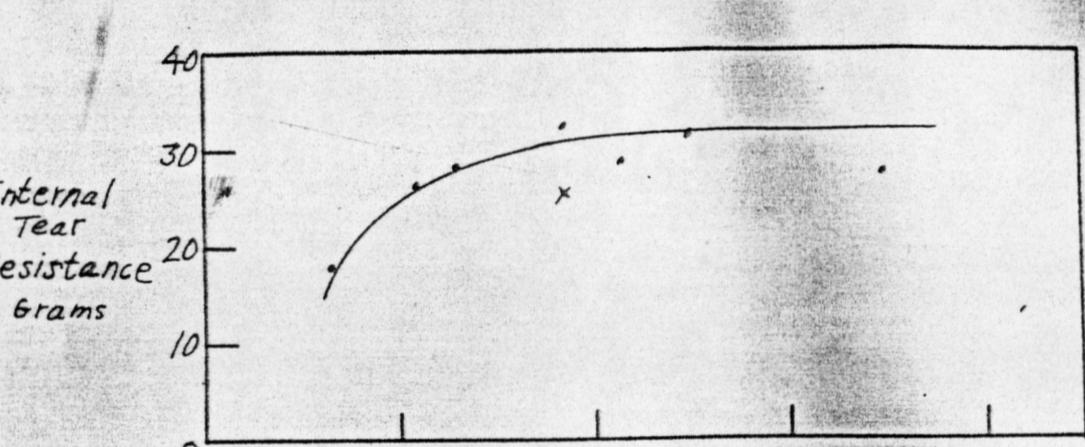
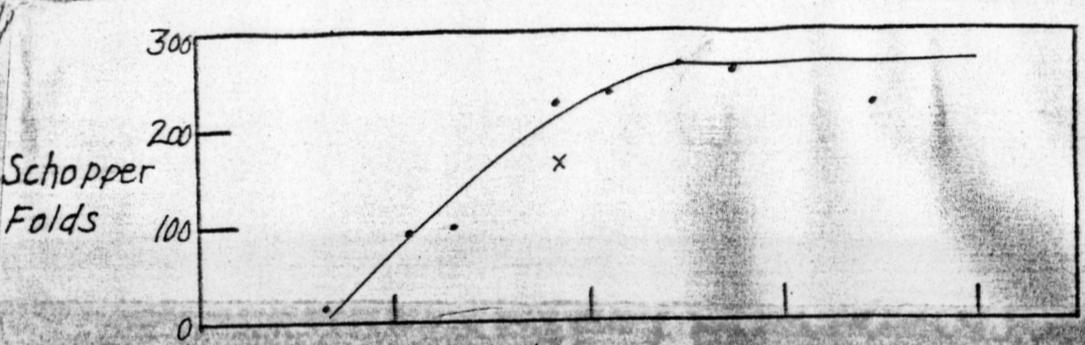
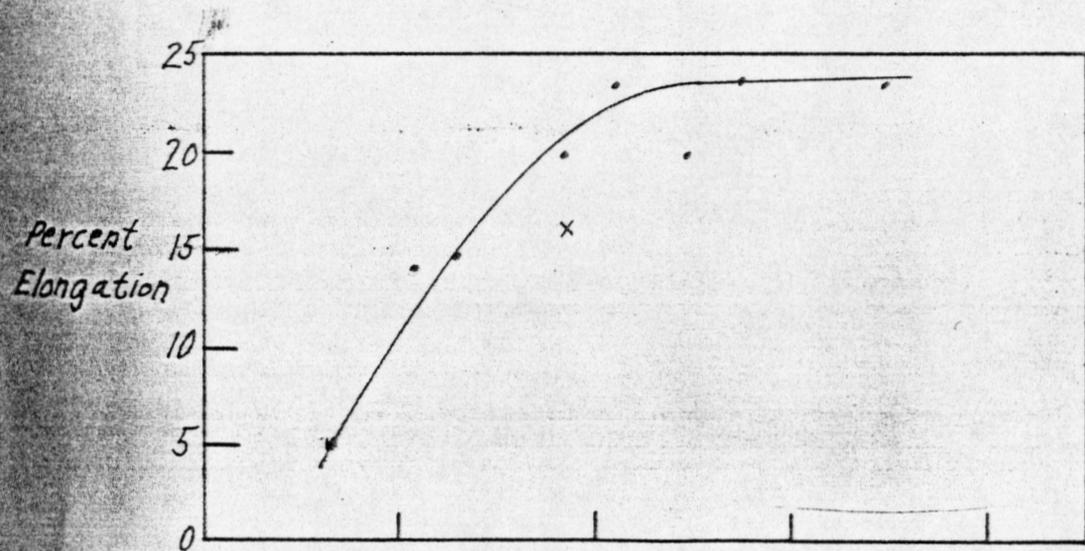
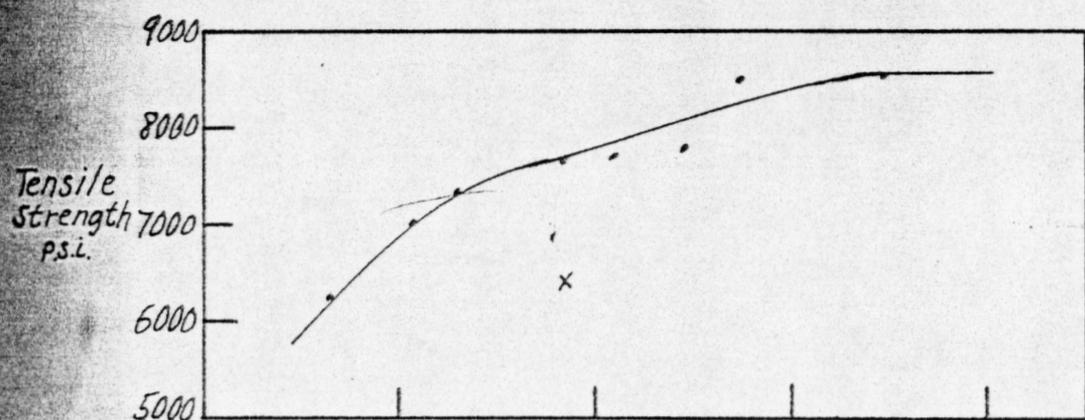
CHANGE IN MECHANICAL PROPERTIES WITH AVERAGE DEGREE OF
POLYMERIZATION

The average values of the mechanical properties of films cast from the fractions were plotted against the average degree of polymerization of those fractions in Graph IV. It is noted that all of the properties improved with the increase in D. P. up to about 200 or 250 where the values remain constant regardless of further increase in the D. P. These results support the findings of Bass and Kauppi (2), Spurlin (51), and Sookne and Harris (50) and the conclusions reached by Mark (33, 34a) in that the tensile strength increases up to a D. P. of 200 above which the average chain length does not further improve the mechanical properties.

GRAPH III

Change in Mechanical Properties with the Change
in Average Degree of Polymerization

Fractions •
Original Material X



FORMATION AND ANALYSIS OF THE BLENDS

Since the average chain length of the fractions affected the physical properties of the films, it was thought that this effect could be minimized by preparing blends having approximately the same average D. P. One distribution curve, that of the original material, having already been determined it was decided to try to keep the average D. P. somewhere near that of the original material or 183. Two other restrictions were placed upon the blends, namely, that they must give smooth curves when the percentage composition was plotted against the D. P. of the components, and that the differential distribution curves should be different.

In order to determine the theoretical composition of the blends trial integral distribution curves were drawn and the percentage of each fraction determined. The average chain length of the blend was then determined by summing the products of percentage times corresponding D. P. and dividing by 100. If this average came within the arbitrary limits established for the blends, a theoretical differential distribution curve was drawn. The theoretical curves do not appear in Graphs V through XV because at scale used the theoretical and experimental curves for the most part coincided.

The blends were prepared by dissolving the calculated weight of each fraction to make a total of 60 grams in 540 grams of

benzene. These solutions were cast into 0.003 inch films and tested and reported as has been previously described.

In order to experimentally determine the composition of the blends, 15 grams of the films were dissolved in 197 grams of ethyl acetate and left standing overnight before being diluted with 788 grams of acetone. Thus a 1.5% solution of ethyl cellulose in a 80:20 acetone-ethyl acetate mixture was formed which was similar to that used in the fractionation of the original material. A 75:25 water-acetone mixture was used as non-solvent for the first two blends before it was found that good control of the fractionation could be obtained by using water alone as the precipitating agent. For the first fraction the non-solvent was added until some haze developed in the solution and a slight precipitate settled within a few minutes. For all subsequent fractions the non-solvent was added until the solution was hazy. The solutions were cooled to 15° C. for 20 hours and then decanted and warmed to 25° C. before more non-solvent was added. The precipitate was recovered in an usable form as has been described, i.e., by dissolving it in a minimum amount of acetone, precipitating into an excess of water, filtering and drying. The last fraction was obtained by evaporation of the remaining liquid.

Fractions of about 10% were readily obtained after the first had been separated, but only when the first fraction was

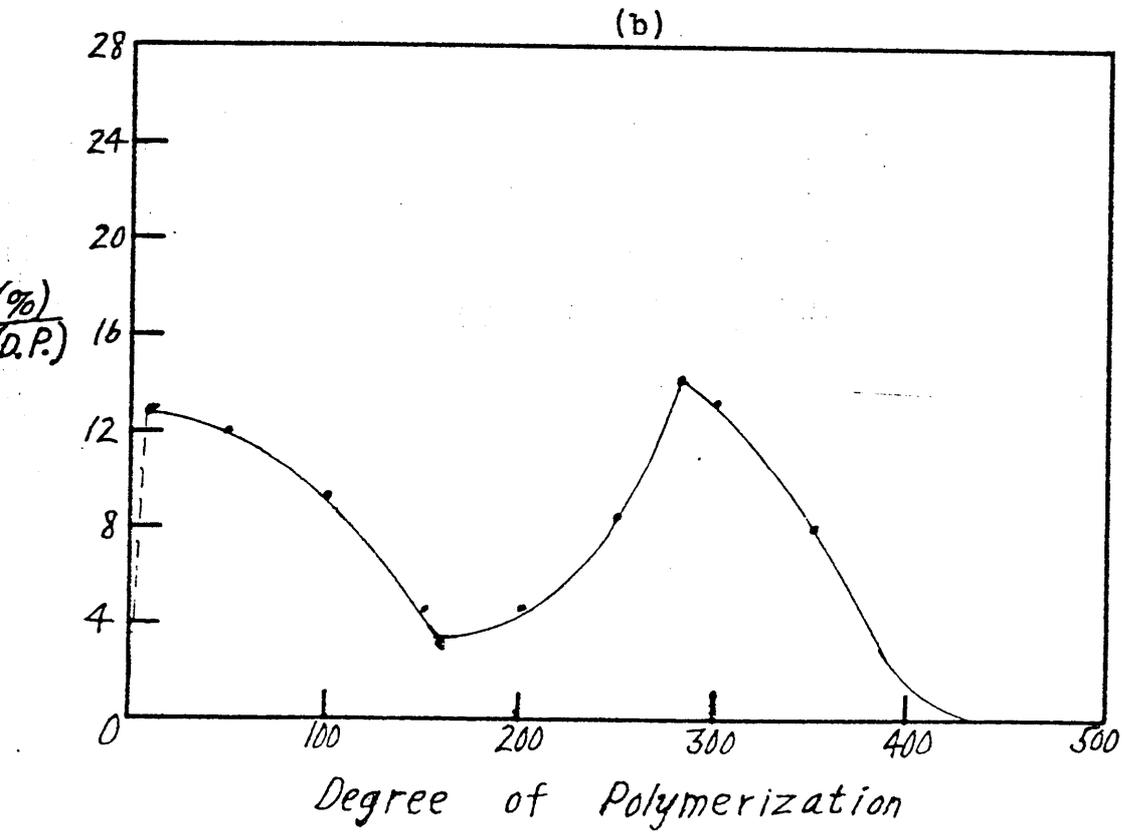
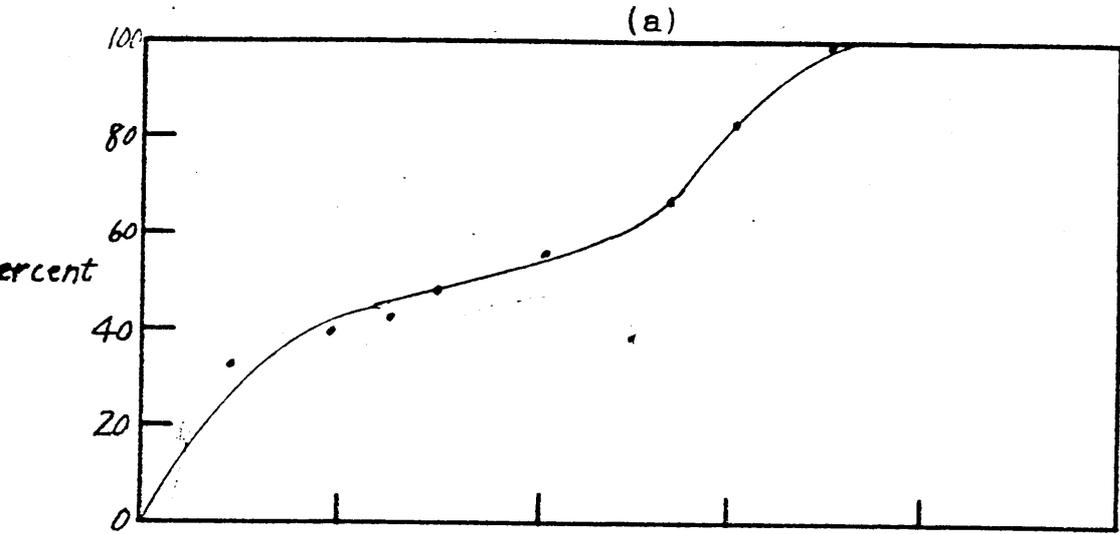
very large, as compared with the percentage of the highest D. P. material used to form the blend was this first fraction refractionated. For refractionation a 1.5% solution of the precipitate was prepared in a 80:20 acetone-ethyl acetate mixture and treated according to previously described procedures.

More detailed information concerning the fractionation of Fraction 5 and Blend 10 is given in Table V. It is noted that the first fraction of Fraction 5 had to be refractionated while that of Blend 10 did not. Distilled water was used as non-solvent in both fractionations. These data are given as examples of the procedures used in analyzing the composition of the blends and fractions. The degree of polymerization of each fraction was determined by viscosity measurements according to the procedure already described. The low D. P. of the first fraction was probably due to the enmeshing of low D. P. material, ash, and other impurities in the first precipitate formed. The solutions were always clearer after the first precipitate had formed than when the solutions were first prepared thus supporting this explanation of the experimentally determined average low D. P. of the first fraction.

The calculated and experimentally determined compositions of the blends are listed in Table VI and the integral and differential distribution curves based upon the experimental data are given in Graphs IV through XIII.

BLEND I

- (a) Integral Distribution
- (b) Differential Distribution

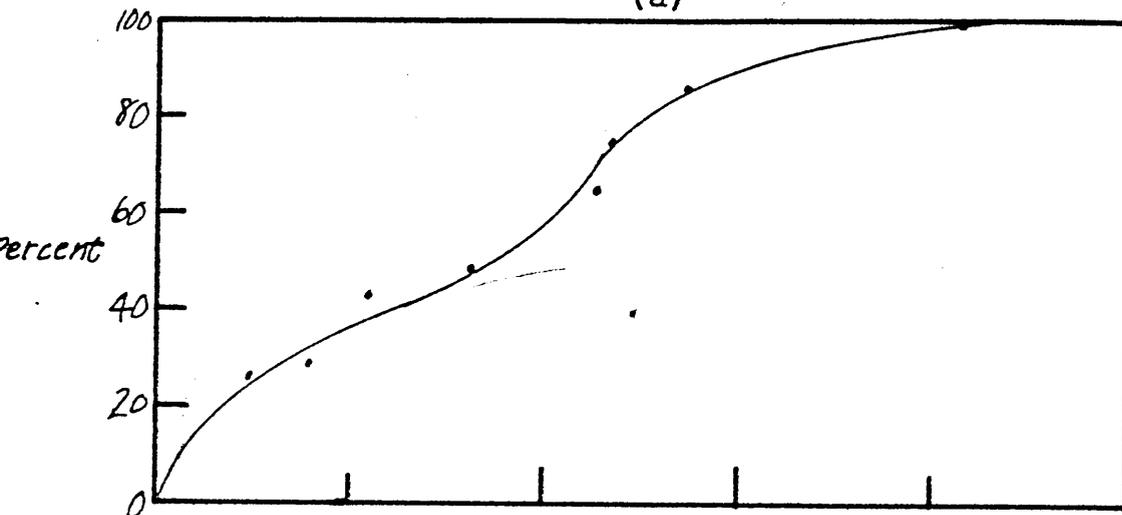


Graph V

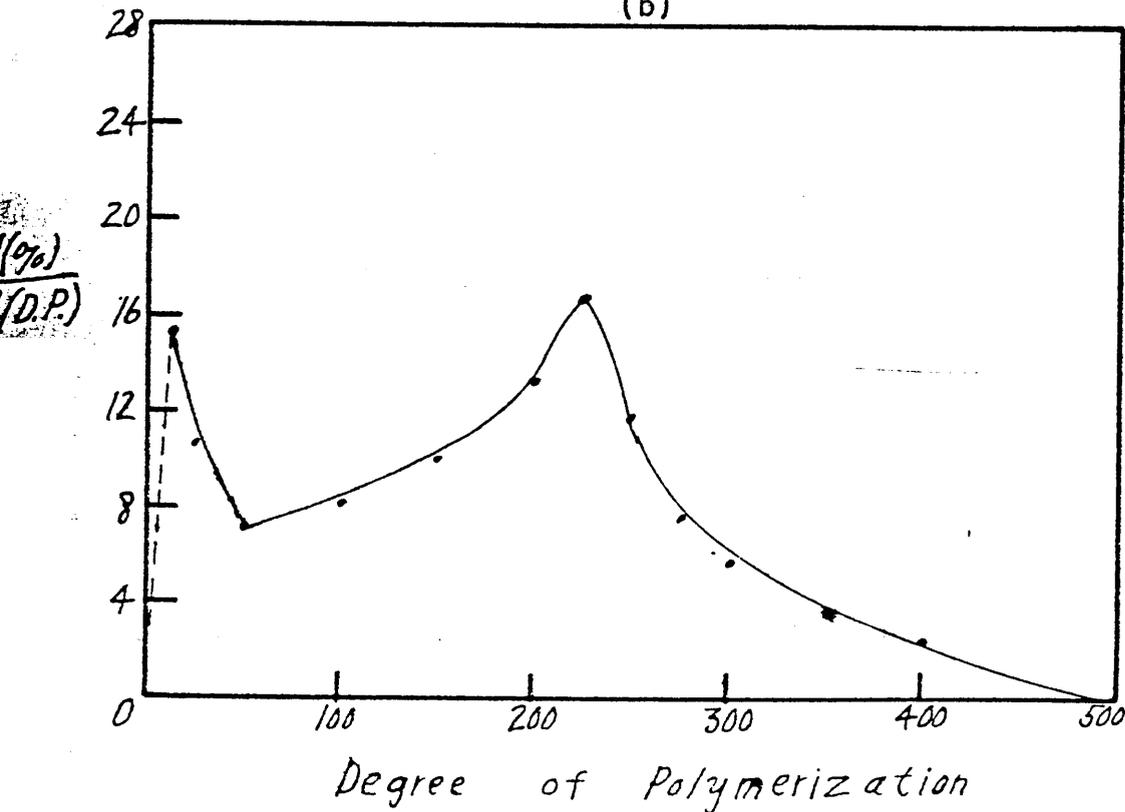
BLEND 2

- (a) Integral Distribution
- (b) Differential Distribution

(a)



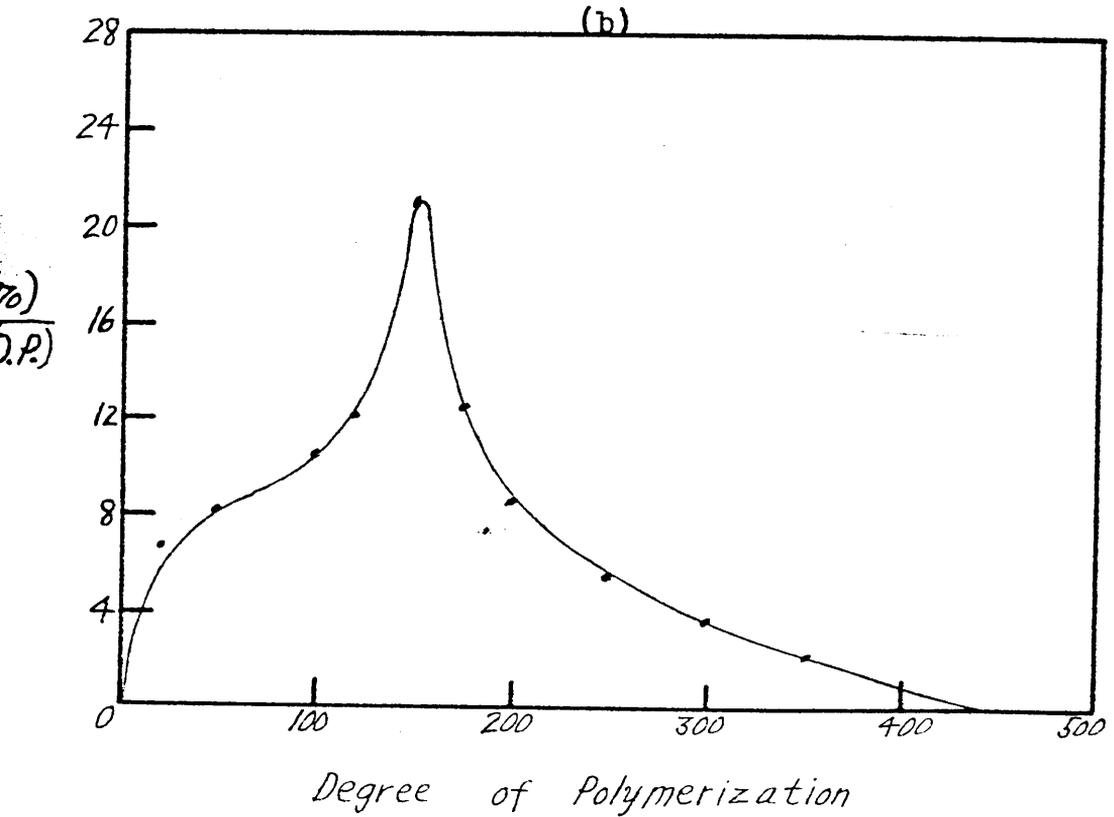
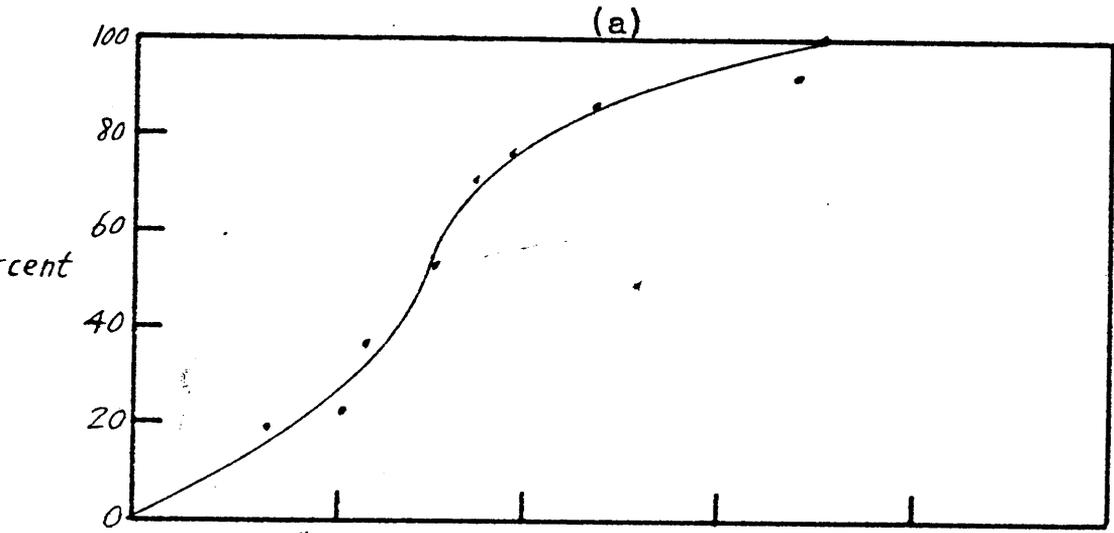
(b)



Graph VI

BLEND 3

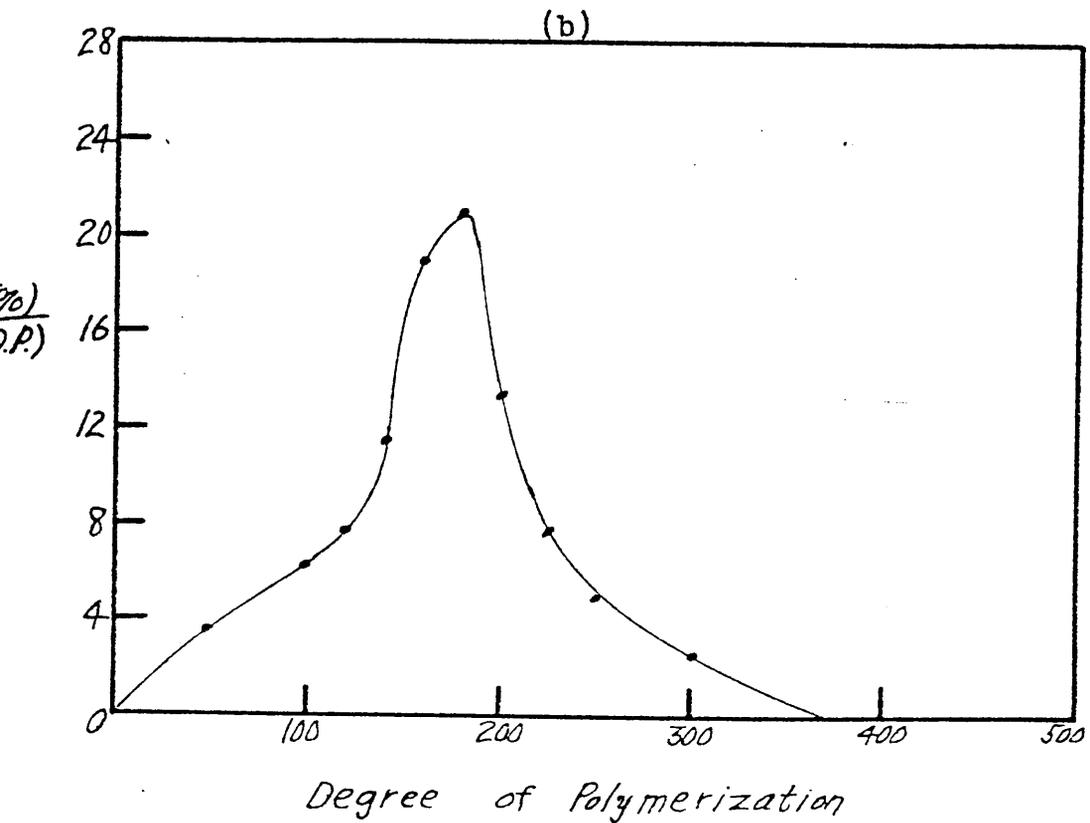
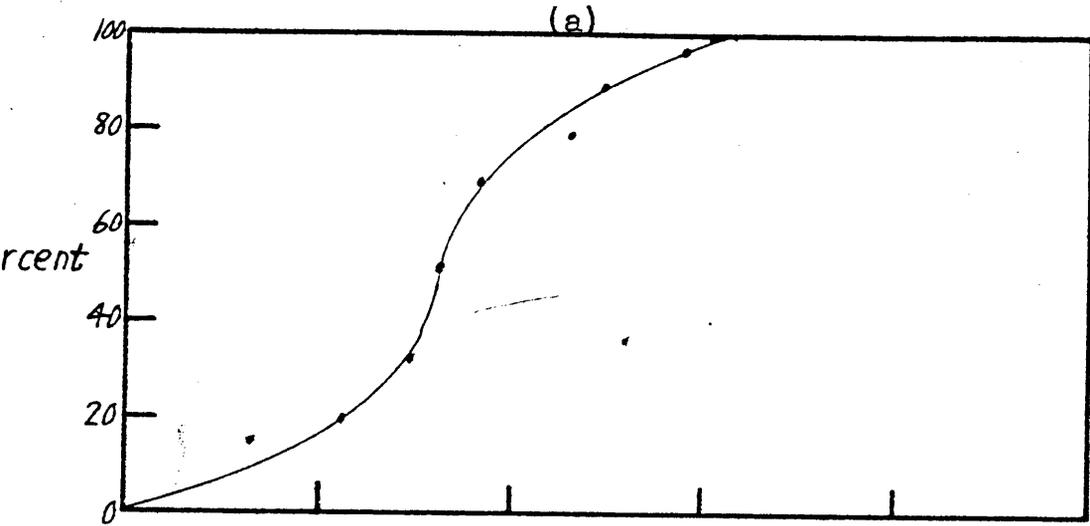
- (a) Integral Distribution
- (b) Differential Distribution



Graph VII

BLEND 4

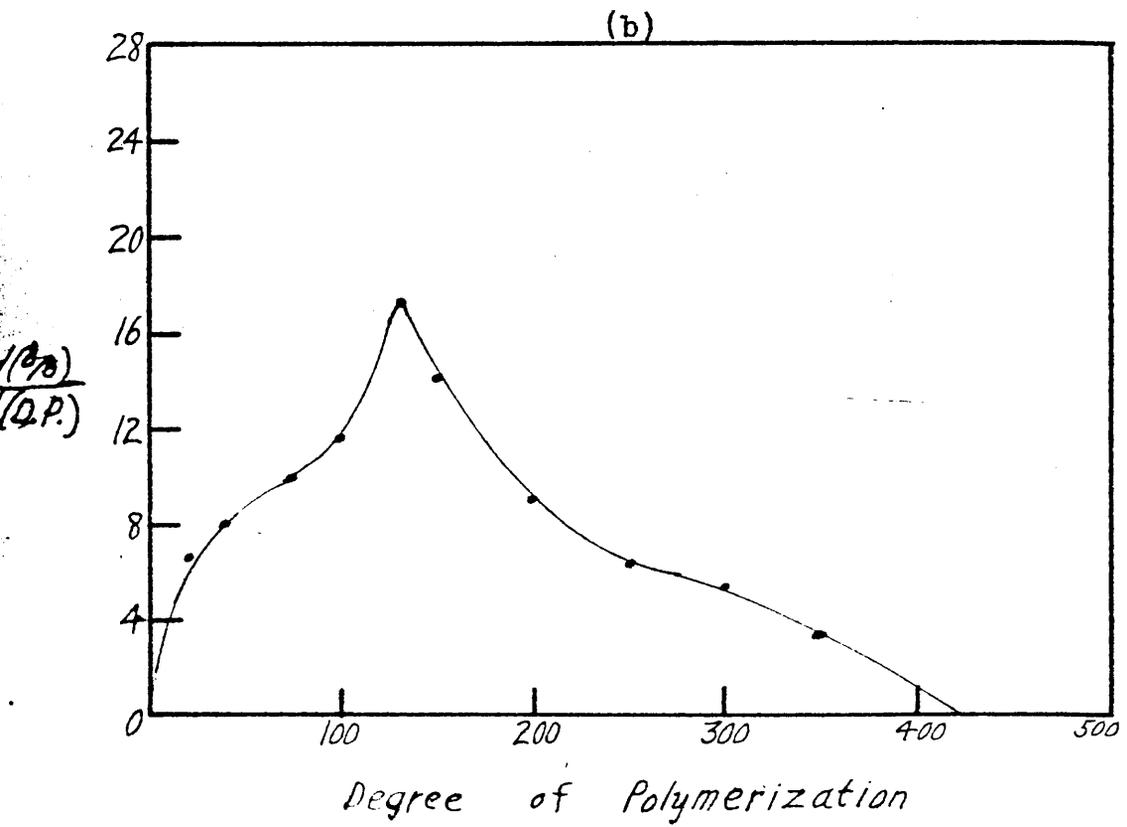
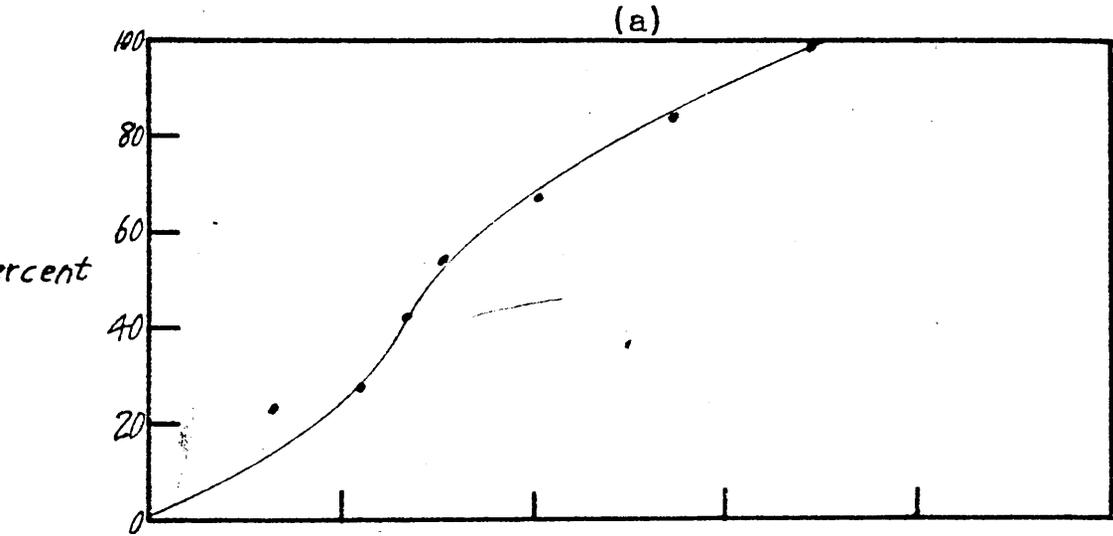
- (a) Integral Distribution
- (b) Differential Distribution



Graph VIII

BLEND 5

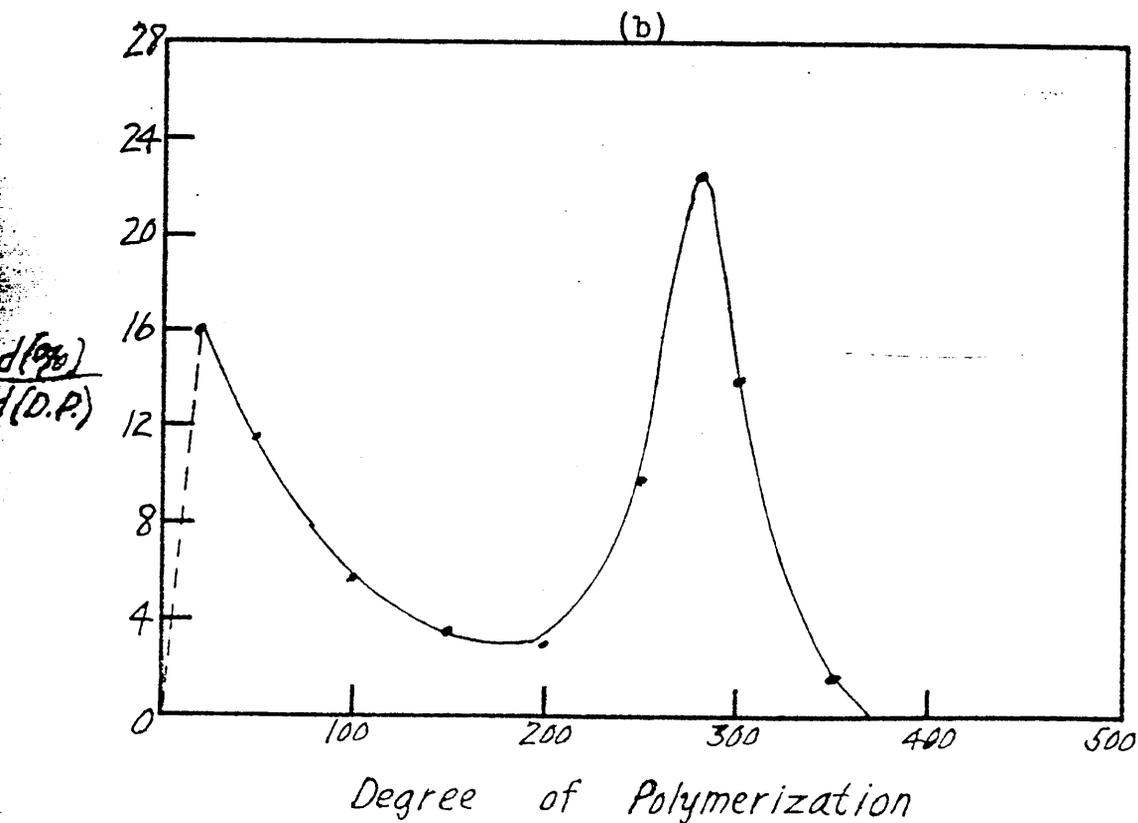
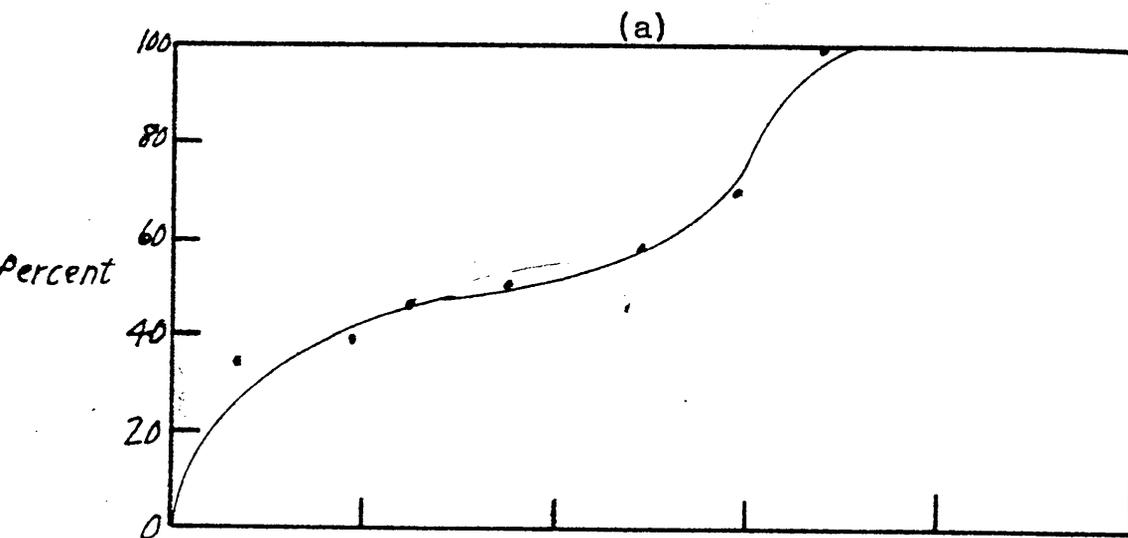
- (a) Integral Distribution
- (b) Differential Distribution



Graph IX

BLEND 6

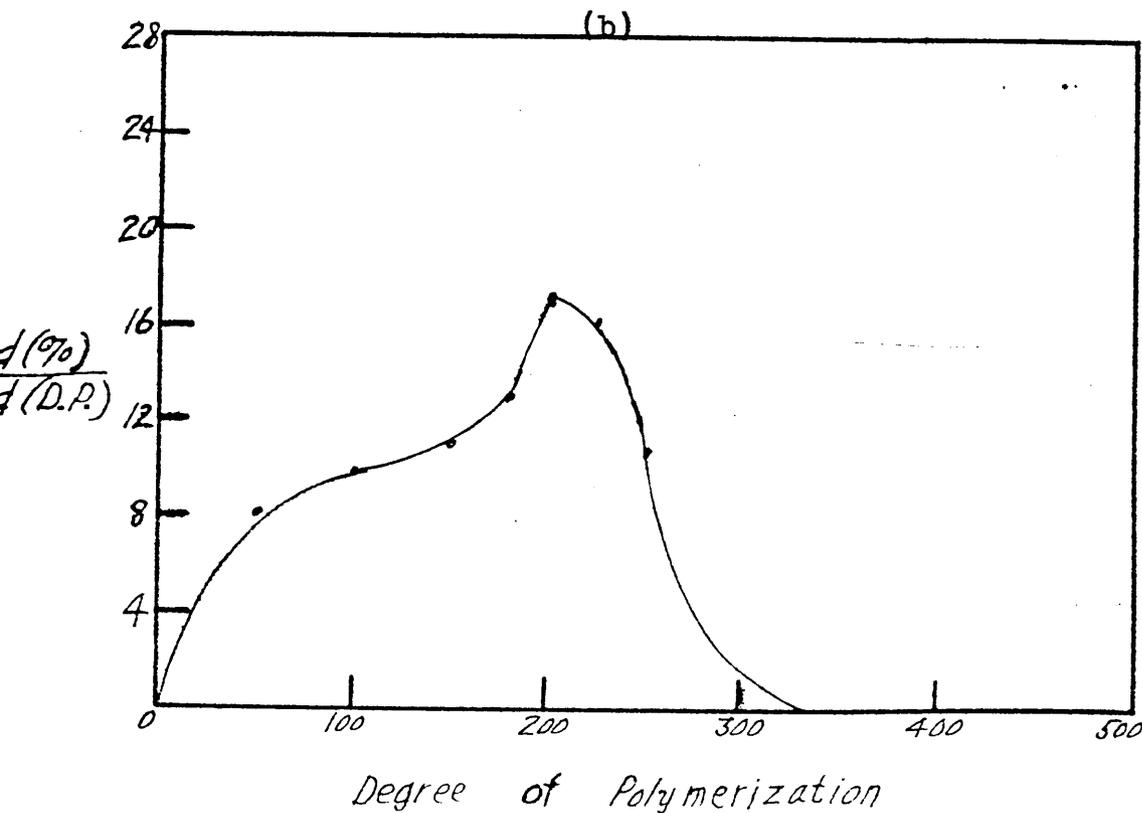
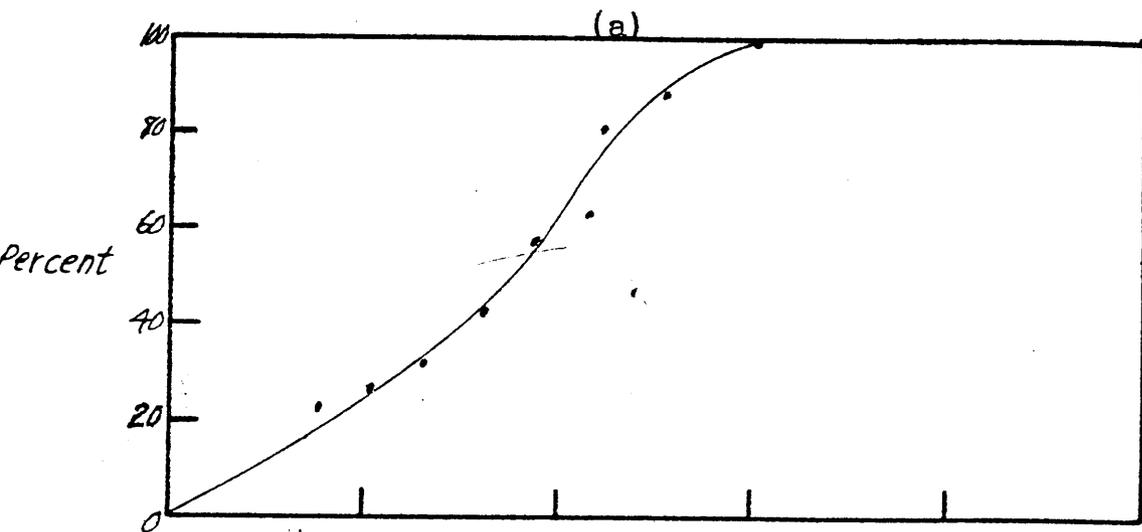
- (a) Integral Distribution
- (b) Differential Distribution



Graph X

BLEND 7

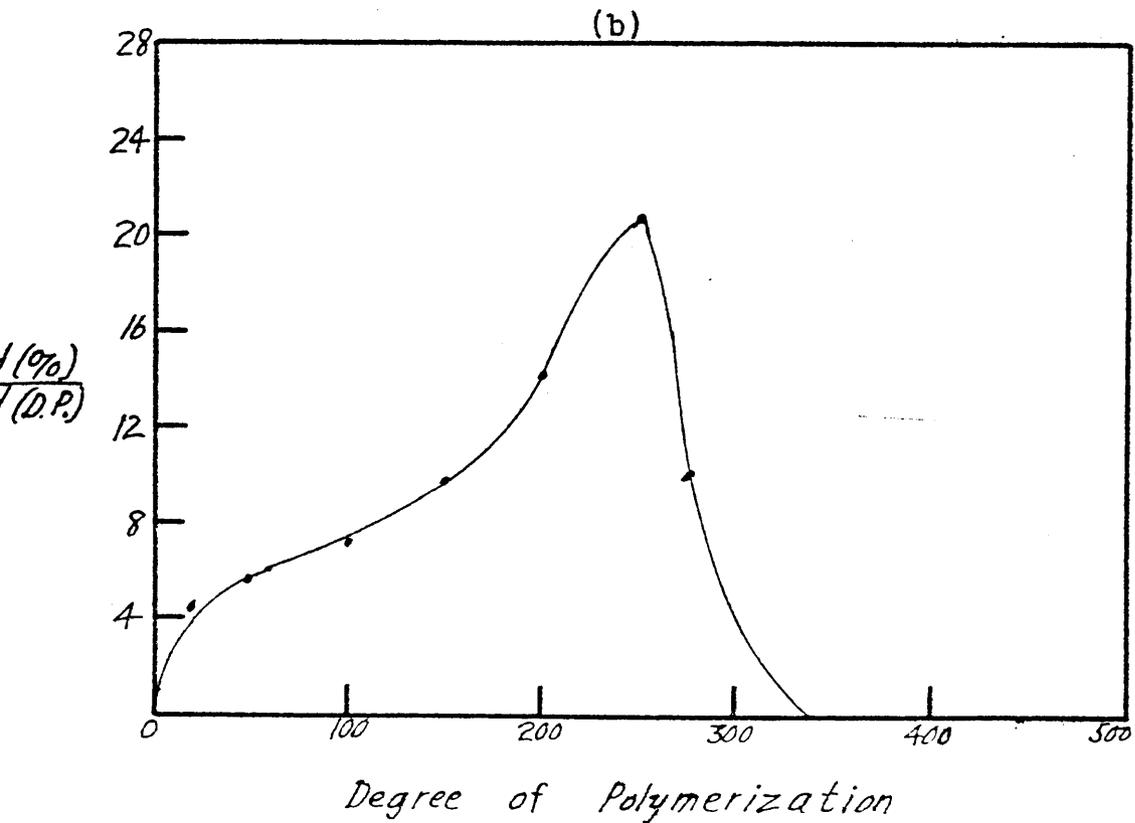
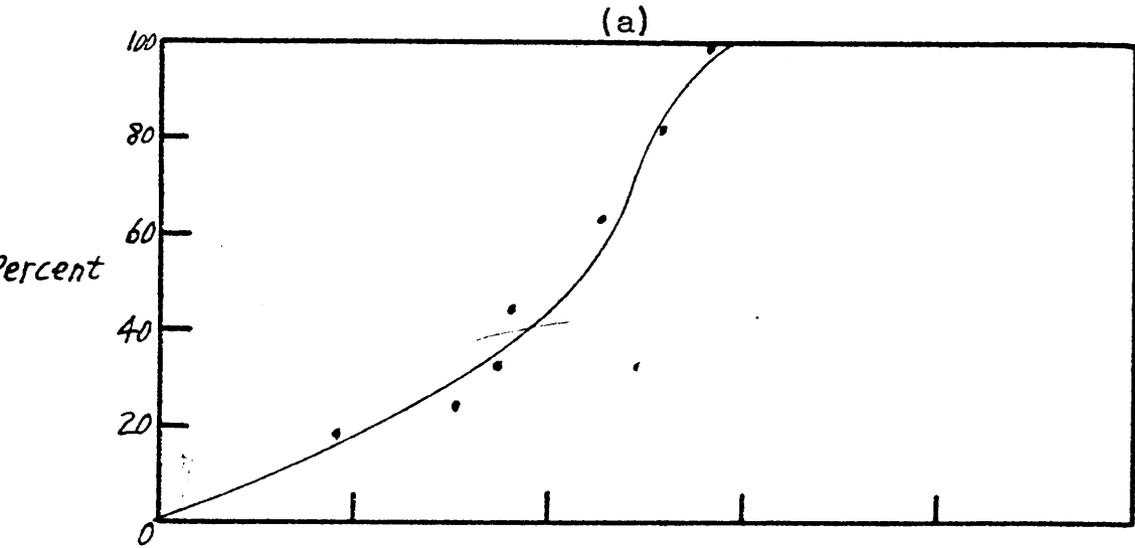
- (a) Integral Distribution
- (b) Differential Distribution



Graph XI

BLEND 8

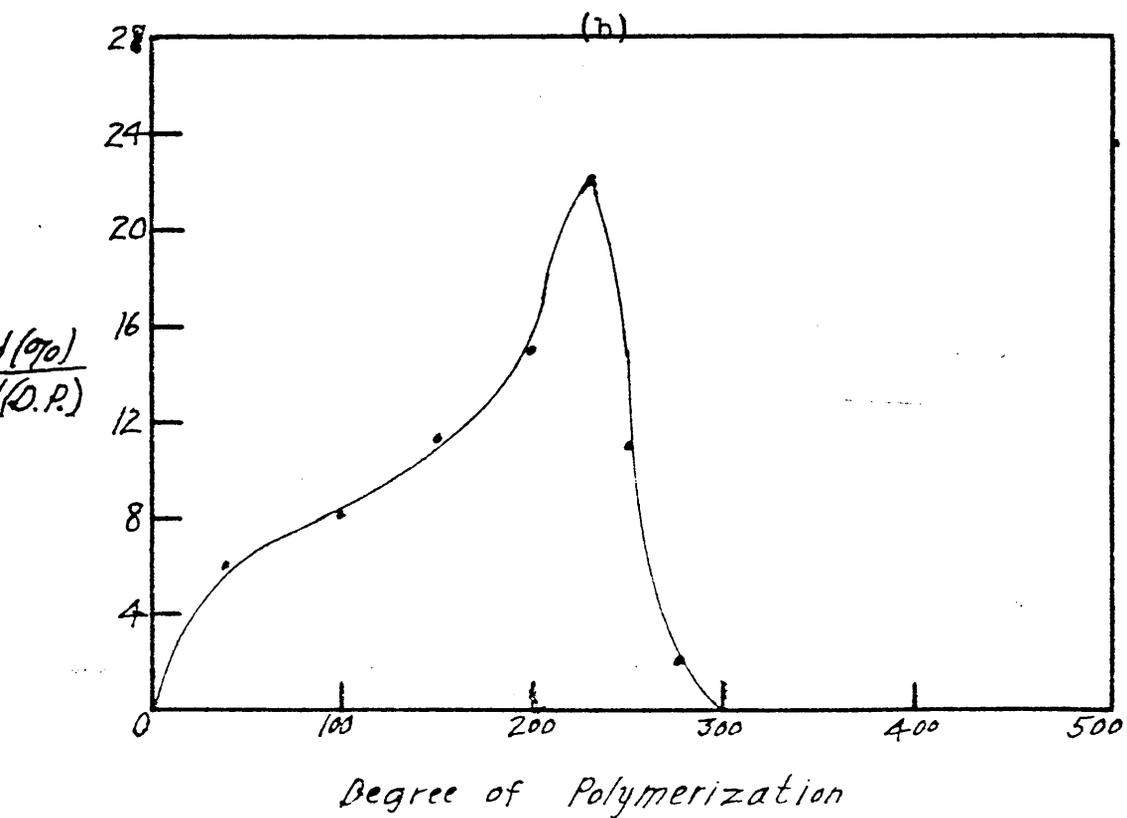
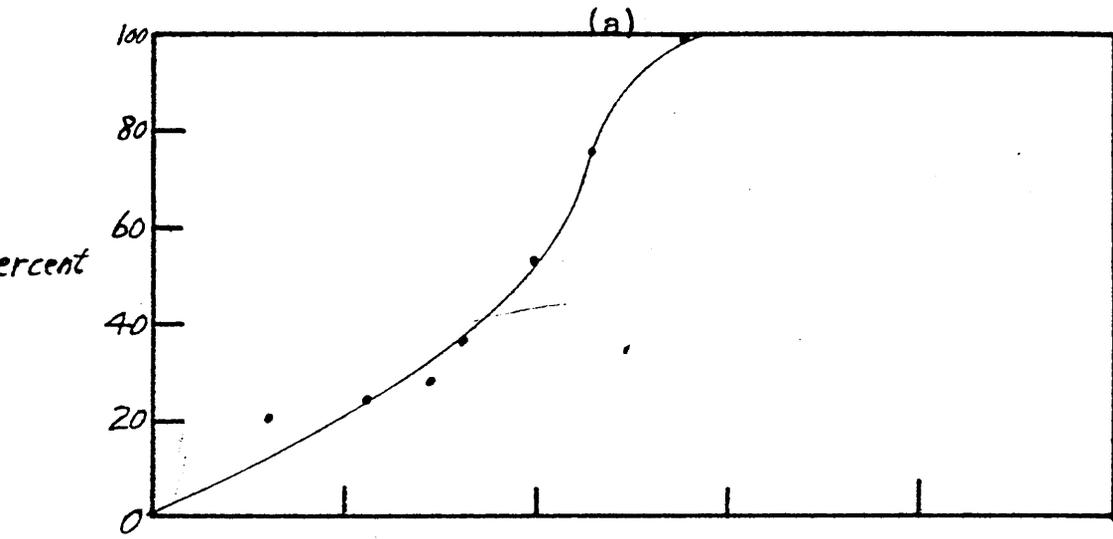
- (a) Integral Distribution
- (b) Differential Distribution



Graph XII

BLEND 9

- (a) Integral Distribution
- (b) Differential Distribution



Graph XIII

BLEND 10

- (a) Integral Distribution
- (b) Differential Distribution

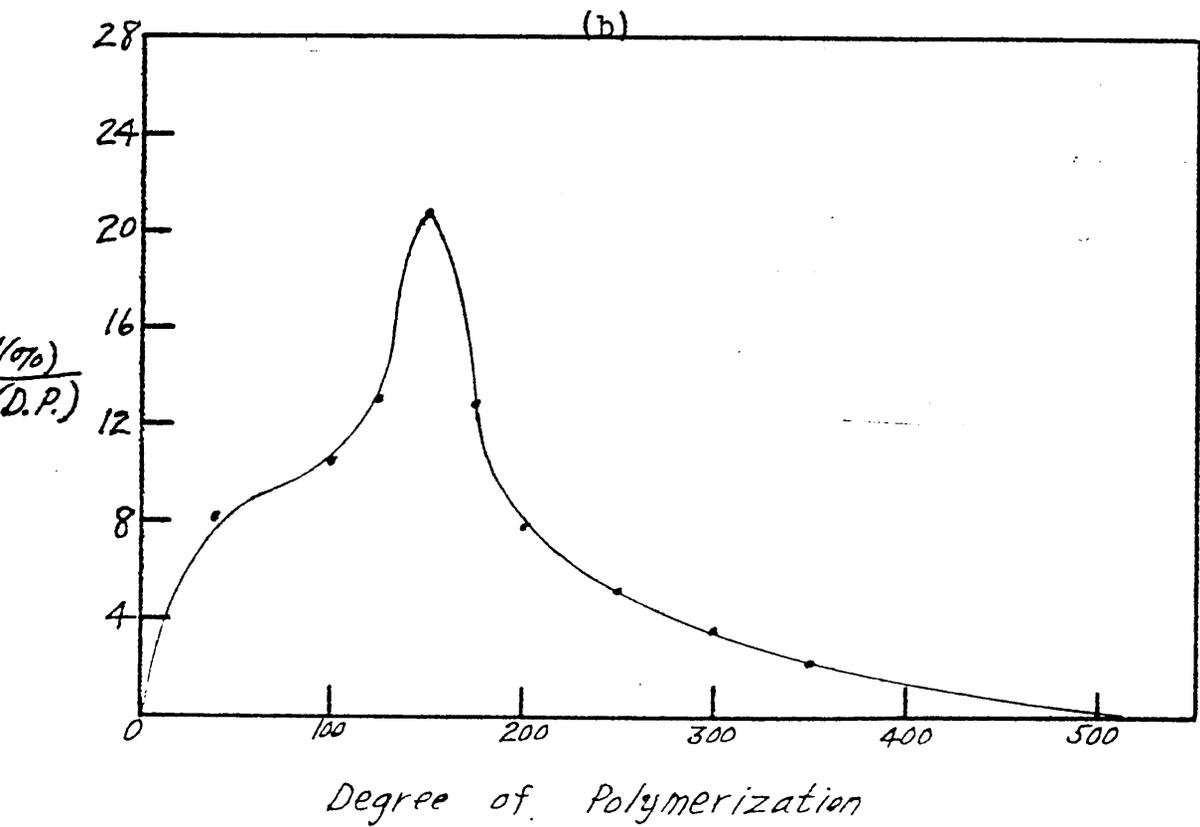
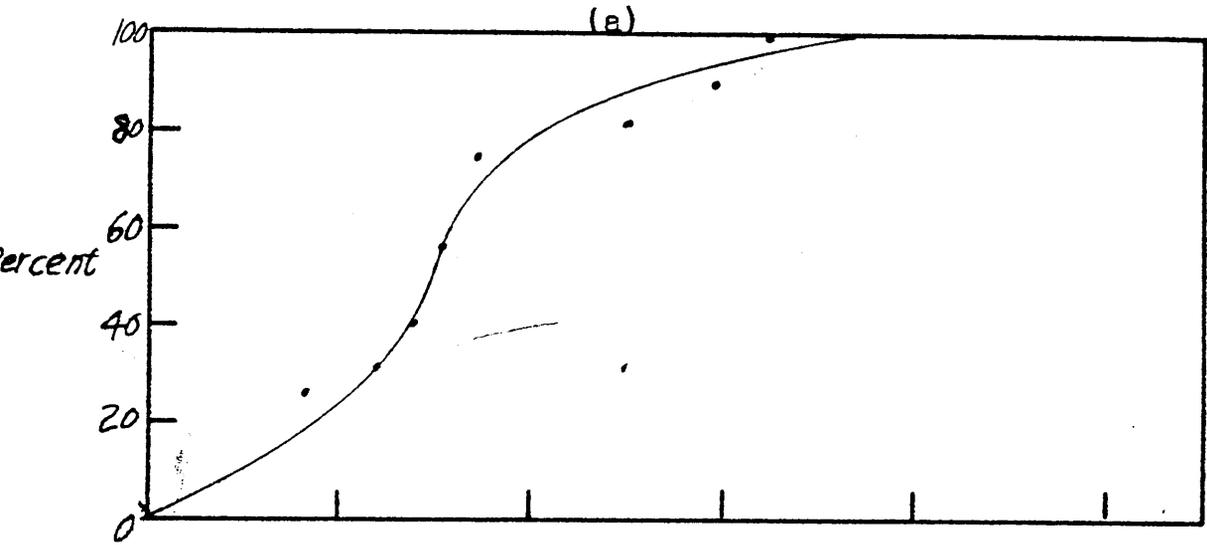


TABLE V

FRACTIONATION OF BLEND 10 AND FRACTION 5

<u>Sample</u>	<u>Weight Solution (grams)</u>	<u>ml. Water Added</u>	<u>Type of Gel</u>	<u>Per-Cent Ppt.</u>	<u>Degree Poly.</u>
B10I	1000	240	Soft*	9.3	295
F5I	1000	270	Soft	45.7	1194
B10II	1185	10	Hard	10.3	324
F5II	1216	12	Soft	19.9	174
B10III	1179	11	Hard	9.8	250
F5III	1217	12	Hard	8.9	157
B10IV	1176	12	Hard	14.1	172
F5IV	1209	10	Hard	2.4	151
B10V	1171	14	Soft	16.4	157
F5V	Evaporated			24.5	91
B10VI	1168	13	Hard	9.0	139
B10VII	1171	15	Hard	5.0	120
B10VIII	Evaporated			26.0	84
Refractionation of F5I:					
F5Ia	443	114	Soft	17.5	206
F5Ib	532	3.5	Hard	10.4	204
F5Ic	523	4.5	Hard	6.3	194
F5Id	520	6.0	Hard	3.4	178
F5Ie	Evaporated			6.7	130

* A soft gel was one which would flow down the sides of the flask while the supernatant liquid was being decanted; A hard gel would not flow down the sides of the flask.

TABLE VI

COMPOSITION OF BLENDS

Blend	Calculated			Found	
	Frac- tion	Per- cent	Degree Poly.	Per- cent	Degree Poly.
1	1	26	349	17.1	353
	2	14	274	16.1	302
	3	8	248	10.6	271
	4	3	212	7.2	208
	5	5	186	6.9	153
	6	1	130	1.9	126
	7	1	109	5.5	97
	8	42	64	34.7	43
	Average		184	Average	194
2	1	35	349	14.2	443
	2	2	274	11.5	274
	3	2	248	9.3	236
	4	4	212	15.9	229
	5	4	186	6.1	164
	6	10	130	12.5	112
	7	6	109	1.6	91
	8	37	64	2.9	80
	Average		192	Average	186
3	1	8	349	8.0	352
	2	4	274	6.4	341
	3	8	248	9.4	238
	4	8	212	5.2	192
	5	46	186	18.0	175
	6	6	130	16.1	155
	7	10	109	14.2	120
	8	11	64	3.4	107
	Average		187	Average	184
4	1	1	349	2.5	309
	2	2	274	8.4	290
	3	12	248	10.4	249
	4	24	212	8.9	231
	5	49	186	18.9	183
	6	7	130	18.6	168
	7	3	109	12.3	148
	8	2	64	3.0	114
	Average		193	Average	190

TABLE VI con't.

Blend	Calculated			Found	
	Frac- tion	Per- cent	Degree Poly.	Per- cent	Degree Poly.
5	1	11	349	17.8	346
	2	6	274	14.8	273
	3	9	248	13.3	202
	4	8	212	11.3	154
	5	29	186	7.0	134
	6	15	130	8.0	124
	7	11	109	4.0	112
	8	11	64	23.7	65
		Average		187	Average
6	1	36	349	30.7	339
	2	5	274	11.3	295
	3	5	248	6.9	246
	4	2	212	5.1	175
	5	2	186	6.9	124
	6	1	130	5.6	93
	7	17	109	33.5	36
	8	33	64		
		Average		192	Average
7	1	0	349	10.5	301
	2	3	274	9.0	253
	3	23	248	17.6	222
	4	32	212	4.5	218
	5	19	186	14.4	186
	6	6	130	1.3	177
	7	9	109	8.7	162
	8	8	64	3.8	139
				4.4	130
			2.8	103	
			23.0	76	
	Average		191	Average	175
8	1	0	349	17.3	286
	2	0	274	19.0	259
	3	47	248	18.8	227
	4	13	212	11.4	181
	5	17	186	8.5	173
	6	5	130	2.8	152
	7	8	109	3.0	129
	8	9	64	19.2	91
		Average		197	Average

TABLE VI con't

<u>Blend</u>	<u>Calculated</u>			<u>Found</u>	
	<u>Frac- tion</u>	<u>Per- cent</u>	<u>Degree Poly.</u>	<u>Per- cent</u>	<u>Degree Poly.</u>
9	1	0	349	24.4	276
	2	2	274	22.7	229
	3	43	248	16.1	192
	4	14	212	8.8	161
	5	17	186	3.5	145
	6	6	130	3.1	111
	7	9	109	21.5	87
	8	9	64		
		Average		197	Average
10	1	6	349	10.3	324
	2	3	274	9.3	295
	3	6	248	9.8	250
	4	6	212	14.1	172
	5	31	186	16.4	157
	6	33	130	9.0	139
	7	15	109	5.0	120
	8	5	64	26.0	84
		Average		176	Average

DISTRIBUTIONS WITHIN THE FRACTIONS

It was realized from the beginning of this investigation that the method of fractionation used to prepare the fractions and to analyze the blends did not give a clean-cut separation according to chain length. It was thought that each fraction contained a relatively narrow band of chain lengths as compared to the wide distribution of the original material (Graph II). However, fractionation of the first six fractions indicated a greater heterogeneity than expected. The last two fractions having an average D. P. of 109 and 64 were not fractionated because the method used to analyze the blends did not satisfactorily fractionate chain lengths of less than 80 glucose units. An example of the proportions of non-solvent to weight of solution is given in Table VI where the values for Fraction 5 are listed in detail. Each fraction and blend had to be handled as a separate problem in fractionation and could not be fractionated according to any previously determined proportions. The results of this analysis of the fractions are listed in Table VII and are shown graphically in Graphs XIV through XVIII.

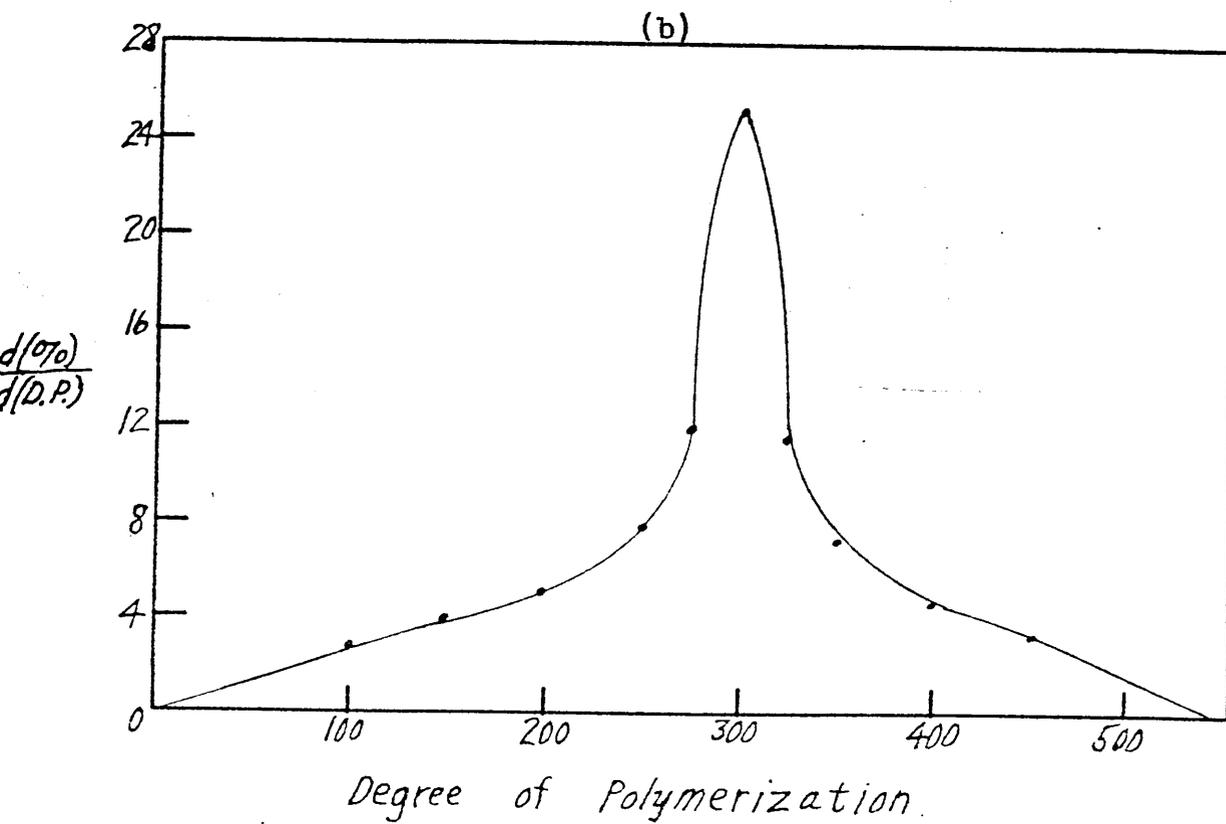
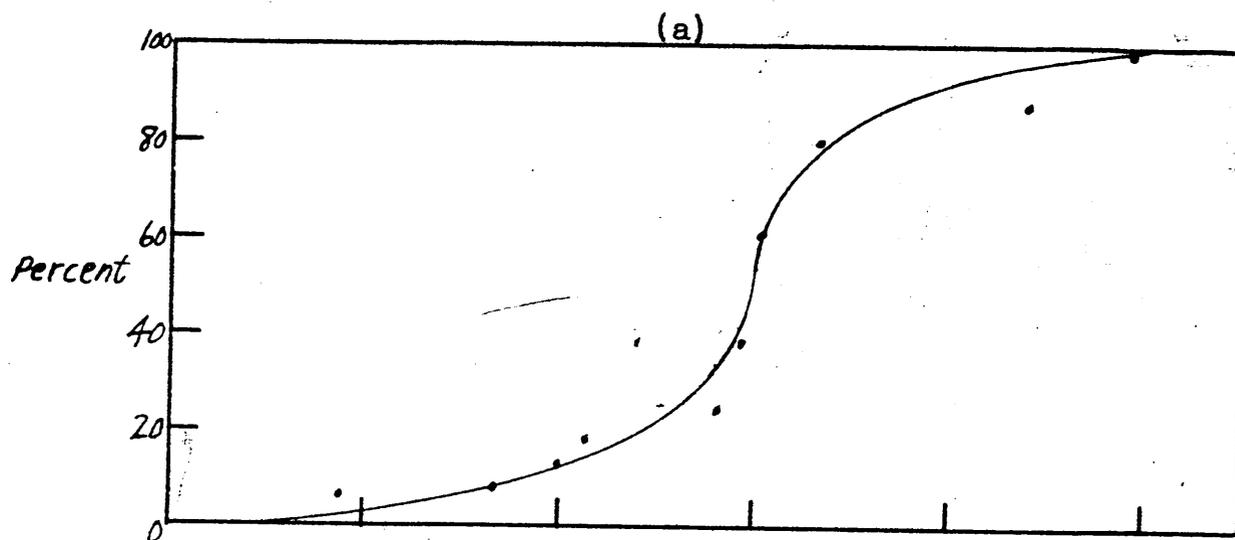
TABLE VII

EXPERIMENTALLY DETERMINED COMPOSITION OF FRACTIONS					
<u>Frac-</u> <u>tion</u>	<u>Per-</u> <u>cent</u>	<u>Degree</u> <u>Poly.</u>	<u>Frac-</u> <u>tion</u>	<u>Per-</u> <u>cent</u>	<u>Degree</u> <u>Poly.</u>
1	11.8	492	2	12.0	379
	8.1	440		32.6	340
	18.9	335		17.8	276
	22.6	305		11.4	243
	12.6	297		7.0	222
	6.6	283		8.1	135
	6.2	214		11.2	100
	4.8	200			
	1.4	166			
	6.9	88			
3	12.0	341	4	11.7	281
	6.4	301		4.3	252
	32.0	278		33.3	219
	2.8	266		13.3	209
	13.6	250		2.0	202
	9.6	211		9.5	193
	6.5	183		7.1	171
	2.7	162		5.5	135
	2.1	139		13.3	83
	12.3	98			
5	17.5	206	6	14.5	162
	10.4	204		21.4	146
	6.3	194		15.1	134
	3.4	178		10.0	114
	19.9	174		10.3	113
	8.9	157		28.8	92
	2.4	151			
	6.7	130			
24.5	91				

Graph XIV

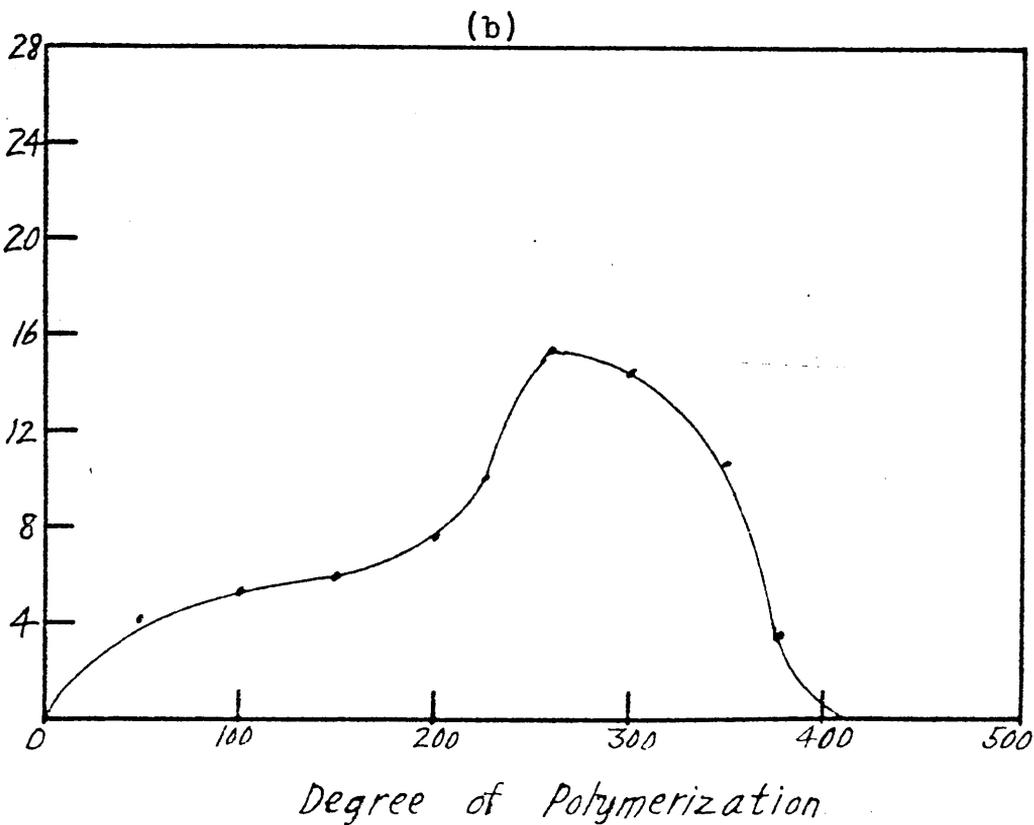
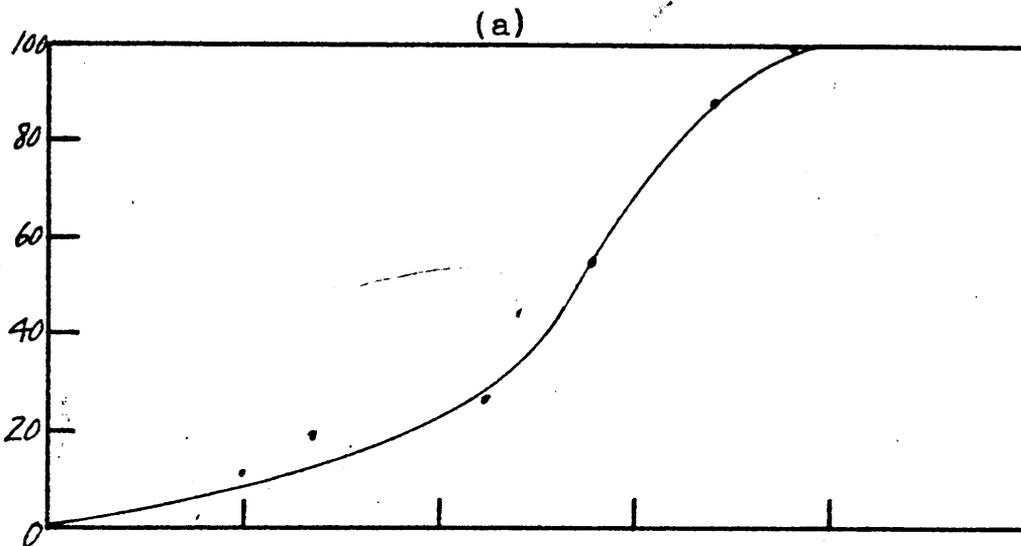
FRACTION 1

- (a) Integral Distribution
- (b) Differential Distribution



Graph XV
FRACTION 2

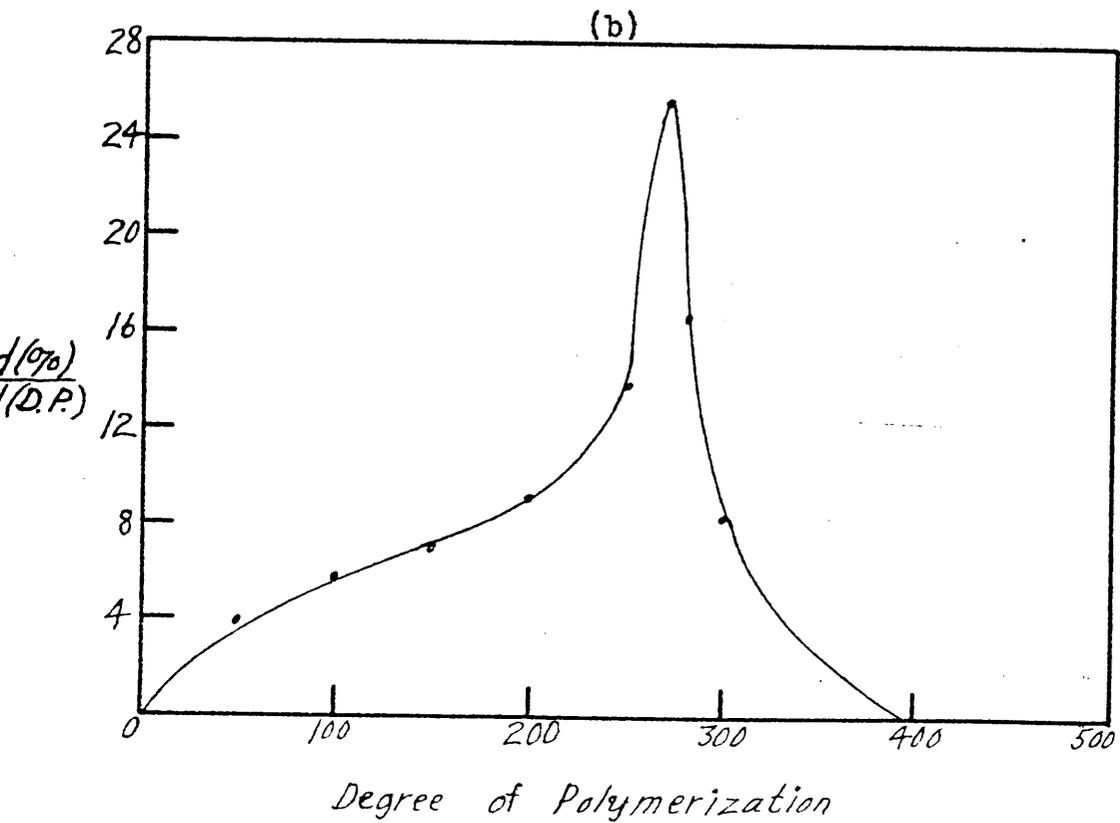
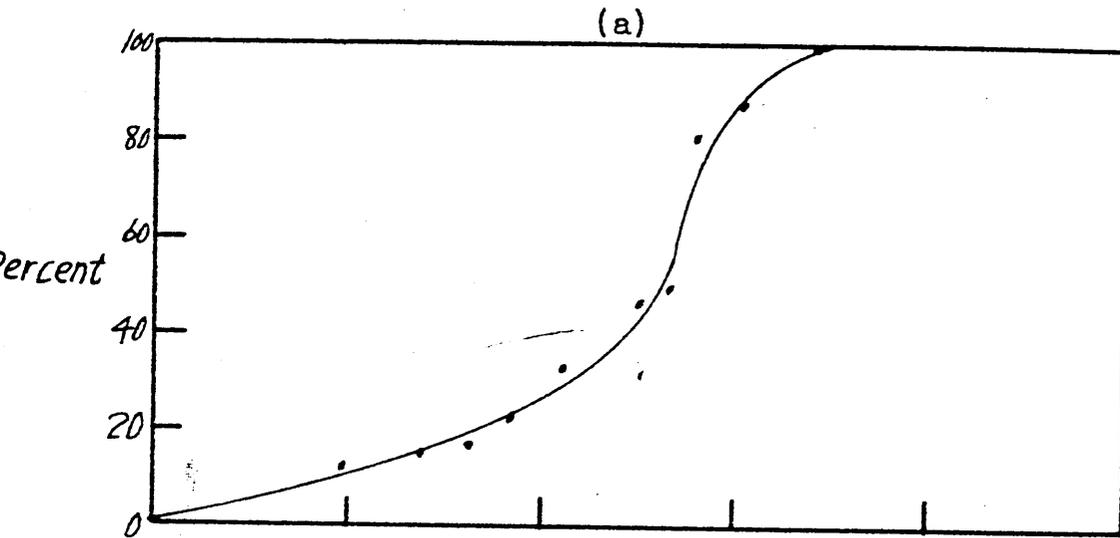
- (a) Integral Distribution
- (b) Differential Distribution



Graph XVI

FRACTION 3

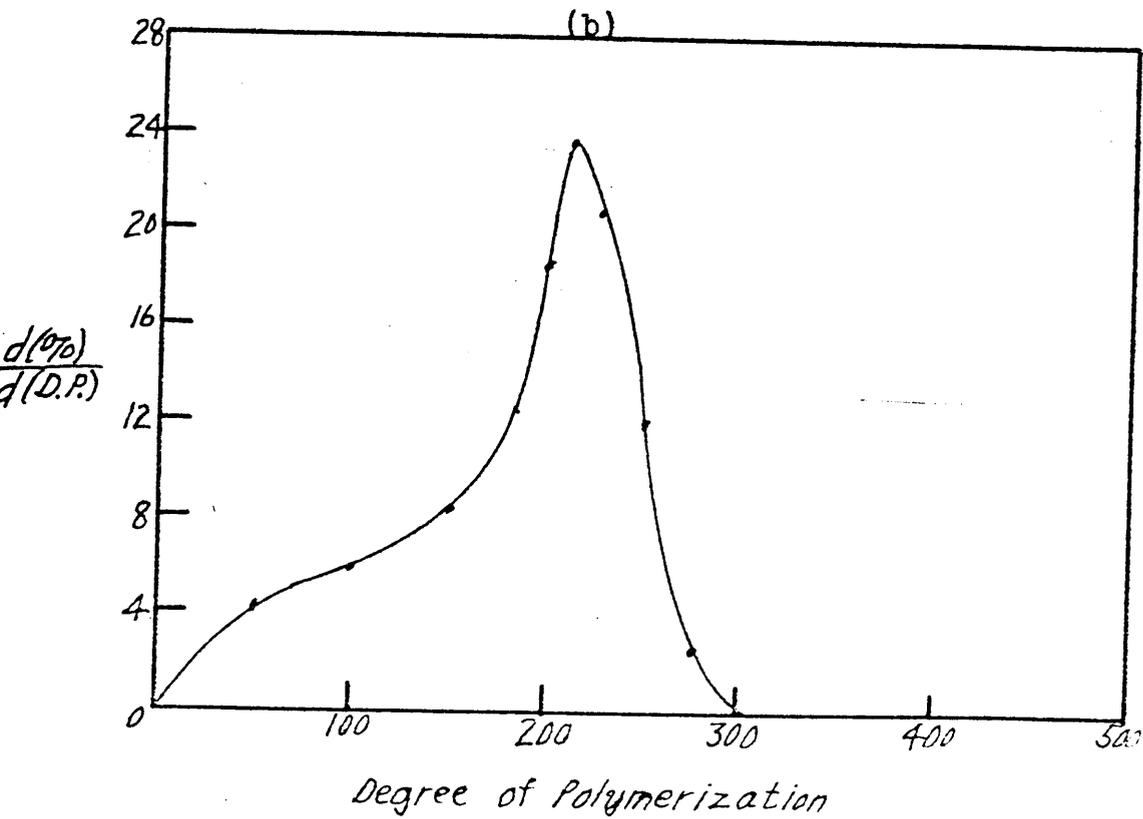
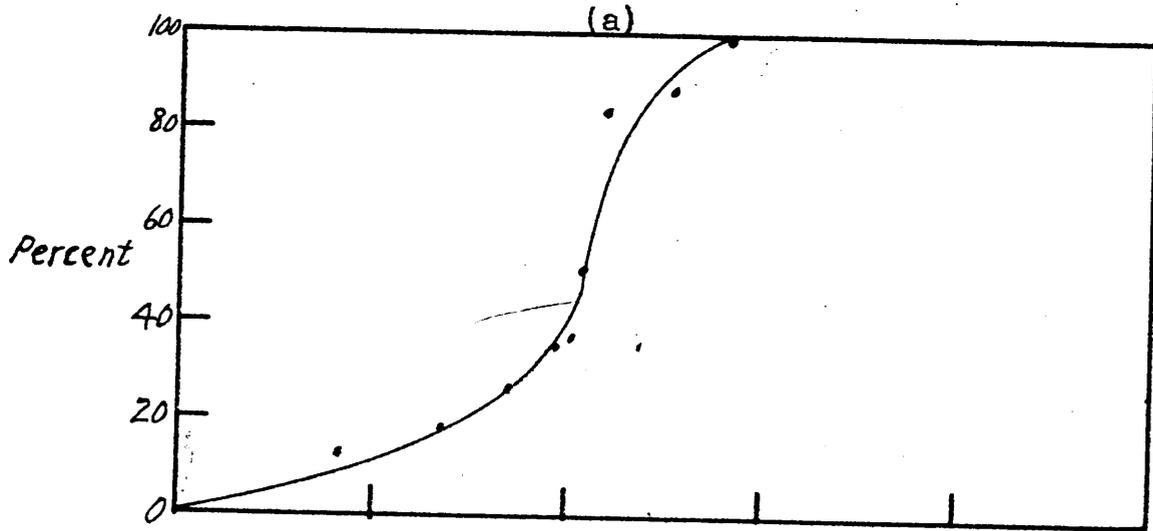
- (a) Integral Distribution
- (b) Differential Distribution



Graph XVII

FRACTION 4

- (a) Integral Distribution
- (b) Differential Distribution

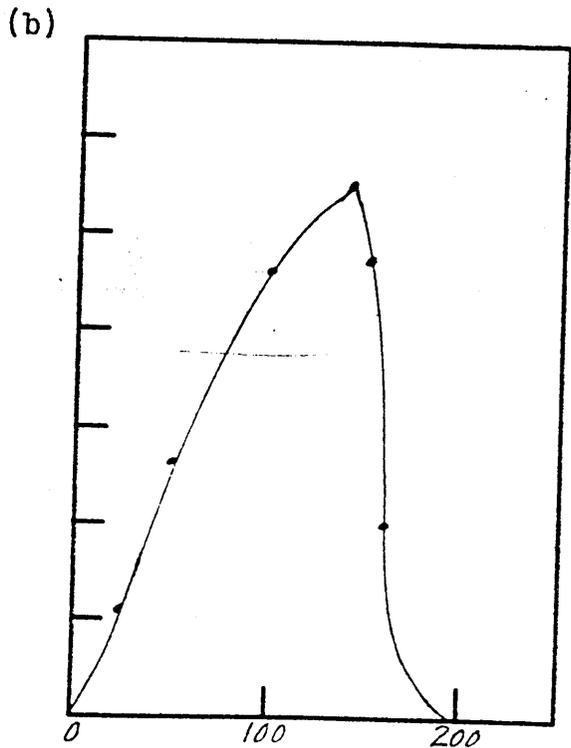
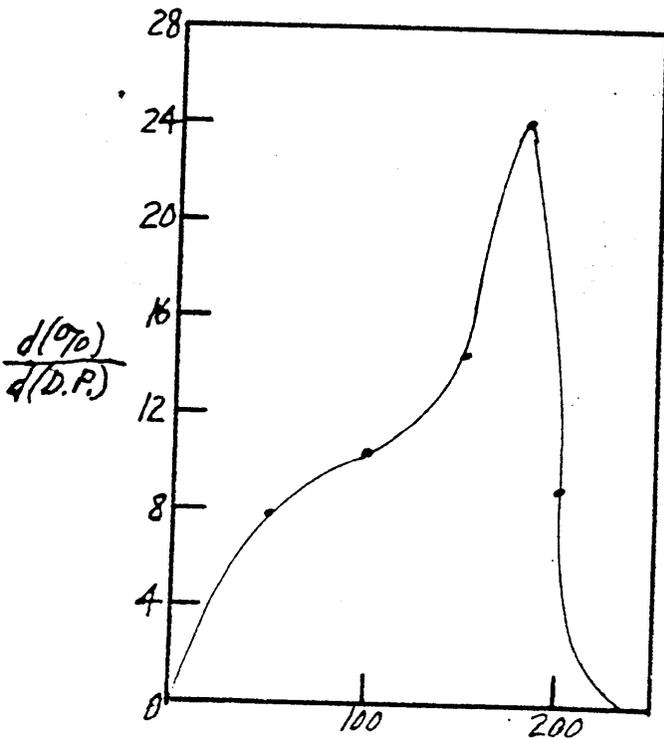
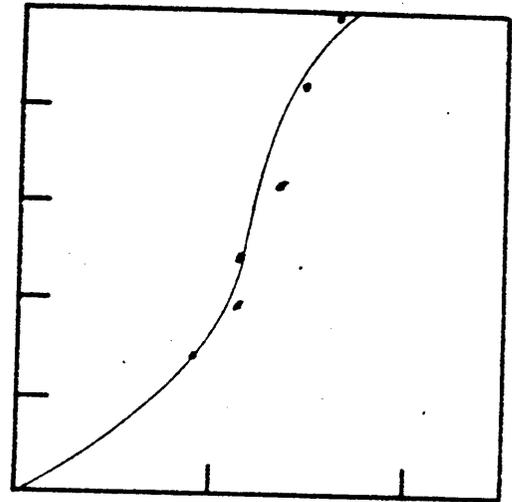
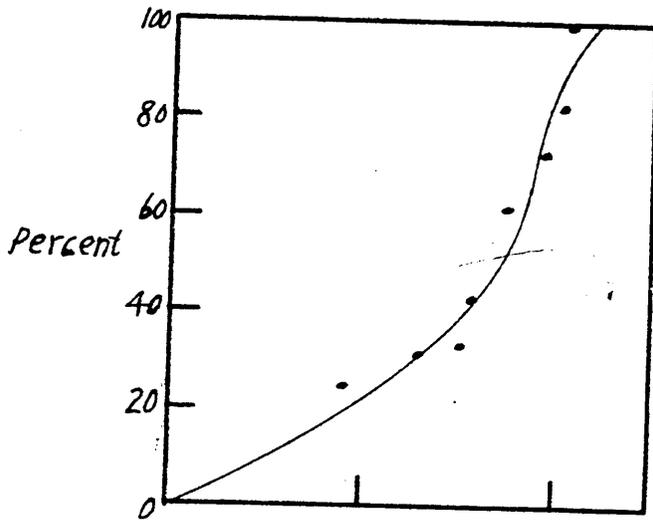


Graph XVIII

FRACTION 5

FRACTION 6

- (a) Integral Distribution
- (b) Differential Distribution



Degree of Polymerization

CORRELATION OF THE MECHANICAL PROPERTIES WITH THE SHAPE OF THE DISTRIBUTION CURVES

Since each blend and fraction had its own peculiarly shaped distribution curve, it was evident that the development of a mathematical equation to express the various distributions would be very difficult if at all possible; therefore, attempts were made to correlate the data in a graphical form. A simple way of doing this is shown in Graph III where the properties are plotted against the average D. P. of the fractions; however, these graphs give no indication of the distributions or heterogeneity within each fraction. The problem became one of finding some way of characterizing the shape of the different distribution curves by one or two sets of numbers.

An attempt was made to express the average width and sharpness of the curve by two numbers derived in the following manner from normalized differential distribution curves. The horizontal and vertical values of points of intersections of the normalized distribution curves and radii at 15° intervals, drawn from the base line at the D. P. of the maximum height, were averaged and called width and sharpness. No constants could be found which would normalize these values and those of the properties for plotting on triangular graph paper. Attempts were made to plot these values on logarithmic and ordinary graph paper with the value of the property being a third number

measured along the line drawn from the intersection of the width and sharpness to the origin. Some modifications of this method of characterizing the curves were also tried without success.

A study of the mechanical properties of the blends showed that there was some correlation with the height of the maximum and with the location of the maximum. The fact that less heterogeneity gives better properties is shown by comparing fraction 5 with the original material, and when blend 4 is compared with this same fraction it is noted that fraction 5 has the better properties. Examination of the distribution curves shows that the maximum of fraction 5 is higher and much narrower than that of blend 4, and that the curve for the original material is very broad and flat. Comparison of some of the other fractions and blends will show differences in properties even though their average D. P. and the position of the maximum may be the same. The sharper or more narrow the maximum the less heterogeneity within the sample and the better the properties.

Theoretically the differential distribution curve of a cellulosic substance containing chains of the same length would be a vertical line. When some material of slightly different chain length is added, the curve changes from a single line to a pencil-like curve. As more and more varied chain lengths are added the curve widens out and the maximum may drop. Thus any

measurement of the ratio of the width of the curve to the height of the maximum would represent the heterogeneity with the sample. On the basis of this reasoning it was decided to determine the average width of the curve and to calculate the ratio of average width to height of maximum; this ratio was called the heterogeneity factor.

All of the differential distribution curves are very broad at the base and some are still rather broad at about half of the height of the maximum. Since the success of this method of characterizing the curves depended upon the width of the peak rather than the width of the base more measurements of the width were taken up in the peak. Therefore, they were made at 0.9, 0.8, 0.6, 0.4, and 0.2 of the height and when added and divided by 5 the average width of the curve was obtained. This number was then divided by the maximum height to give a measure of the heterogeneity. All readings were taken from curves drawn to the same scale, which was about twice that used to prepare the graphs shown in this report.

Attempts at plotting these values on coordinate, logarithmic, and semi-logarithmic paper showed that the correlation of properties was better when the heterogeneity was plotted on the logarithmic scale, the D. P. of the maximum along the coordinate scale, and the properties measured in centimeters along the line drawn from the point of intersection and the

origin. However, three values were being plotted on two axis paper so these points had no real meaning. Since the lines drawn from the points of intersection and the origin represented the ratio of heterogeneity to D. P. of the maximum, this ratio was determined mathematically by dividing the logarithm of the heterogeneity by the D. P. of the maximum. This ratio was plotted against the values of the properties on coordinate paper and the points were grouped so that smooth curved lines could be drawn through them.

It is noted that the differential distribution curves for blends 1, 2 and 6 have two peaks which indicates large quantities of low and of high D. P. material were used to make these blends. Thus these are the result of merging two separate distributions. The mathematical characterization of these two curves was done in much the same manner as for the single peaked curves in that each peak was treated as a separate curve. The two logarithms of heterogeneity were added which is another way of multiplying the probabilities expressed by the "two" distributions. Since two maxima existed the average D. P. was obtained by dividing the difference in D. P. by two. The calculation of these values for blend 6 is given below as sample calculation of the characterization of the curves.

Height of Maximum	16	22.3
D. P. of Maximum	20	280

Measurements of width were taken at:

0.9 x 16 = 14.4	23	0.9 x 22.3 = 20.07	24
.8 x 16 = 12.8	32	.8 x 22.3 = 17.84	34
.6 x 16 = 9.6	53	.6 x 22.3 = 13.38	42
.4 x 16 = 6.4	85	.4 x 22.3 = 8.92	68
.2 x 16 = 3.2	<u>164</u>	.2 x 22.3 = 4.46	<u>116</u>
	357		284

$$357 \times 1/5 = 71.4 \text{ avg. width}$$

$$284 \times 1/5 = 56.8 \text{ avg. width}$$

$$\frac{71.4}{16} = 4.4625 \text{ Heterogeneity}$$

$$\frac{56.8}{22.3} = 2.547 \text{ Heterogeneity}$$

$$\frac{280 - 20}{2} = 130 \text{ D. P. of Maximum}$$

$$\log 2.547 = 0.4060$$

$$\log 4.463 = \frac{0.6496}{1.1556}$$

$$\frac{130}{1.1556} = 113 = \text{Shape Factor}$$

The essential measurements and calculated values for characterizing the 17 distributions tested in this investigation are listed in Table VIII.

An attempt was made to locate the lines through the points in Graph XIX mathematically according to the method of averages (10) by plotting these same values on logarithmic paper. The logarithm of the shape factor and properties were averaged; the constants in the equation $\log y = \log a + b \log x$ were determined; and the straight line constructed. The coordinates of this line were transferred to the regular graph paper and a

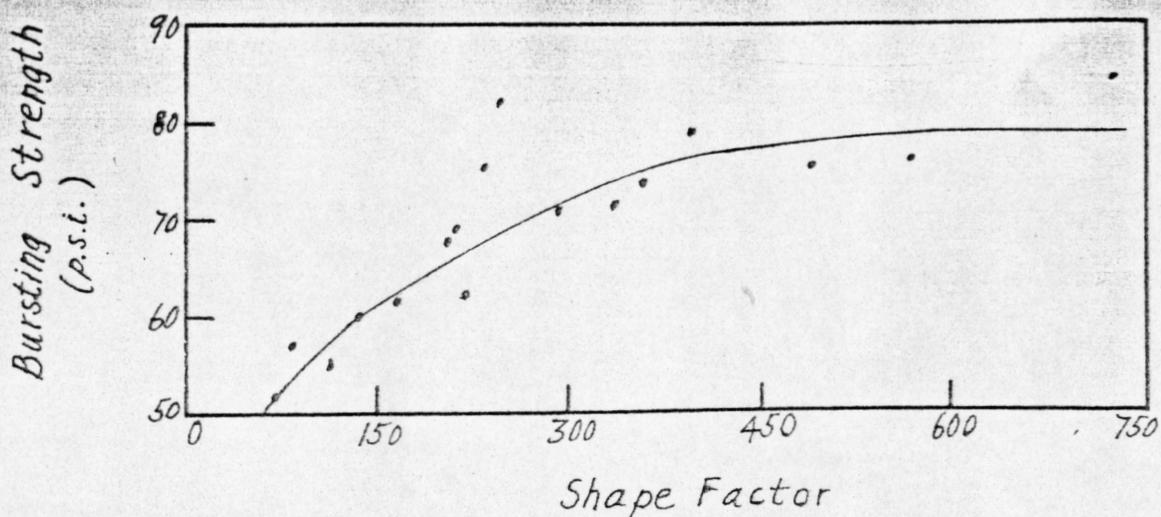
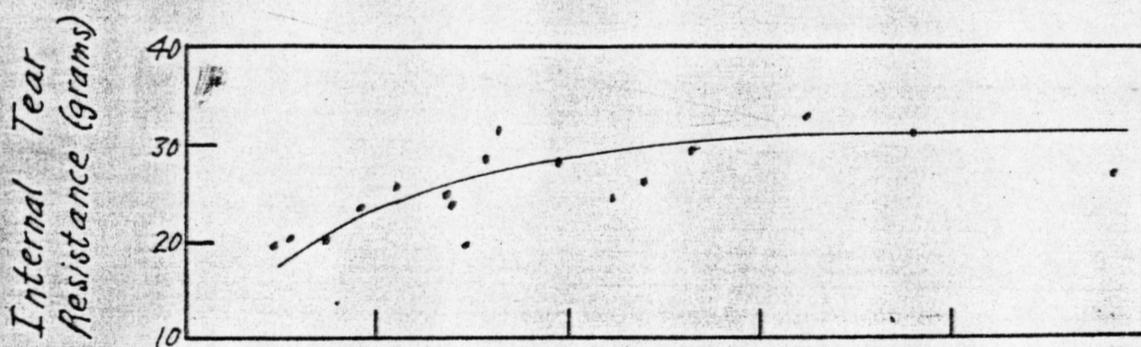
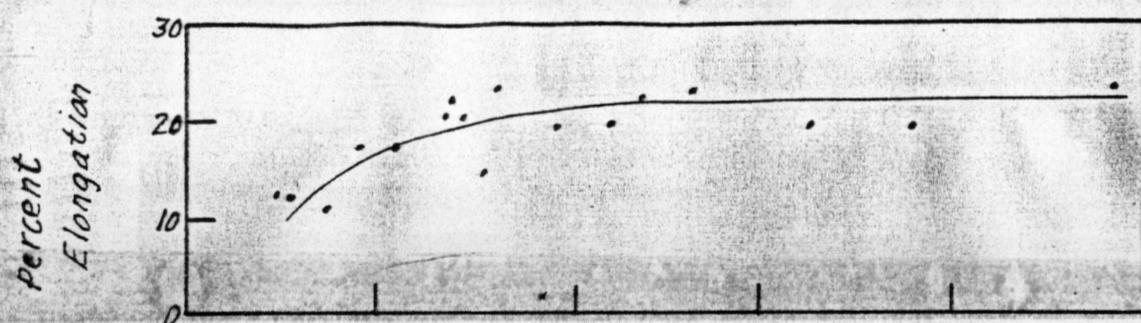
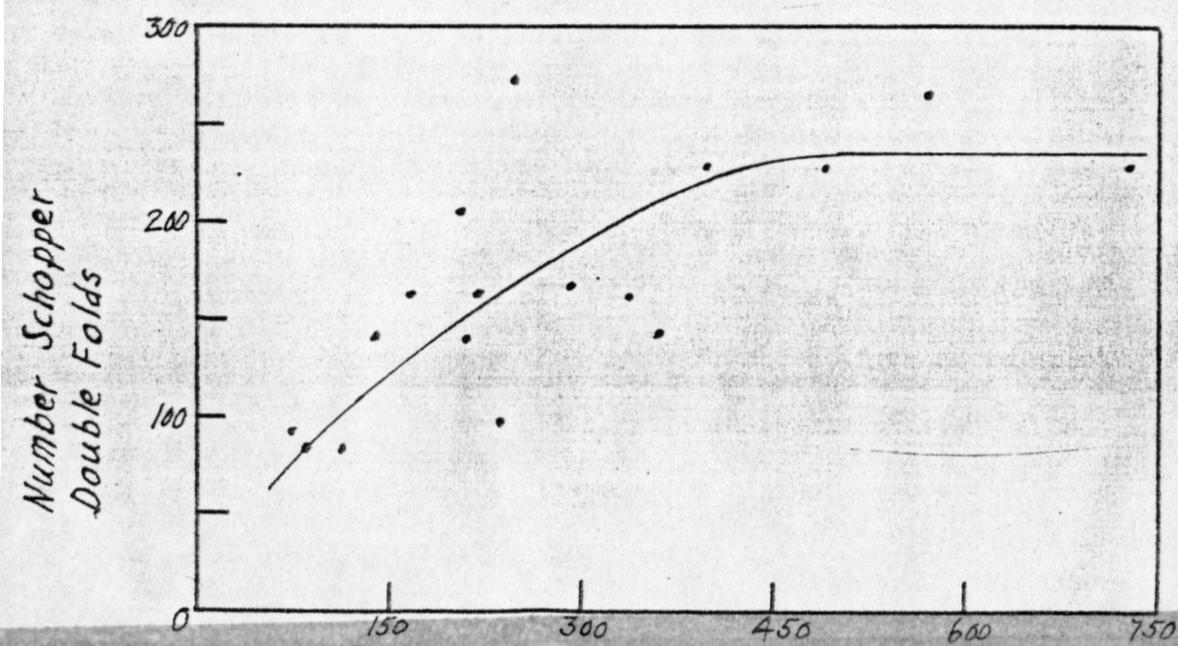
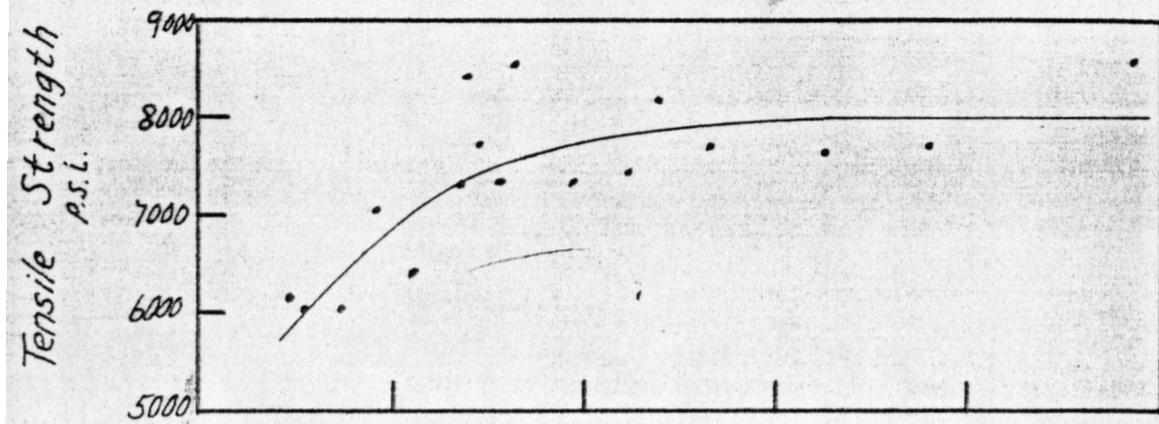
TABLE VIII

DATA FOR CHARACTERIZING THE DISTRIBUTION CURVES

<u>Sample</u>	<u>Height of Max.</u>	<u>D. P. of Max.</u>	<u>Avg. Width</u>	<u>Width Height</u>	<u>Log. Heter.</u>	<u>Shape Factor</u>
F 1	25.1	300	64.8	2.582	0.4119	728
F 2	15.4	260	173.4	11.260	1.0515	247
F 3	25.5	270	75.8	2.973	0.4731	571
F 4	23.8	210	80.6	3.387	0.5297	397
F 5	24.5	180	57.0	2.326	0.3666	491
F 6	22.2	140	87.4	3.940	0.5951	235
Original	14.4	200	238.0	16.527	1.2182	164
B 1	14.3	280	112.4	7.860	0.8954	
	13.0	20	109.0	8.384	0.9235	72
B 2	16.7	225	121.5	2.586	0.4125	
	15.2	12	39.3	7.275	0.8618	85
B 3	21.0	150	101.0	4.809	0.6821	220
B 4	21.0	180	87.0	4.143	0.6163	292
B 5	17.3	130	144.0	8.323	0.9203	141
B 6	22.3	280	56.8	2.547	0.4060	
	16.0	20	71.4	4.463	0.6496	113
B 7	17.1	200	158.0	9.239	0.9656	207
B 8	20.7	250	116.0	5.603	0.7484	334
B 9	22.2	230	97.0	4.369	0.6404	359
B 10	20.6	150	107.0	5.195	0.7156	210

smooth curve drawn through the points. This curve did not level off for the high values and neither could it be extrapolated to zero within the experimental range. Both of these requirements must be met if the line is to follow the experimental data as shown in Graph III where all of the physical properties become nearly constant when the average D. P. is about 200 or above and the lower end of the line indicates a rapid decrease in mechanical properties. The method of least squares (10) was also tried by first plotting the values on logarithmic paper and solving for the constants in equation $y = a + bx$ and drawing the straight line on the logarithmic paper as before. When these coordinates were transferred a curved line was drawn through the points but again the theoretical requirements of the curves were not met. The curves in Graph XIX are the best which could be drawn by visual inspection and they show that there is a correlation between the mechanical properties of ethyl cellulose films and the shape of the distribution curves.

Correlation of Mechanical Properties of Ethyl Cellulose Films with Shape of Distribution Curves



Shape Factor

DISCUSSION OF RESULTS

Comparison of the average degree of polymerization of the fractions obtained from a five gallon batch, Table I, with the average D. P. of the composites of the eight fractions as listed in Table IV shows that the fractionation procedure used gives reproducible results. The ethoxyl content was found to be the same for all the fractions so the degree of substitution did not enter into the separation. Examination of Graphs XIV through XVIII shows that this original fractionation was not very sharp especially on the low D. P. side (the curves are skewed to the right) which means that there was considerable enmeshing of short chains within the longer ones during the period of coalescence and settling. Fraction 1, which was refractionated in the original procedure, shows a sharper distribution than do the others. The method of fractionating the blends and fractions gave a cleaner separation of the chain lengths than that obtained in the original procedure as will be explained later.

Examination of Table IV and Graph III shows that there is an improvement of mechanical properties of the films with an increase in the average D. P. of the fractions from 64 to about 200. Above this the properties remained nearly constant within the D. P. range tested. Extrapolation of the lower end of these curves indicates that the property in question would not be

measureable should the average D. P. fall below 50. These curves follow the general shape of those experimentally determined by Bass and Kauppi (2), who also worked with ethyl cellulose, by Sookne and Harris (50), who worked with cellulose acetate, and by Spurlin (51), who fractionated and tested half-second cellulose nitrate. This lower limit at which mechanical properties are measureable falls within the limits of 40 to 80 predicted by Mark (33, 34a).

It is noted in Graph III that the mechanical properties of the original material fell below that of the fractions of the same or higher average D. P., and that only the last fraction with an average D. P. of 64 had poorer values for all the properties than did the original material. This corresponds to the findings of Sookne and Harris (50) that the fractions had better mechanical properties than the original material. The Schopper fold and internal tear resistance values for the first fraction fell below the maximum although it had the highest average D. P. probably because of the impurities present in that fraction. These impurities, which gave the dried material a slightly greyish color, were enmeshed during the formation of the aggregates and could not be removed by washing with water.

The poor mechanical properties of the 64 D. P. material show very clearly the lack of flexibility and strength in material composed of short chains. Some of this brittleness may also be

due to the accumulation of impurities in this residue fraction and also to any degradation products formed during the evaporation.

In the D. P. range tested the adhesion between the chains was sufficient to give appreciable tensile strength, internal tear resistance, and bursting strength to the films. However, those properties which in some way test the brittleness of the material, the elongation, and folding endurance were greatly affected by the decrease in average chain length from 212 to 64.

An examination of Table V shows that the experimentally determined composition of the blends agreed very closely with the calculated composition which is what Douglas and Stoops (11) found when blending vinyl ester resins. Except for Blends 1, 2, and 6 the percentage of experimentally determined low D. P. material exceeded that theoretically put in the blend. This is taken as another indication of the enmeshing of the low D. P. material with the long chains and the accumulation of the short chains from all of the original fractions used in the blend. This also indicated that a sharper separation of the chain lengths was obtained when using a 1.5% rather than a 3% solution of ethyl cellulose. Blends 1, 2, and 6 contained large amounts of both 64 and 349 D. P. material so that a two-peak distribution was obtained with these blends although the average D. P. was the same as for the other blends.

A practical and rather simple method of characterizing the shape of the distribution curves was developed when it was observed in Graphs II, IV-XIII, and XIV - XVIII, that Fractions 1, 3, 4, and Blends 3, 4, 8, 9, 10 had the better properties and that the peaks of their maxima were a little higher than those of the other fractions and blends. It was also noted that when the D. P. of the maximum was 180 or better the values of the properties were a little higher. Fraction 5 had better properties than the original material and Blend 4 although the average D. P. was the same. Examination of Graphs II, VII, and XVII showed that Fraction 5 was more homogeneous in its composition than the original material and that it had a sharper peak than Blend 4. The average width of the curves was determined and the ratio of width to height of maximum calculated and called the "Heterogeneity". The ratio of the D. P. of the maximum to the logarithm of the "Heterogeneity" gave a number which was called the "Shape Factor".

Some of the pertinent data has been collected from preceding tables and summarized in Table IX in order to make correlation of the curve characteristics and mechanical properties a little easier. All blends or fractions having the same average D. P. are grouped together and are compared with members of the same group so as to eliminate the effect of increasing D. P. upon the physical properties.

TABLE IX

CURVE CHARACTERISTICS AND PHYSICAL PROPERTIES

	Avg. D. P. 190				Avg. D. P. 183		
	B 4	B 5	B 8	B 9	Orig.	F 5	B 3
Height	21	17.3	20.7	22.2	14.4	24.5	21.0
D. P. of Max.	180	130	250	230	200	180	150
Avg. Width	87	144	116	97	238	57	101
% D.P. below 91	16.9	23.7	19.2	21.5	24.7	24.5	19.4
Tensile Str.	7360	7040	7470	8200	6440	7670	7740
% Elongation	19.7	17.4	19.7	22.2	17.2	19.5	20.6
Folding Endur.	166	142	163	142	163	229	164
Internal Tear	28.0	23.5	24.5	26.0	25.5	32.5	17.7
Bursting Str.	70.9	60.1	71.4	74.2	61.7	75.7	62.6

In Table IX it is observed that Blend 9 has, except for Schopper
 Folds, the best mechanical properties in the 190 D. P. group, and
 that it has the greatest maximum height, second highest D. P. of
 the maximum, next to smallest average width, and next to the great-
 est amount of low D. P. material. In the 183 D. P. group, Frac-
 tion 5 has the better properties, highest maximum, narrowest
 average width, and next to greatest amount of low D. P. material.
 It is noted that there is no direct correlation between the amount
 of low D. P. material and the physical properties when the average
 D. P. is held constant which in part contradicts the conclusion
 reached by Mark (34a), "The shape of the distribution curve seems
 to have no definite effect on the ultimate strength except that
 a comparatively small amount (between 10 and 15 per cent by

weight) of constituents having a polymerization degree below 150 are definitely detrimental to the mechanical properties of the sample." Study of Tables IV, V and VII gives a broader view and supports the conclusion that the amount of low D. P. material (91 or below) has to equal about 30% of the total weight before it appreciably lowers the mechanical properties.

It has already been pointed out and is observed again in Table IX that the average width of the distribution curve does have some effect on the physical properties as noted with the original material, Blend 5 and Fraction 5. There is also some correlation between the position and height of the maximum and the properties; these characteristics of the curves determine their shape which in turn has a definite effect on the ultimate strength and this is another contradiction of Mark's statement as quoted above. Spurlin (51a) also states that "the optimum physical properties may be obtained by increasing the molecular weight regardless of the degree of polymolecularity; the degree of polymolecularity is then not an important consideration." However, when these characteristic properties of a distribution curve are combined and plotted against the five mechanical properties as in Graph XIX the effect of the shape of the distribution curve upon the mechanical properties becomes very apparent.

The smooth lines drawn through the points in Graph XIX give the best correlation between the shape of the distribution curves

and the mechanical properties that has been developed to date. It is realized that the correlation is not so good in the case of the folding endurance test and that the correlation of tensile strength with the shape factor could be greatly improved. At the same time it is noted that only seventeen distribution curves have been so characterized and that this is too few to give a complete picture of the correlation. However, a start has been made and some conclusions can be drawn from these curves.

In Graph XIX it is observed that the properties improve as the shape factor increased up to a value of 450 except for the elongation which leveled off at 375. These curves are similar to those observed in Graph III, but in this case more than the average D. P. is considered since four of the blends (4, 5, 8, and 9) have the same average D. P. Combined in the shape factor is the "heterogeneity" of the material and the D. P. of the maximum.

The effect of polymolecularity is especially noticeable in the correlation of Schopper Folds with the "shape factor" in Graph XIX, particularly in Blends 1, 2, and 6 which contain large quantities of both high and low D. P. material; yet according to the average D. P. of the sample the number of folds should have been 80 to 100 higher. Sookne and Harris (50) noted this same sensitiveness of fold resistance to the molecular heterogeneity, and Spurlin (51) found that when the distribution curve contained

two peaks only about half of the expected number of Schopper Folds were obtained.

Examination of Table IV shows the percent elongation, tensile strength, and bursting strength are also sensitive to this heterogeneity, while the internal tear resistance of Blends 1, 2, and 6 is nearly the same as for the other blends. From the values of the "shape factor" given in Table VIII and an examination of Graph XIX, it is noted that these three blends fall along the lower ends of the curves. The fact that these two-peak blends fit into the curves of Graph XIX so well is good evidence that the method of characterizing the shape of the distribution curves developed during this investigation is theoretically sound. However, until more families of distribution curves are similarly studied Alfrey's (1a) statement that the strength properties "are almost entirely controlled by the gross features of the molecular weight distribution curve, rather than by fine details" is still the best generalization that can be made.

CONCLUSIONS

1. Fractionation of ethyl cellulose solutions in five gallon batches has been controlled so as to give reproducible results according to the average degree of polymerization.
2. The mechanical properties of the films improved with increasing D. P. of the fractions up to 200-250 and then exhibited little improvement for any further increase in the average degree of polymerization. By neglecting the effect of shape of distribution curves, the mechanical properties may be predicted when the average degree of polymerization is known.
3. It is possible to prepare and to test films prepared from ethyl cellulose having an average D. P. of 64 which is in the D. P. range where it was predicted the mechanical properties could not be measured.
4. It is necessary to refractionate the fractions in order to reduce the polymolecularity within the fraction.
5. Prediction of the mechanical properties depends upon three factors, the average D. P. of the material, the D. P. of the maximum, and the polymolecularity.
6. When the average degree of polymerization is held constant (below 200-250), prediction of the mechanical properties depends upon the polymolecularity and D. P. of the maximum.

7. The correlation so far obtained limits predictions to a few generalizations.

There is no direct correlation between the amount of low D. P. material (D. P. of 100 or less) and the mechanical properties when the average D. P. of the samples is the same until about 30% of the total weight has been added.

When the average D. P. and the position of the maxima are the same, the sample with the sharper peak will have the better properties.

A shift of the maximum to a higher D. P. without increasing the average D. P. will not necessarily mean an improvement in the mechanical properties.

The mechanical properties depend more upon the gross characteristics of the curve than upon fine details such as smoothness and general contour.

SUGGESTIONS FOR FUTURE STUDY

1. A satisfactory method of fractionating the low D. P. residues should be developed so that this material could be further investigated and used in preparing blends.
2. The fractions need to be refractionated so as to eliminate the relatively large amounts of low D. P. material and tests run to determine the effect of this low D. P. material on the physical properties.
3. More families of distribution curves need to be studied to determine the effect of small changes upon the mechanical properties and the subsequent correlation.
4. Films of a different thickness should be prepared and tested to determine the effect of film thickness upon the correlation of properties with the shape of the distribution curve.
5. Other film-forming solvents should be investigated to determine the effect of the solvent upon the correlation of mechanical properties with the distribution.

BIBLIOGRAPHY

1. Alfrey, T., Mechanical Behavior of High Polymers, Vol. VI of High Polymers, Interscience Publishers, Inc., New York, 1948, pp 507-8.
(a) Ibid., pp 498-9
2. Bass, S. L. and Kauppi, T. A., *Ind. Eng. Chem.*, 29, 679-86 (1937); 30, 74-9 (1938)
3. Blom, A. V., *Kolloid-Z*, 61, 235-9 (1932); 65, 223-8 (1933)
4. Busse, W. F., Lessig, E. T., Loughborough, D. L., and Larrick, L., *J. Applied Phys.*, 13, 715-24 (1942)
5. Carroll, S. J., *Can. p. 374*, 698 June 28, 1938 to *Can. Kodak Co., Ltd.*
6. Carswell, T. S. and Mason, H. E., *Symposium on Plastics*, A.S.T.M., Philadelphia, 1944
7. Clark, E. P., *J.A.C.S.* 51, 1479 (1928); *J.A.O.A.C.* 15, 136-40 (1932); *ibid* 22, 622 (1939)
8. Cragg, L. H. and Hammerschlag, H., *Chem. Rev.* 39, 81 (1946)
9. D'ans and Jager, *Cellulosechem*, 6, 146 (1925)
10. Davis, D. S., Empirical Equations and Nomography, McGraw-Hill Book Co., New York 1943, pp 4-33
11. Douglas, S. D. and Stoops, W. N., *Ind. Eng. Chem.* 28, 1152-5 (1936)
12. Dreyfus, H., F.P. 462274 (1914)
13. Ethocel TF and Ethocel, Dow Coating Materials, Dow Chemical Company, Midland, Mich. 1947
14. Flory, P. J., *J.A.C.S.* 62, 1057 (1940)
15. Frey-Wyssling, A. and Muhlethaler, K., *J. Polymer Sci.* 1, 172-4 (1946)
16. Gloor, W. E., *Ind. Eng. Chem.* 27, 1163 (1935)

17. Haward, R. W., *Trans. Faraday Soc.* 38 394-403 (1942)
18. Haworth, W. W., *Helv. Chim. Acta.* 11, 547 (1928)
19. Hercules Ethyl Cellulose, Properties and Uses, Hercules Powder Co., Wilmington, Del., 1944
20. Ibid; Hercules Ethyl Cellulose, Formulations with Resins and Plasticizers, Hercules Powder Co., Wilmington, Del., 1940
21. Herzog, R. O. and Deripasko, A., *Celluloschem.* 13, 25 (1932)
22. Hess, K., Die Chemie der Zellulose und ihrer Begleiter, Akademische Verlagsgesellschaft, m.b.H., Leipzig (1928)
23. Hess, K. Tógus, C. and Schwarzkopf, C., *Z. physik Chem.*, A 162. 189 (1932)
24. Heuser, E., The Chemistry of Cellulose, John Wiley and Sons, Inc., New York, 1944
 - (a) Ibid., p 409
25. Hildebrand, J. H., Solubility of Non-Electrolytes, Am. Chem. Soc. Monograph No. 17, 2nd Ed., Reinhold, New York, 1936
26. Huggins, M. L. in Cellulose and Cellulose Derivatives, Ed. by Ott, E., Vol V of High Polymers, Interscience Publishers, Inc., New York, 1946, pp 953-5
 - (a) Ibid., p 927
27. Kodak-Pathe, F.P. 836154 Jan. 12, 1939
- 281 Leuchs, O., D.R.P. 322586 issued to Farbenfabriken vorm F. Bayer & Co., 1920
29. Lilienfeld, L., E.P. 12854 (1912)
30. Lovell, E. L. and Hibbert, H., *J.A.C.S.*, 63, 2070-2 (1941)
31. Mahoney, J. F. and Purves, C. B., *J.A.C.S.* 64, 15 (1942)
32. Mark, H., *J. Phys. Chem.*, 44, 779 (1940)
33. Mark, H. in Cellulose and Cellulose Derivatives, ed. by Ott, E., Vol V of High Polymers, Interscience Publishers, Inc., New York, 1946, pp 990-1043

(a) *Ibid.*, p 937

34. Mark, H., *Paper Trade J.*, 113, 28 (1941)
(a) *Ind. Eng. Chem.*, 34, 1343-8 (1942)
35. Marsh, J. T., and Wood, F. C., An Introduction to the Chemistry of Cellulose, D. Van Nostrand Co., Inc., New York, 1939
36. Meyer, K. H. and Lotmar, W., *Helv. Chim. Acta.*, 19, 68 (1936)
37. Meyer, K. H. and Mark, H., Aufbau der hochpolymeren organischen Naturstoffe, Akademische Verlagsgesellschaft, m.b.H., Leipzig (1930)
38. Meyer, K. H. and Misch. L., *Ber.* 70, 266 (1937); *Helv. Chim. Acta.*, 20, 232 (1937)
39. Meyer, K. H. and van der Wyk, A., *Helv. Chim. Acta.*, 20, 1313 (1937)
40. McNeer, R. D., Master's Thesis submitted to the Virginia Polytechnic Institute Faculty (1948)
41. Monsanto Plasticizers, Monsanto Chemical Co., St. Louis, 1949
42. Morey, D. R. and Tambllyn, J. W., *J. Phys. and Coll. Chem.*, 51, 721-46 (1947)
43. Ohl, F., *Kunstseide*, 12, 468 (1930)
44. Okamura, I., *Cellulosechem*, 14, 135 (1933)
45. Ott, E., Ed., Cellulose and Cellulose Derivatives, Vol V, High Polymers, Interscience Publishers Inc., New York, 1946
46. Pfeiffer, G. H. and Osborn, R. H., in Cellulose and Cellulose Derivatives, Vol V, High Polymers, Interscience Publishers Inc., New York, 1946, pp 978-85
47. Rocha, H. J., *Kolloid-Beiheft*, 30, 230-48 (1930)
48. Rogovin, Z. and Glazman, S., *J. Applied Chem.*, U.S.S.R., 8, 1237-46 (1935) CA: 30: 6554, 7329
49. Sheppard, S. E., and Newsome, P.T., *J. Soc. Chem. Ind.*, 56, 256-61E (1937)

50. Sookne, A. M., and Harris, M., Textile Research 13, No. 3, 17-31; J. Research Nat'l. Bur. Standards 30, 1-14 (1943)
51. Spurlin, H. M., Ind. Eng. Chem., 30, 538-42 (1938) (a)
Cellulose and Cellulose Derivatives, Vol V, High Polymers, Interscience Publishers Inc., New York, 1946, pp 932-7
52. Staudinger, H., Die hochmolekularen organischen Verbindungen, J. Springer, Berlin, 1932
53. Staudinger, H. and Reinecke, F., Ann. 535, 47-100 (1938)
54. Ushakov, S. N., Shneer, I. M., Demina, E. N., Ijboldina, Ch., Rev. gen. mat. plastiques 13, 301-4 (1937); C. A. 32: 3603; Ushakov, S. N., Geller, I. M. and Demina, E. N., Plasticheskie Massy, Sbornik Statei 1939 58-69; Khim. Referat. Zhur. 1940 No. 3, 102 CA: 32: 3146
55. White, E. V., U.S.P. 2, 235, 783 to The Dow Chemical Co., March 18, 1941
56. Wiggan, D. P., Hercules Powder Company, Personal Communication
57. Zeisel, B., Monatsh 6, 989-96 (1885)
58. Granville, W. A., Smith, P. F., and Longley, W. R., Elements of Calculus, Ginn and Co., New York, 1946 p 121

THE CORRELATION OF MECHANICAL PROPERTIES OF ETHYL
CELLULOSE FILMS WITH SHAPE OF DISTRIBUTION CURVES

by

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INTRODUCTION

The polymolecularity of cellulose and its derivatives has been recognized and studied for several decades. The usual commercially produced ethyl cellulose containing between 43.5 and 50% ethoxy is soluble in most of the organic and inorganic solvents except for the straight chain hydrocarbons and water. The longer the cellulosic chain, or the larger the degree of polymerization, the less soluble the ethyl cellulose becomes which is the basis for the method of fractional precipitation of high polymers (2). This method of separating polymers into fractions having decreasing degrees of polymerization was developed for ethyl cellulose by using a 80:20 mixture of acetone and ethyl acetate as the solvent and a 75:25 water-acetone mixture as the non-solvent (9).

Several studies have been made of the effect of increasing chain length and of the effect of blending high and low D. P.

material upon the physical properties of cellulose derivatives (1, 5, 7, 10, 4, 3). Sookne and Harris (4) found that a coherent film of cellulose acetate could not be formed if the D. P. was 30 or below but above that there was a rapid improvement of mechanical properties up to about a D. P. of 150. Spurlin (12) found that films cast from half-second cellulose nitrate fractions of higher viscosities were superior in folding endurance tests, but when about equal quantities of low and high D. P. material were blended the number of Schopper Folds was reduced by 50%. He also concluded that the best mechanical properties were obtained by increasing the D. P. regardless of the polymolecularity. Mark (6) concluded that there is a lower limit of between 40 and 80 D. P. below which the mechanical properties are not measureable and that above this the properties improve rapidly with increasing D. P. to about 200-250 beyond which the property improvement is slight with further increases in chain length. He also concluded that the shape of the distribution curve has no effect on the strength of the films except when 10 to 15% by weight material with a D. P. of 150 or less is contained in the sample.

It is the purpose of this paper to show that when the average D. P. is kept below 200-250 the shape of the distribution curve for ethyl cellulose does have a great effect upon the mechanical properties and that the optimum mechanical properties can be

obtained by changing the shape of the curve without increasing the average degree of polymerization.

MATERIALS AND MECHANICAL TESTS

The ethyl cellulose used throughout this investigation was a commercial grade type E200 with 48.7% ethoxy content and with a viscosity of 169 centipoises in 5% solution obtained from Hercules Powder Company. The benzene, 99-100% purified, was obtained from Baker and Adamson while the other solvents, CP acetone, commercial grade ethyl acetate, and reagent grade n-butyl acetate were obtained from Commercial Solvents Corporation.

For all the mechanical tests applied to the films both the testing machine and the technique used complied with the requirements of the respective ASTM. All specimens tested were visibly free of foreign particles and blemishes and were cut from at least three different films to the size specified for each test. Standard Laboratory Atmosphere, 50 - 2% R.H. at 77 - 1.8°F., ASTM D 618-46T was maintained for all tests and all films were conditioned for at least 40 hours. The Schopper Type Tensile Strength and Elongation Tester complied with the specification of ASTM D 882-46T; the Schopper Type Folding Endurance Tester met the requirements of ASTM D 634-43; the Kullen Tester met the requirements of ASTM D 774-46 for the Bursting Strength of Paper;

and the Elmendorf Tearing Tester filled the requirements of ASTM D 689-44.

EXPERIMENTAL

METHOD OF FRACTIONATION

A method for fractional precipitation of a 3% solution of ethyl cellulose in 80:20 acetone-ethyl acetate mixture by the addition of the precipitating agent, 75:25 water-acetone (9), was slightly modified from the original 900 gram batch to a 10,800 gram batch. Eleven such batches were fractionated and then fractions of the same average D. P. were combined by re-dissolving them in acetone and precipitating into an excess of water, filtering and drying. The average D. P. of each composite was experimentally determined and is the value used throughout this investigation.

The fractions, obtained above, and the blends were analyzed for polymolecularity by a similar fractionation method. A 1000 gram solution containing 1.5% ethyl cellulose in a 80:20 acetone-ethyl acetate mixture was fractionally precipitated by the addition of water. As each fraction and blend had its own type of heterogeneity no set procedure could be established, and the non-solvent was added until the solutions became hazy. When the first fraction was relatively larger than the amount of highest

D. P. material added, it was refractionated by redissolving in 80:20 acetone-ethyl acetate mixture and fractionally precipitating with water.

The polymolecularity of the original material, fractions, and blends is given in Table I.

DEGREE OF POLYMERIZATION AND OF SUBSTITUTION DETERMINED

In order to show that the ethyl cellulose had actually been separated into groups according to chain length, viscosity measurements of a 0.01% solution were made and the data so obtained substituted in Staudinger's (14) equation and the degree of polymerization calculated. The constant of proportionality, K_p , for ethyl cellulose dissolved in n-butyl acetate at 40°C. was calculated as 10.57×10^{-4} from information given by Staudinger and Reineke (15).

As there is always the possibility that variations in the degree of substitution might cause the precipitation rather than the chain length, the ethoxy content of the fractions was determined (9) by a modification of Zeisel's method (16). This test showed that the ethoxy content of the fractions was nearly the same (greatest deviation from the mean was 0.5%).

PREPARATION OF FILMS

Films were cast from a benzene solution (free of air bubbles) onto plate glass and given an uniform thickness by means of a

TABLE I

POLYMOLECULARITY OF MATERIALS TESTED					
<u>Sample</u>	<u>Per- cent</u>	<u>Degree Poly.</u>	<u>Sample</u>	<u>Per- cent</u>	<u>Degree Poly.</u>
Orig.	14.7	346	F 1	11.8	492
	7.9	310		8.1	440
	10.7	280		18.9	335
	9.4	226		22.6	305
	8.7	189		12.6	297
	7.2	143		6.6	283
	10.6	110		6.2	214
	21.5	67		4.8	200
			1.4	166	
			6.9	88	
	Average	183		Average	349
F 2	12.0	379	F 3	12.0	341
	32.6	340		6.4	301
	17.8	276		32.0	278
	11.4	243		2.8	266
	7.0	222		13.6	250
	8.1	135		9.6	211
	11.2	100		6.5	183
			2.7	162	
			2.1	139	
			12.3	98	
	Average	274		Average	248
F 4	11.7	281	F 5	17.5	206
	4.3	252		10.4	204
	33.3	219		6.3	194
	13.3	209		3.4	178
	2.0	202		19.9	174
	9.5	193		8.9	157
	7.1	171		2.4	151
	5.5	135		6.7	130
13.3	83	24.5	91		
	Average	212		Average	186
F 6	14.5	162	B 1	17.1	353
	21.4	146		16.1	302
	15.1	134		10.6	271
	10.0	114		7.2	208
	10.3	113		6.9	153
	28.8	92		1.9	126
				5.5	97
		34.7	43		
	Average	130		Average	194

TABLE I con't.

<u>Sample</u>	<u>Per- cent</u>	<u>Degree Poly.</u>	<u>Sample</u>	<u>Per- cent</u>	<u>Degree Poly.</u>
B 2	14.2	443	B 3	8.0	352
	11.5	274		6.4	341
	9.3	236		9.4	238
	15.9	229		5.2	192
	6.1	164		18.0	175
	12.5	112		16.1	155
	1.6	91		14.2	120
	2.9	80		3.4	107
	26.0	50		19.4	70
	Average	186		Average	184
B 4	2.9	309	B 5	17.8	346
	8.4	290		14.8	273
	10.4	249		13.3	202
	8.9	231		11.3	154
	18.9	183		7.0	134
	18.6	168		8.0	124
	12.3	148		4.0	112
	3.0	114		23.7	65
	1.9	82			
	15.0	65			
	Average	190		Average	190
B 6	30.7	339	B 7	10.5	301
	11.3	295		9.0	253
	6.9	246		17.6	222
	5.1	175		4.5	218
	6.9	124		14.4	186
	5.6	93		1.3	177
	33.5	36		8.7	162
	Average	187		3.8	139
				4.4	130
B 8	17.3	286		2.8	103
	19.0	259		23.0	76
	18.8	227		Average	175
	11.4	181			
	8.5	173	B 9	24.4	276
	2.8	152		22.7	229
	3.0	129		16.1	192
	19.2	91		8.8	161
	Average	190		3.5	145
				3.1	111
B 10	10.3	324		21.5	87
	9.3	295		Average	190
	9.8	250			
	14.1	172			
	16.4	157			
	9.0	139			
	5.0	120			
	26.0	84			
	Average	153			

leveling device which was a piece of 2 cm. diameter glass tubing with a single wire loop on each end to serve as runners. Wire of differing diameters was needed as it was not always practical to use the same concentration for all casting solutions due to their differing viscosities. The relationship between wet thickness or the diameter of the wire used to make the loops and the concentration of the solution to produce 0.003 inch films is given in Table II.

TABLE II

<u>WET THICKNESS REQUIRED TO GIVE 0.003 INCH FILMS</u>			
<u>Fraction</u>	<u>Average D.P.</u>	<u>Conc. of Solution</u>	<u>Inches Wet Thickness</u>
1	349	5%	0.106
2	274	9%	0.063
3	248	9%	0.063
4	212	9%	0.063
5	186*	10%	0.051
6	130	10%	0.051
7	109	10%	0.063
8	64	15%	0.051

* Approximate average D.P. for blends and for original material which were cast with the same wet thickness.

The glass plate with the wet film was placed in a 30-40°C. drying oven for 45 minutes. All films were stripped from the plates in the same direction they were leveled by applying a steady pull to a loosened edge whose film-glass interface had

been wetted with a few milliliters of water. However, the films formed from Fraction 8 could not be pulled from the plates because of breaking and cracking so these were allowed to soak free from the glass plates with water. These films were then conditioned and tested.

MECHANICAL TESTS

For all tests except the Bursting Strength Test (which did not require it) specimens were cut parallel to and normal to the direction of leveling and stripping. These directions are hereafter called "With" and "Cross". The values obtained from each direction were arithmetically averaged separately and then averaged together to give the final value for the test.

The results of all mechanical property tests are summarized in Table III. The average values of the mechanical properties of films cast from the fractions and original material were plotted against the average D. P. of those fractions in Graph I where it is noted that all of the properties improved with the increase in D. P. up to about 200 or 250 where the values remained constant regardless of further increase in D. P.

PREPARATION OF BLENDS

Three restrictions were placed upon the preparation of blends from the eight fractions. The average D. P. of all the blends must be below 200 and nearly the same so as to minimize the effect of increasing D. P. noted above. Since the original

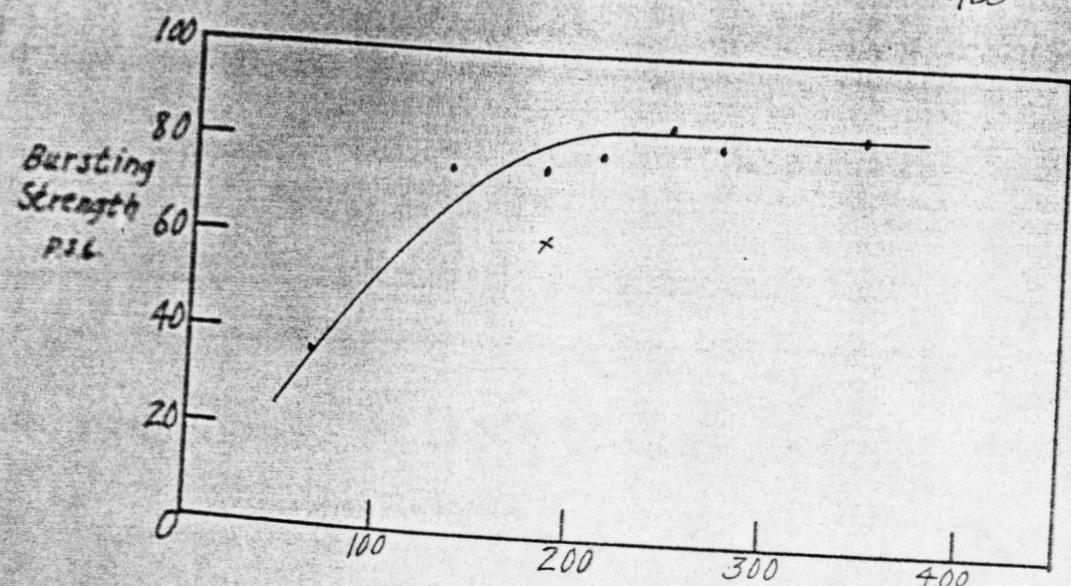
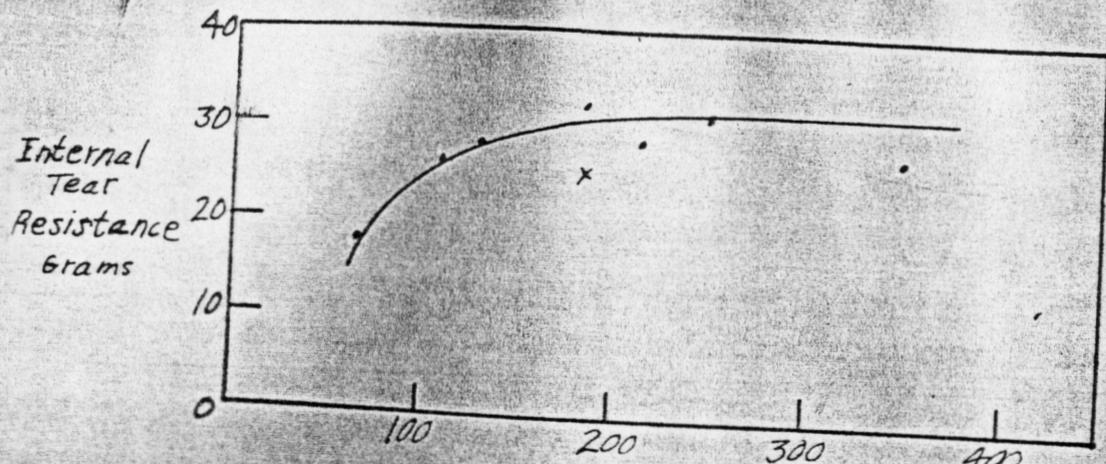
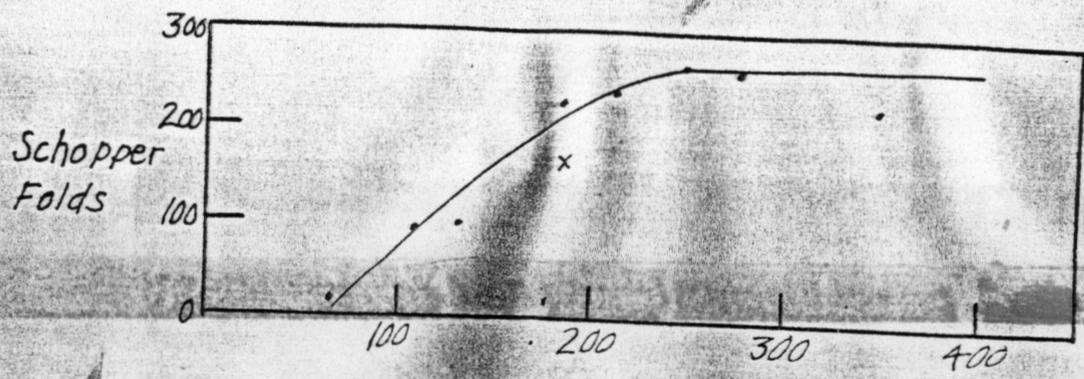
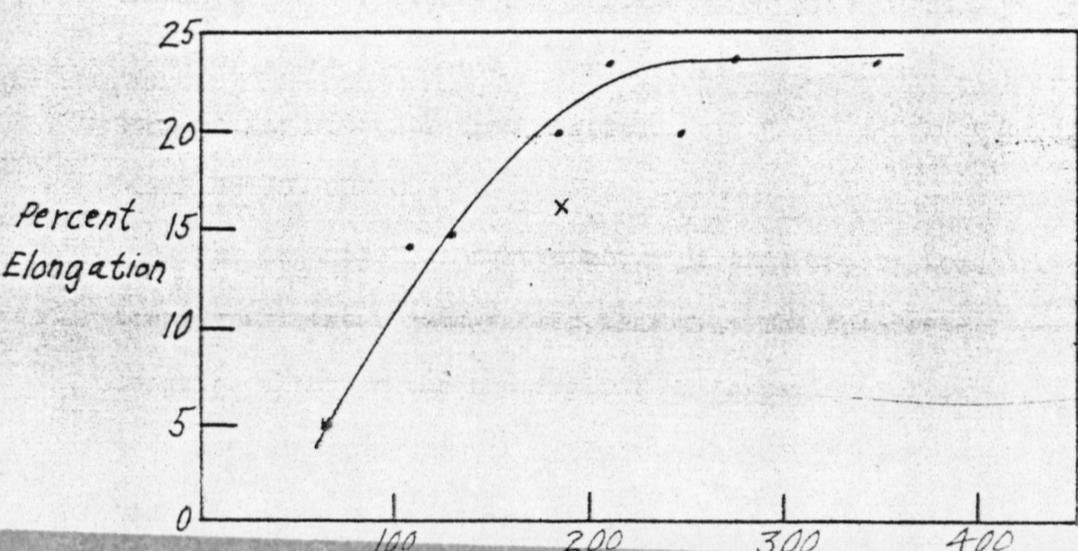
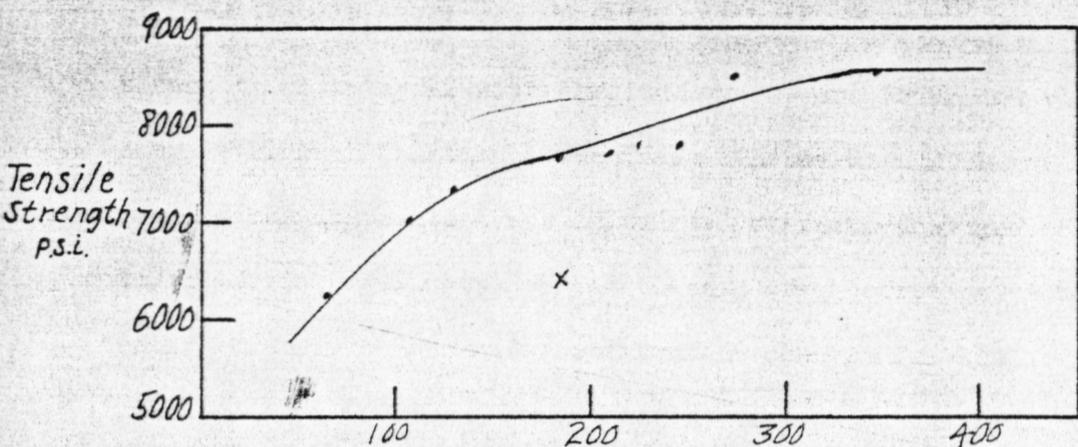
TABLE III

MECHANICAL PROPERTIES OF 0.003 INCH ETHYL CELLULOSE FILMS SUMMARIZED

Sample	Tensile-Strength (p.s.i.)		Percent Elongation No. Schopper Folds Resistance (grams)		Internal Tear		Bursting Strength (p.s.i.)				
	Avg. D.P.	With Cross AVE.	8770 8580	8780 8580	24.3 23.5	24.6 22.6		205 226	247 205	25.8 28.3	27.0
F 1	242	8780	8580	8780	24.3	24.6	205	247	25.8	28.3	84.5
F 2	274	8720	8570	8420	24.8	22.6	292	251	30.5	32.6	82.5
F 3	248	7320	7660	7720	19.2	19.9	246	286	35.2	28.2	75.6
F 4	212	7390	8030	7710	23.7	22.6	196	261	29.1	29.3	79.2
F 5	186	7700	7650	7670	21.5	17.6	210	248	32.0	33.0	75.7
F 6	130	7450	7270	7360	14.0	15.2	92	104	32.6	24.0	75.6
F 7	109	6730	7340	6530	17.0	11.0	83	101	27.0	26.0	56.4
F 8	64	6580	5890	6230	4.2	5.6	20	17	18.0	18.0	35.7
Original	183	6720	6170	6440	16.2	18.2	153	172	25.3	25.8	61.7
B 1	194	6640	5730	6180	10.2	15.0	107	78	19.5	19.7	52.0
B 2	186	6200	5820	6020	10.7	13.7	83	83	20.3	19.5	57.6
B 3	184	7740	7740	7740	21.5	19.8	151	177	20.8	17.7	62.6
B 4	190	6900	7830	7360	20.7	18.7	151	181	27.3	28.7	70.9
B 5	190	7080	6980	7040	16.3	18.5	136	148	22.8	24.0	60.1
B 6	187	6020	6060	6040	10.5	11.5	79	84	19.7	19.6	55.1
B 7	175	7410	7210	7310	20.5	21.2	185	225	23.5	26.5	68.1
B 8	190	6880	8060	7470	21.2	18.2	153	172	24.0	24.5	71.7
B 9	190	8400	8000	8200	21.7	22.5	138	145	26.5	25.5	74.2
B 10	153	8100	8760	8430	23.3	21.0	142	138	23.5	24.5	69.1

GRAPH I

CHANGE IN MECHANICAL PROPERTIES WITH THE CHANGE IN AVERAGE DEGREE OF POLYMERIZATION



Degree of Polymerization

material had an average D. P. of 183 and its distribution had been determined (9), the average D. P. of the blends was kept reasonably close to this value. The other restrictions were that the blends must give smooth curves when the percentage composition was plotted against the D. P. of the components, integral distribution, and that the differential distribution curves should be different.

In order to determine the theoretical composition of the blends trial integral distribution curves were drawn and the percentage of each fraction determined. The average D. P. of this theoretical composition was calculated statistically and if within the arbitrary limits for the blends, the theoretical differential distribution curve was drawn and checked for similarity with those previously calculated. If these were different, the amount of each fraction was calculated to give a total of 60 grams of ethyl cellulose to be dissolved in sufficient benzene to give the concentration desired.

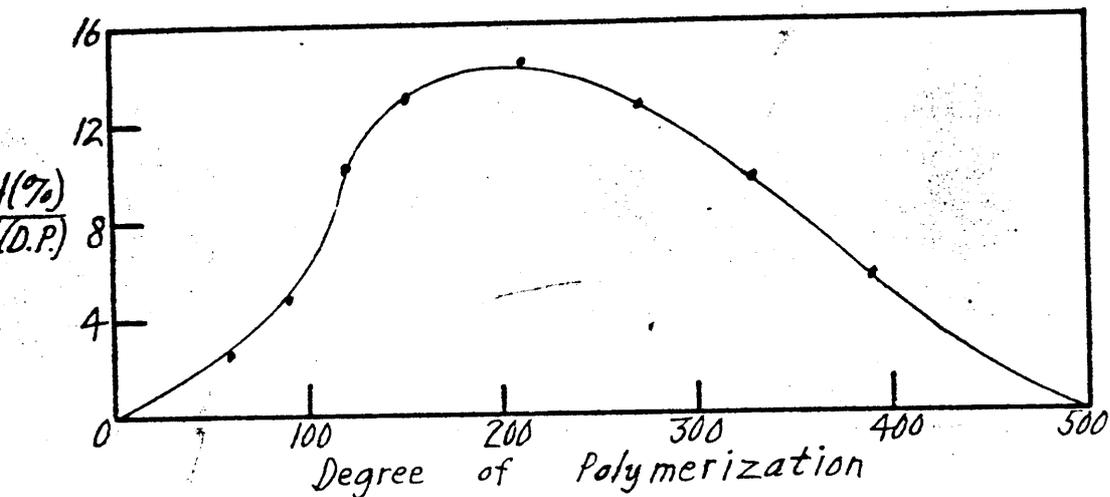
DISTRIBUTION CURVES

The distribution curves shown in this report were drawn from experimental data rather than from the theoretical composition although the theoretical and experimental curves often coincided. The method of analyzing the blends and fractions has already been described.

When the accumulative percentages of Table I were plotted against the corresponding degree of polymerization, the integral distribution curves were obtained. The slopes of the tangents to these integral curves as read on the scale of a tangentometer were plotted against the D. P. to give the differential distribution curves as shown in Graphs II through XVIII. These curves may be converted to the percentage curve by estimating the area under the curve according to Simpson's Rule and then dividing the area of the increments by the total area. These values when plotted against the D. P. will give a normalized curve from which the percentage of each chain length present may be read directly from the ordinate.

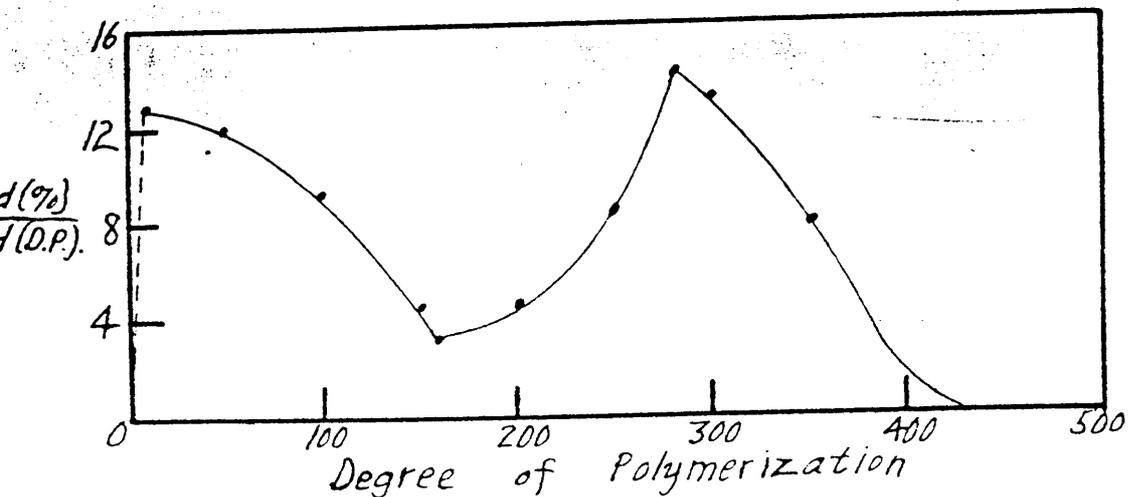
GRAPH II

DISTRIBUTION IN ORIGINAL MATERIAL



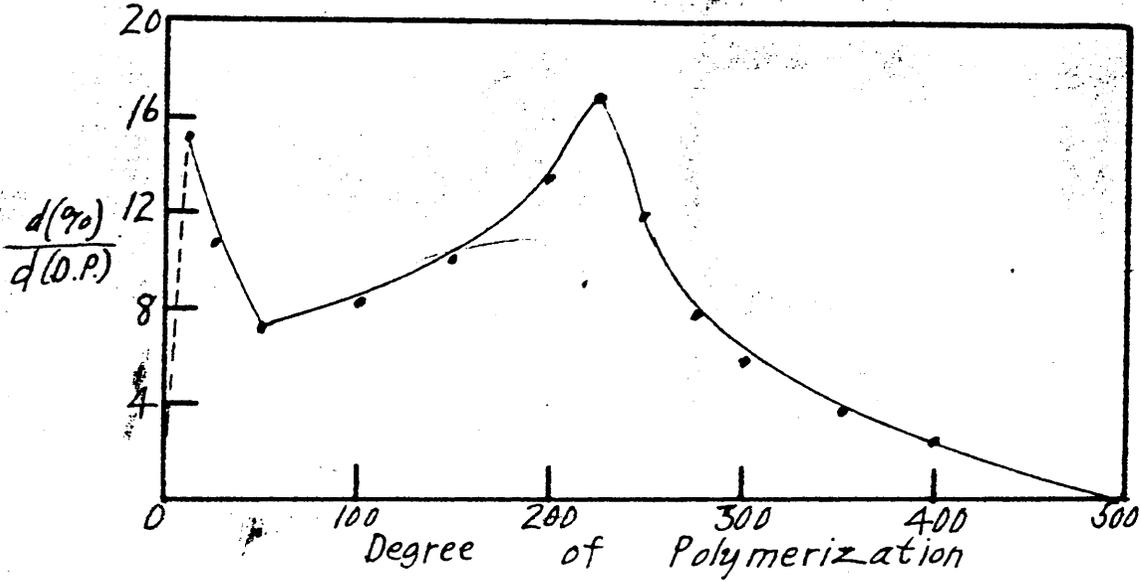
GRAPH III

DISTRIBUTION IN BLEND 1



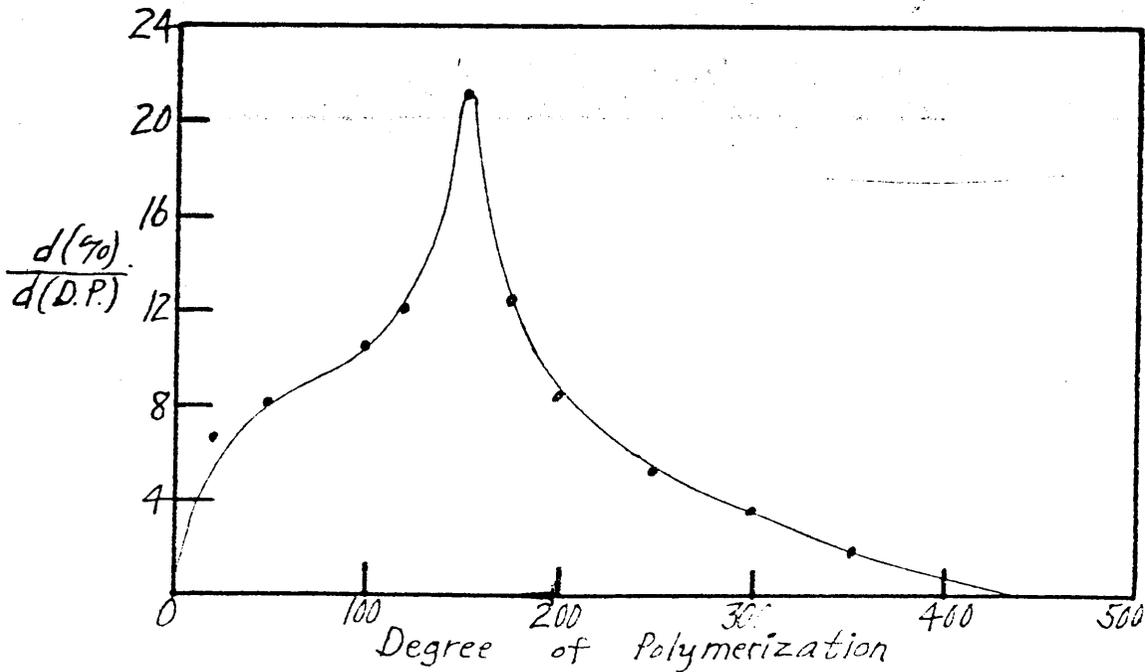
GRAPH IV

DISTRIBUTION IN BLEND 2



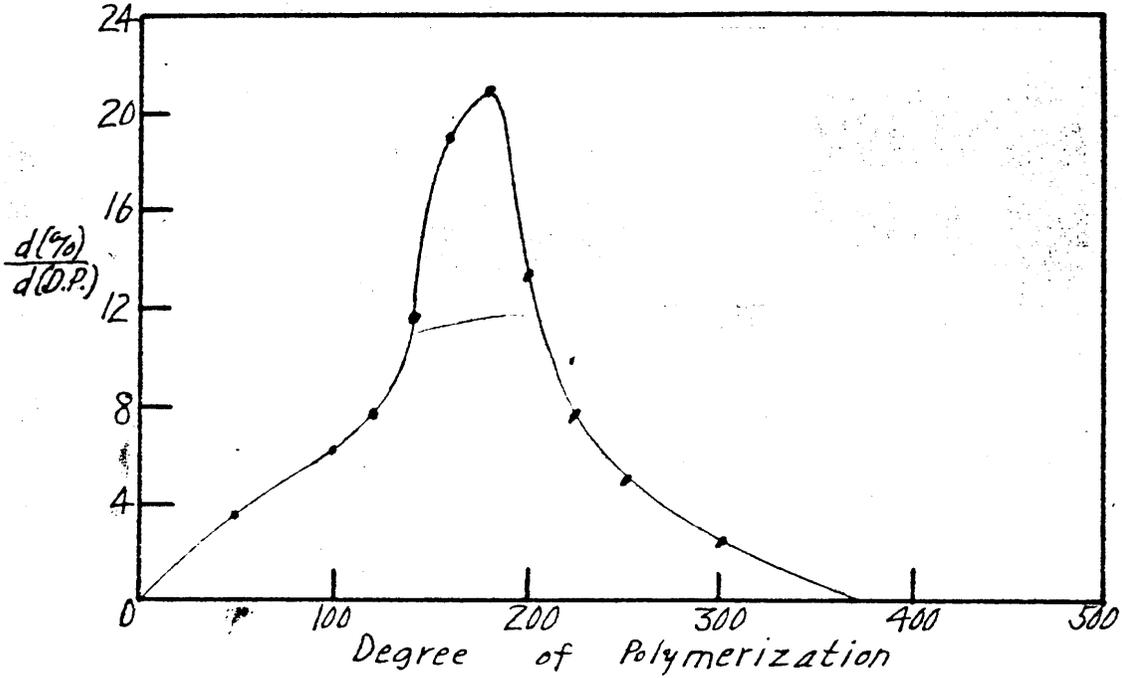
GRAPH V

DISTRIBUTION IN BLEND 3



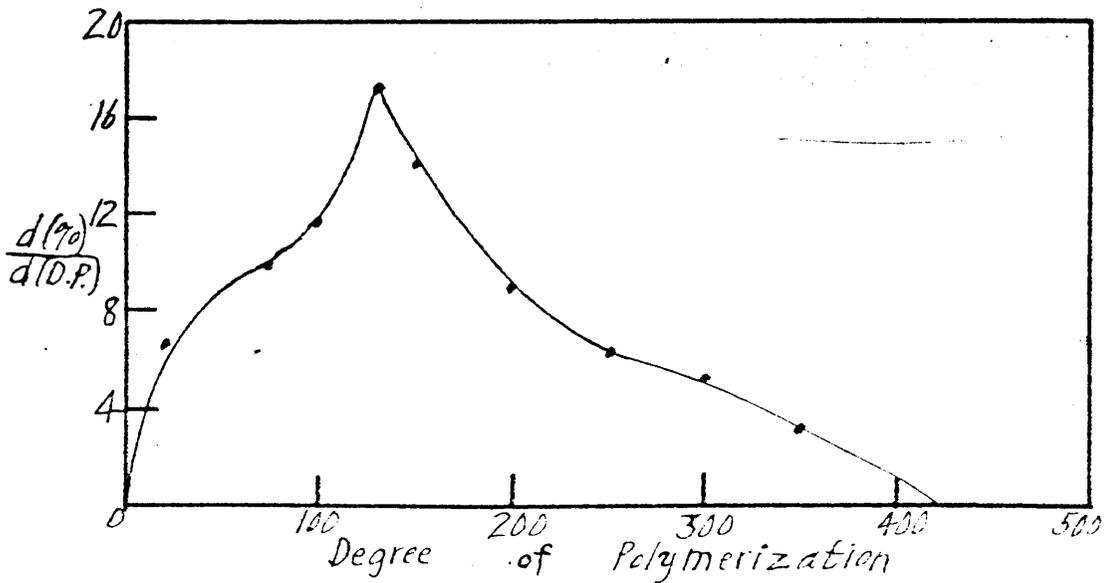
GRAPH VI

DISTRIBUTION IN BLEND 4



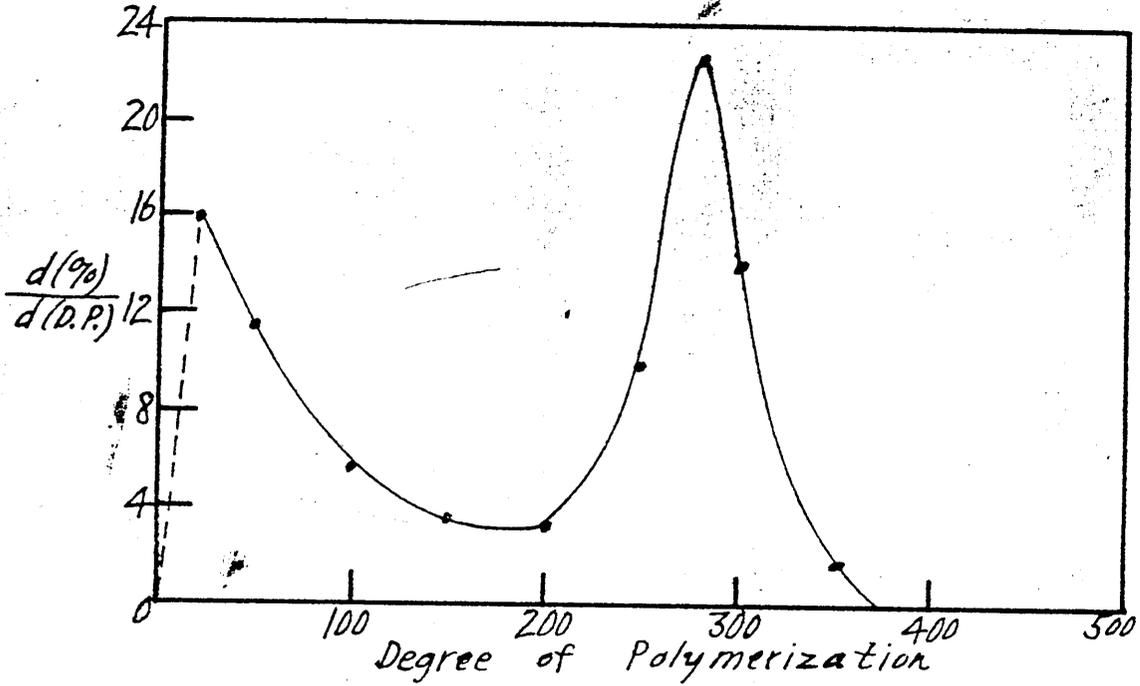
GRAPH VII

DISTRIBUTION IN BLEND 5



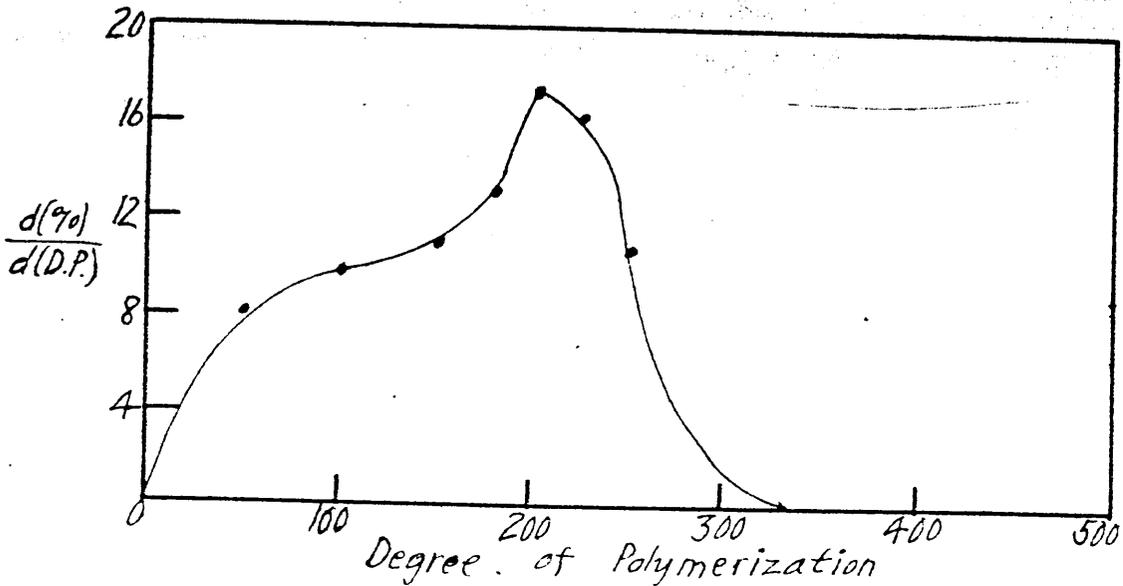
GRAPH VIII

DISTRIBUTION IN BLEND 6



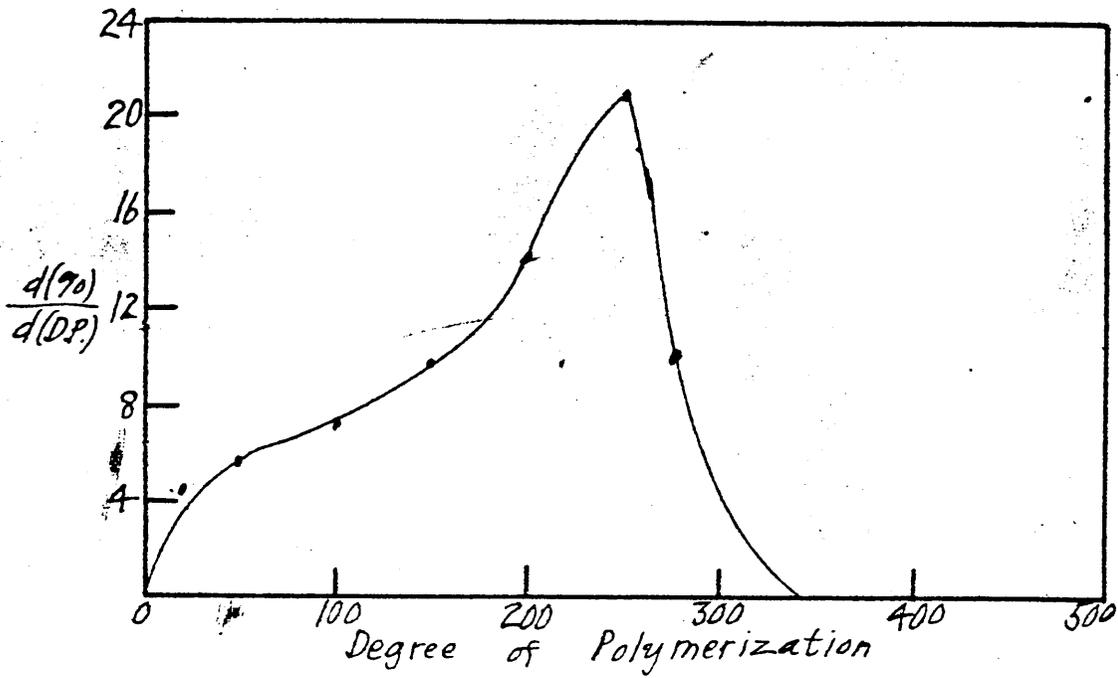
GRAPH IX

DISTRIBUTION IN BLEND 7



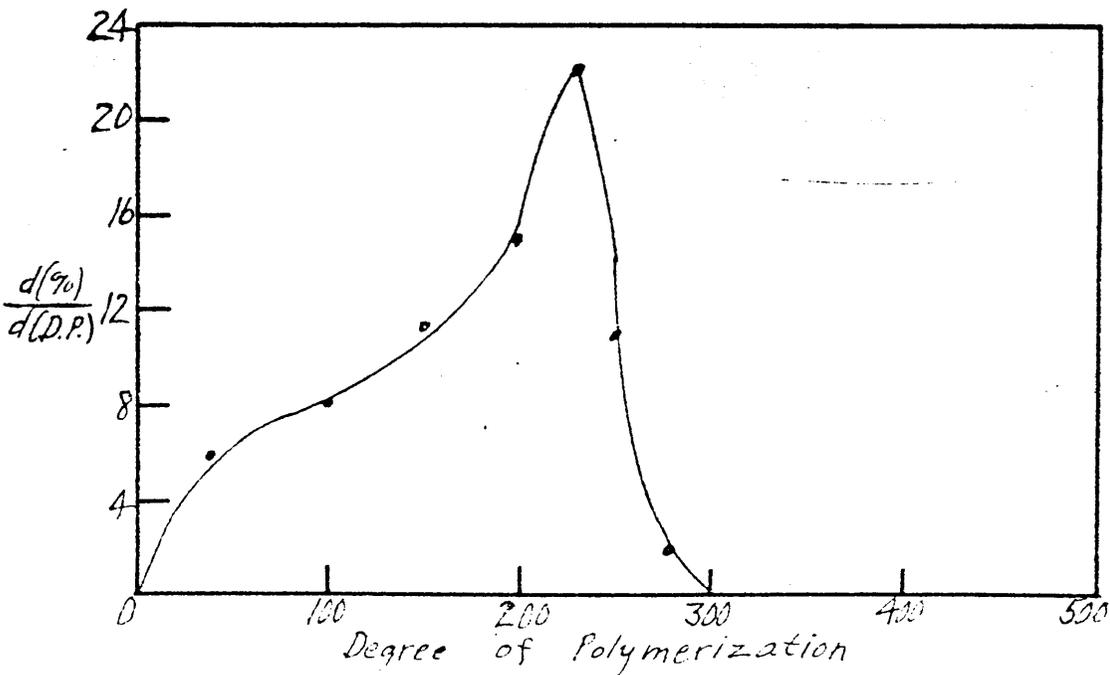
GRAPH X

DISTRIBUTION IN BLEND 8



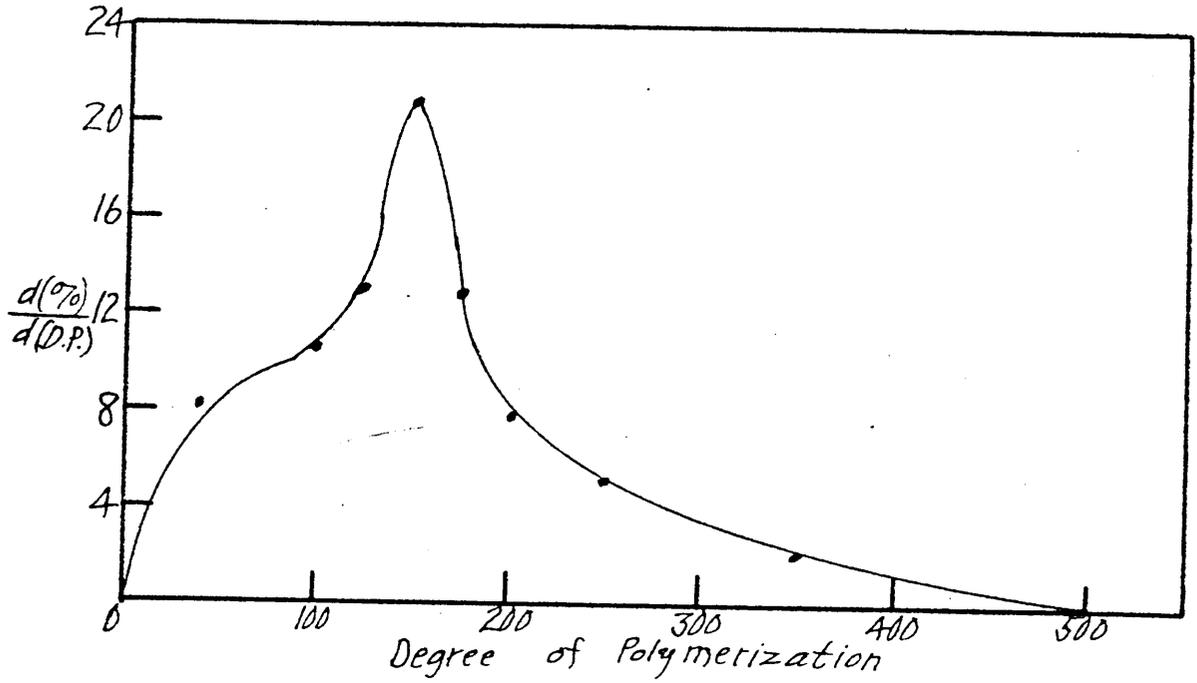
GRAPH XI

DISTRIBUTION IN BLEND 9



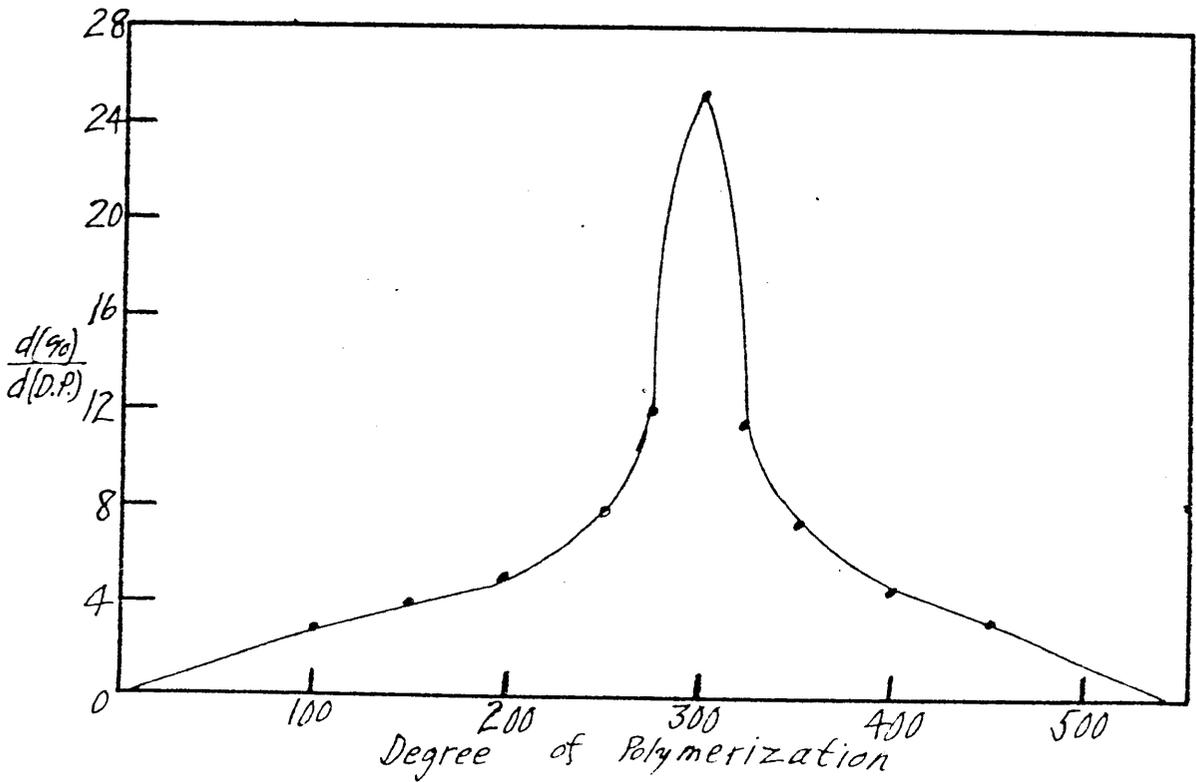
GRAPH XII

DISTRIBUTION IN BLEND 10



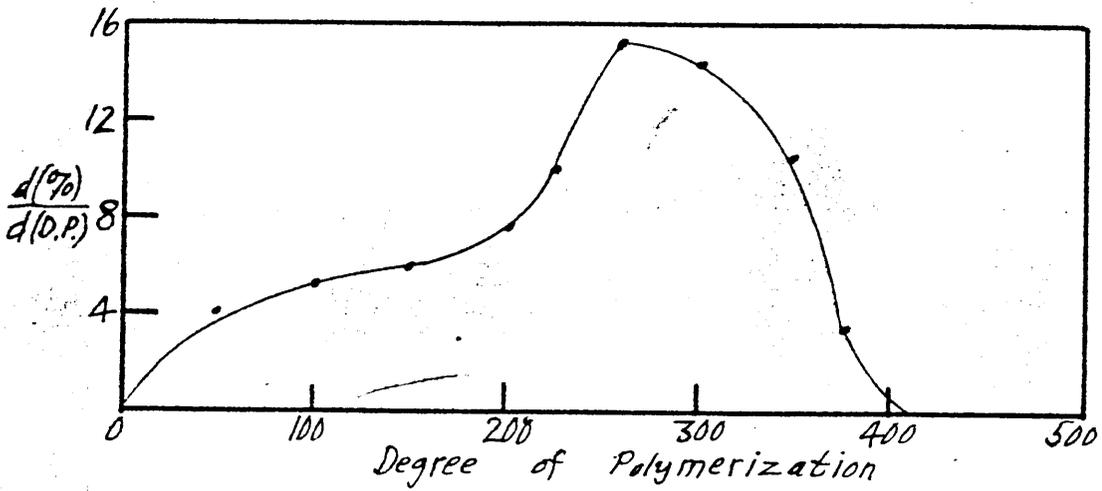
GRAPH XIII

DISTRIBUTION IN FRACTION 1



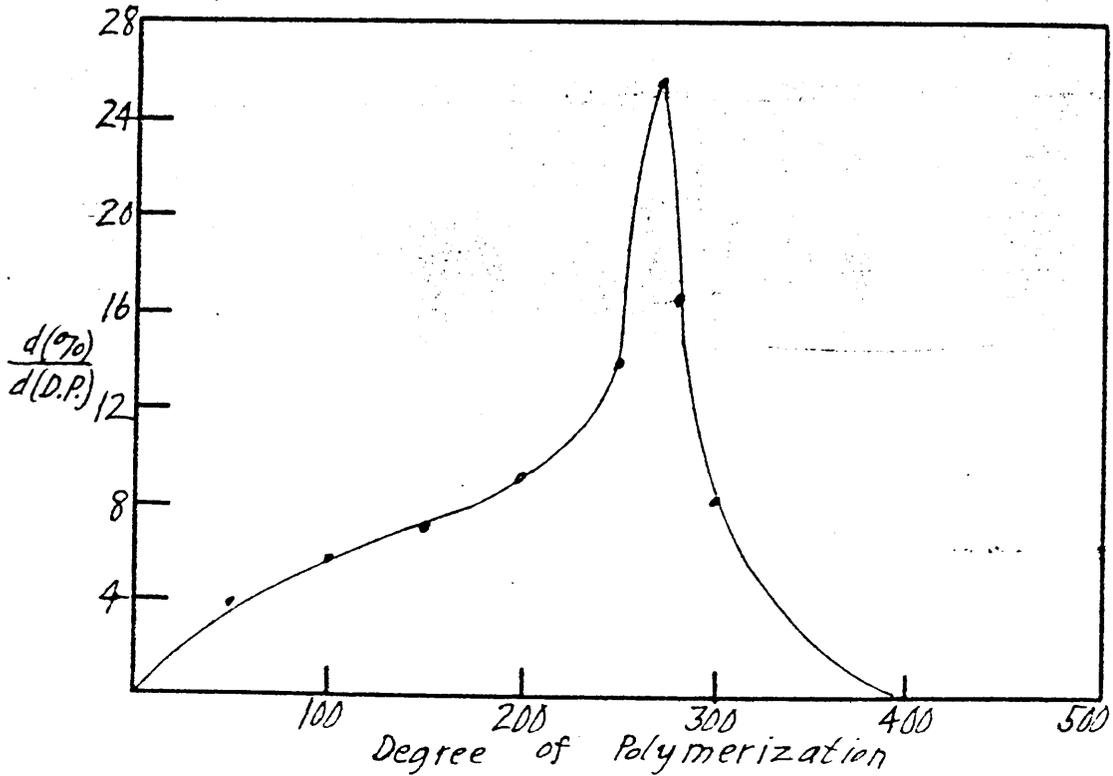
GRAPH XIV

DISTRIBUTION IN FRACTION 2



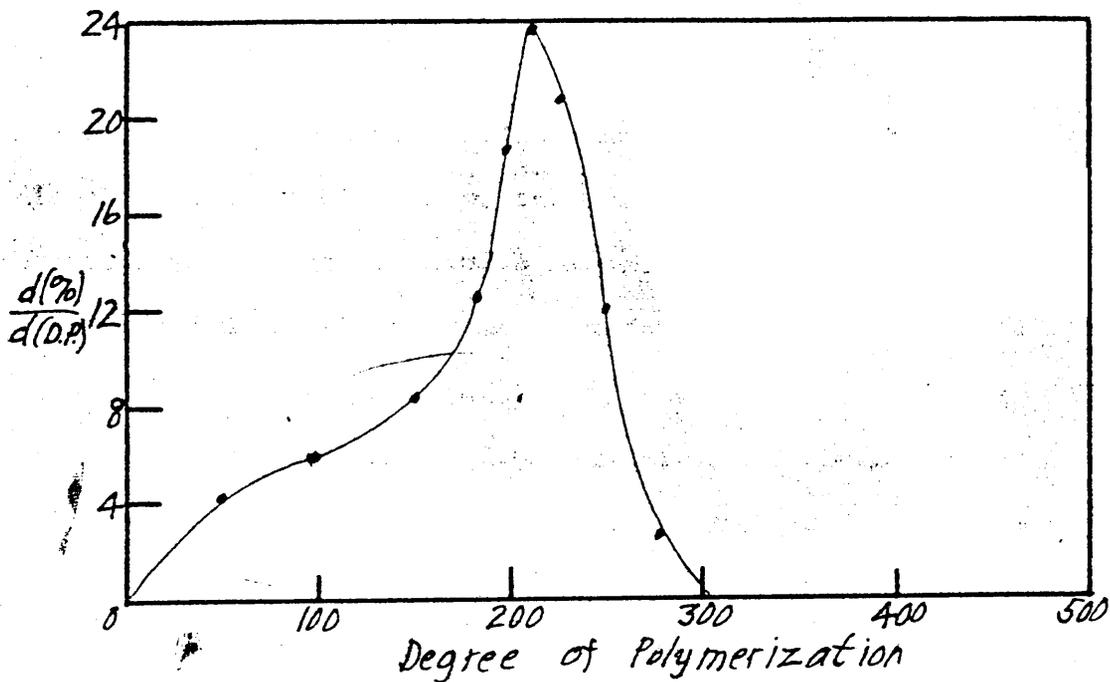
GRAPH XV

DISTRIBUTION IN FRACTION 3



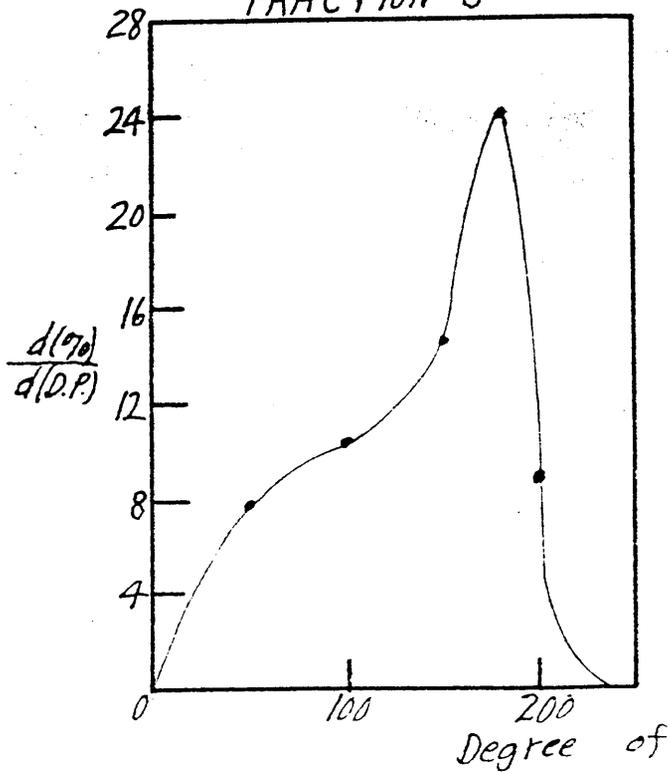
GRAPH XVI

DISTRIBUTION IN FRACTION 4



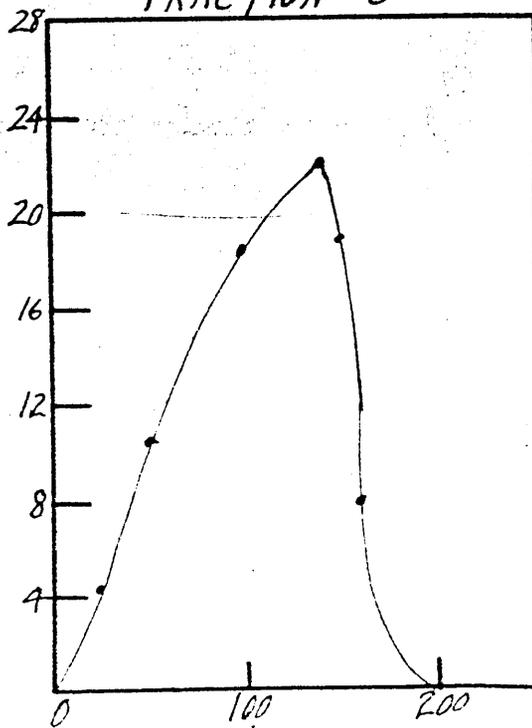
GRAPH XVII

DISTRIBUTION IN FRACTION 5



GRAPH XVIII

DISTRIBUTION IN FRACTION 6



CORRELATION OF THE MECHANICAL PROPERTIES WITH THE SHAPE OF THE DISTRIBUTION CURVES

Since each blend and fraction had its own peculiarly shaped distribution curve, it was evident that the development of a mathematical equation to express the various distributions would be difficult if at all possible; therefore, a graphical correlation of the data was developed.

A study of the mechanical properties of the blends showed that there was some correlation between the height of the maximum and the location of the maximum. The fact that less heterogeneity gives better properties is noted when comparing Fraction 5 with the original material, and when Blend 4 is compared with this same fraction it is noted that Fraction 5 has the better properties. Examination of the distribution curves shows that the maximum of Fraction 5 is higher and much narrower than that of Blend 4, and that the curve for the original material is very broad and flat. In other words, the sharper the maximum the less heterogeneity within the sample and the better the properties.

Theoretically the differential distribution curve of a cellulose derivative containing chains of one length only would be a vertical line. When some material of slightly different chain length is added, the curve changes from a single line to a pencil-like curve. As more and more varied chain lengths are added the curve widens out and the maximum may drop. Thus any

measurement of the ratio of the width of the curve to the height of the maximum would represent the heterogeneity within the sample. On the basis of this reasoning, measurements of the width of the peak were taken at 0.9, 0.8, 0.6, 0.4, and 0.2 of the height of the peak since the success of this method of characterizing the curves depended upon the width of the peak rather than the width of the base. The average of these widths was calculated and then divided by the maximum height to give a measure of the heterogeneity.

By a trial and error method it was found that when the D.P. of the maximum was divided by the logarithm of the "heterogeneity" and this ratio or "shape factor" plotted against the values of the properties, the points were so grouped that smooth curved lines could be drawn through them as in Graph XIX. The essential measurements and calculated values for characterizing the 17 distributions tested in this investigation are listed in Table IV.

It is noted that the differential distribution curves for Blends 1, 2, and 6 have two peaks which indicates that large quantities of low and of high D. P. material were used to make these blends. Thus they are the result of merging two separate distributions, and their "shape factors" were also merged. Since two maxima existed the average D. P. was obtained by dividing the difference in D. P. by two; the two logarithms of "heterogeneity" were added; and these combined values used to calculate the "shape factor".

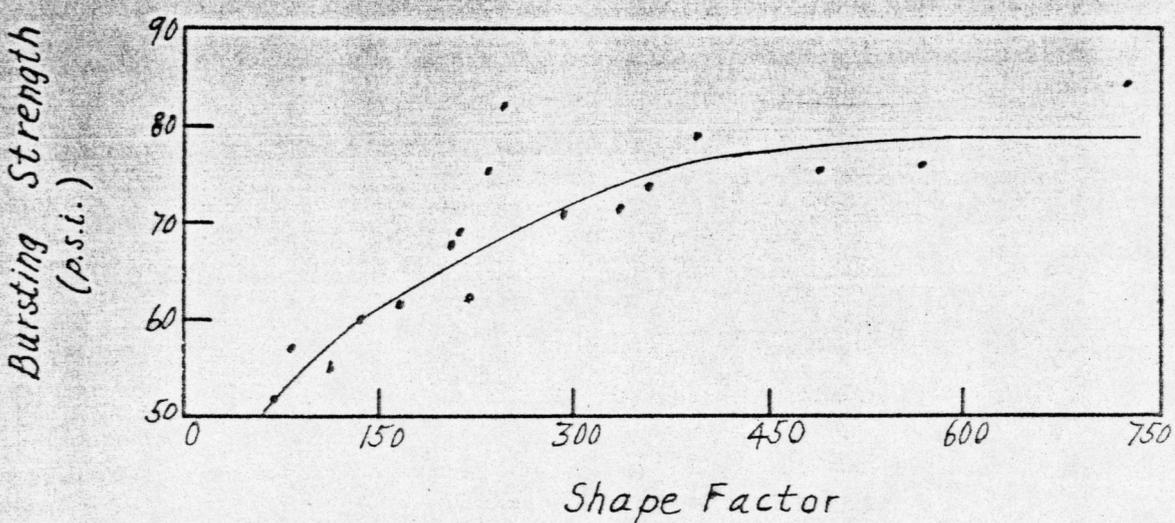
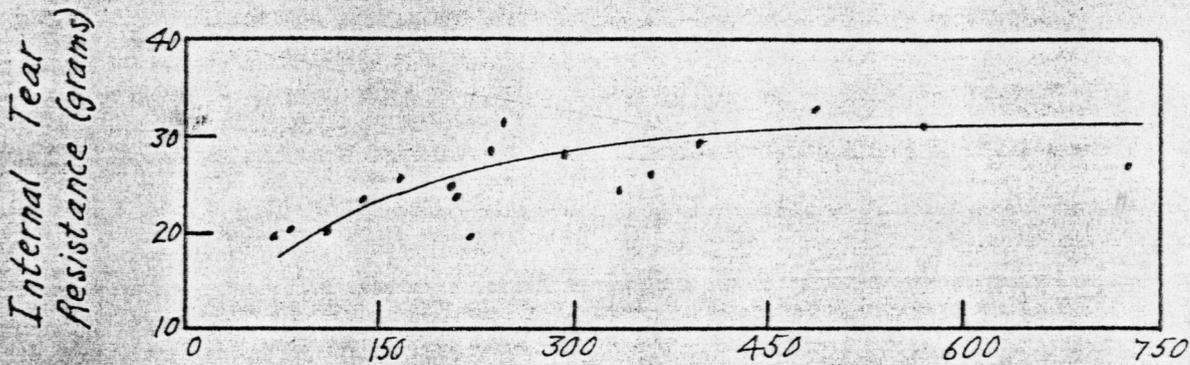
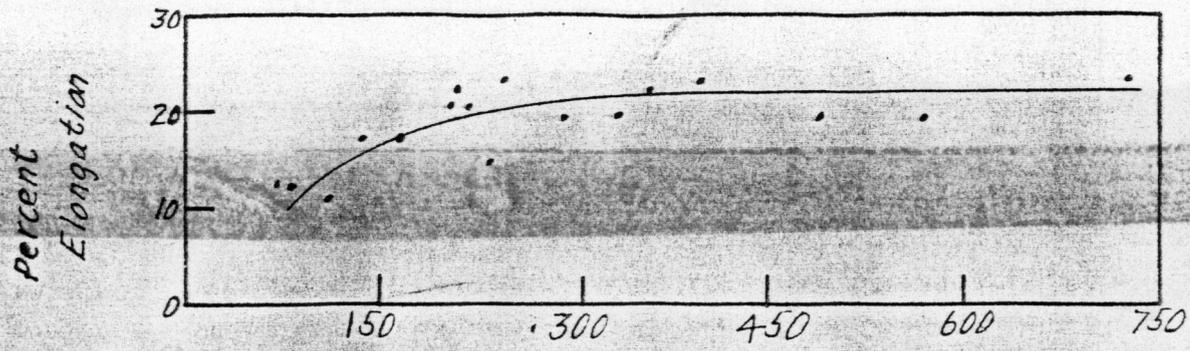
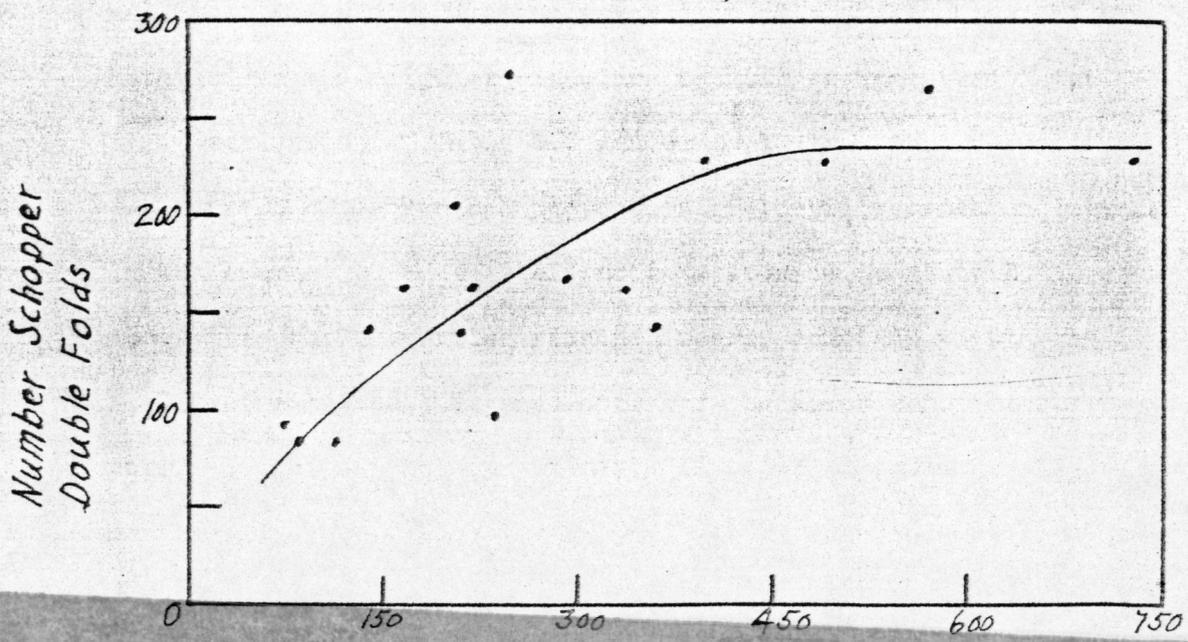
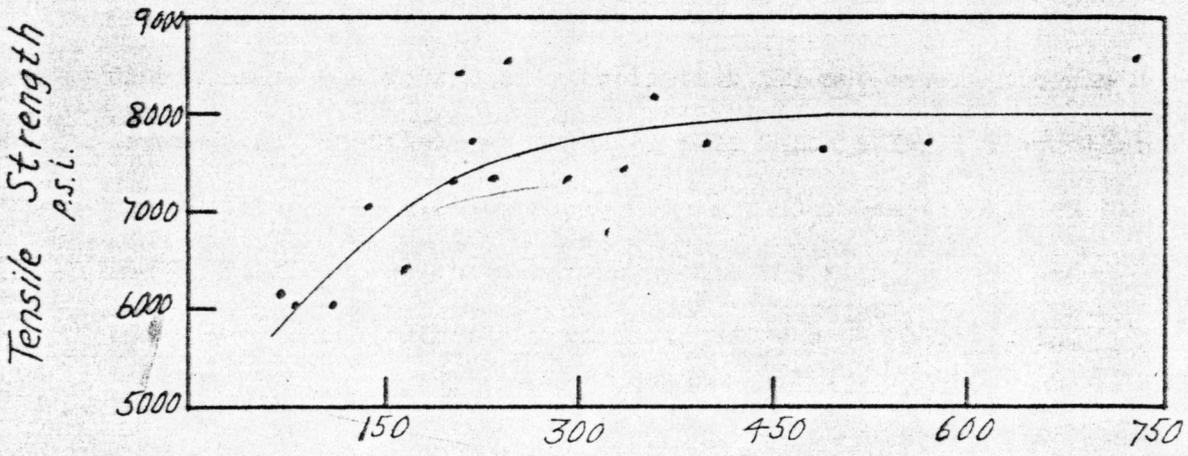
TABLE IV

DATA FOR CHARACTERIZING THE DISTRIBUTION CURVES

<u>Sample</u>	<u>Height of Max.</u>	<u>D. P. of Max.</u>	<u>Avg. Width</u>	<u>Width Height</u>	<u>Log. Heter.</u>	<u>Shape Factor</u>
F 1	25.1	300	64.8	2.582	0.4119	728
F 2	15.4	260	173.4	11.260	1.0515	247
F 3	25.5	270	75.8	2.973	0.4731	571
F 4	23.8	210	80.6	3.387	0.5297	397
F 5	24.5	180	57.0	2.326	0.3666	491
F 6	22.2	140	87.4	3.940	0.5951	235
Original	14.4	200	238.0	16.527	1.2182	164
B 1	14.3	280	112.4	7.860	0.8954	
	13.0	20	109.0	8.384	0.9235	72
B 2	16.7	225	121.5	2.586	0.4125	
	15.2	12	39.3	7.275	0.8618	85
B 3	21.0	150	101.0	4.809	0.6821	220
B 4	21.0	180	87.0	4.143	0.6163	292
B 5	17.3	130	144.0	8.323	0.9203	141
B 6	22.3	280	56.8	2.547	0.4060	
	16.0	20	71.4	4.463	0.6496	113
B 7	17.1	200	158.0	9.239	0.9656	207
B 8	20.7	250	116.0	5.603	0.7484	334
B 9	22.2	230	97.0	4.369	0.6404	359
B 10	20.6	150	107.0	5.195	0.7156	210

GRAPH XIX

CORRELATION OF MECHANICAL PROPERTIES OF ETHYL CELLULOSE FILMS WITH SHAPE OF DISTRIBUTION CURVES



Shape Factor

DISCUSSION OF RESULTS

Comparison of the average degree of polymerization of the fractions obtained from a five gallon batch with the average D. P. of the composites of the eight fractions as listed in Table I shows that the fractionation procedure used gives reproducible results. The ethoxy content was found to be the same for all the fractions so the degree of substitution did not enter into the separation. Examination of Graphs XIII through XVIII shows that this original fractionation was not very sharp especially on the low D. P. side (the curves are skewed to the right) which means that there was considerable enmeshing of short chains by the longer ones during the period of coalescence and settling. Fraction 1, which was refractionated, shows a sharper distribution than do the others. The method of fractionating the blends and fractions gave a cleaner separation of the chain lengths than obtained in the original procedure as will be explained later.

Examination of Table III and Graph I shows that there is an improvement of mechanical properties of the films with an increase in the average D. P. of the fractions from 64 to about 200. Above this the properties remained nearly constant within the D. P. range tested. Extrapolation of the lower end of these curves indicates that the property in question would not be measureable should the average D. P. fall below 50. These curves

follow the general shape of those experimentally determined by Bass and Kauppi (1) who also worked with ethyl cellulose, by Sookne and Harris (11), who worked with cellulose acetate, and by Spurlin (12), who fractionated and tested half-second cellulose nitrate. This lower limit at which mechanical properties are measureable falls within the limits of 40 to 80 predicted by Mark (6, 8).

It is noted in Graph I that the mechanical properties of the original material fell below that of the fractions of the same or higher average D. P., and that only the last fraction with an average D. P. of 64 had poorer values for all the properties than did the original material. This corresponds to the findings of Sookne and Harris (11) that the fractions had better mechanical properties than the original material. The Schopper fold and internal tear resistance values for the first fraction fell below the maximum although it had the highest average D. P. probably because of the impurities present in that fraction. These impurities, which gave the dried material a slightly greyish color, were enmeshed during the formation of the aggregates and could not be removed by washing with water.

The poor mechanical properties of the 64 D. P. material show very clearly the lack of flexibility and strength in material composed of short chains. Some of this brittleness may also be due to the accumulation of impurities in this residue fraction

particularly in the form of degradation products formed during the evaporation.

Except for Blends 1, 2, and 6 the percentage of experimentally determined low D. P. material exceeded that theoretically put in the blend. This is another indication of the enmeshing of the low D. P. material with the long chains and the accumulation of the short chains from all of the fractions used to make the blends. This also indicated that a sharper separation of the chain lengths was obtained when using a 1.5% rather than a 3% solution of ethyl cellulose. Large quantities of both 64 and 349 D. P. material were placed in these three blends to produce two-peak distributions while keeping the average D. P. the same as for the other blends.

A practical and rather simple method of characterizing the shape of the distribution curves was developed when it was observed in Graphs II through XVIII that Fractions 1, 3, 4, and Blends 3, 4, 8, 9, 10 had the better properties and that the peaks of their maxima were slightly higher than those of the other fractions and blends. It was also noted that when the D.P. of the maximum was 180 or better the values of the properties were a little higher. Fraction 5 had better properties than Blend 4 and the original material although the average D. P. was the same; Fraction 5 was more homogeneous in its composition than the original material and it had a sharper peak than Blend 4.

Some of the pertinent data has been collected from preceding tables and summarized in Table V in order to facilitate the correlation of the curve characteristics and mechanical properties.

TABLE V

CURVE CHARACTERISTICS AND PHYSICAL PROPERTIES

	<u>B 3</u>	<u>B 4</u>	<u>B 5</u>	<u>B 8</u>	<u>B 9</u>	<u>Orig.</u>	<u>F 5</u>
Height	21.0	21	17.3	20.7	22.2	14.4	24.5
D.P. of Max.	150	180	130	250	230	200	180
Avg. Width	101	87	144	116	97	238	57
% D.P. below 91	19.4	16.9	23.7	19.2	21.5	24.7	24.5
Tensile Str.	7740	7360	7040	7470	8200	6440	7670
% Elongation	20.6	19.7	17.4	19.7	22.2	17.2	19.5
Folding Endur.	164	166	142	163	142	163	229
Internal Tear	17.7	28.0	23.5	24.5	26.0	25.5	32.5
Bursting Str.	62.6	70.9	60.1	71.4	74.2	61.7	75.7

In Table V it is observed that Blend 9 has, except for Schopper Folds, the best mechanical properties, and that it has the greatest maximum height, second highest D. P. of the maximum, next to smallest average width, and next to the greatest amount of low D. P. material. That there is no direct correlation between the amount of low D. P. material and the physical properties when the average D. P. is held constant partially contradicts the conclusion reached by Mark (6), "The shape of the distribution curve seems to have no definite effect on the

ultimate strength except that a comparatively small amount (between 10 and 15 per cent by weight) of constituents having a polymerization degree below 150 are definitely detrimental to the mechanical properties of the sample." Study of Tables I and III gives a broader view and supports the conclusion that the amount of low D. P. material (91 or below) has to equal about 30% of the total weight before it appreciably lowers the mechanical properties.

It has already been pointed out and is observed again in Table V that the average width of the distribution curve does have some effect on the physical properties as noted with the original material, Blend 5 and Fraction 5. There is also some correlation between the position and height of the maximum and the properties; these characteristics of the curves determine their shape which in turn has a definite effect on the ultimate strength and this is another contradiction of Mark's statement as quoted above. Spurlin (13) also states that "the optimum physical properties may be obtained by increasing the molecular weight regardless of the degree of polymolecularity; the degree of polymolecularity is then not an important consideration." However, when these characteristic properties of a distribution curve are combined and plotted against the five mechanical properties as in Graph XIX the effect of the shape of the distribution curve upon the mechanical properties becomes very apparent.

The smooth lines drawn through the points in Graph XIX give the best correlation between the shape of the distribution curves and the mechanical properties that has been developed to date. It is realized that the correlation is not so good in the case of the folding endurance test and that the correlation of tensile strength with the shape factor could be improved. At the same time it is noted that only seventeen distributions have been so characterized and that this is too few to give a complete picture of the correlation. However, a start has been made and some conclusions can be drawn from these curves.

In Graph XIX it is observed that the properties improve as the "shape factor" increased up to a value of 450 except for the elongation which leveled off at 375. These curves are similar to those observed in Graph I, but in this case more than the average D. P. is considered since four of the blends (4, 5, 8, and 9) have the same average D. P. Combined in the "shape factor" is the "heterogeneity" of the material and the position of the maximum.

The effect of polymolecularity is especially noticeable in the correlation of Schopper Folds with the "shape factor" in Graph XIX, particularly in Blends 1, 2, and 6 which contain large quantities of both high and low D. P. material; yet according to the average D. P. of the sample the number of folds should have been 80 to 100 higher. Soime and Harris (11) noted this

same sensitiveness of fold resistance to the molecular heterogeneity, and Spurlin (12) found that when the distribution curve contained two peaks only about half of the expected number of Schopper Folds was obtained.

Examination of Table III shows that the percent elongation, tensile strength, and bursting strength are also sensitive to this heterogeneity while the internal tear resistance of Blends 1, 2, and 6 is nearly the same as for the other blends. From the values of the "shape factor" given in Table IV and an examination of Graph XIX, it is noted that these three blends fall along the lower ends of the curves. The fact that these two-peak blends fit into the curves of Graph XIX so well is good evidence that the method of characterizing the shape of the distribution curves developed during this investigation is sound and that there is a correlation between the shape of the distribution curves and the mechanical properties of ethyl cellulose films.

CONCLUSIONS

1. Fractionation of ethyl cellulose solutions in five gallon batches has been controlled so as to give reproducible results according to the average degree of polymerization.
2. The mechanical properties of the films improved with increasing D. P. of the fractions up to 200-250 and then exhibited little improvement for any further increase in the average degree of polymerization. By neglecting the effect of shape of distribution curves, the mechanical properties may be predicted when the average degree of polymerization is known.
3. It is possible to prepare and to test films prepared from ethyl cellulose having an average D. P. of 64 which is in the D. P. range where it was predicted the mechanical properties could not be measured.
4. It is necessary to refractionate the fractions in order to reduce the polymolecularity within the fraction.
5. Prediction of the mechanical properties depends upon three factors, the average D. P. of the material, the D. P. of the maximum, and the polymolecularity.
6. When the average degree of polymerization is held constant (below 200-250), prediction of the mechanical properties depends upon the polymolecularity and D. P. of the maximum.

7. The correlation so far obtained limits predictions to a few generalizations.

There is no direct correlation between the amount of low D. P. material (D. P. of 100 or less) and the mechanical properties when the average D. P. of the samples is the same until about 30% of the total weight has been added.

When the average D. P. and the position of the maxima are the same, the sample with the sharper peak will have the better properties.

A shift of the maximum to a higher D. P. without increasing the average D. P. will not necessarily mean an improvement in the mechanical properties.

The mechanical properties depend more upon the gross characteristics of the curve than upon fine details such as smoothness and general contour.

BIBLIOGRAPHY

1. Bass, S. L. and Kauppi, T. A., *Ind. Eng. Chem.*, 29, 679-86 (1937); 30, 74-9 (1938)
2. Cragg, L. H. and Hammerschlag, H., *Chem. Rev.* 39, 81 (1946)
3. Douglas, S. D. and Stoops, W. N., *Ind. Eng. Chem.* 28, 1152-5 (1936)
4. Gloor, W. E., *Ind. Eng. Chem.* 27, 1163 (1935)
5. Herzog, R. O. and Deripasko, A., *Celluloschem.* 13, 25 (1932)
6. Mark, H., *Ind., Eng., Chem.*, 34, 1343-8 (1942)
7. Mark, H. *Paper Trade J.*, 113, 26 (1941)
8. Mark, H., in Cellulose and Cellulose Derivatives, Ed. By Ott, E., Vol V of High Polymers, Interscience Publishers, Inc., New York, 1946, pp 990-1043
9. McKeer, R. D., Master's Thesis submitted to the Virginia Polytechnic Institute Faculty (1948)
10. Rocha, E. J., *Kolloid-Beihefte*, 30, 230-48 (1930)
11. Sookne, A. M. and Harris, M. *Textile Research* 13, No. 3, 17-31; *J. Research Nat'l. Bur. Standards* 30, 1-14 (1943)
12. Spurlin, H. M., *Ind. Eng. Chem.*, 30, 538-42 (1938)
13. Spurlin, H. M., in Cellulose and Cellulose Derivatives, Ed. by Ott, E., Vol V, High Polymers, Interscience Publishers, Inc., New York, 1946, p 937
14. Staudinger, H., Die hochmolekularen organischen Verbindungen, J. Springer, Berlin 1932
15. Staudinger, H. and Reinecke, F., *Ann.* 535, 47-100 (1936)
16. Zeisel, S., *Monatsh* 6, 989-96 (1885)