A CORRELATION OF THE MECHANICAL PROPERTIES OF CELLULOSE
NITRATE FILMS AS A FUNCTION OF THE SHAPE
OF THE DISTRIBUTION CURVE

by

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I. ACKNOWLEDGMENT

II. INTRODUCTION

In order to be able to study variation in the shape of the distribution curve of a polymeric material there are two possible methods of attack, in that one might search through a whole series of samples of the polymer until there is obtained a group of compounds of the same analytical composition but with distribution curves which vary in the range desired, or one might prepare a series of fractions (from a given raw material) which do not vary in analytical composition, but which cover the whole range of chain length values. By proper combination of such fractions it would then be possible to prepare artificially a polymer mixture whose distribution curve could be arbitrarily varied. The fractionation procedure was the one chosen for this investigation.

It is apparent that three experimental tasks have to be dealt with: (a) the analytical determination of the inhomogeneity; (b) the preparation of pure fractions; and (c) the suitable selection and quantitative determination of the physical properties to be investigated.

The last problem offers comparatively little difficulty. It frequently happens that one particular property exceeds all others in importance and may therefore be chosen as the main object of the investigation. It should be emphasized, however, that there is little known at the present time about which special characteristic of a solid high polymer reacts most sensitively to a change of the molecular distribution at a constant average degree of polymerization.

III.   CELLULOSE AND CELLULOSE NITRATE

STRUCTURE AND NITRATION OF CELLULOSE

The name cellulose does not denote a chemically well-defined and homogeneous substance; it serves for the characterization of products which, although having certain features in common, differ considerably from each other and should be regarded as homologous polymers. Cellulose, chemically speaking, is a polysaccharide of sufficient chain length to be insoluble in water or dilute acids and alkalies, consisting of glucose anhydride units linked together through the 1 and 4 carbon atoms with a beta-glucosidal linkage and giving a typical X-ray diagram. The empirical formula $(C_6H_{10}O_5)_n$ gives cellulose a molecular weight of 162 for each glucose anhydride unit present in the linear polymer. Each unit contains three hydroxyl groups in positions 2, 3 and 6 (figure 1). Since two hydroxyl groups are secondary and one is primary, these groups show differences in reactivity which are very evident in topochemical reactions while not so marked in permutoidal reactions, as for example, in the formation of the nitrate esters.

The nitration of cellulose is usually accomplished using mixtures of nitric and sulfuric acids and water. The basic chemical reaction involved in the preparation of the theoretical cellulose trinitrate may be represented by the equation:

$$\left[C_6H_7O_2(OH)_3\right]_x + 3xHNO_3 \rightleftharpoons \left[C_6H_7O_2(ONO_2)_3\right]_x + 3xH_2O$$
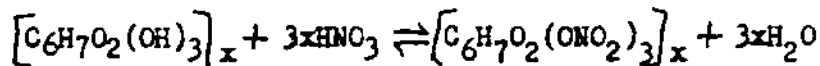
The actual mechanism and chemical reactions involved are infinitely more complex. The equilibrium reaction is shifted rather easily by changes in the composition of the nitrating acid and the reaction conditions. It is
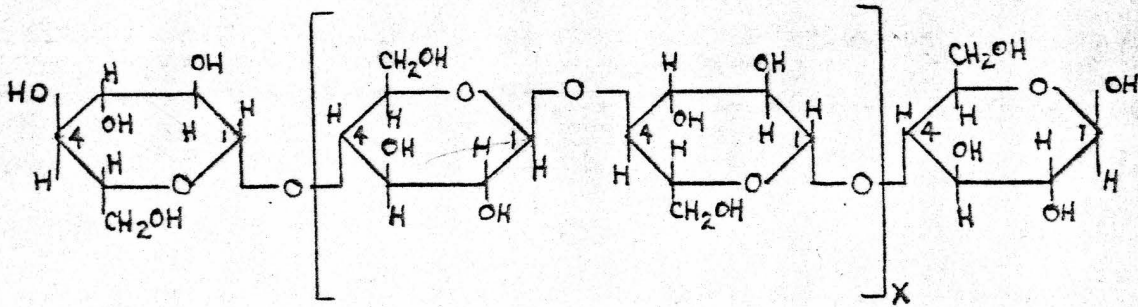
Figure 1. Theoretical configuration of the cellulose molecule. Degree of polymerization (D.P.) = X+2. At the left of the drawing·is shown a secondary alcohol configuration, the non-reducing end group. At the right is shown the hemiacetal configuration, only one of the several configurations possible for the reducing-end group.

(Taken from "Advancing Fronts in Chemistry", Vol. I., High Polymers. Edited by Twiss. Reinhold Publishing Corporation (1945), p. 79.)

possible to obtain nitrates of any desired degree of substitution averaging between zero and three nitrate groups per glucose unit by adjusting the nitrating conditions. In general, the esterification reaction is accompanied by some degradation of the cellulose as the result of the hydrolysis of the glucosidic linkages.

It is difficult to cite specifically the influence of the reaction conditions and the role of each constituent in the system on the nature and mechanism of the reaction. Water in the nitrating acid plays many roles, some of which are to increase the reactivity of the cellulose, reduce the viscosity of the nitrating acid, and control the effective concentration of the nitric acid. In addition to being the esterifying agent, the nitric acid also has a swelling and hydrolyzing action on the cellulose. The principal function of the sulfuric acid is to serve as a dehydrating agent and thereby maintain the effective concentration of nitric acid approximately constant. It has been shown by Berl (5) and Tomonari (67) that the sulfuric acid may be replaced by other dehydrating acids, particularly phosphoric acid. Brissaud (7) and Darzens (18) reported a method using a mixture of nitric acid, acetic anhydride and chloroform. Trogus (68) used a mixture of nitric acid and acetic acid, obtaining a nitrogen content of 12 percent.

It is possible to accomplish the introduction of the nitrate group by the use of nitrogen pentoxide (16,17,33,61). The vapors of nitric acid anhydride dissolved in carbon tetrachloride were permitted to act on cellulose at a temperature of 13° C in the absence of light. In this manner it was possible to obtain a nitrate with 14.12 percent nitrogen content. The yield amounted to 99.3 percent of the theoretical (61).

It is seen that under certain conditions the theoretical value of
the trinitrate (14.14 percent nitrogen) has been very closely approached.
This may be due to the elimination of the formation of sulfuric acid
esters. It might also be assumed that the absence of sulfuric acid de-
creases the hydrolyzing action of the nitration mixture upon the nitrate.

FRACTIONATION OF CELLULOSE AND CELLULOSE DERIVATIVES

In a discussion of the methods used to separate the different degrees of polymerization of cellulose and cellulose derivatives, the methods employed may be conveniently classified on the basis of the separation principle (15). A review of the literature has shown that the solubility methods, especially fractional precipitation and fractional solution, have been more widely used than diffusion, ultracentrifugal, chromatographic adsorption, and ultrafiltration methods (55).

The early theories of solubility fractionation of Brønsted (8) and Schulz (58,59) have been followed by a thermodynamic approach developed by Flory (24,25,26), Gee (28), and Huggins (34,35,36). In the thermodynamic approach, entropies and heats of mixing are calculated for the solution and precipitate phases, and these are used in the thermodynamics of equilibrium between the two phases.

A theory has been proposed by Morey and Tamblyn (48) to explain the reverse-order precipitation in which the low molecular weight chains were precipitated first (47). Other examples of this type have not been reported, although one case of precipitation without any preference as to molecular weight was reported by Battista and Sisson (4).

The efficiency of fractionation is a prime essential of practical importance which should be carefully examined in the course of the development of theories. However, the emphasis has been placed particularly on the proper concentration of the polymer present in the solution while the importance of the solvent-precipitant system has not been fully investigated.

METHODS OF DETERMINATION OF THE MOLECULAR
WEIGHT OF CELLULOSE NITRATE

The methods used for the determination of the average chain length
of cellulose nitrate are physical methods and are applicable to the
substance in a state of molecular dispersion. The cryoscopic methods of
molecular weight determination, methods dependent on boiling point ele-
vations and freezing point depressions, are impractical; since in order
to obtain measurable effects with substances of high molecular weight, it
would be necessary to work at concentrations at which the van't Hoff re-
lation no longer holds. Certain chemical methods such as end-group
determinations are useful for cellulose itself but cannot be applied to
cellulose nitrate.

Methods of determining the average molecular weight of cellulose
nitrate may be found in the recent texts (19, 32, 51); and in spite of
the criticisms of the Staudinger viscosity method (1, 37, 41, 42, 60), it
is, due to convenience, ease of determination and simplicity, still of
practical value.

The recent modification of Staudinger's method by Kraemer (39) is
purported to be a more reliable method for calculating molecular weights
from viscosity measurements. Kraemer expressed the viscosity measure-
ments extrapolated to zero concentration as intrinsic viscosities:

$$[\eta] = \left(\frac{\log_e \eta_r}{c}\right)_{c \to 0}$$

in which "η_r" is the viscosity of the solution relative to that of the
solvent and "c" is the concentration in grams of solute per 100 cc of
solution.

One disadvantage of the Kraemer modification has been the fact that several viscosity determinations at different concentrations were necessary in order to extrapolate accurately to zero concentration. However, Coppick (14) has shown that it is possible to obtain similar results using one viscosity measurement with an accuracy approximating that of the most accurate measurements extrapolated to infinite dilution.

IV.   THE INFLUENCE OF THE AVERAGE MOLECULAR WEIGHT ON THE
PHYSICAL PROPERTIES OF CELLULOSE NITRATE

INTRODUCTION

It is well known that practically all natural and synthetic linear high polymers consist of a more or less nonuniform mixture of molecules having different chain lengths, different internal structures of the chains, and sometimes even different end-groups. If the molecules are not strictly linear, it is necessary to consider a different amount of branching or cross-linking for a comparison of various molecules of the same sample. In making observations on osmotic behavior, diffusion, viscosity, etc., it is always necessary to interpret the experimental results by introducing certain average values for size, shape, and chemical constitution of the elementary particles of the material. The number average "M_n" and the weight average "M_w" molecular weight, and the corresponding polymerisation degrees "P_n" and "P_w", are particularly useful and important. Although it is now possible to tie up these average values with the osmotic behavior and the intrinsic viscosity of the material, it is not yet possible to bring them into reasonable agreement with the most important properties of the material in a more concentrated state, such as the flowing properties of concentrated solutions and the mechanical properties of the high polymeric gels as fibers or films.

INFLUENCE OF AVERAGE MOLECULAR WEIGHT

It is known that for a given structure the sum total of the attractive forces between neighboring chains will be a function of the chain length. The chemical considerations of behavior must therefore be modified by variation in chain length.

It is also of interest to study the relationship between degree of polymerization, and fold resistance and tensile strength. The tensile strength of cotton, ramie, or flax fibers increases rapidly as the degree of polymerization increases from 200 to 600. Contrasted with this behavior, cellulose-derivative films or filaments deposited show measurable strength and flexibility with a degree of polymerization of less than 200. On the basis of molecular weights of polymers other than cellulose, such as the polyesters of Carothers and Hill (12) and the vinyl esters of Douglas and Stoops (20), it would appear that the lower limit for film formation would occur at a number average degree of polymerization, P_n, nearer 50 or a weight average degree of polymerization, P_w, of about 100 (52). The weight average degree of polymerization values are those most easily correlated with viscosities, which are the measurements from which molecular weights are usually calculated. Native cellulose fibers all have approximately the same tensile strength, although the P_w varies from 1000 to 3000; similarly in the case of cellulose derivative filaments or films deposited from solution, it is found that an upper limit of molecular weight exists above which further improvement in molecular weight does not result in improvement of tensile strength. Fold resistance increases somewhat more than tensile strength with increase in

molecular weight. It may be summarized that, in general, a P_w of approximately 100 is required for measurable tensile strength and that tensile strength increases with further increase in chain length until a maximum is approached with a degree of polymerization of about 600 to 800 (45).

The Two-Phase Structure of High Polymers

Experimental evidence of the last several years points in the direction that all high polymers in the solid state are complicated two-(or even multi-) phase systems. For example, a rubber band or a cellulosic film is certainly well defined from the point of view of the chemical unit which builds up the chains of the polymer (isoprene or anhydroglucose); it may be well characterized in respect to its average degree of polymerization and even to its chain length distribution curve. Nevertheless, it is possible to produce fibers and films of very widely varying properties from these polymers solely by varying the supermolecular structure of the system, that is, the way in which the individual chains are connected with each other by intermolecular forces (2,3,9,10, 12,27,30,40,46,62,63).

Chemical and physical investigation of all types of high polymers have shown that there are two extreme cases to be considered first:

(a) the completely organized or crystallized state, and

(b) the completely disordered or amorphous state.

Organized or Crystallized State

X-ray, birefringence, swelling, thermal behavior and chemical reactivity of rubbers, plastics and fibers indicate that most of those materials contain portions, inside of which the individual chains are arranged in a three-dimensional lattice. In the interior of such a crystallite, each atom occupies a definite equilibrium position around which it carries out more or less regular vibrations. No shifting and

no rotations are possible. The equilibrium positions are periodically distributed according to a three-dimensional pattern.

Thus, the interior of these organized areas shows all characteristic qualities of a crystal. Their surface does not, since there is no indication for the existence of sharp angles, plane faces or even for a definite external shape as a result of these crystallites. It seems that a bundle of chains which is very highly organized over a certain length, say 25 Å, can lose its internal regularity over another distance, say 200 Å, and regain it afterwards. This means that one and the same individual chain can belong to a crystallized area, go through an amorphous portion and re-enter another crystallite.

It is obvious that ordered and disordered chains are not clearly separated from each other but are interconnected by through-going chains. This complex structure of the interface between crystallized and amorphous portions causes the gradual melting zone of high polymers and effects their swelling and setting properties.

The Effect of Crystallization

With the present knowledge it can be stated that the crystallized areas give to the material a high modulus of elasticity, rigidity, and ultimate tensile strength, while the disordered parts are responsible for its flexibility, recovery, elongation, and swelling (44). For example, a sample of a completely crystallized cellulose of a polymerization degree of 1000 should have a modulus of elasticity of about 5×10^{12} dynes per square centimeter and an ultimate tensile strength of about 15 grams per denier. Its elongation to break, however, should be very low, about

one percent. The same sample in a completely disordered state should have a modulus of about 5×10^{10} dynes per square centimeter and an ultimate tensile strength of less than one gram per denier.

Any individual sample somehow combines the properties of its completely organized and completely disordered portions, but it is also greatly influenced in its properties by the material having intermediate degrees of orientation. These areas of intermediate randomness can be considered as not having had the chance during the formation of the film either to remain in their original, complete disorder or to reach a fully organized state. They may be compared with a quenched alloy in which a meta-stable arrangement of atoms is maintained, because the molecular rearrangement is so slow that no changes are taking place although the system is far from being in equilibrium. If the internal mobility of the chains is increased by appropriate measures, such as swelling or temperature increase, a certain amount of rearrangement will take place and the sample will undergo a change of its internal structure, of its external shape, and of its physical properties.

If the areas of intermediate organization are nearer to the amorphous state, the chains in them will tend to approach complete disorder as soon as they acquire sufficient mobility to do so; the result will be a shrinking of the sample if it is swollen or heated. On the other hand, if the metastable portions have a tendency to be transformed into crystallites, any appropriate change of the external conditions, such as dehydration, stretching, or cooling, will induce them to crystallize and the properties will change accordingly.

Thus, samples of high polymers are complicated systems of a certain intrinsic metastability which makes them very sensitive against any

change of the external conditions such as humidity, temperature, presence of swelling agents, etc.

To produce crystallization, one can bring the chains into a more favorable elongated shape by stretching, where upon crystallization sets in immediately. However, as soon as the external force is released, the random kinetic molecular movement destroys the regularity again; the crystallites revert to a more random structure because the intermolecular forces between the chains are weak and the sample contracts. This reversible crystallizability is the main reason for the typical elasticity of rubber and other related compounds.

Disordered or Amorphous State

Experimental evidence shows that there is always a certain amount of disordered material between the crystallites. In some cases, such as rubber, it has been observed (44) that the segments of the individual chains can be arranged completely at random so that a high degree of disorder is characteristic for the amorphous areas of these substances. Inside of these disordered areas, the geometrical arrangement of the units of a chain can be compared with a liquid; certain average distances are maintained, but there is no strict three-dimensional periodicity prevailing.

Furthermore, there are not only oscillations of single atoms or atom groups possible, but there is a certain degree of rotational and translational freedom which permits processes of rearrangement and relaxation in comparatively short times. In other cases, however, particularly if distinct groups of intermolecular forces are regularly distributed along

the chains (polar groups), it seems that there is always a certain amount of regularity left inside of sufficiently small volumes (about 10 $\overset{o}{A}$ cubed).

There are several ways to force the chains into a more random state. The sample can be heated which, by increasing the average kinetic energy, makes the chains more capable of escaping the organising action of the intermolecular forces. By treatment with a swelling agent, the points of attraction between the chains become solvated and the intermolecular forces are directly weakened. A third method is mechanical relaxation which relaxes the external forces, straightens out the chains, and therefore favors randomness.

Intermediate States

Complete organization and complete randomness are the two extreme states in which a given (small) volume of any high polymer can appear, but they are not the only ones (44). There is a continuous variation in the degree of randomness between these two extremes; and large portions of a sample, such as a film, are in an intermediate or mesomorphous state in which the tendency for crystallization and for randomization balance each other under the given experimental conditions.

If the forces between the chains are strong and regularly distributed, and if the chains are fitting easily into a lattice, crystallinity of the material is favored. If, on the other hand, the forces are weak and irregular, and the fitting of the chains is poor, randomness is preferably to be expected.

Alteration of Orientation and Randomness Through Processing

Under given conditions concerning the structure of the chains, the presence of reasonably strong intermolecular forces and chains which can fit together, operations such as stretching, rolling, and annealing favor crystallinity and orientation, while processes such as shrinking, swelling, quenching, etc., bring the system into a more amorphous and disordered state (44).

Each sample, such as cellulose or a cellulosic derivative film, is the result of a series of operations, some of which are favoring crystallization while others are intending to bring the chains into a more randomized state. Hence, each individual film is a mixture of completely organized areas, completely disordered portions, and portions having intermediate degrees of internal organization.

Tensile Strength of Cellulose Nitrate

In order to begin a discussion of the tensile strength of cellulose nitrate, it is necessary to present two theoretical cases (43). The first case assumes that the rupture is due only to a break of the chains themselves, that is, a rupture of the primary valences; while the second case assumes that the rupture is due solely to slippage of the individual chains along each other breaking the secondary valence forces.

Rupture of Primary Valences

The problem thus involves an approximation of the tensile strength. It was assumed that a fiber or film consisting of infinitely long cellulose chains is subjected to a stress at its ends parallel to the direction of the chains. Each chain passes through the entire section under tension so that if the fiber or film is torn, all the chains must be torn and cannot slip over each other. If the chains are parallel, it follows from the projection of the native cellulose unit lattice, the individual cross section of a chain amounts to 33×10^{-16} cm^2, and thus, the number of chains passing perpendicularly through the unit cross section of 1 cm^2 is 3×10^{14} (43).

The force necessary to break one cellulose chain must be calculated. It is obvious that the most labile linkages in the chain will be the -C-O-C- bridges which connect the glucose rings. The energy of the -C-O- bond is about 90 kg-cal per mole or 6×10^{-12} ergs per individual bond, and it is approximately equal to the force necessary to separate the atoms and the distance from the equilibrium position to the point

where the interatomic attractive force is essentially zero. If 1.5 $\overset{o}{A}$ is the equilibrium distance of the -C-O- bond and 4.0 $\overset{o}{A}$ is the distance at which the bond can be considered broken, it can be easily calculated that the tenacity of one single cellulose chain is 2.4×10^{-4} dynes. The tensile strength of this idealized sample is the product of the number of cellulose chains and the tenacity. This theoretical tensile strength is 7.2×10^{10} dynes per cm^2 or approximately 60 grams per denier. This is about eight times higher than the maximum values measured with well-oriented and highly-crystallized natural and synthetic fibers such as flax, hemp, or viscose rayon.

The previously given rough calculation has been refined by de Boer (6), who, from a knowledge of the potential energy atomic distance curve, calculated still higher values for the tenacity of an idealized cellulose sample. This result can be taken as an indication that all real samples break according to a different mechanism.

Rupture of Secondary Valence Forces

It is assumed that three theoretical samples of parallel cellulose chains exist (43). In sample A, the overlapping of the chains is at random; in sample B, there is no overlapping of the chains; and in sample C, there is a regular overlapping of the chains. Of these three samples, a minimum tenacity obviously exists in sample B. The tenacity of this cross-section can be figured as before, taking into account only the secondary valence forces, as approximately 2 grams per denier.

The value calculated is in fair agreement with the tenacity of very dry, poorly oriented viscose or acetate rayon filaments.

To account for the higher tenacities which are obtained if fibers of better orientation are investigated, it seems reasonable to assume that, as the chains and crystallites become more and more parallel, the probability of finding one cross section which contains only chain ends will decrease very rapidly. With an increase in the overlapping of the chains, the ragged cross-sectional area over which only secondary valence forces need to be broken will increase, and with it, the number of bonds which will need to be broken will be larger also. Thus, if the primary valence bonds are so strong that they do not rupture, then secondary valence forces must be opened up over a much larger area because the chains are overlapping each other in an irregular manner. Instead of breaking 3×10^{14} secondary valence bonds along a smooth cross section at the same instant, those parts of the chains which overlap must tear loose and slip along each other.

Slippage of Chains

In order for two chains to slip along each other, it is not necessary that the full strength of the secondary valence forces along the whole distance of 3.5 $\overset{o}{A}$ be overcome and that the attracting groups be completely removed from each other's sphere of action. It is only necessary that the chains become uncoupled. This requires a certain activation energy to carry out the elementary step of slippage under the influence of stress. This concept of slippage is similar to that of Eyring (22) in his treatment of viscosity of liquids as a rate phenomenon.

In well-oriented fibers it must be supposed that the chains which are of limited length are associated over part of their length to form a

lattice-type arrangement as a result of the interaction forces between the polar groups present. Rupture of the filament or film can occur as the result of chains slipping over each other. In artificial fibers prepared from material which has been carefully treated and in which the orientation is good, the internal cohesion of the chains is so considerable that the tenacities approach those of the natural fibers.

It seems reasonable to believe that artificial fibers never reach theoretical values because of the lack of perfect orientation and the presence of imperfections in the crystalline and amorphous portions of the chains. If a thin slice is taken from a filament or film, certain parts of the cross section are well crystallized, oriented, and overlapped and therefore will stand the stress which is applied to them. Other portions, however, which are of less favorable structure, having less orientation and less overlapping, will give way at the expense of the stronger portions. As a result, the stress in these portions will increase unduly and produce the break earlier than if the whole cross section were homogeneous. Thus, the rupture of a high polymeric system has to be treated by assuming that it begins at the weakest point and progresses gradually to the stronger portions, the strength of which may be completely prevented from adding to the numerical value of the tenacity.

Summary of Early Experimental Work

Carothers (11,13) was one of the first to establish a connection between the average chain length of a high polymer and its tenacity, showing that a critical minimum polymerization of about 50 is necessary

in order to produce films or filaments. With a degree of polymerization greater than this minimum, the tenacity increases rapidly as the chain length increases up to a polymerization degree of about 300. Above this value, the rate of increase decreases and at some fairly definite range in the polymerization degree, a further increase in tenacity is not obtained by increasing the average degree of polymerization. The exact shape of this average chain length-tenacity curve depends distinctly upon the chemical character of the system and upon the conditions at which the sample was prepared.

In 1933, Jones and Miles (38) published results showing the effects of the average degree of polymerization on the tensile strength and elongation of cellulose nitrate films. Included in this work was a statistical study of the results which showed that if a large number of samples was used for testing, the results were distributed normally, that is, a normal distribution of the values was obtained.

Further, a study of the effect of the solvent used on the resultant tensile strength was made, and it was shown that according to the solvent or solvent mixture used, the tensile strength varies quite markedly. In this particular study, a cellulose nitrate designated as H.I.776 having a nitrogen content of 12.24 percent was used. Some of the results obtained are given in Table 1. It is interesting to note that acetone and ethyl acetate solutions gave films of high tensile strength. The values for elongation do not seem to follow the tensile strength in any logical manner.

More recently, Ott (53) has stated that there should be a range of polymerization degree in which the number of imperfections in any test sample caused both by crystallization tendencies and by the operation of

TABLE I

TENSILE STRENGTH AND ELONGATION OF FILMS
PREPARED FROM COMMON SOLVENTS

Cellulose Nitrate	Solvent	Tensile Strength psi	Percent Elongation
H.X.776	Acetone	12,190	14.0
H.X.776	Ethyl Acetate	11,612	16.0
H.X.776	Cyclohexanone	10,520	10.0
H.X.776	Cellosolve	8,190	10.7
H.X.776	Methyl Alcohol	*	*
H.X.776	Methyl Alcohol - Ethyl formate 1:1	9,270	6.0

* Too brittle to test.

chance would be so great that the tensile strength would be little greater than zero. With an increase in the polymerization degree, the crystallizing tendencies are diminished and the number of chain ends in a small volume decreases very rapidly. Therefore, the tensile strength should increase quite abruptly. This abrupt rise could be considered as a transition between the state of negligible tensile strength and a state in which the chains are so long that the probability of chain ends being concentrated in one region is very small.

Observed tensile strengths versus chain-length curves for cellulose nitrate show, according to Ott (53), no measurable tensile strength up to a weight-average polymerization degree of about 100. There is a rapid increase in tensile strength up to a "P_W" of about 250, and as the "P_W" increases above this value, the rate at which the tensile strength increases becomes slower. Above a "P_W" of about 600, the increase is usually very slight.

Mark has stated (45) that in order to obtain mechanical strength at all, the material must have a certain minimum degree of polymerization. This critical minimum value ranges between 40 and 80. He further states, "As soon as this critical value of the chain length is surpassed, the material starts to show mechanical strength, and the increase of tenacity is roughly proportional to the average degree of polymerization. This proportionality holds up to a polymerization degree of about 250; then the curve flattens out gradually, until when it has reached a polymerization degree of about 600 or 700, the mechanical properties no longer depend to any appreciable extent upon the chain length."

Further information concerning this minimum lower limit of polymerization degree necessary for film formation is given by Gloor (29) as

being from 30 to 40 for a cellulose nitrate having a nitrogen content of
12.0 percent. He pointed out that this is below the limit of chain
length as given by Carothers and van Natta (13). However, it should be
realized that this work of Carothers and van Natta was a study of poly-
esters obtained by polycondensation reactions from ω-hydroxydecanoic
acid, and the results cannot be used indiscriminately to characterize all
high polymers regardless of the type and nature of the recurring unit.

In general, it may be said that the mechanical properties such as
tensile strength (tenacity) and elongation, folding endurance, etc., are
practically non-existent for a cellulose nitrate which has a very low
average degree of polymerization. This minimum value of the polymeri-
zation degree is thought to be somewhere below 50. Beyond this critical
range and up to an average polymerization degree of 200 to 300, the
mechanical properties increase quite markedly with increased chain length.
Finally, after an average polymerization degree of about 250 is reached,
the curve of the mechanical property plotted versus chain length flattens
out and approaches a constant value, above which the average chain length
does not further influence the mechanical properties to any considerable
degree.

It should be emphasized that in most cases the curves which have been
given relating mechanical properties to chain length have not represented
experimentally determined curves entirely. In addition, if fractionated
materials were used, the quantities available were small. Consequently,
the information represents more a picture of extrapolated knowledge
rather than established facts.

V. THE EFFECT OF THE SHAPE OF THE DISTRIBUTION CURVE ON THE
MECHANICAL PROPERTIES OF CELLULOSE NITRATE

During the early study of cellulose derivatives, it was realised
that any given sample consists of a mixture of molecules of widely
differing chain lengths. The significance of this fact in the inter-
relationships between mechanical properties and the average polymeri-
sation degree as the degree of polymolecularity is changed must be
considered. It is possible that either a very uniform or a very poly-
molecular product will have mechanical properties impossible to realise
with the other extreme, and the quantitative relationships between such
properties, as tensile strength and flexibility of films, may differ as
the degree of polymolecularity is changed.

As soon as it became evident that cellulose derivatives could be
fractionated into portions differing greatly in viscosity and other physi-
cal properties, the question arose as to whether a mixture of high- and
low-molecular weight material had better or poorer mechanical properties
than a more uniform product. Cellulose derivatives were fractionated,
and the tensile strength and elongation of films or filaments made from
the fractions or mixtures of them were used to characterise the products.

The results of much of this early work (31,49,54) seemed to indicate
a definite advantage of blends of high- and low-molecular weight material
over uniform fractions having the same viscosity in solution as the blends.
This conclusion is diametrically opposed to that indicated by more recent
work. It is probable that the early investigators made too few experi-
ments on too poorly fractionated materials actually to decide the point.

One of the early studies of the influence of the chain length distri-
bution on the properties of viscose staple fibers was reported by Schieber
(56,57) who investigated eleven staple fibers and reached the general con-
clusion that the outstanding point is the detrimental influence of

moderate amounts (5 to 15 percent) of chains below a certain critical polymerization degree (for viscose staple fiber around 70 to 100). The distribution curves were worked out by nitration of the fibers and fractionation of the nitrate by selective solubility in acetic ester-alcohol mixtures. This method gave interesting chain length diagrams of great analytical importance but did not permit one to prepare synthetic distribution curves of distinct shapes, convert them into films or fila-ments, and study their properties.

The work of Eisenhut (21) indicated similar conclusions concerning the detrimental effect of short chain material.

Schulz (58,59) showed that, on the basis of fractionation experience, the molecular weight distribution of a cellulose derivative such as cellu-lose nitrate is more uniform than that of synthetic polymers such as polystyrene and polyisobutylene. Staudinger (66) ascribed these differ-ences in distribution to differences in their method of preparation. Cellulose nitrate is prepared by the degradation of a relatively uniform high molecular weight linear natural polymer, and in the process, low molecular weight portions are formed only in small amounts. Flory (23) and Schulz (58,59) gave expressions for calculating molecular weight distributions for polymers, which agree substantially with one another and with Schulz's data for fractionated polystyrene and polyisobutylene.

The points brought out above apply even to cellulose derivatives of relatively low molecular weight. Flory (23) showed that the molecular weight distribution of cellulose products will approach that of the synthetic polymers the more the cellulose is degraded. In spite of this fact, Spurlin's fraction data (65) on a low viscosity cellulose nitrate show less molecular heterogeneity than is calculated for a condensation

polymer of the same average degree of polymerization.

Ott (50) believes, in view of the fact that experimental data and calculation of molecular weight distribution of synthetic polymers agree, the difference in the distributions of cellulosic polymers and synthetic polymers appears to be significant. He further concludes that cellulose derivatives will always show a greater uniformity in molecular weight distribution than synthetic polymers, and as a result, the cellulose derivatives when properly prepared will be expected to suffer less from the disadvantages associated with the presence of low molecular weight fractions.

More recently, the data of Sookne and Harris (64) on cellulose acetate are interesting in that they present the idea that the strengths of the blends which they prepared are an additive property of the fractions employed. The assumption was made that the fractions were perfectly homogeneous. The fractions used were refractionated three times, but even this does not insure perfect homogeneity. This work was carried out as an approach to the problem of the harmful influence of low molecular weight material on the mechanical properties of blends, but the blends prepared consisted of only two fractions. Thus, it is not possible to draw differential curves nor to correlate the mechanical properties as a function of the shape of such distribution curves.

The above criticism also applies to the work of Spurlin (65) who applied a similar procedure in the preparation of his blends.

From a review of the literature available on this problem, only this conclusion can be drawn, that in order for a polymer to exhibit any mechanical strength, the average degree of polymerization must have a certain minimum value somewhere between 40 and 100 (45,53). Further, there is no

known definite effect of the shape of the differential distribution
curve on the mechanical properties except for the fact that a compara-
tively small amount between 10 and 15 percent by weight of constituents,
having a polymerization degree below 150, is definitely detrimental for
the mechanical properties of the sample (45).

VI. EXPERIMENTAL PROCEDURE AND RESULTS

MATERIALS USED

The high-viscosity cellulose nitrate was Lot 1379, RS Type 600 - 1000 seconds, obtained from Hercules Powder Company, Parlin, New Jersey. The nitrogen content was reported to be 12.07 percent.

The low-viscosity cellulose nitrate was Lot 6226, RS Type $\frac{1}{2}$-second, obtained from Hercules Powder Company, Parlin, New Jersey.

The acetone was chemically pure grade obtained from Commercial Solvents Corporation, Peoria, Illinois.

The ethyl acetate was technical grade obtained from Commercial Solvents Corporation, Peoria, Illinois.

The n-butyl acetate was technical grade obtained from Eastman Kodak Company, Rochester, New York.

The n-heptane was commercial grade obtained from Phillips Petroleum Company, Bartlesville, Oklahoma.

FRACTIONATION PROCEDURES AND DETERMINATIONS OF DEGREE
OF POLYMERIZATION

Fractionation of High Viscosity Cellulose Nitrate

The primary purpose of the development of a reproducible fractionation procedure for the fractionation of cellulose nitrate was to permit sufficient quantities of fractions of different average degrees of polymerization to be accumulated in order that the blends to be prepared might have different differential distribution curves. A search of the literature did not reveal a method of fractionation which could be applied successfully to the large batch fractionations which this investigation required. Furthermore, since there was no reference in the literature which indicated the quantities of material needed to permit the flexibility desired in changing the shape of the distribution curve, it was impossible to make any estimation of the quantity of each fraction required in such a study.

The fractionation procedure which was used was that of fractional precipitation combined with a temperature decrease (55). This method used ethyl acetate as the solvent, and a concentration of 2.5 percent of cellulose nitrate, RS Type 600 - 1000 seconds, in this solvent gave a solution which could be easily handled. The non-solvent used, n-heptane, was added to the ethyl acetate solution in sufficient quantity to cause a permanent turbidity without precipitation at 25 degrees Centigrade. The quantity of n-heptane necessary to produce turbidity had been previously determined by small scale experiments (55). Upon addition of the n-heptane, the temperature of the solvent-non-solvent-polymer mixture

was decreased to approximately 23 degrees. The temperature of solution was allowed to rise to 25 degrees while stirring the solution.

A total of twenty-four fractionations was run. The ethyl acetate-cellulose nitrate solution was composed of 7,064 grams of ethyl acetate and 181 grams of oven-dry cellulose nitrate. To this solution was added 6,699 grams of n-heptane. After the addition of the n-heptane, the mixture was stirred vigorously for two to three hours before being placed at 15 degrees Centigrade. The period of standing for the first and second fractions was 45 hours and for subsequent fractions, 21 hours.

After standing for the required period of time, the supernatant liquid was decanted into another container and heated to 25 degrees before the addition of more non-solvent. The precipitate was dissolved in acetone and recovered in the form of flocks by pouring the acetone solution into water. The fraction thus obtained was dried at 55 degrees overnight, and to this was added sufficient ethyl alcohol to wet it thoroughly. The alcohol-wet cellulose nitrate fraction was then stored at 15 degrees in the dark for a period of approximately six months.

By the use of the above fractional precipitation procedure, a total of nine fractions was obtained, averaging 92 percent of the total weight of cellulose nitrate. Due to the economic necessity of recovering the ethyl acetate and heptane, the residual portion of the cellulose nitrate was not recovered.

By using the Staudinger viscosity method to determine the degree of polymerization of the fractions obtained, a sample consisting of approximately .0500 grams of cellulose nitrate was placed in a small weighing bottle, dried for one hour at 100 degrees Centigrade, cooled in a desiccator, and weighed accurately. The sample was then transferred to a large

Pyrex test tube, to which was added 50 ml of n-butyl acetate. The test tube was stoppered with a cork which had been previously extracted with n-butyl acetate to remove soluble fats and waxes. After the test tube had been well shaken, it was allowed to stand long enough for the cellulose nitrate to dissolve. The time of standing was varied as necessary to obtain complete solution.

After the sample was dissolved, the test tube and the Ostwald-Fenske viscosimeter were suspended in a water bath maintained at 20.0 ± .1 degrees Centigrade for at least 30 minutes before the transfer of 5 ml of the solution into the viscosimeter. Five successive readings agreeing within 0.2 second were taken of the time for the flow through the viscosimeter of the solution and of the pure solvent. From these times, the specific viscosities of the samples were calculated by assuming the density of the very dilute solution and of the solvent to be essentially the same. The average degrees of polymerization were calculated from Standinger's equation.

Sample Calculation

Weight of sample   0.0508 grams

Volume of butyl acetate   50 ml.

Viscosity of solvent   57.7 sec.

Viscosity of solution   105.4 sec.

Value of $K_{(m)}$ = 14×10^{-4}

$$\eta_{sp} = \frac{\text{Viscosity of solution}}{\text{Viscosity of solvent}} - 1$$

Substituting into Staudinger's equation

$$\frac{\eta_{sp}}{c} = K_m \cdot P$$

where "c" is concentration in grams per liter and "P" is the degree of polymerization.

$$P = \frac{\eta_{sp}}{c \cdot K_m}$$

$$P = \frac{\frac{105.4}{57.7} - 1}{\frac{.0508}{50} \times 1000 \times 14 \times 10^{-4}}$$

$$P = 581$$

The results obtained from one large scale fractionation, together with the average degree of polymerization determined for each fraction, are given in Table 1.

The control of the temperature of the viscosity bath at 20 degrees was found to be difficult due to the temperature changes in the laboratory. Therefore, a series of determinations was made at 35 degrees for the solvent, another series for the solutions. From these the "η_{sp}" could be calculated. Determinations were also made on the same solutions at 20 degrees. The average degree of polymerization was calculated on the basis of the 20-degree measurements using the Staudinger constant, 14×10^{-4}. Assuming that the same average degree of polymerization existed for the solutions at 35 degrees, a new constant for use at this higher temperature was calculated to be 12.2×10^{-4}. This new constant was used throughout the remainder of this investigation.

TABLE 1

SAMPLE OF FRACTIONS OBTAINED IN LARGE SCALE PROCEDURE

Fraction Number	Percent Obtained	Average D.P.
1	19.7	550
2	17.4	535
3	13.0	505
4	6.9	465
5	6.9	415
6	7.1	380
7	7.8	275
8	8.5	220
9	2.7	165

Total percent obtained 90.0

It was realized that even storage of the cellulose nitrate fractions in ethyl alcohol at 15 degrees Centigrade, in the dark, would not prevent the occurrence of some degradation. Therefore, it was necessary to combine all portions of corresponding fractions by dissolving them in acetone and reprecipitating by pouring the viscous acetone solution into water.

Some small scale refractionations had indicated that by a refractionation of the first fraction, a higher average degree of polymerisation than 550 could be obtained. This indication was found prior to storing the fractionated material.

A portion of the first fraction was dissolved in acetone and distilled water was used as the precipitant. The precipitated portion obtained was separated and recovered in the usual manner, but upon the determination of the viscosity, it was found that the average degree of polymerization had not increased. It had been decreased to 510. An attempt was made to refractionate another portion of the first fraction using ethyl acetate as the solvent and n-heptane as the precipitant. This resulted in a precipitated portion having an average degree of polymerisation of 465. Recognizing that the first fraction was badly degraded, no further attempts were made to improve the average degree of polymerization, and this fraction was not used in any of the mechanical tests.

Duplicate viscosity determinations were made on each of the other eight fractions obtained from the large batch fractionations, and since the average degree of polymerisation for each fraction varied only a small amount from the previously determined values, these fractions were used in film formation and testing, as will be described in the following section. It should be noted that in this redetermination of the

viscosities, fractions five and six were found to have the same average degree of polymerization. The determinations on fraction five were 344 and 346; and on fraction six, 344 and 345.

Therefore, from the fractionation of the high viscosity cellulose nitrate, seven fractions ranging in average degree of polymerization from 520 to 165 were available for mechanical testing.

Fractionation of Low Viscosity Cellulose Nitrate

The purpose of fractionating the low viscosity cellulose nitrate, with an average degree of polymerization of 60, was to obtain a small amount of material which might have an average degree of polymerization of 50 or less. It was not necessary that the results be reproducible, since one large batch would supply enough material for testing the mechanical properties and for use in the artificial blends.

It was estimated that 100 grams of material, having an average degree of polymerization of 50 or slightly below, would be sufficient. Therefore, it was decided to dissolve 400 grams of the low viscosity cellulose nitrate in 3600 grams of acetone and to add a sufficient quantity of water to produce a permanent turbidity in the mixture at 25 degrees Centigrade. This required 650 cc of distilled water. The acetone-water-nitrocellulose mixture was then allowed to stand for 20 hours at a temperature of 15 degrees Centigrade. Two distinct phases were obtained. The supernatant liquid was separated, placed under reduced pressure and evaporated, thus recovering the soluble portion of this material. A viscosity determination revealed that the average degree of

polymerization was 55, and the weight of the dry material was 221 grams.

The precipitated phase was highly solvated, and it was recovered by redissolving in acetone and pouring into water. The average degree of polymerization of this material was 75.

Since the average degree of polymerization of the soluble portion obtained in this fractionation procedure was above 50, it was decided to subject the material to another fractionation. This was accomplished in a similar manner as before by dissolving the 221 grams of cellulose nitrate in 1980 grams of acetone, and to this solution was added 600 cc of distilled water. After standing for 20 hours at 15 degrees Centigrade, the solution had separated into two phases. The precipitated phase was again highly solvated, and it was difficult to separate the supernatant liquid from the precipitated phase. However, the separation was accomplished by the use of a large separatory funnel.

The supernatant liquid was again placed under reduced pressure and the soluble material was recovered. This portion, weighing 81 grams, had an average degree of polymerization of 30; and the precipitated phase, recovered by dissolving in acetone and pouring into water, was found to have an average degree of polymerization of 71.

This precipitated portion of the low viscosity material was combined with the precipitated portion from the previous fractionation, since the difference in the average degrees of polymerization was only four units. This is well within the usual experimental errors involved.

Thus, it was possible to obtain two fractions from the low viscosity cellulose nitrate having average degrees of polymerization of 75 and 30, respectively.

Presentation of Data from Fractionation Procedures

The immediate outcome of any fractionation procedure is a table which lists the weight percent and corresponding average degree of polymerization of each fraction obtained. The simplest way of presenting such data is to convert this data directly into a curve, plotting the cumulative weight percent of the fractionated material against its average degree of polymerization. This leads to a curve such as the integral distribution curve presented in Graph 1, which represents the distribution in the high viscosity cellulose nitrate.

The differential distribution curve is obtained by a point by point graphical determination of the slope of the curve using a tangentometer. The resultant values in degrees are translated into tangents, and the values of the tangents are plotted against the corresponding degrees of polymerization.

In this differential distribution curve, the shape is an indication of the heterogeneity of the sample with respect to the degree of polymerization. Thus, the shape of this particular differential curve indicates that the sample contains a preponderance of material having a degree of polymerization between 450 and 650 with a maximum at 500.

The integral distribution curve and the corresponding graphically obtained differential distribution curve for the low viscosity cellulose nitrate (see Graph 2) was obtained by a similar method as described for the large scale fractionation of this material, and this method will be described more fully under the section, "Formation and Analysis of Blends".
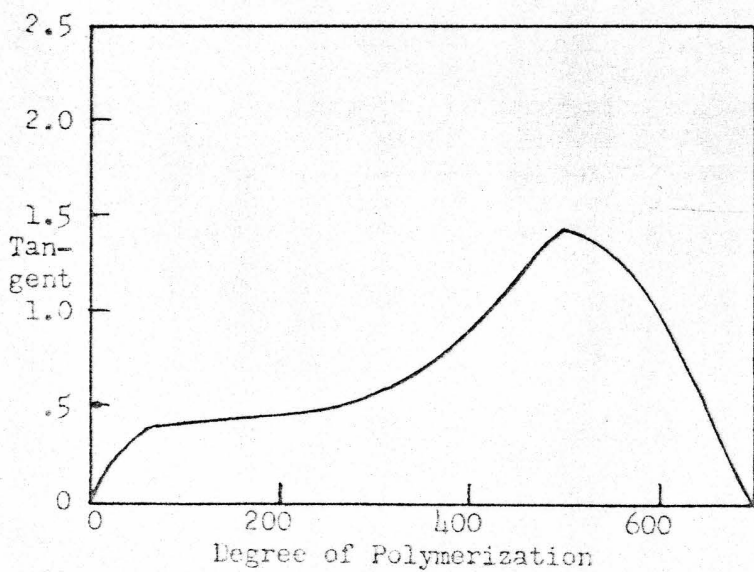
GRAPH 1

Original Blend

Average Degree of Polymerization 420

Integral Distribution Curve
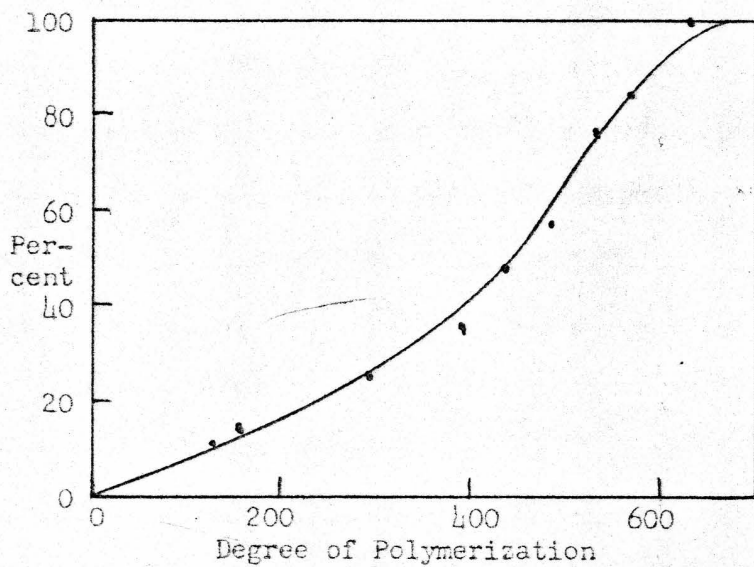
Differential Distribution Curve

FORMATION OF FILMS AND MECHANICAL TESTING OF FRACTIONS

It was realized that each of the fractions obtained by a single fractionation while having a different average degree of polymerization from the other fractions, was still a rather heterogeneous material. However, it was thought that the information gained from subjecting these fractions to the same mechanical tests as would be used for the synthetic blends would be of considerable value, especially since very little actual experimental data is available in the literature.

The determination of the mechanical properties of cellulose nitrate in film form requires that the cellulose nitrate first be dissolved in a suitable solvent or solvents from which a free film may be cast. The search for a suitable solvent revealed the fact that any solvent mixture containing a considerable percentage of acetone was not satisfactory due to the "blushing" of the film. This "blushing" was apparently caused by the lowering of the surface temperature of the film sufficiently to cause condensation of the atmospheric moisture upon the film surface.

The initial films were obtained by pouring a quantity of the cellulose nitrate solution on a glass plate. The solution was spread to a uniform thickness by drawing a glass rod equipped with wire spacers at each end slowly along the glass plate. The solvent mixture was allowed to dry at room temperature. All of the films cast in this manner were opaque because of "blushing". Solvent mixtures composed of different amounts of acetone, ethyl alcohol, ethyl acetate and toluene were used without success.

It was then decided to use a solution composed of 30 percent acetone, 63 percent commercial ethyl acetate, and 7 percent oven-dry cellulose

nitrate. The films were obtained by spreading the solution evenly by means of the glass rod, after which the glass plates were placed in an air convection oven at 55 degrees Centigrade for one hour. These films were transparent after drying and adhered to the glass plate so that it was necessary to soak the film loose from the glass plate with distilled water. These films contained numerous small bubbles on the surface, and it was believed that these were due to the rapid evaporation of the solvent mixture. Therefore, it was decided to test the use of commercial ethyl acetate as the solvent for the cellulose nitrate and to dry the films in an oven regulated at 35 to 45 degrees Centigrade for one hour. This procedure gave transparent films which were free from the blemishes previously encountered and was used as the standard procedure in the formation of all films.

Solutions composed of 7 percent oven-dry cellulose nitrate and 93 percent commercial ethyl acetate were used to cast films of 0.0025 inches thickness from the fractions which had an average degree of polymerization greater than 200. The wire spacers used were .081 inches in diameter. The three fractions having average degrees of polymerization of 165, 75, and 30, were cast from ethyl acetate solutions containing 17.2 percent, 20.3 percent, and 30.0 percent dry cellulose nitrate. The films, 0.0025 inches thick, were obtained by the use of wire spacers which had diameters of 0.031, 0.025, and 0.021 inches, respectively. These differences in solution concentration were necessary due to the range in the viscosities of the different fractions, and the concentrations were varied as necessary to obtain the required 0.0025 inches film thickness.

The films cast in this manner were removed from the glass plate by the use of a water bead with the exception of the very low viscosity

fraction. This fraction having an average degree of polymerization of 30 was very brittle, and in order not to tear the films, it was necessary to soak them loose before any attempt was made to remove them from the glass plate.

Immediately after the films were removed from the glass plates, they were placed between sheets of paper toweling and pressed flat with a glass plate. This removed the water clinging to the surface of the films and prevented them from curling into a roll.

After pressing, the films were placed in the conditioning room for at least 40 hours prior to testing, under conditions of constant temperature 77±1.8 degrees Fahrenheit and constant relative humidity of 50±2 percent. These are the standard atmospheric conditions set forth by A.S.T.M. Designation: D 618-46T.

Mechanical Tests Applied to Films

The testing machines employed in the tests were the Schopper Type Tensile Strength and Elongation Tester, the Schopper Type Folding Endurance Tester, the Mullen Bursting Strength Tester and the Elmendorf Tearing Strength Tester. It should be noted that these machines were designed for the testing of paper products, and in the tests, the paper products were to be tested in two principal directions: one direction parallel to the formation of the paper sheet, and the other normal to the formation of the paper sheet. The samples cut with their length in the parallel direction were designated as "machine direction" or "with direction", and the samples cut with their length at right angles to the machine direction were designated as "cross machine direction" or

"cross direction". In accordance with these directions, the results obtained from the specimens cut in the direction that the cellulose nitrate solution was spread, using the glass rod, are designated as "with values". Those obtained from specimens cut at right angles are designated as "cross values".

The Schopper Type Tensile Strength and Elongation Tester

The tensile breaking strength of a film is the load required to pull the specimen apart. It is usually expressed as the maximum tensile load per unit area of the original cross-section. In these tests the twenty specimens were cut 0.5 inches wide and 6 inches long from at least four different films. Each sample was measured with a dial micrometer. Specimens having a thickness differing from 0.0025 inches by more than 0.0002 inches were discarded, and other specimens were prepared as replacements.

The procedure used for testing was that set forth in A.S.T.M. Designation: D 822-46T. The maximum, minimum, and mean values, together with the average deviation and calculated tensile strength in pounds per square inch in the "with" and "cross" directions for each fraction tested, are given in Tables 2a and 2b.

The corresponding values obtained for the elongation, including the calculated percent elongation based on a distance of 4 inches between the steel clamps, are given in Tables 3a and 3b.

The Schopper Type Folding Endurance Tester

The Schopper Fold Tester is commonly used to test the wear or fold resistance of a film under tension. The specimen is clamped under tension

TABLE 2a

TENSILE STRENGTH OF FRACTIONS
"WITH" VALUES

Average D.P. of Fraction	Maximum Reading	Minimum Reading	Mean	Average Deviation	Calculated Tensile Strength psi
520	14.7	12.8	13.9	0.5	11,100
465	14.2	11.8	13.5	0.7	10,800
390	16.2	12.7	14.5	0.6	11,600
345	15.8	13.7	15.5	0.5	12,400
265	13.8	11.8	13.2	0.6	10,600
215	16.0	11.3	13.2	1.0	10,600
165	14.6	12.9	13.7	0.6	11,000
75	14.0	12.5	13.3	0.4	10,600
30*	8.2	5.4	6.4	0.9	5,100

Twenty samples of film, 0.5 inches wide and 0.0025 inches thick, from each fraction were tested.

* Only four samples of this fraction were tested.

TABLE 2b

TENSILE STRENGTH OF FRACTIONS
"CROSS" VALUES

Average D.P. of Fraction	Maximum Reading	Minimum Reading	Mean	Average Deviation	Calculated Tensile Strength psi
520	14.1	11.9	13.4	0.3	10,700
465	15.4	12.7	13.8	0.7	11,000
390	16.4	12.7	14.4	0.7	11,500
345	15.8	13.4	14.5	0.6	11,600
265	16.8	10.6	13.2	1.6	10,600
215	15.0	11.9	12.9	1.1	10,300
165	14.6	12.4	13.6	0.5	10,900
75	13.3	11.3	12.5	0.4	10,000
30*	6.4	3.2	5.0	1.2	4,000

Twenty samples of film, 0.5 inches wide and 0.0025 inches thick, from each fraction were tested.

* Only four samples of this fraction were tested.

TABLE 3a

ELONGATION OF FRACTIONS
"WITH" VALUES

Average D.P. of Fraction	Maximum Reading	Minimum Reading	Mean	Average Deviation	Percent Elongation
520	0.25	0.13	0.17	0.03	4.3
465	0.54	0.12	0.30	0.09	7.3
390	0.68	0.14	0.25	0.10	6.3
345	0.41	0.15	0.27	0.05	6.8
265	0.53	0.16	0.27	0.08	6.8
215	0.38	0.12	0.22	0.06	5.5
165	0.57	0.15	0.31	0.08	7.8
75	0.55	0.18	0.34	0.09	8.5
30*	0.07	0.04	0.05	0.01	1.3

Twenty samples of film, 0.5 inches wide and 0.0025 inches thick, from each fraction were tested. The percent elongation calculated is based on a distance of four inches between the clamps.

* Only four samples of this fraction were tested.

TABLE 3b

ELONGATION OF FRACTIONS
"CROSS" VALUES

Average D.P. of Fraction	Maximum Reading	Minimum Reading	Mean	Average Deviation	Percent Elongation
520	0.36	0.13	0.20	0.05	4.0
465	0.51	0.13	0.28	0.09	7.0
390	0.65	0.14	0.28	0.06	7.0
345	0.44	0.14	0.29	0.07	7.3
265	0.45	0.17	0.31	0.07	7.8
215	0.44	0.06	0.22	0.06	5.5
165	0.45	0.15	0.28	0.08	7.0
75	0.37	0.12	0.25	0.07	6.3
30*	0.05	0.01	0.03	0.01	0.8

Twenty samples of film, 0.5 inches wide and 0.0025 inches thick, from each fraction were tested. The percent elongation calculated is based on a distance of four inches between the clamps.

* Only four samples of this fraction were tested.

between two sets of jaws and folded back and forth perpendicularly to the plane of the specimen. The number of double folds required to break the film at the point of binding is automatically recorded on the counter. Twenty specimens, cut in each of the two directions, were tested according to the procedure set forth by the A.S.T.M. Designation: D 643-43. The maximum, minimum, mean, and average deviation for each fraction tested are given in Tables 4a and 4b.

The Mullen Bursting Strength Tester

In making this test the specimen is firmly clamped beneath a metal ring while pressure is applied underneath until it bursts. This particular type of tester employs hydraulic pressure by utilizing a rubber diaphragm. The hydraulic pressure is generated by a motor-driven piston forcing a liquid, usually glycerine, into the pressure chamber of the apparatus at the rate of 75 ml per minute. Ten tests were carried out according to the procedure set forth by the A.S.T.M. Designation: D 774-46. The maximum, minimum, mean, and average deviation for each fraction tested are given in Table 5.

The Elmendorf Tearing Strength Tester

This tester is the instrument in most general use for determining the tearing strength of films. It consists of a pendulum carrying a movable jaw, which, initially is in line with the fixed jaw. The specimens are clamped in the two jaws and a slit made by means of a knife attached to the instrument. The pendulum is released and in its swing, tears the paper. A pointer on a scale indicates the force required.

TABLE 4a

FOLDING ENDURANCE OF FRACTIONS
"WITH" VALUES

Average D.P. of Fraction	Maximum Reading	Minimum Reading	Mean	Average Deviation
520	82	34	53.3	10.7
465	91	28	55.8	11.3
390	68	20	41.2	9.3
345	49	21	35.2	7.2
265	79	30	55.0	13.7
215	90	32	55.4	10.8
165	94	27	51.5	16.6
75	37	21	30.0	4.4
30*	—	—	—	—

Twenty samples of film, 0.0025 inches thick, from each fraction were tested.

* Too brittle for testing.

TABLE 4b

FOLDING ENDURANCE OF FRACTIONS
"CROSS" VALUES

Average D.P. of Fraction	Maximum Reading	Minimum Reading	Mean	Average Deviation
520	87	24	48.1	12.9
465	91	32	54.4	10.0
390	68	25	42.9	7.8
345	80	22	38.6	9.6
265	91	34	63.4	15.5
215	90	38	59.6	9.3
165	90	27	57.6	16.0
75	35	21	29.8	2.8
30*	---	---	---	---

Twenty samples of film, 0.0025 inches thick, from each fraction were tested.

* Too brittle for testing.

TABLE 5

BURSTING STRENGTH OF FRACTIONS

Average D.P. of Fraction	Maximum Reading	Minimum Reading	Mean psi	Average Deviation
520	99	59	78.9	12.8
465	76	50	65.1	6.5
390	89	47	63.0	12.0
345	92	62	77.0	10.0
265	87	63	75.5	5.6
215	84	57	71.8	7.5
165	85	74	79.8	3.0
75	75	50	62.8	6.2
30	33	18	26.0	5.5

Ten samples of film, 0.0025 inches thick, from each fraction were tested.

The instrument is designed to show the force in grams required when 16 sheets are torn simultaneously. Five tests were made in which 16 sheets of film 0.0025 inches thick were used. The tests were carried out according to the procedure described by the A.S.T.M. Designation: D 689-44. The maximum, minimum, mean, and average deviation for each fraction tested are given in Table 6a and 6b.

To permit a complete survey of the data obtained by these mechanical tests on the fractions, the values obtained for "with" and "cross" specimens are averaged, and a summary of the average values for each test is given in Table 7. Plots of the data were made and are given in Graph 2a and 2b.

TABLE 6a

TEARING STRENGTH OF FRACTIONS
"WITH" VALUES

Average D.P. of Fraction	Maximum Reading	Minimum Reading	Mean Grams	Average Deviation
520	29	25	27.8	1.5
465	29	28	28.4	0.5
390	29	26	27.7	1.3
345	27	25	26.4	0.7
265	26	24	25.4	0.7
215	31	26	28.6	1.5
165	25	25	25.0	0.0
75	23	22	22.6	0.5
30*	--	--	--	--

Five samples, each composed of 16 sheets of film, 0.0025 inches thick, from each fraction were tested.

* Too brittle for testing.

TABLE 6b

TEARING STRENGTH OF FRACTIONS
"CROSS" VALUES

Average D.P. of Fraction	Maximum Reading	Minimum Reading	Mean Grams	Average Deviation
520	29	27	27.8	0.6
465	28	26	27.2	0.8
390	26	24	24.8	0.6
365	28	27	27.4	0.5
265	29	25	27.0	0.8
215	30	26	28.6	1.3
165	27	26	26.6	0.5
75	23	22	22.4	0.5
30*	—	—	—	—

Five samples, each composed of 16 sheets of film, 0.0025 inches thick, from each fraction were tested.

* Too brittle for testing.

TABLE 7

SUMMARY OF AVERAGE VALUES FOR FRACTIONS

Average D.P. of Fraction	Tensile Strength psi	Percent Elongation	Schopper Folds	Bursting Strength psi	Tear Strength grams
520	10,900	4.2	50.7	78.9	27.8
465	10,900	7.2	55.1	65.1	27.8
390	11,550	6.7	42.1	63.0	26.2
345	12,000	7.1	36.9	77.0	26.9
265	10,600	7.3	59.2	75.5	26.2
215	10,450	5.5	57.5	71.8	28.6
165	10,950	7.4	54.6	79.8	25.8
75	10,300	7.4	29.9	62.8	22.5
30	4,550	1.1	*	26.0	*

* Too brittle for testing.

GRAPH 2a

Results of Mechanical Tests on Fractions
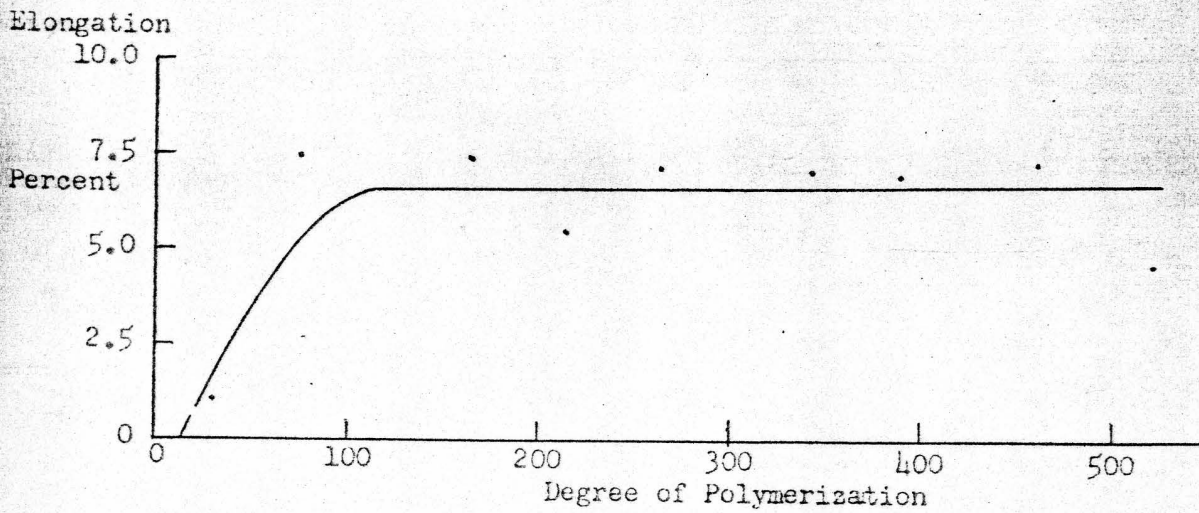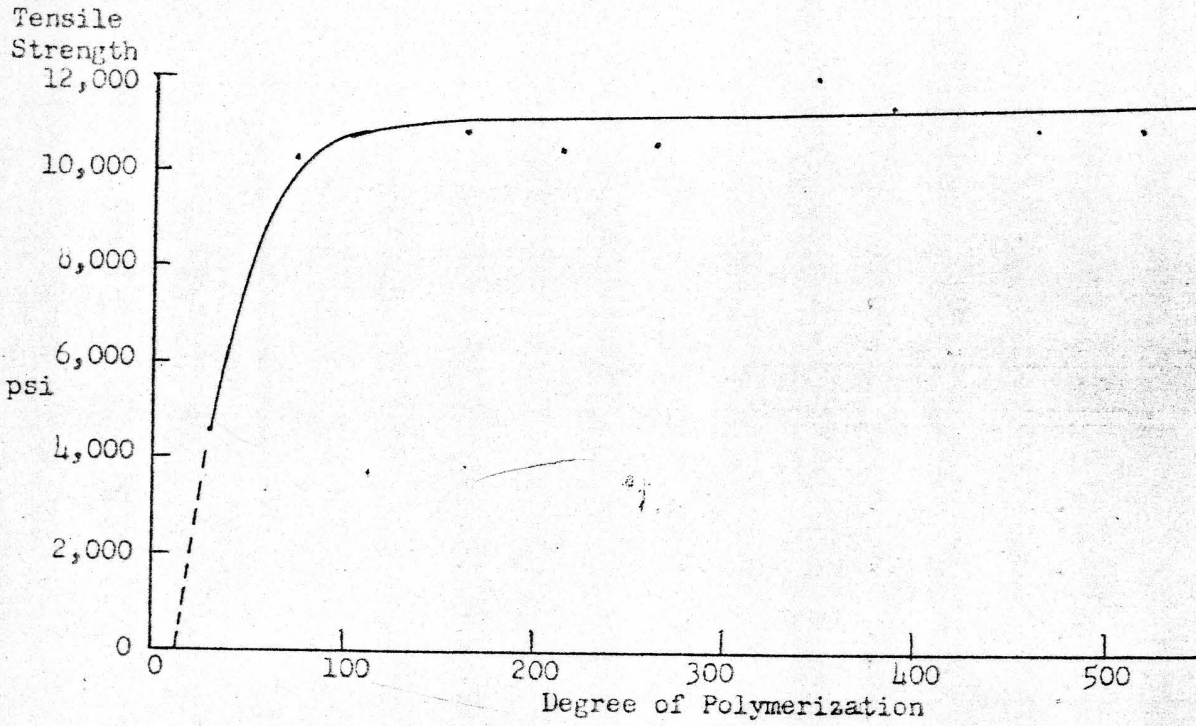
GRAPH 2b

Schopper Folds vs Degree of Polymerization
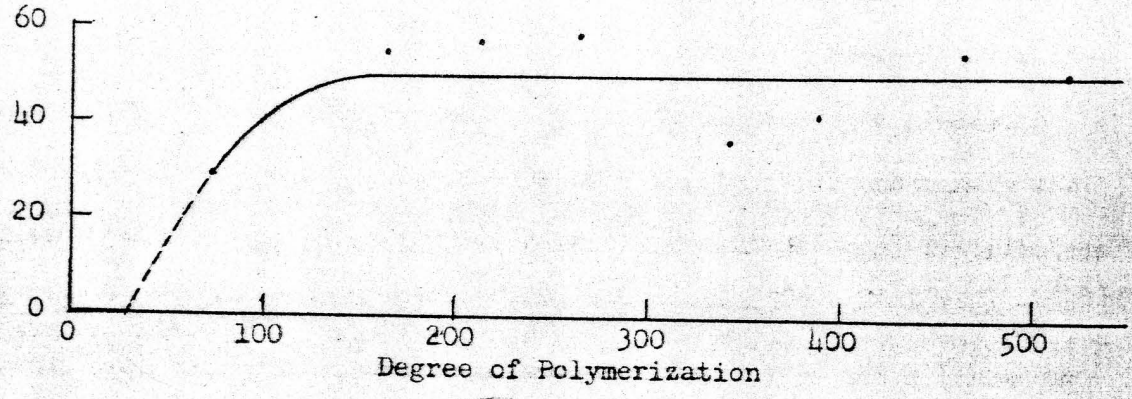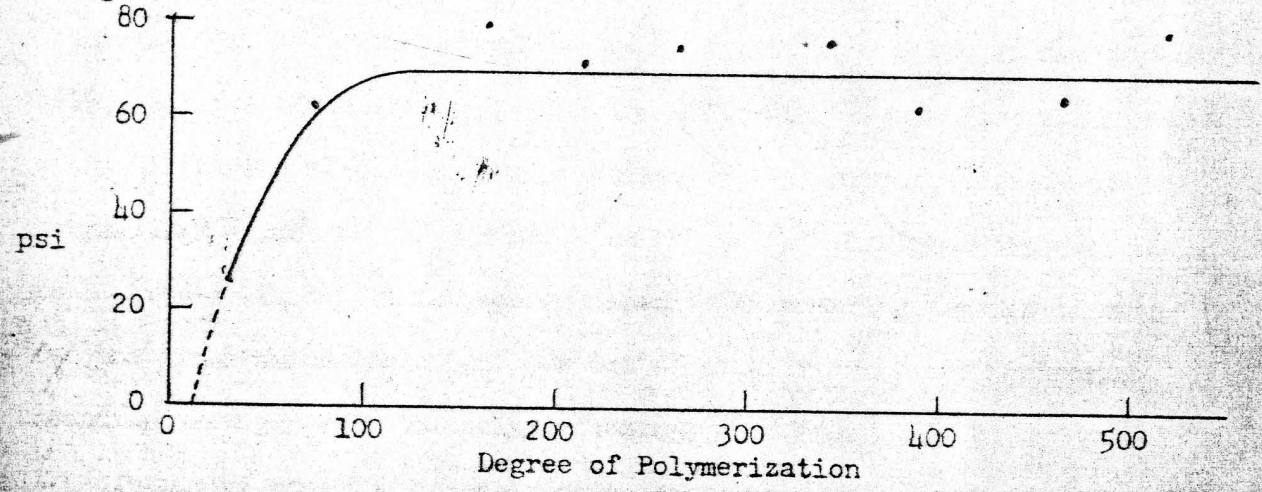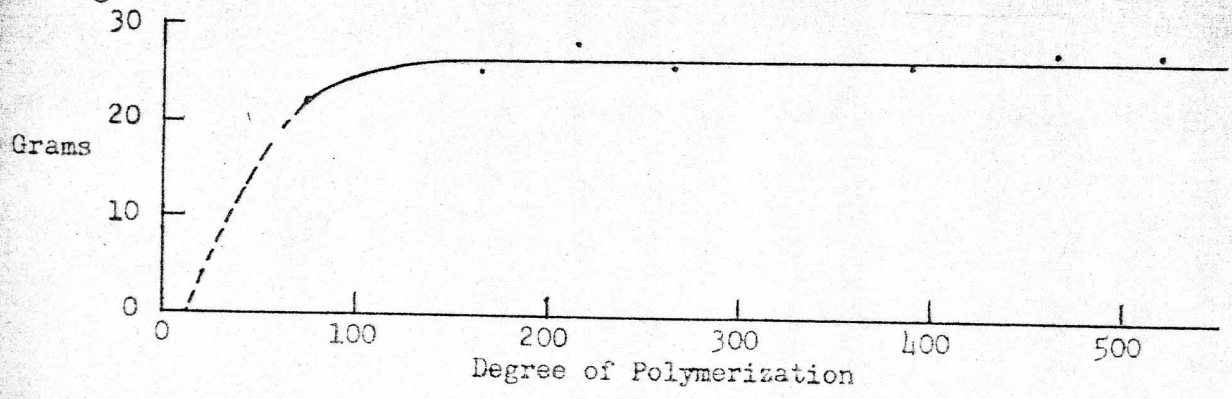
Burst Strength (psi) vs Degree of Polymerization

Tear Strength (Grams) vs Degree of Polymerization

PREPARATION, TESTING, AND ANALYSIS OF BLENDS

In order to attack the problem of the effect of the shape of the distribution curve on the mechanical properties of cellulose nitrate, it was necessary to place some restrictions on the blends to be prepared synthetically from the fractions available. First, it was necessary that the blends be so prepared as to give a fairly smooth integral distribution curve from which a differential distribution curve could be graphically obtained, each different from the others. This could be accomplished by the trial and error method of plotting a curve of the cumulative weight percentages of the fractions to be used against the average degree of polymerization of the fractions, and comparing the curves which resulted.

Secondly, it was necessary to choose an average degree of polymerization for the blends so that while the shapes of the distribution curves of the different blends were to be different, the average degrees of polymerization for the blends could be held within a narrow range of 10 to 20 units. This could be accomplished by calculating a weighted mean for the blend using the weight percent of each fraction and its corresponding average degree of polymerization.

It was planned in the early stages of this problem to use as the average degree of polymerization the same average for the blends as that of the original high viscosity material. However, after a careful consideration of the fractions available, it was found that only two were available which had average degrees of polymerization above the average of 420 as determined for the original blend. The remainder of the fractions had average degrees of polymerization below that of 420 units, and in order to add any quantity of very low average D.P. material, it

would be necessary to use a very large percentage of the highest average D.P. material. For example, if it were decided to make up a blend containing 20 percent of 75 D.P. fraction, it would be necessary to add 69 percent of the 520 D.P. fraction in order to keep the average degree of polymerization of the blend at 420. The remaining 11 percent of all other fractions which could be added to such a blend would not give a smooth differential distribution curve containing one maximum as was evident from a plot of such a proposed composition.

In order to obtain more flexibility in the formulations of the synthetic blends, it was decided to select as the average degree of polymerization the value of 250 units. This value would permit the use of five fractions which had average D.P.'s above the desired average and of four fractions which had average D.P.'s below this value. Furthermore, since it was planned to analyze each blend tested, the value of 250 would also permit the use of the original low viscosity material which had an average D.P. of 60.

It was then decided to prepare three blends which had markedly different distribution curves but the same average degree of polymerization. These curves were calculated using different quantities of all fractions and the low viscosity original blend. From the curves, the weight percentages of the different materials were determined and Blends 1, 2, and 3 were prepared.

A total of 60 grams of each blend was prepared, and the ethyl acetate solutions of the blends were made up with 10 percent by weight of the synthetic cellulose nitrate blend. Films were cast using 0.064 inch wire spacers to obtain clear films 0.0025 inches thick. The procedures used for casting, conditioning, and testing were those previously described

for the fractions. The results obtained from the tests of Blends 1, 2, and 3 are given in Tables 8a through 12b, and a summary of the average values is given in Table 13.

Immediately following the completion of the mechanical tests, a sample of 20 grams of each blend was taken for analysis by fractionation. The general procedure followed in the analysis of these three blends was to prepare a 2 percent solution of the sample in ethyl acetate and by the use of n-heptane as the precipitant and a time of standing of 21 hours at 15 degrees Centigrade, it was possible to obtain eight fractions. The ethyl acetate-heptane solution was then evaporated to dryness under reduced pressure and the material recovered was redissolved in acetone. A similar procedure was carried out for the acetone solution, again using n-heptane as the precipitant, and it was possible to obtain two to four more fractions depending on the amounts of the different fractions in that particular blend. The final fraction was obtained by complete evaporation of the acetone and heptane under reduced pressure. It was necessary to refractionate the first fractions obtained in these procedures using an acetone-water system.

The results of the fractionation procedures for Blends 1, 2, and 3 are given in Graphs 3, 4, and 5. It is immediately evident from the distribution curves that the fractions being used are not homogeneous fractions inasmuch as distribution curves having two maxima were obtained for each of these blends. There is again evidence of further degradation, especially in the fractions of higher average D.P. since the calculated averages were 250 and the average D.P.'s obtained from viscosity measurements were in the range of 220. This large a deviation can hardly be attributed to experimental error.

TABLE 8a

TENSILE STRENGTH OF BLENDS
"WITH" VALUES

Blend Number	Average D.P. of Blend	Maximum Reading	Minimum Reading	Mean	Average Deviation	Calculated Tensile Strength psi
Orig.	420	16.0	12.2	14.0	0.6	11,200
Orig.	60	13.9	10.0	12.3	0.7	9,800
1	218	14.6	11.5	12.9	0.8	10,300
2	222	14.7	12.0	13.1	0.7	10,500
3	216	15.9	11.6	13.5	1.0	10,800
4	106	13.2	10.0	11.5	0.6	9,200
5	103	16.1	11.3	12.7	0.9	10,200
6	106	14.0	12.6	13.3	0.4	10,600
7	101	15.4	12.0	13.8	0.9	11,000
8	100	15.4	12.7	13.8	0.4	11,000
9	106	14.1	12.8	13.5	0.4	10,800

Twenty samples of film, 0.5 inches wide and 0.0025 inches thick, from each blend were tested.

TABLE 8b

TENSILE STRENGTH OF BLENDS
"CROSS" VALUES

Blend Number	Average D.P. of Blend	Maximum Reading	Minimum Reading	Mean	Average Deviation	Calculated Tensile Strength psi
Orig.	420	15.8	11.9	13.5	0.8	10,800
Orig.	60	13.0	10.0	11.7	0.7	9,400
1	218	14.5	11.3	12.7	0.8	10,200
2	222	15.6	11.7	12.8	0.8	10,200
3	216	15.4	12.3	13.8	0.6	11,000
4	106	13.0	9.9	11.5	1.1	9,200
5	103	15.0	11.8	13.2	0.9	10,600
6	106	14.3	12.2	13.4	0.7	10,700
7	101	15.0	12.7	13.4	0.4	10,700
8	100	15.0	12.5	13.8	0.6	11,000
9	106	14.2	12.3	13.2	0.4	10,600

Twenty samples of film, 0.5 inches wide and 0.0025 inches thick, of each blend were tested.

TABLE 9a

ELONGATION OF BLENDS
"WITH" VALUES

Blend Number	Average D.P. of Blend	Maximum Reading	Minimum Reading	Mean	Average Deviation	Percent Elongation
Orig.	420	0.57	0.11	0.28	0.08	7.0
Orig.	60	0.33	0.11	0.21	0.06	5.3
1	218	0.71	0.15	0.35	0.11	8.8
2	222	0.38	0.13	0.23	0.06	5.8
3	216	0.54	0.17	0.26	0.08	6.5
4	106	0.33	0.13	0.20	0.05	5.0
5	103	0.54	0.14	0.31	0.07	7.8
6	106	0.60	0.18	0.33	0.07	8.3
7	101	0.65	0.19	0.37	0.10	9.3
8	100	0.78	0.14	0.36	0.11	9.0
9	106	0.83	0.17	0.38	0.11	9.5

Twenty samples of film, 0.5 inches wide and 0.0025 inches thick, from each blend were tested. The percent elongation calculated is based on a distance of four inches between the clamps.

TABLE 9b

ELONGATION OF BLENDS
"CROSS" VALUES

Blend Number	Average D.P. of Blend	Maximum Reading	Minimum Reading	Mean	Average Deviation	Percent Elongation
Orig.	420	0.57	0.15	0.30	0.11	7.5
Orig.	60	0.27	0.10	0.19	0.05	4.8
1	218	0.61	0.18	0.34	0.11	8.5
2	222	0.53	0.12	0.22	0.06	5.5
3	216	0.49	0.18	0.33	0.08	8.3
4	106	0.40	0.10	0.22	0.06	5.5
5	103	0.79	0.14	0.40	0.10	10.0
6	106	0.51	0.14	0.32	0.09	8.0
7	101	0.58	0.21	0.36	0.09	9.0
8	100	0.62	0.16	0.35	0.07	8.8
9	106	0.48	0.16	0.35	0.06	8.8

Twenty samples of film, 0.5 inches wide and 0.0025 inches thick, from each blend were tested. The percent elongation calculated is based on a distance of four inches between the clamps.

TABLE 10a

FOLDING ENDURANCE OF BLENDS
"WITH" VALUES

Blend Number	Average D.P. of Blend	Maximum Reading	Minimum Reading	Mean	Average Deviation
Orig.	420	67	43	54.0	9.0
Orig.	60	61	27	38.2	6.6
1	218	87	44	59.4	8.7
2	222	58	32	43.5	5.3
3	216	61	34	45.4	5.7
4	106	41	22	31.7	5.1
5	103	50	27	36.5	7.3
6	106	61	28	41.8	9.1
7	101	65	25	42.8	9.0
8	100	56	32	42.4	6.3
9	106	65	35	48.4	6.2

Twenty samples of film, 0.0025 inches thick, from each blend were tested.

TABLE 10b

FOLDING ENDURANCE OF BLENDS
"CROSS" VALUES

Blend Number	Average D.P. of Blend	Maximum Reading	Minimum Reading	Mean	Average Deviation
Orig.	420	68	32	54.0	12.0
Orig.	60	47	21	34.5	5.3
1	218	75	30	55.7	9.8
2	222	68	32	43.6	7.3
3	216	56	31	42.1	5.2
4	106	53	22	32.1	5.5
5	103	51	27	37.7	5.3
6	106	52	30	40.4	6.1
7	101	78	28	42.8	10.0
8	100	58	39	46.5	4.1
9	106	75	39	52.6	9.1

Twenty samples of film, 0.0025 inches thick, from each blend were tested.

TABLE 11

BURSTING STRENGTH OF BLENDS

Blend Number	Average D.P. of Blend	Maximum Reading	Minimum Reading	Mean psi	Average Deviation
Orig.	420	81	58	67.0	5.4
Orig.	60	75	42	58.0	10.0
1	218	88	55	69.9	8.3
2	222	86	60	78.3	9.1
3	216	88	65	78.3	3.8
4	106	54	40	44.5	3.1
5	103	84	50	64.8	7.2
6	106	76	55	61.0	5.0
7	101	89	40	59.3	12.5
8	100	83	59	69.0	8.4
9	106	88	42	68.0	11.4

Ten samples of film, 2.5 inches square and 0.0025 inches thick, from each blend were tested.

TABLE 12a

TEARING STRENGTH OF BLENDS
"WITH" VALUES

Blend Number	Average D.P. of Blend	Maximum Reading	Minimum Reading	Mean Force Grams	Average Deviation
Orig.	420	26	23	24.6	0.9
Orig.	60	23	21	21.6	0.9
1	218	25	23	24.2	0.6
2	222	27	25	26.2	1.0
3	216	28	26	26.8	0.8
4	106	23	22	22.8	0.3
5	103	25	23	24.0	0.8
6	106	25	24	24.4	0.5
7	101	25	24	24.4	0.5
8	100	26	24	24.8	0.6
9	106	26	24	25.2	0.6

Five samples, each composed of 16 sheets of film, 0.0025 inches thick, from each blend were tested.

TABLE 12b

TEARING STRENGTH OF BLENDS
"CROSS" VALUES

Blend Number	Average D.P. of Blend	Maximum Reading	Minimum Reading	Mean Force Grams	Average Deviation
Orig.	420	27	25	26.2	0.6
Orig.	60	23	22	22.2	0.3
1	218	27	25	26.0	0.4
2	222	28	25	26.6	0.9
3	216	27	25	25.8	0.8
4	106	21	20	20.2	0.3
5	103	26	24	25.0	0.4
6	106	25	23	24.0	0.8
7	101	26	24	25.0	0.8
8	100	27	26	26.2	0.3
9	106	25	23	24.0	0.4

Five samples, each composed of 16 sheets of film, 0.0025 inches thick, from each blend were tested.

TABLE 13

SUMMARY OF AVERAGE VALUES FOR BLENDS

| Blend Number	Average D.P. of Blend	Tensile Strength psi	Percent Elongation	Schopper Folds	Bursting Strength psi	Tear Strength grams
Orig.	420	11,000	7.3	54.0	67.0	25.4
Orig.	60	9,600	5.1	36.4	58.0	21.9
1	218	10,250	8.7	57.6	69.9	25.1
2	222	10,350	5.7	43.6	78.3	26.4
3	216	10,900	7.4	43.8	78.3	26.3
4	106	9,200	5.3	31.9	44.5	21.5
5	103	10,400	8.9	37.1	64.8	24.5
6	106	10,650	8.2	41.1	61.0	24.2
7	101	10,850	9.2	42.8	59.3	24.7
8	100	11,000	8.9	44.5	69.0	25.5
9	106	10,700	9.2	50.5	68.0	24.6

GRAPH 3

Blend Number 1

Average Degree of Polymerization 218

Integral Distribution Curve
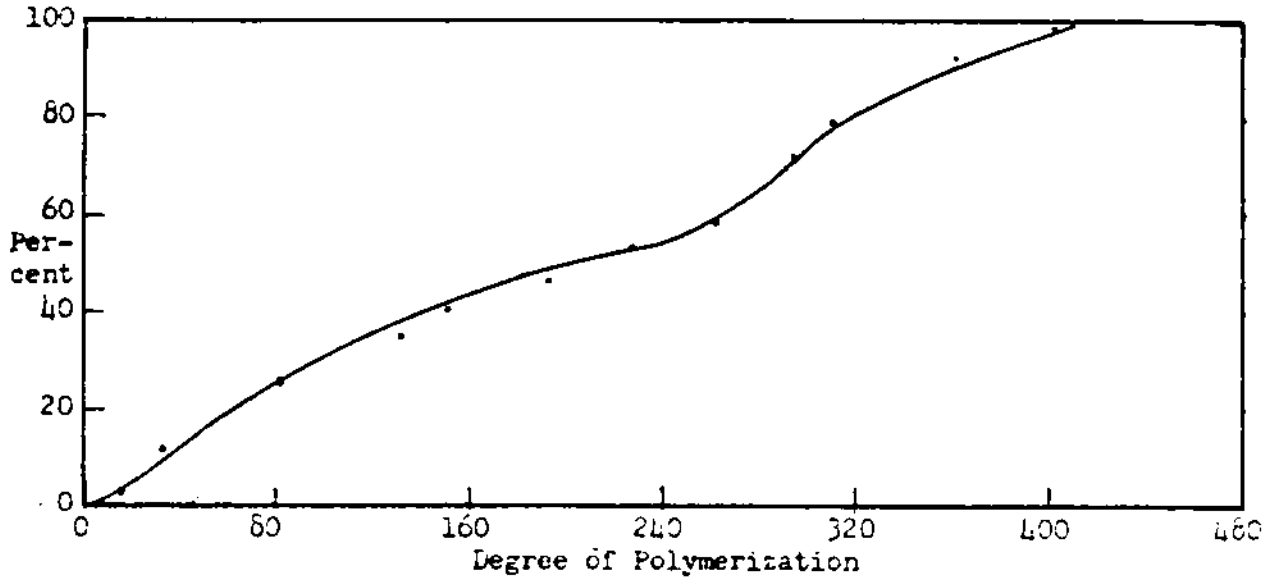
Differential Distribution Curve
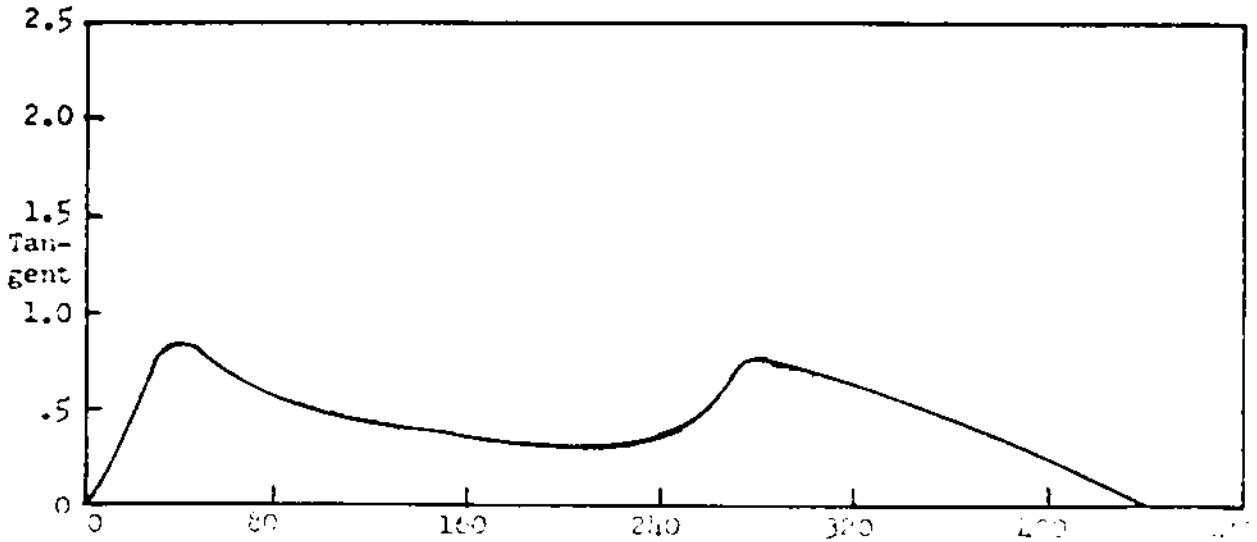
GRAPH 4

Blend Number 2

Average Degree of Polymerization 222

Integral Distribution Curve
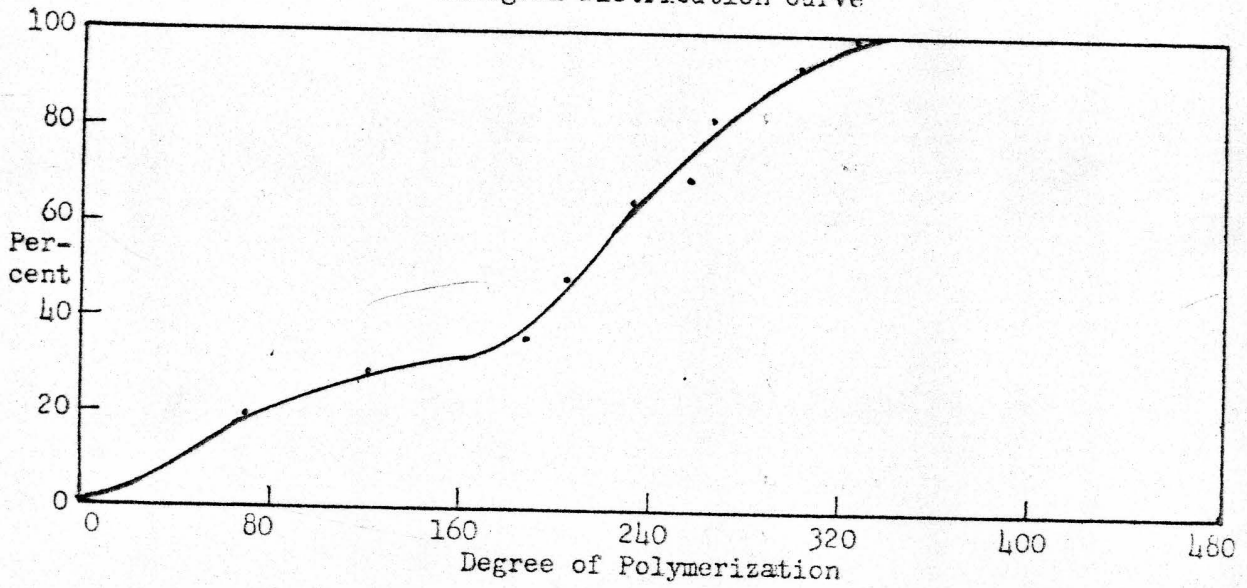
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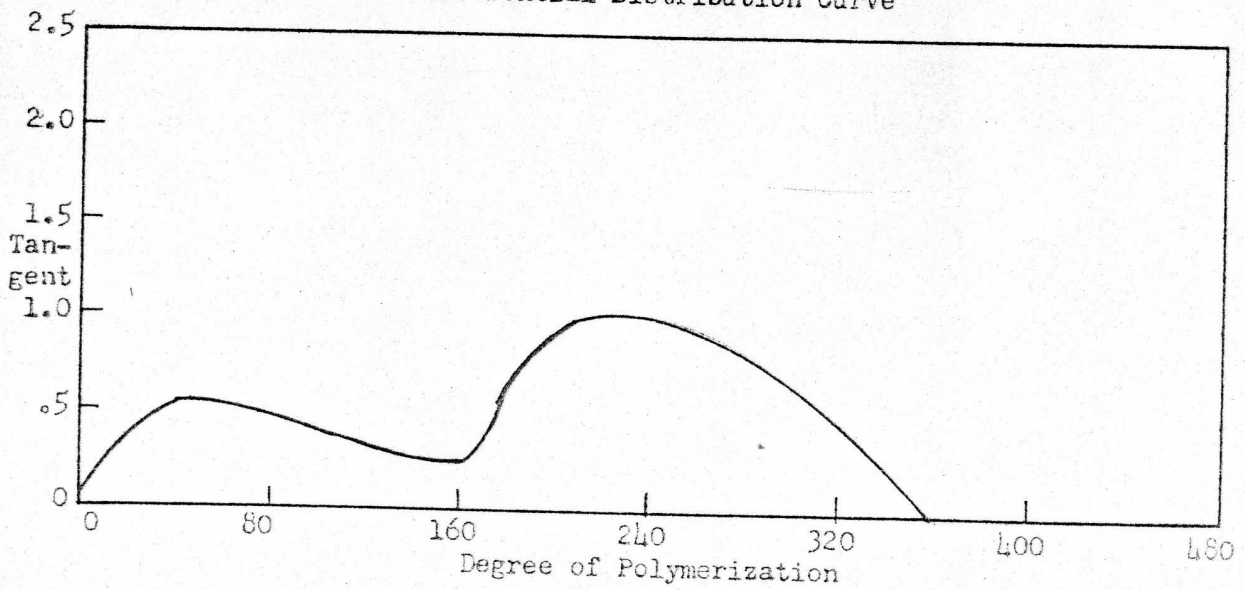
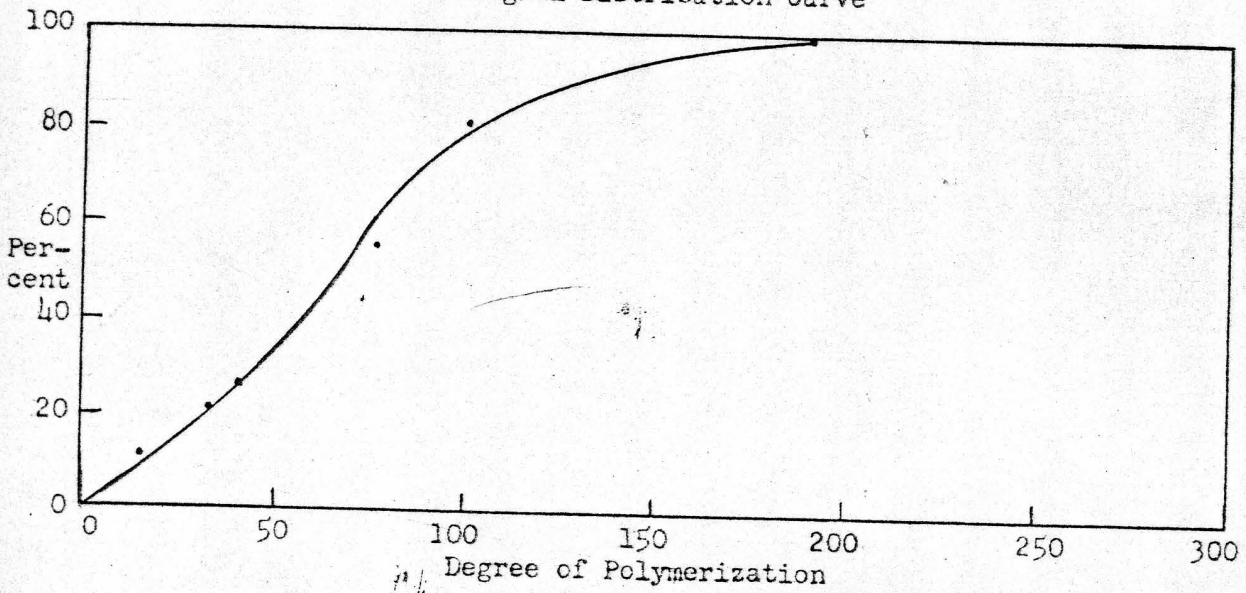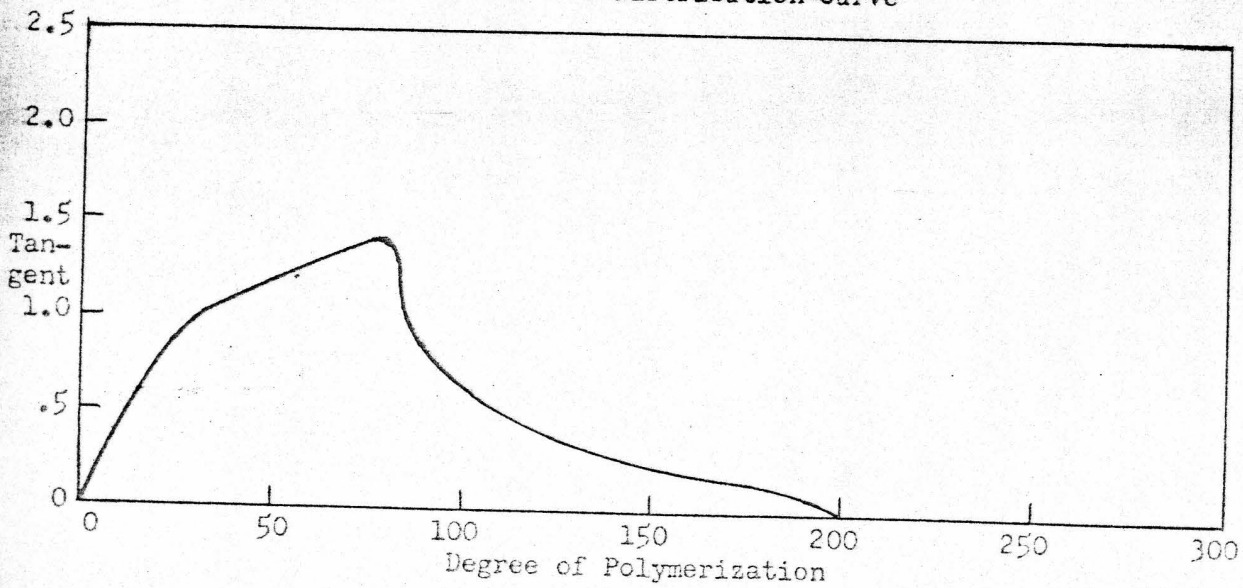# GRAPH 5

Blend Number 3

Average Degree of Polymerization 216

Integral Distribution Curve
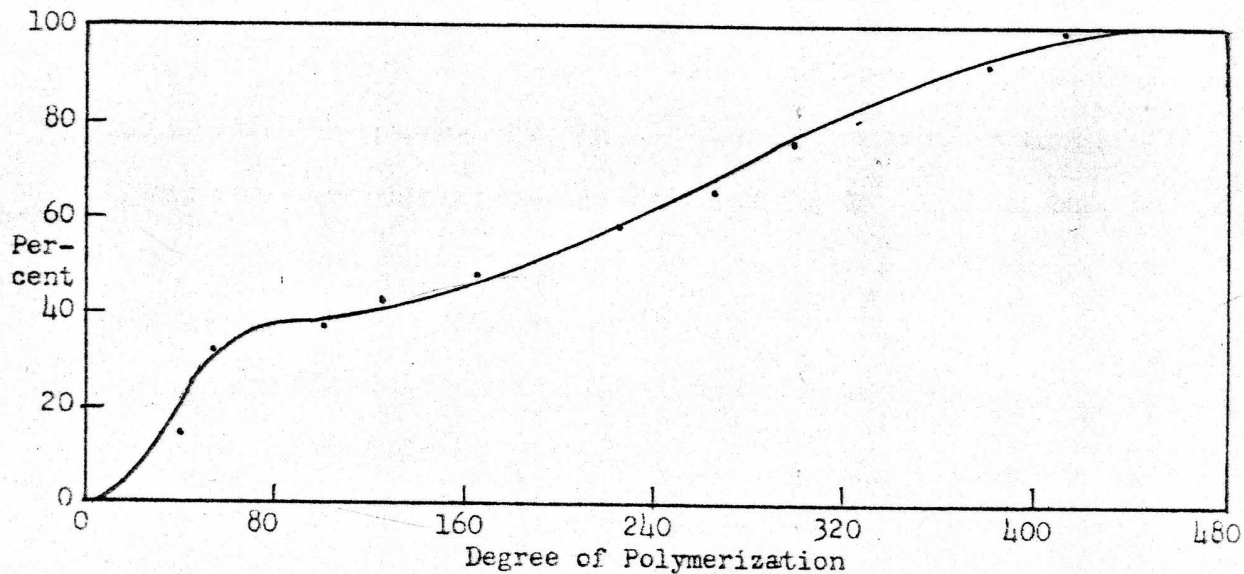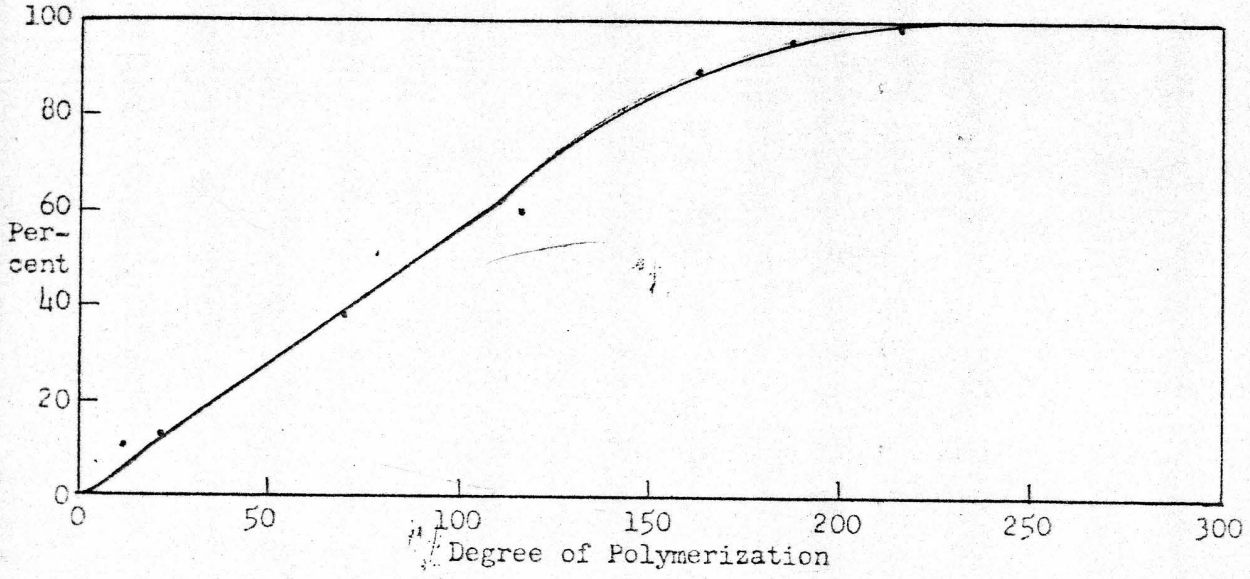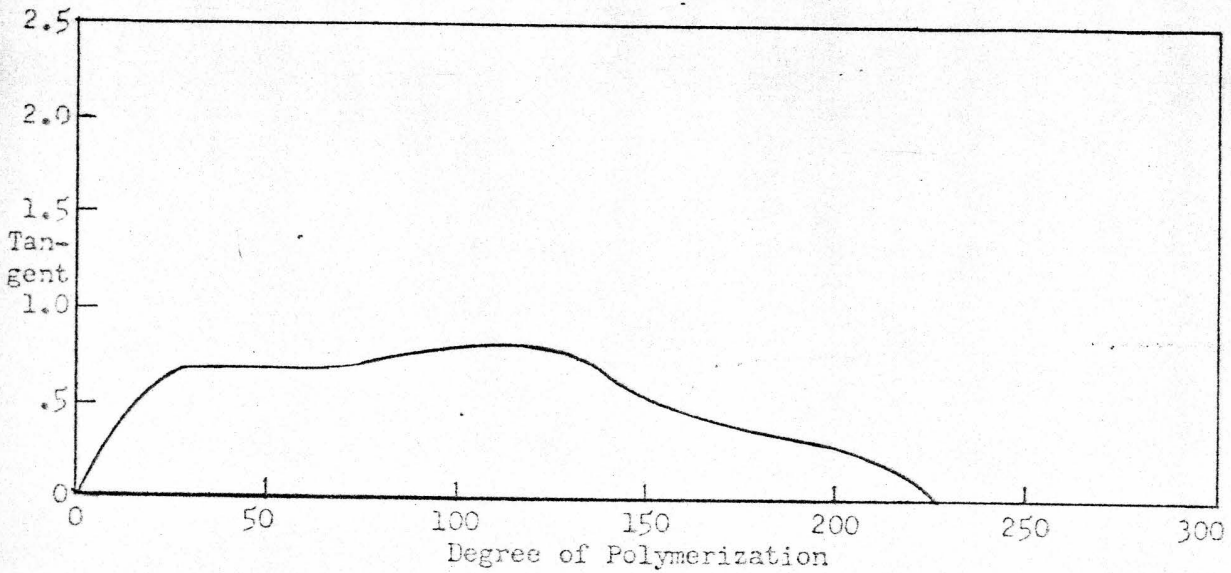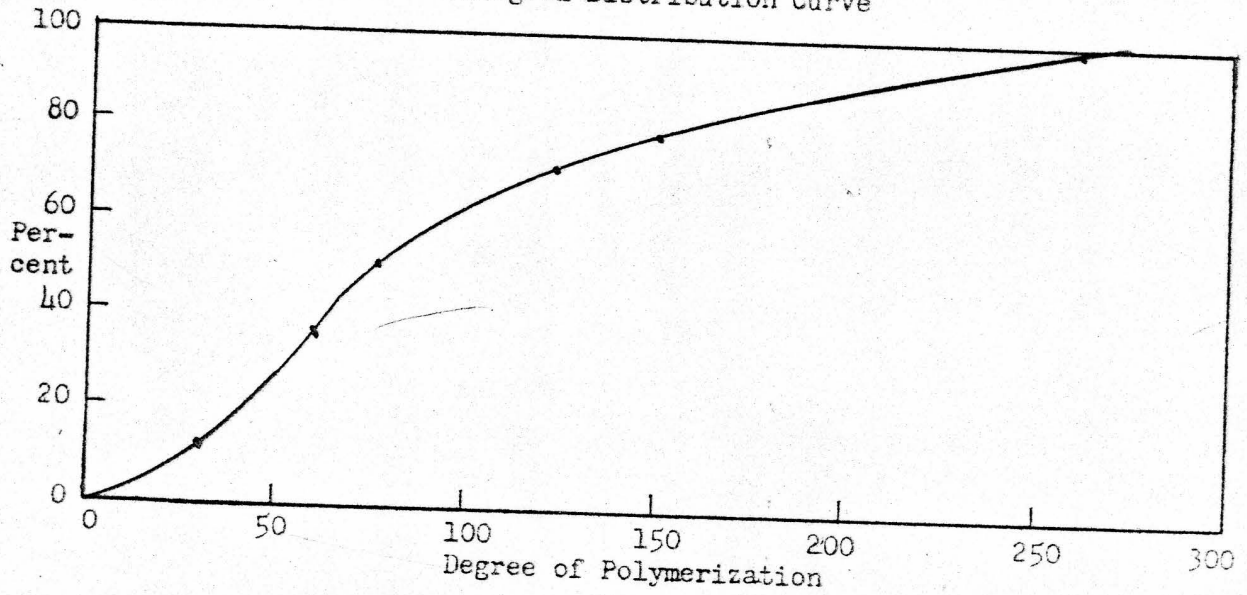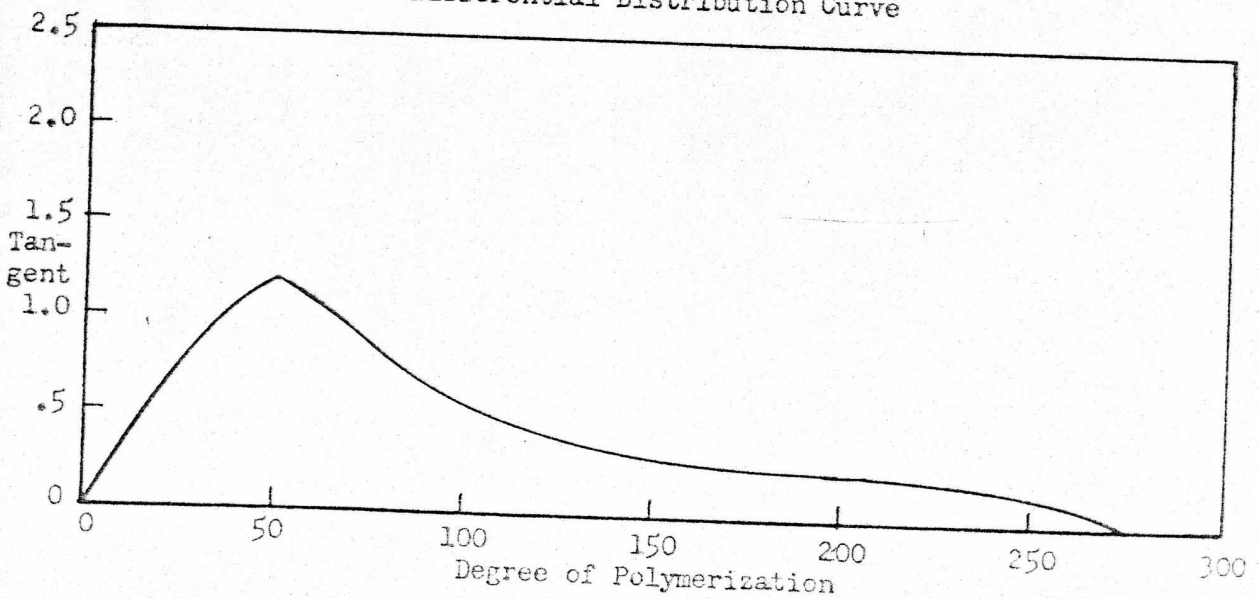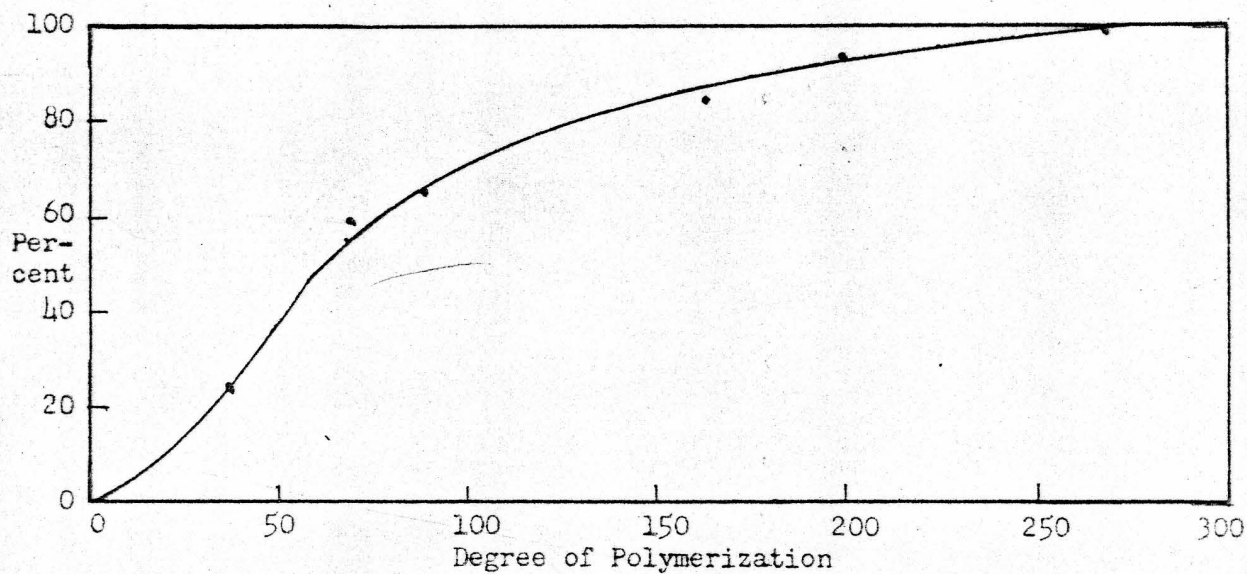

Differential Distribution Curve
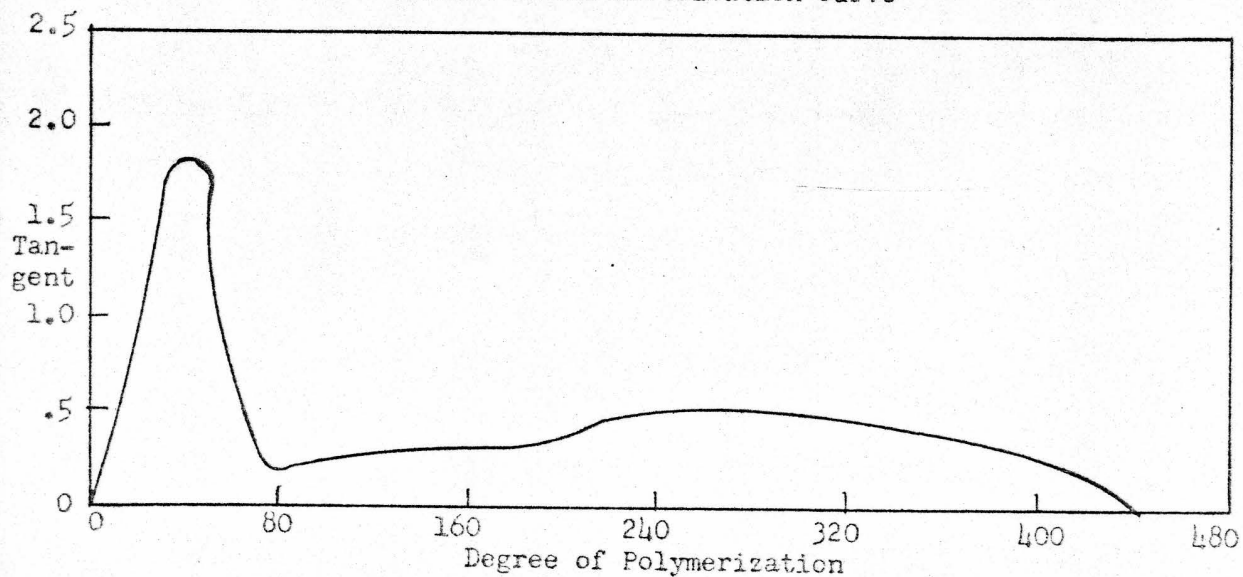
A study of the results obtained from the mechanical tests revealed an indication that as long as the average degree of polymerization was as high as 220, the differences in the mechanical properties were not markedly different regardless of the shape of the differential distribution curve.

A series of six blends which had an average degree of polymerization of 100 were then prepared. The fractions which were used in this series of blends were those having average D.P.'s of 30, 75, 215, and 265, and these were supplemented by using the low viscosity original blend. Only a small quantity of the fraction having an average D.P. of 165 was available. This quantity being insufficient for use in all blends, it was decided not to use this fraction.

The blends were calculated in the same manner as previously stated, and the calculated average was set at 110 in order to allow for the amount of degradation which had occurred since the viscosities of the fractions had been determined. A total of 100 grams of each blend was prepared, and the ethyl acetate solutions containing 16.7 percent by weight of the blend were used for the formation of the films. The films were cast using 0.031 inch wire spacers to obtain clear films 0.0025 inches thick. The procedures used for casting, conditioning, and testing were previously described. The results of these tests are given as Blends 4 through 9, in Tables 8a through 12b, and a summary of the average values is given in Table 13.

The analysis of these blends was carried out using a 5 gram sample of the blend dissolved in 495 grams of acetone. To the solution was added enough distilled water to just cause the formation of very small visible particles at a temperature of 25 degrees Centigrade. By allowing

the solution to stand at 15 degrees Centigrade for 12 hours, it was possible to separate off the supernatant liquid. The supernatant liquid was treated in the customary manner to obtain subsequent fractions. The precipitated phase was redissolved in acetone, and by the addition of distilled water at least three fractions were obtained. The final fractions were obtained by a complete removal of the acetone and water under reduced pressure. The results obtained in this procedure are shown in Graphs 6 through 11.

The mechanical tests for the original high viscosity and low viscosity cellulose nitrates were obtained by the use of the previously described procedures for casting, conditioning, and testing of fractions. The ethyl acetate solution of the high viscosity cellulose nitrate was prepared as a 7 percent solution and cast using 0.061 inch wire spacers, and the solution of the low viscosity cellulose nitrate was prepared as a 20.0 percent solution and cast using 0.025 inch wire spacers.

An analysis of the low viscosity cellulose nitrate was carried out using acetone and water as the solvent and precipitant. No refractionation of the first fraction was made. The results of this fractionation are given in Graph 12.

It was thought that if some method of correlation of the mechanical properties of the blends with the shape of the differential distribution could be found, it might be interesting to observe whether the results obtained from the testing of some of the fractions might also fit into the system of correlation. If the distributions of the fractions having average D.P.'s of 75, 165, 215, and 265 were determined, then these fractions could possibly be treated as blends of different average degrees of polymerization from the nine blends prepared synthetically.

GRAPH 6

Blend Number 4

Average Degree of Polymerization 106

Integral Distribution Curve
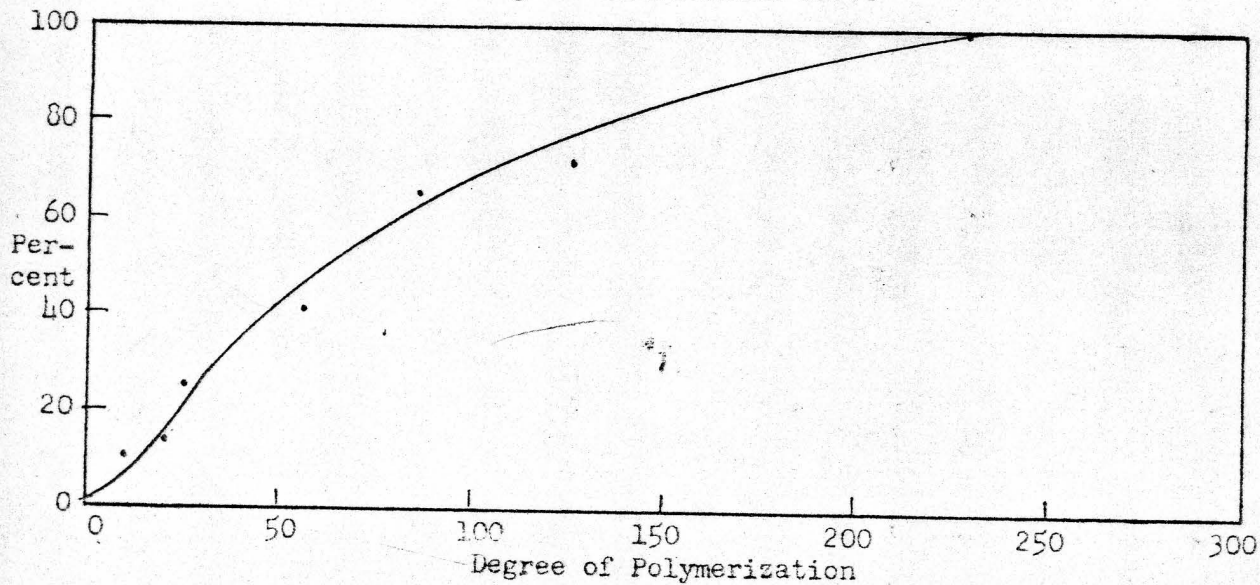
Differential Distribution Curve
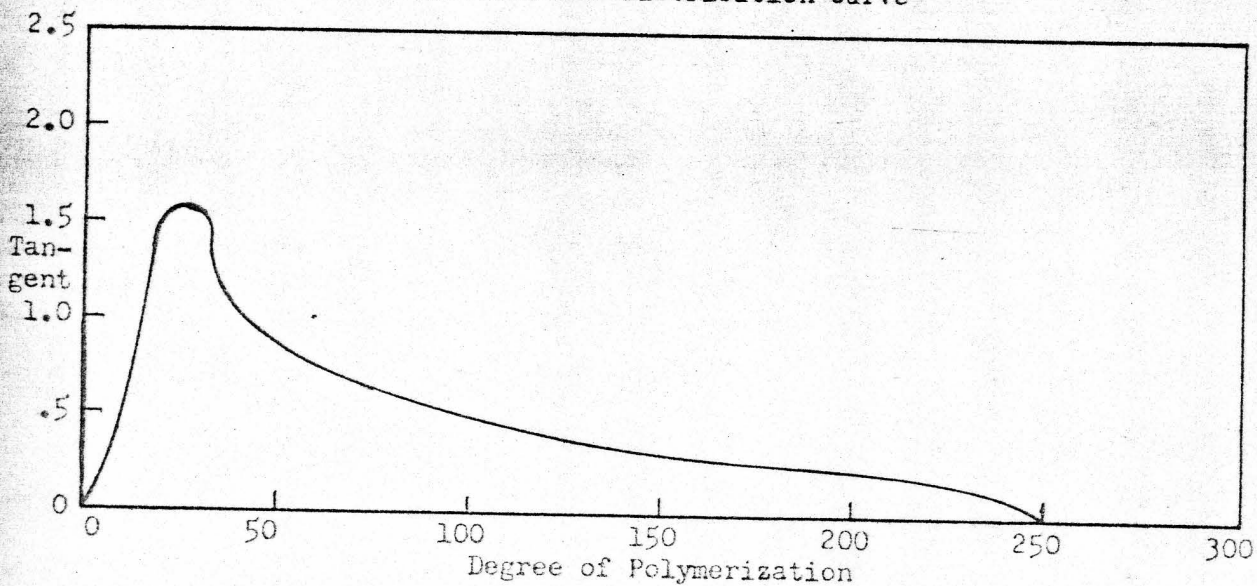
GRAPH 7

Blend Number 5

Average Degree of Polymerization 103

Integral Distribution Curve
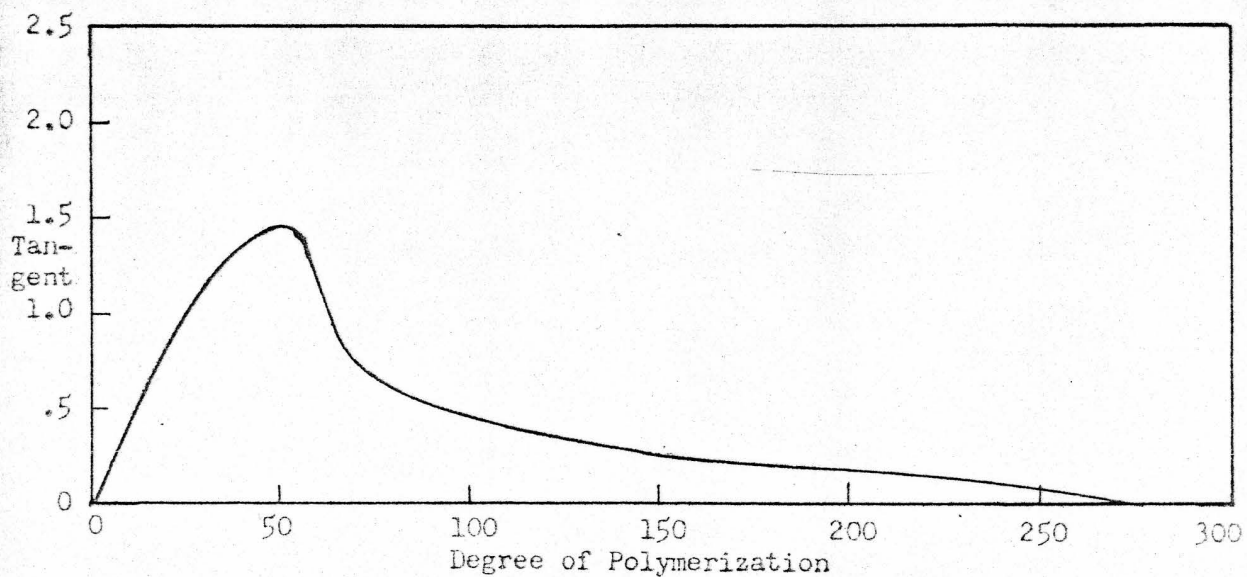

Differential Distribution Curve

GRAPH 8

Blend Number 6

Average Degree of Polymerization 106

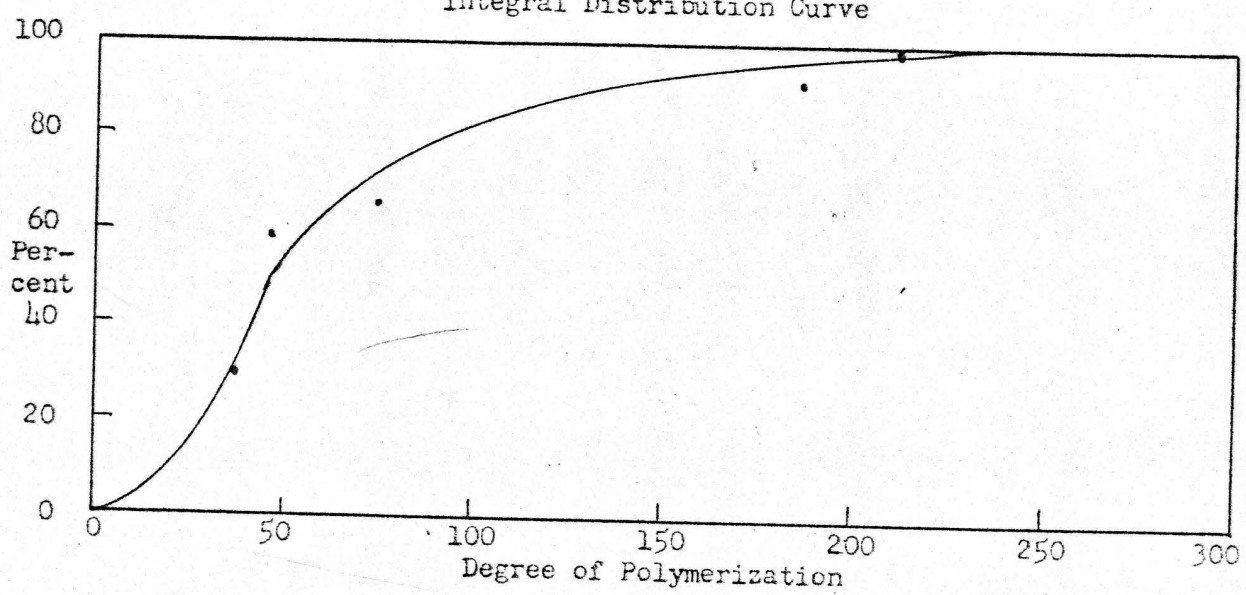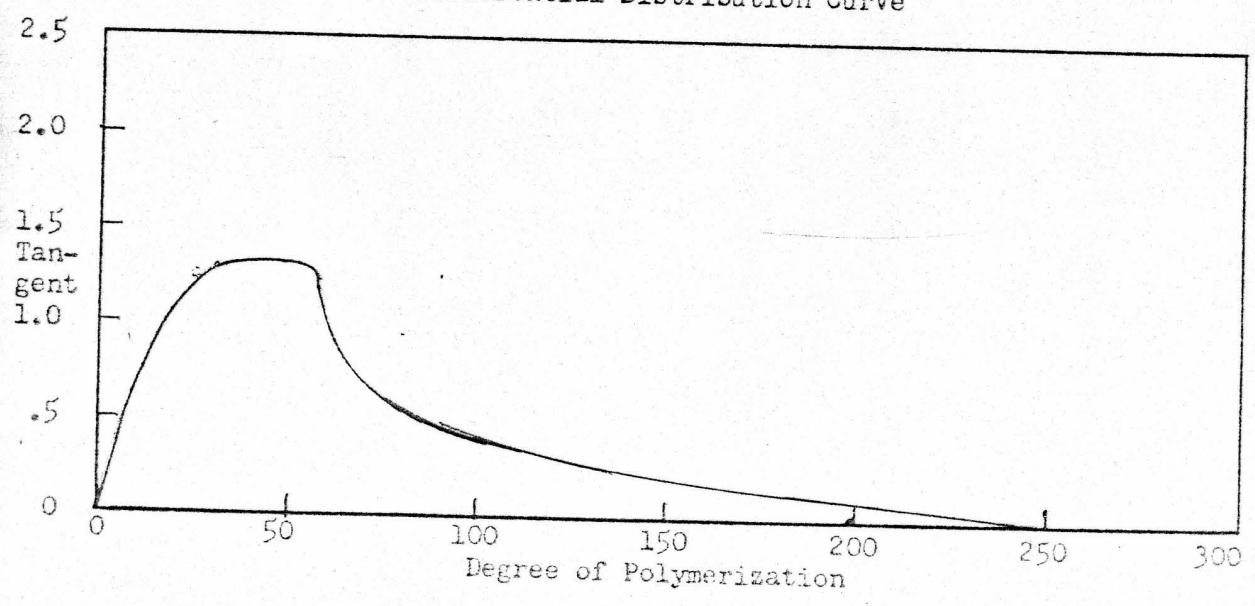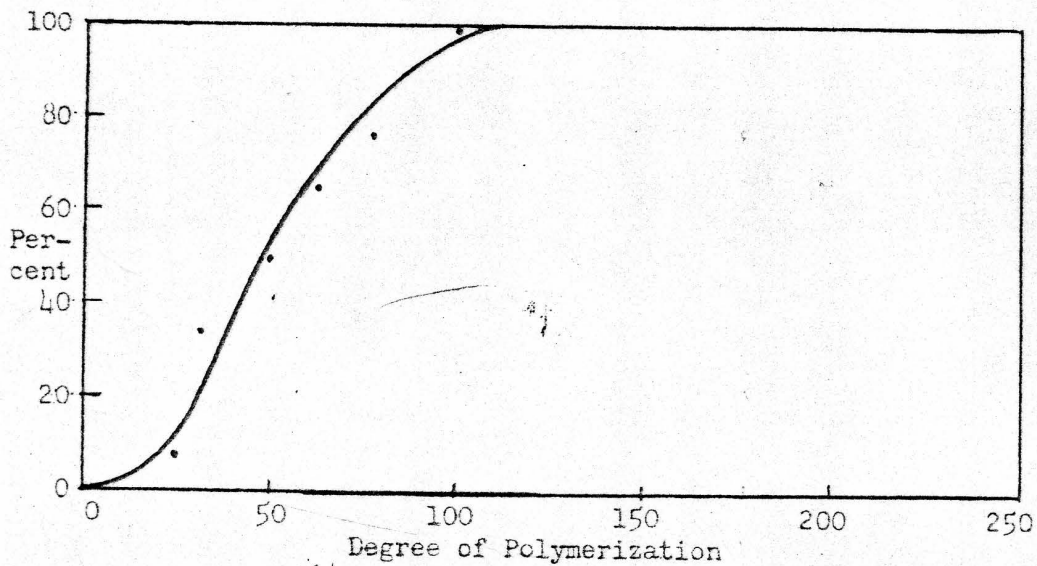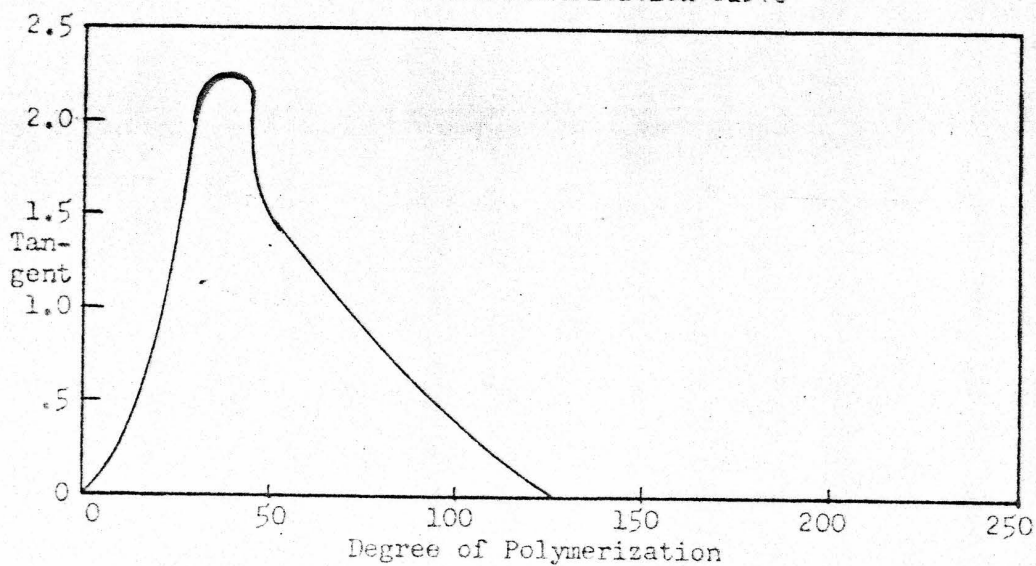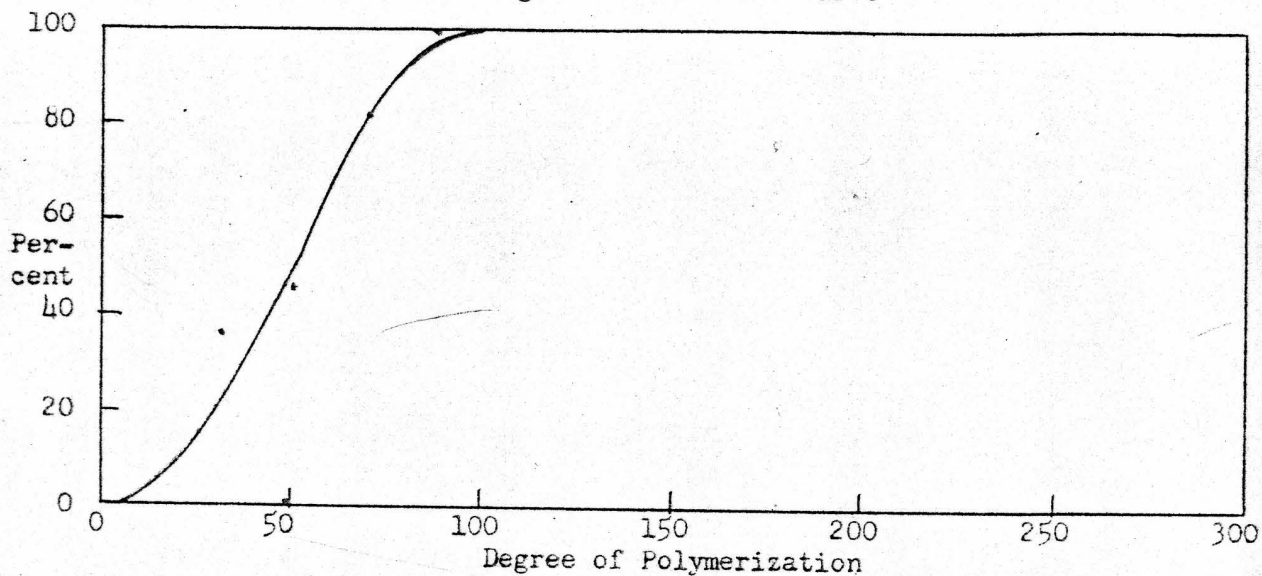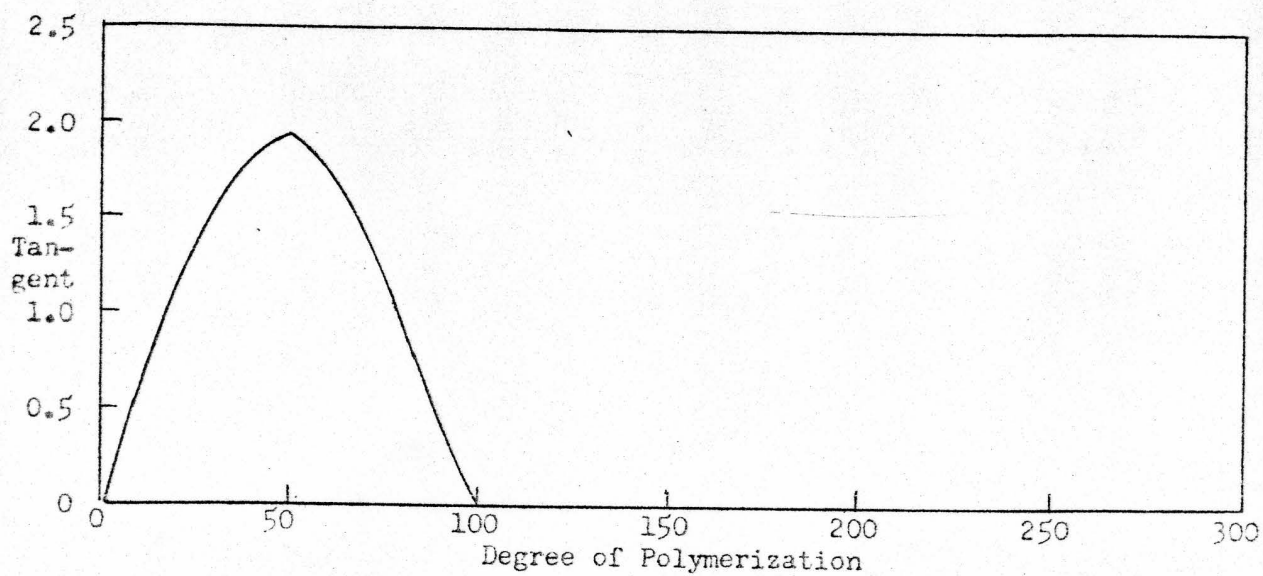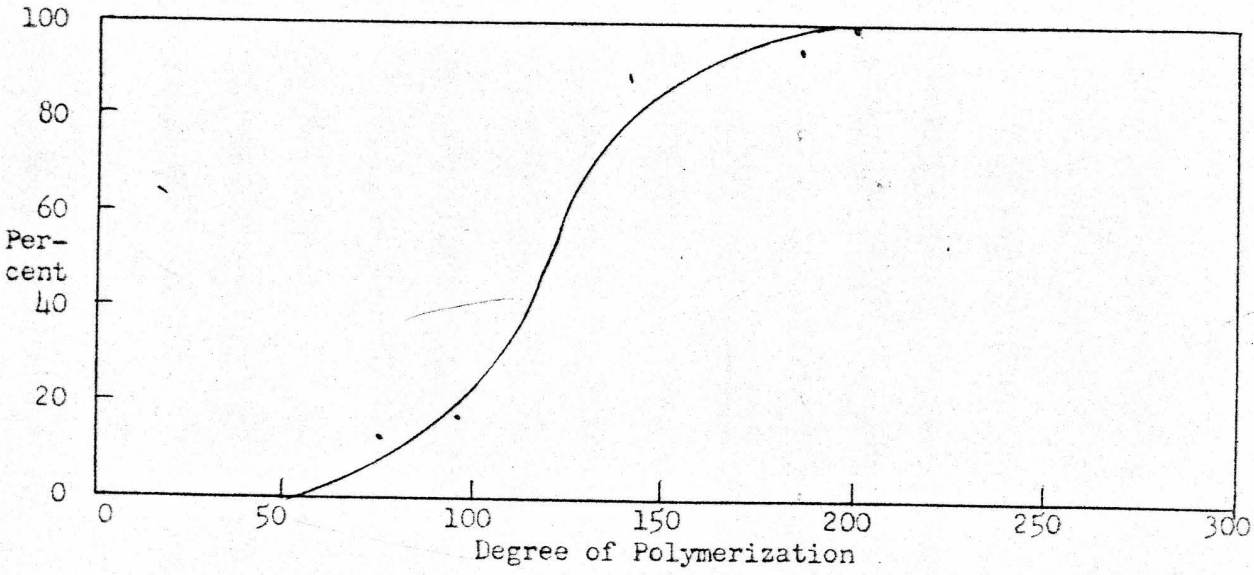Integral Distribution Curve

Differential Distribution Curve

GRAPH 9

Blend Number 7

Average Degree of Polymerization 101

Integral Distribution Curve

Differential Distribution Curve
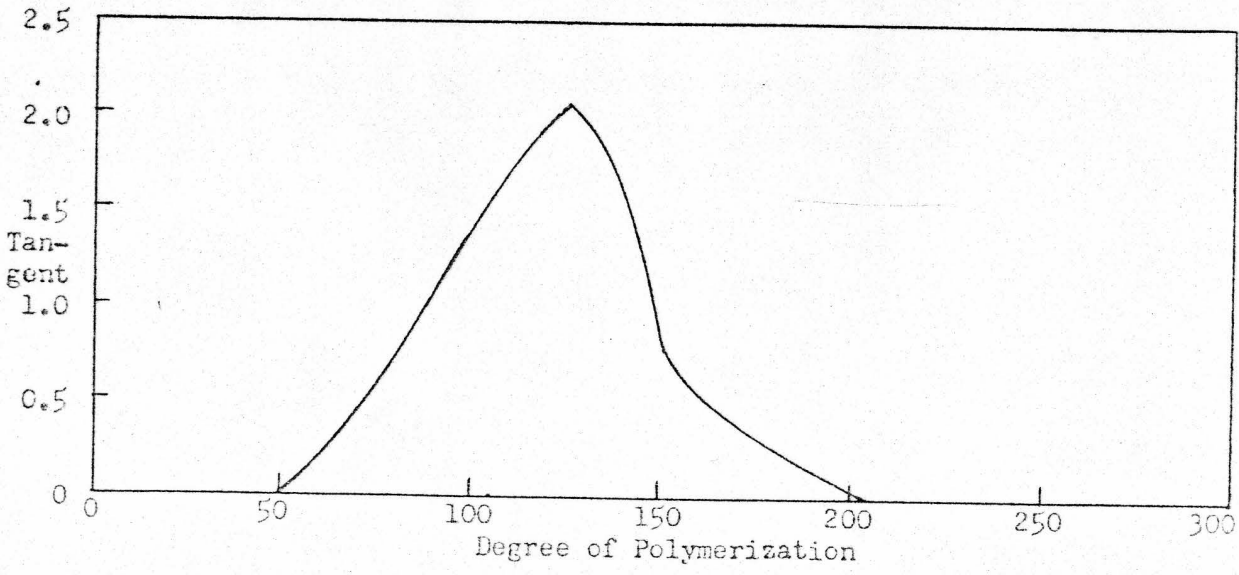
GRAPH 10

Blend Number 8
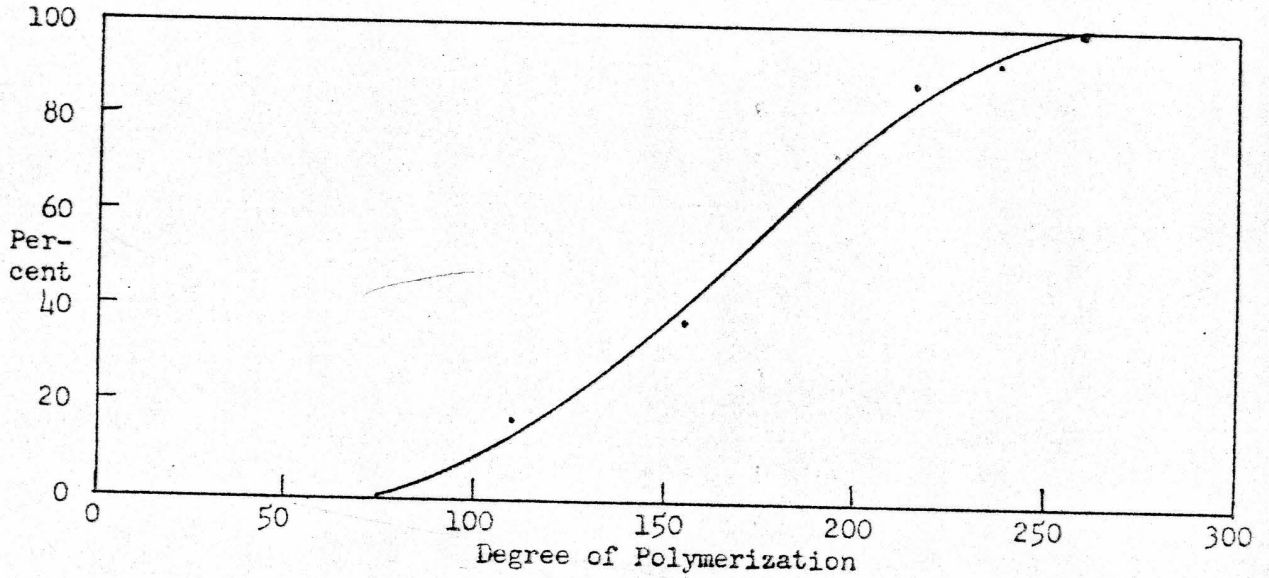
Average Degree of Polymerization 100

Integral Distribution Curve

Differential Distribution Curve

GRAPH 11

Blend Number 9

Average Degree of Polymerization 106

Integral Distribution Curve

Degree of Polymerization

Differential Distribution Curve

Degree of Polymerization

GRAPH 12

Original Blend

Average Degree of Polymerization 60

Integral Distribution Curve

Differential Distribution Curve

Therefore, the four fractions mentioned were fractionated using acetone and heptane as the solvent and precipitant. Even in a 1 percent solution it was necessary to refractionate the first fractions. The results of these fractionations are shown in Graphs 13, 14, 15, and 16.
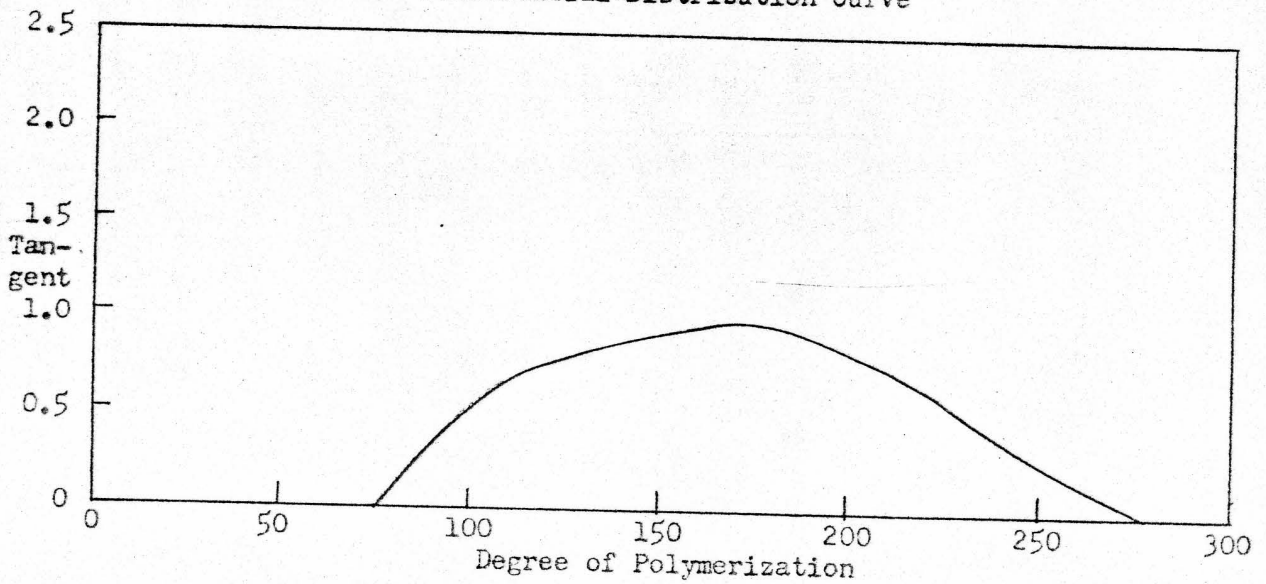
GRAPH 13

Fraction

Average Degree of Polymerization 75

Integral Distribution Curve

Differential Distribution Curve

GRAPH 14

Fraction

Average Degree of Polymerization 165

Integral Distribution Curve

Differential Distribution Curve

GRAPH 15

Fraction

Average Degree of Polymerization 215

Integral Distribution Curve

Differential Distribution Curve
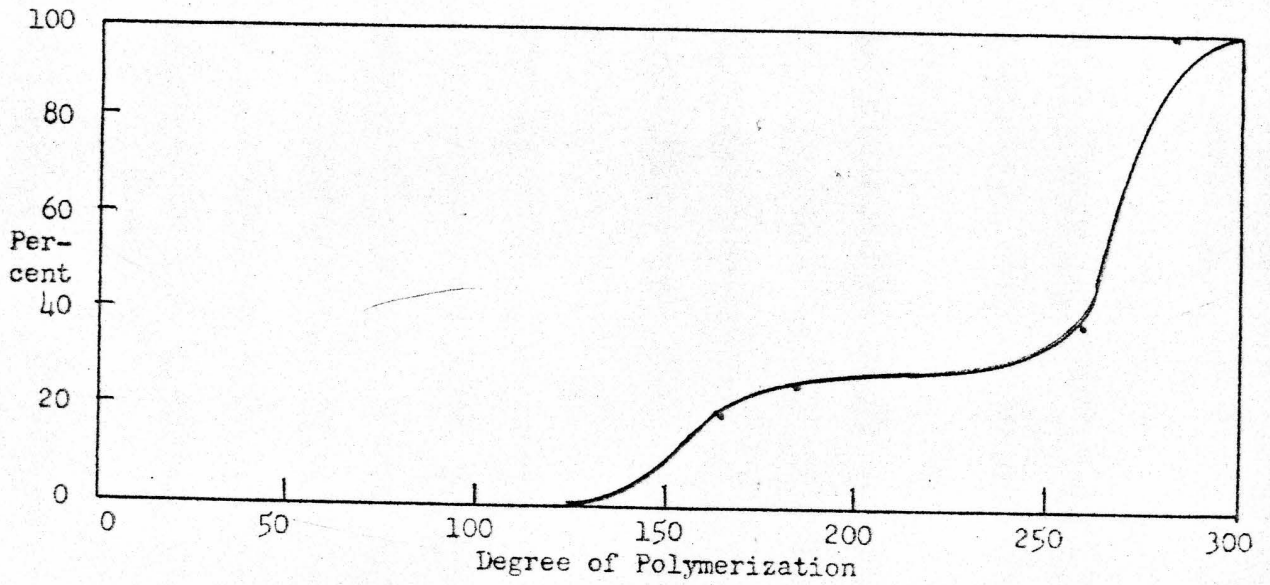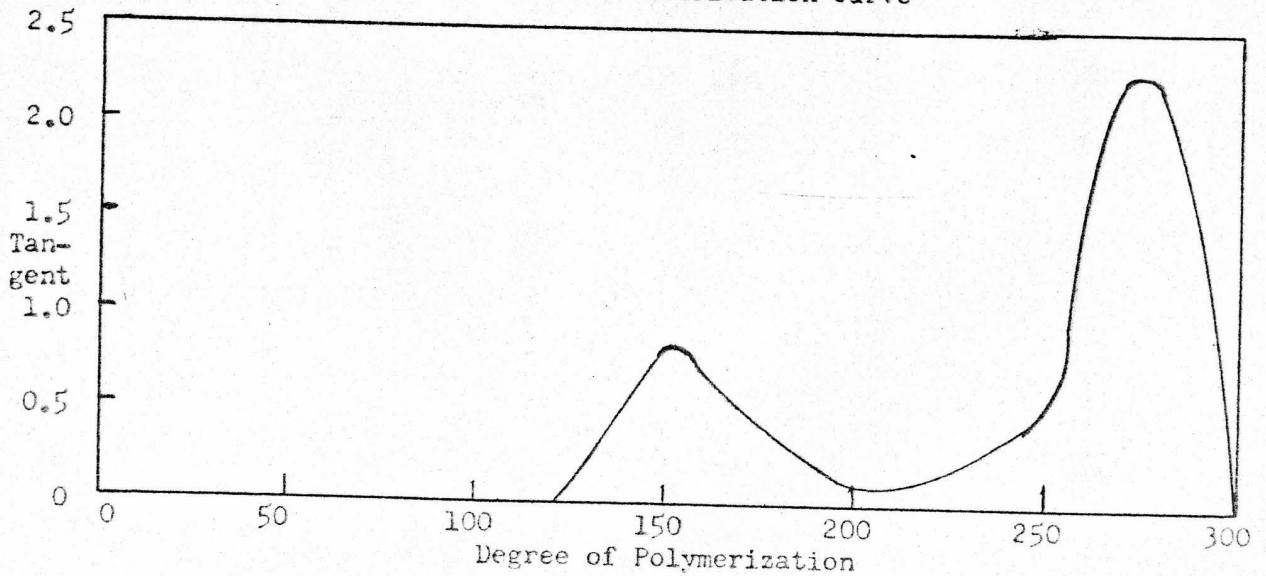
GRAPH 16

Fraction

Average Degree of Polymerization 265

Integral Distribution Curve

Differential Distribution Curve

The problem of the correlation of the data obtained from such a series of blends having different distribution curves, including three blends and one fraction which had distribution curves with two maxima, had not been considered by those workers who had previously prepared blends of two fractions (20,64,65). Therefore, the solution to the problem was by no means readily apparent.

At the same time, work paralleling the work on cellulose nitrate was being carried out on ethyl cellulose (42a), and a method of correlating the mechanical properties with a calculated "shape factor" was used successfully.

The "shape factor" may be defined as the number resulting from the division of the maximum degree of polymerization obtained from the differential distribution curve by the logarithm of the heterogeneity, a measure of the average width. It should be emphasized that the calculation is of an empirical nature, but it does permit the correlation of the data.

As a sample calculation of the "shape factor", the data given in Graph 6 on Blend 4 may be considered. In this particular blend, there is one maximum which occurs at a D.P. of 25. The total height at this maximum in terms of the tangent values, the ordinate, is 1.55. The width of the curve is measured in terms of D.P. at five different points along the total height of the curve at the maximum. These points are 0.9, 0.8, 0.6, 0.4, and 0.2 of the total height. These values of the width are shown with the remainder of the calculations in Table 14. A mean value of these five readings was calculated, and this mean or "average width" was divided by the total height, thus obtaining "H", the heterogeneity. In order to calculate the shape factor, the D.P. of

TABLE 14

CALCULATION OF SHAPE FACTOR
BLEND 4

Fraction of Total Height	Tangent Value	Width of Curve in D.P.	Difference
1.0	1.55	-	—
.9	1.41	30 - 20	10
.8	1.24	35 - 17	18
.6	0.93	45 - 12	33
.4	0.62	77 - 9	68
.2	0.31	154 - 5	149
		Total Width	278
		Average Width	55.6

$$H = \frac{55.6}{1.55} = 35.9$$

$$\log H = 1.555$$

$$\text{Maximum D.P.} = 25$$

$$\text{Shape Factor} = \frac{25}{1.555} = 16.1$$

the maximum is divided by the common logarithm of the heterogeneity.

Similar calculations were made for the other blends and fractions which contained one maximum in their respective differential distribution curves. It was necessary to alter the calculation of the shape factor for those differential distribution curves which had two maxima. The calculation was made as follows: The measurements of the width were made in the same manner, and if the 0.2 measurement was below the curve, then that portion of the curve between the maxima was extrapolated to zero. This extrapolation indicated, then, that two separate distributions existed but overlapped each other at some points. The "H" values were calculated separately and then the common logarithms were added. The difference between the two maxima was obtained; this difference was divided by two, and entered in the table as the maximum. The values of log H, the D.P. at the maximum, and the shape factor for the blends and the four fractions are given in Table 15.

Plots of the mechanical properties and the shape factors are given in Graph 17a and 17b for each of the properties determined in this investigation.
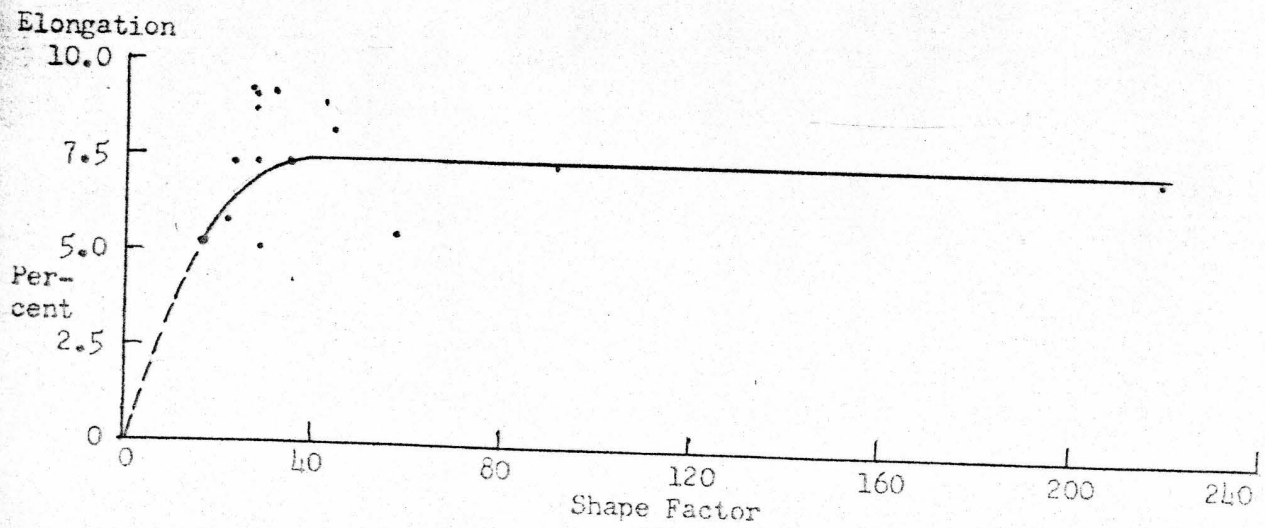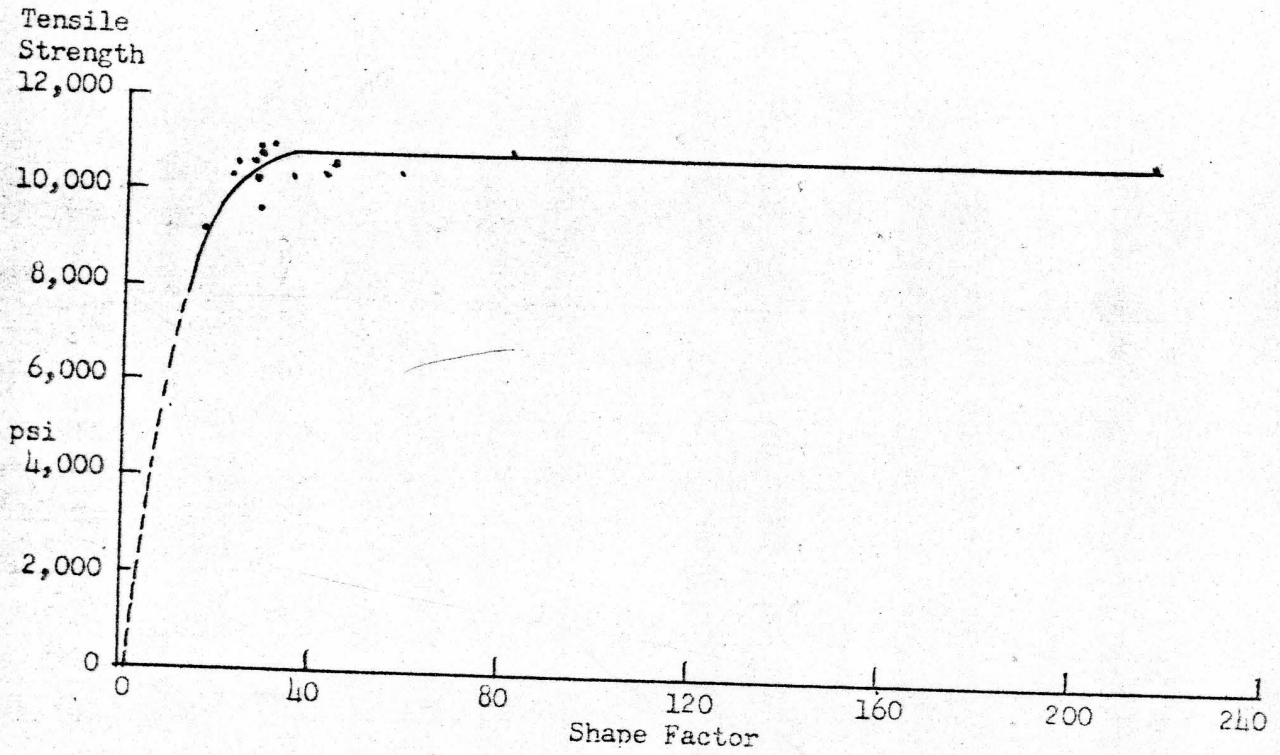
TABLE 15

HETEROGENEITY AND SHAPE FACTORS

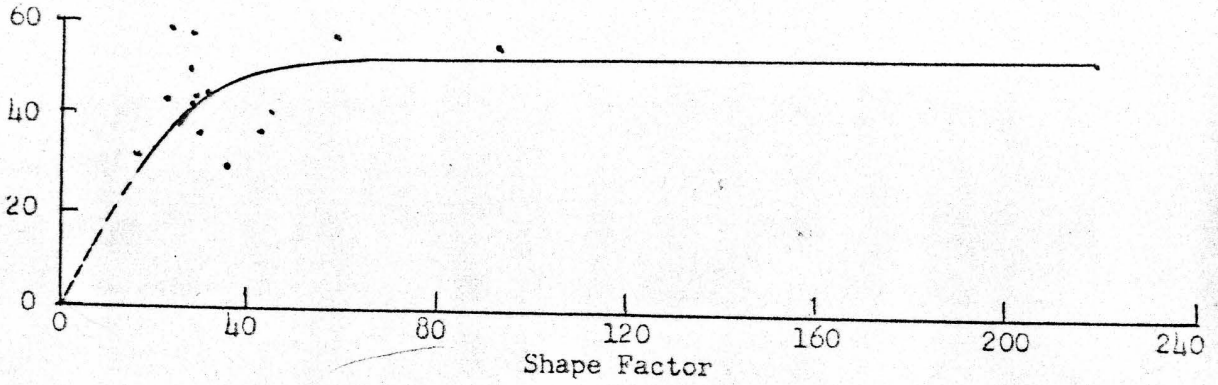| Blends	log H	D.P. at Maximum	Shape Factor
Orig.D.P.420	2.290	500	218.3
Orig.D.P.60	1.333	38	28.5
1*	4.365	120	27.5
2*	4.361	95	22.0
3*	3.912	110	28.1
4	1.555	25	16.1
5	1.739	73	42.0
6	2.263	100	44.2
7	1.810	50	23.6
8	1.646	50	30.4
9	1.703	45	26.4
D.P. of Fractions			
75	1.430	50	35.0
165	1.368	125	91.4
215	2.079	120	57.7
265*	2.728	63	22.9

* Differential distribution curves showed two maxima.

GRAPH 17a

Correlation of Results of Mechanical Tests on Synthetic Blends with Shape Factor of Distribution Curve
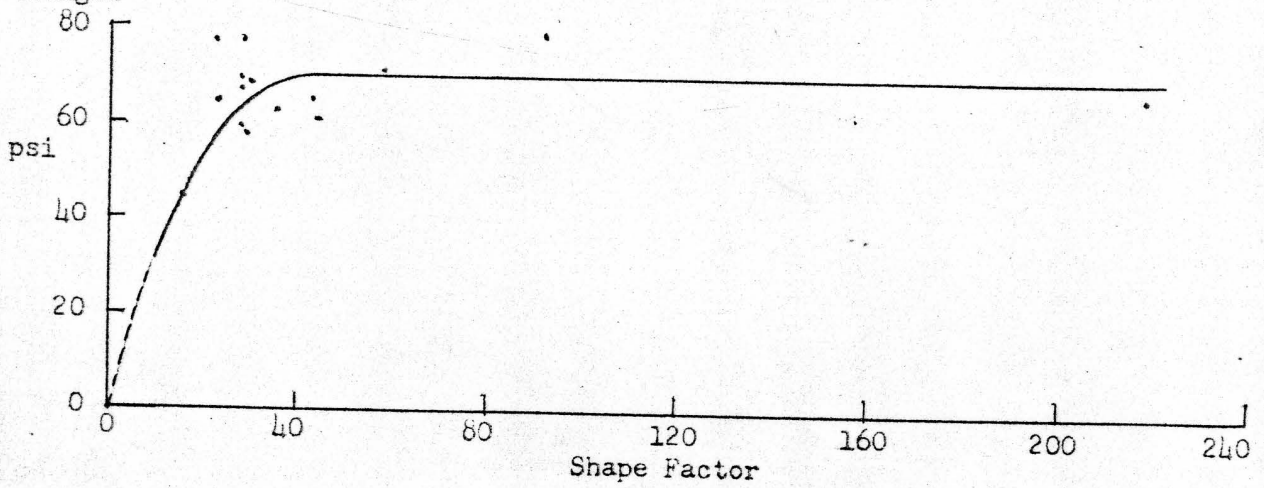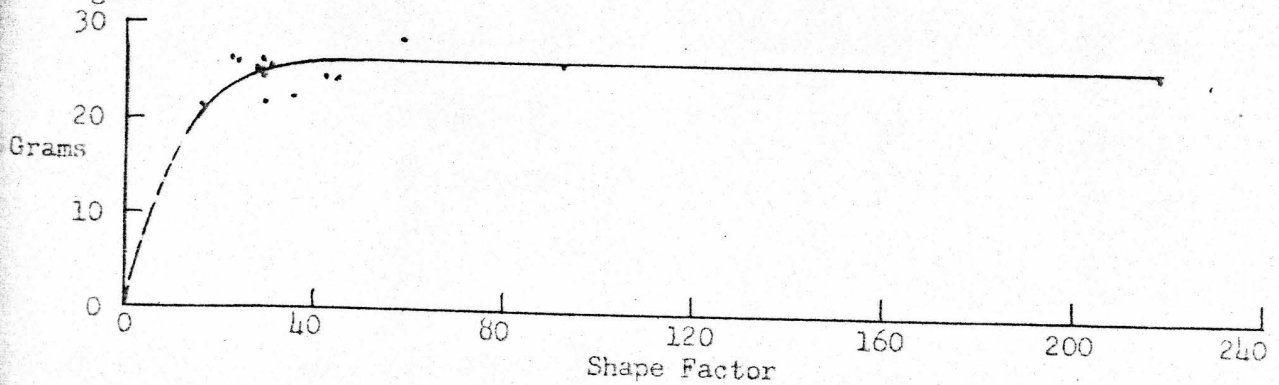
GRAPH 17b

VIII. DISCUSSION OF RESULTS

The results of this investigation are discussed under five separate divisions in order to permit an orderliness in presenting the discussion and the conclusions derived therefrom.

1. The results of the mechanical tests on the films deposited from ethyl acetate solutions have shown that any fraction having an average degree of polymerization greater than 50 shows considerable mechanical strength. The tensile strength of a fraction which has an average degree of polymerization of 30 is not zero. This material in the form of films is very brittle, but with careful handling, test samples can be prepared and an average tensile strength of 4,500 psi was calculated from the average results of eight samples. According to experimental results and theory, the tensile strength increases very rapidly as the average degree of polymerization is increased. The increase as determined by experiment is more rapid than theory demands, and the change in the rate of increase in the tensile strength occurs in the region of 100. Above 100, the rate of increase in the tensile strength decreases, and above 200 as the average degree of polymerization increases, there is practically no further increase in the tensile strength.

The results obtained for percentages of elongation follow very closely those obtained for the tensile strength. The rate of increase is again rapid up to an average degree of polymerization of 100, and the elongation does not increase appreciably above this value.

The values obtained for the Schopper Folding Endurance test show a wide variation which is apparently inherent in this type of test. It is a well established fact that unmodified cellulose nitrate films are brittle. Conclusions drawn from Schopper Folding tests alone are subject

to considerable doubt as to their accuracy. However, if the results of
the Schopper Folding tests are in line with the results of other mechani-
cal strength tests, then a more completely rounded picture is available
for theoretical consideration. Therefore, it may be said that in spite
of the large variability involved, similar conclusions as stated above
for the tensile strength and elongation may be said to hold for the
folding endurance tests.

The Mullen Bursting Strength tests show a considerable variation in
the films tested from the various fractions. It should be remembered
that this test was primarily designed for the testing of paper products,
and a modification of this basic tester might prove to be more useful
in determining the burst strength of such films as those prepared in
this investigation.

It is still possible, however, to state that in view of the experi-
mental results obtained from the burst test, a similar relation exists
for this test as for those previously discussed.

The results obtained from the use of the Elmendorf Tearing Strength
Tester indicate that this test is not very sensitive to changes in the
average degree of polymerization throughout the range of polymerization
studied. It is unfortunate that no materials having average degrees of
polymerization between 75 and 165, and between 30 and 75, were available
for testing. The tests do indicate what is believed to be a significant
decrease for the sample which had an average degree of polymerization of
75. Since the value obtained for this test was 22.5 grams, this is an
indication that any fraction having an average degree of polymerization
between 50 and 75 should exhibit some tear strength. Only in fractions
having an average degree of polymerization below 50 should the tear

strength value be close to zero.

From the experimental values obtained, it may be concluded that, as in the other mechanical tests, a certain minimum average degree of polymerization is necessary for a fraction to show any resistance to tearing. This minimum value is just above 30. The resistance to tearing increases rapidly as the average degree of polymerization increases to a value of about 75. Above an average value of 75, the resistance to tear increases more slowly, and above 150, no appreciable increase is observed.

2. In the first series of synthetic blends prepared, Blends 1, 2, and 3, it was planned to have the blends skewed toward the low D.P. side in order to get an indication of the harmful effects caused by the presence of a large percentage of low D.P. material. From the plots of the analytical curves obtained by fractionation, Graphs 3, 4, and 5, each of the three blends contained at least 20 percent of material having an average degree of polymerization below 80, and Blend 3 had 37 percent of material having an average of 80 or below. Since all theoretical discussions on the subject of polymolecularity and the effect of low molecular weight material had presented the idea of the presence of this low D.P. material affecting adversely the mechanical properties, it was not expected that the mechanical properties should show almost no differences. For example, the average tensile strengths for the blends were 10,250 psi for Blend 1, 10,350 psi for Blend 2, and 10,900 psi for Blend 3. Similar results were obtained for each of the other properties tested, and in every case the values approximated those obtained for the fraction having an average D.P. of 215. (Refer to Tables 7 and 13.) It was readily seen from these results that any material having an average degree of

polymerization above 200 was not affected adversely by the presence of as much as 35 percent of material having a D.P. of 80 or below. This conclusion was again contrary to theory.

3. It was not intended that the three blends should contain two maxima in their differential distribution curves. Due to the unavoidable degradation during storage of the fractions, the distributions were such that upon analysis, two maxima were obtained. It had been stated by Douglas and Stoops (20) that if a mixture of fractions of vinyl ester resins was made such that the differential distribution curve should have two maxima, only one maximum was found upon fractionation of the mixture. This statement was made regarding vinyl esters, and no such information concerning cellulose esters has been found. Therefore, it was rather unusual to obtain such results from the fractionations of these three blends.

Thus, despite the fact that the two-peak distributions were not planned, it is evident from the results of the fractionations that cellulose nitrate blends which have distributions resulting in two maxima in the differential distribution curves, can be fractionated in such a manner as to obtain two maxima in the differential distribution curve.

It was necessary to carry out these fractionations in one percent solutions in order to decrease the amount of low D.P. material which might be occluded in the higher D.P. fractions. The refractionation of the first fractions was still necessary in order to eliminate the low D.P. material that was occluded in the fractional precipitation from the one percent solution.

4. The preparation of the second series of blends which had an average degree of polymerization of 100 was somewhat hindered by the

lack of fractions which had average D.P.'s in the range between 75 and 215. This deficiency could not be rectified since the highest D.P. material available from the low viscosity original blend was 75, and no material in this range was available from the high viscosity original blend in sufficient quantity for use. Since it was believed to be more important to investigate the effect of skewing the differential distribution curve to the right, thus placing the emphasis on the weight percentages of low D.P. material, this deficiency was not of any great consequence.

The results obtained from the mechanical tests of these six blends indicated that the shape of the distribution curve had a marked influence on the properties of these blends. For example, Blend 4 which had the same average degree of polymerization as the other five blends showed distinctly inferior properties in all of the mechanical tests. Furthermore, the distribution curves of Blends 4 and 8 can be superimposed one upon the other above a D.P. of 75. The difference in the mechanical properties were so marked that these differences could only be attributed to the differences in the shapes of the two distribution curves below 75 and the positions of the maxima. The mechanical properties of the other blends showed in some cases considerable variation, but the shapes of the differential distribution curves were so different that no simple correlation of the data was possible. No conclusion could be drawn except the presence of a considerable quantity of very low D.P. material exerted a harmful effect on the mechanical properties of films prepared from these blends.

5. It was realized that no simple relation was available which would permit the data to be correlated with the different shapes of the

differential distribution curves. The problem was to arrive at some method which would permit a simple plot of the data against some function which expressed the shape of the differential distribution curve. Such a function was the so-called "shape factor" which has been previously defined as the quotient of the D.P. of the maximum divided by the common logarithm of the heterogeneity.

By the use of this function as a measure of the shape of the differential distribution curve, it has been possible to prepare plots of the data obtained from the mechanical testing of the films prepared from nine synthetic blends, the two original commercially obtained blends and the four fractions analyzed. From these plots, as given in Graphs 17a and 17b, it may be concluded that the value of a mechanical property increases as the shape factor increases up to a value of the "shape factor" of about 30. Above a "shape factor" of about 30, very little increase is obtained in the mechanical property under consideration. It should be noted that, in general, a large value of the "shape factor" implies either a sharp maximum, that is a narrow range of heterogeneity in the polymeric material, and/or a high average degree of polymerization.

IX. CONCLUSIONS

The results of this investigation on the effect of the shape of the differential distribution curve on the mechanical properties of cellulose nitrate films may be summarized in the following manner:

1. The results of mechanical tests on the films obtained from the fractions show that a minimum average degree of polymerization must be present before any mechanical strength is observed. Contrary to theory, this minimum is in the range of 30 for cellulose nitrate and varies somewhat according to the particular strength property under consideration. The tensile strength and percent elongation increase quite rapidly as the average degree of polymerization is increased up to a certain value which, contrary to the theoretically proposed value of 250, has been determined as being about 100. Above an average degree of polymerization of 100, these values do not increase markedly.

The Schopper Folding Endurance, Mullen Bursting Strength, and Elmendorf Tearing Strength Testers show similar results to a greater or lesser extent dependent upon the variability involved in the particular test and the overall sensitivity of the testing machine to the range in the polymerization studied.

It should be realized that the conclusions drawn from this work are the results obtained from films deposited from ethyl acetate solutions and should not be applied to films deposited from any and all other solvents and solvent mixtures. Furthermore, it is realized that the fractions used were non-homogeneous, but an improvement in the homogeneity would probably result in the shifting of the region of abrupt change in the mechanical properties still farther from the theoretical values.

2. A study of the results obtained from the mechanical testing of
Blends 1, 2, and 3 indicate that the influence of the presence of as much
as 20 percent of material having an average degree of polymerization be-
low 40 is very slight. In fact, according to these experiments, the
effect of as much as 35 percent of low D.P. material is negligible pro-
vided the average degree of polymerization is maintained above 200.
This is again contrary to the statements in the literature (45,53).

3. A second conclusion which can be drawn from Blends 1, 2, and
3, is that blends which contain two maxima in the plots of their differ-
ential distribution curves can be successfully analyzed. Such fraction-
ations must be carried out in dilute solution and in even a one percent
solution it may be necessary to refractionate the first and possibly the
second fractions.

4. A study of the second series of synthetically prepared blends,
those six having average degrees of polymerization of 100, has shown
conclusively the harmful effects of the presence of a quantity of very
low D.P. material on the mechanical properties of films prepared from
such blends. The extent of decrease in the strength properties is easily
shown by a comparison of Blends 4 and 8 (Graphs 6 and 10) which have
distributions very similar above a D.P. of about 75. However, the differ-
ences in the distribution curves in the region below 75 are reflected
markedly in the mechanical properties. For example, Blend 4 which has
a maximum at 25 in the differential distribution curve shows a tensile
strength of 9,200 psi. Blend 8, however, shows a maximum at a D.P. of
50, and has a tensile strength of 11,000 psi. The other mechanical
properties exhibit similar results.

5. It has been shown that a correlation of the mechanical properties with the shapes of the differential distribution curves of the synthetic blends may be obtained by the use of the "shape factor". The calculation of the shape factor is admitted to be an empirical calculation. However, it permits some measure of the heterogeneity present in the blend sample and allows the correlation of blends not only of the same average degree of polymerization but also of different average degrees of polymerization, including the low viscosity original blend having an average D.P. of 60 and the high viscosity original blend having an average D.P. of 420.

The conclusions derived from this investigation may be applied only to cellulose nitrate having a nitrogen content of 12 percent. A cellulose nitrate having a different nitrogen content from 12 percent may show somewhat different mechanical properties in the same range of average polymerization degree due to the differences in the strength of the secondary valence forces. The change in the mechanical properties may be similar to that found for the solubility of cellulose nitrates of different degrees of substitution (32). Data to prove or disprove the reliability of this statement are not available at this time.

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THE MECHANICAL PROPERTIES OF CELLULOSE NITRATE FILMS AS A FUNCTION OF THE SHAPE OF THE DISTRIBUTION CURVE

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INTRODUCTION

The object of this investigation was to study the manner in which the physical and mechanical properties of cellulose nitrate films vary as the proportions of the various chain lengths are changed and in that manner attempt to arrive at a correlation between the shape of the distribution curve and those properties. The initial phases of this investigation were directed toward the development of a reproducible method of fractionation to be used to separate a quantity of cellulose nitrate into a series of fractions which do not vary in analytical composition, but which cover a wide range of chain length values.

The problem of the effect of the shape of the distribution curve has been discussed by Mark (5,6), Meyer (7), and Ott (8) from the theoretical point of view. However, very little experimental work (1,2,10,11) is available in the literature.

FRACTIONATION PROCEDURES

Fractionation of High Viscosity Cellulose Nitrate

It had previously been found (9) that ethyl acetate (commercial grade) was a satisfactory solvent for the RS Type 600-1000 second cellulose nitrate, and n-heptane (commercial grade) was satisfactory as the non-solvent. The fractionation procedure consisted of the addition of sufficient quantity of n-heptane to a solution of ethyl acetate containing 2.5 percent by weight oven-dry cellulose nitrate to cause a permanent turbidity without precipitation at 25 degrees Centigrade. The solvent-non-solvent polymer mixture was then permitted to stand for a period of time at 15 degrees Centigrade to allow sufficient time for the formation of two separate and distinct phases. The liquid or supernatant phase was decanted into another container, warmed to 25 degrees Centigrade before the addition of more non-solvent. The precipitate phase was dissolved in acetone and recovered in the form of flocks by pouring the acetone solution into water.

By the use of this fractionation procedure, twenty-four large scale fractionations were run. Each batch consisted of 7,064 grams of ethyl acetate and 18.1 grams of oven-dry cellulose nitrate. For the precipitation of the first fraction it was necessary to add 6,699 grams of n-heptane. The fractions thus obtained were dried at 55 degrees Centigrade, wetted with ethyl alcohol, and stored at 15 degrees Centigrade in the dark for a period of approximately six months.

By the use of the fractionation procedure described above, it was possible to obtain nine fractions whose average degrees of polymerization

as determined by the Staudinger viscosity method covered a range from 165 units to 550 units (9). The combined weights of the fractions recovered averaged 92 percent of total weight of the cellulose nitrate. The residual portion of the cellulose nitrate soluble in the mother liquor was not recovered. The results obtained from one large scale fractionation together with the average degree of polymerization determined for each fraction are given in Table 1.

It was realized that even storage of the alcohol-wet cellulose nitrate fractions at 15 degrees Centigrade, in the dark, would not prevent the occurrence of some degradation. Therefore, it was necessary to combine all portions of corresponding fractions by dissolving them in acetone and precipitating by pouring the viscous acetone solution into water, in order to obtain a fraction from which a sample representative of the entity could be taken for a redetermination of the average degree of polymerization prior to the mechanical testing.

Duplicate viscosity determinations were made on each of the fractions obtained from the large scale fractionation procedure. It was found that the first fraction was badly degraded, and since attempts to improve the average degree of polymerization were unsuccessful, the first fraction was not used in the mechanical testing. The viscosity determinations also indicated that fractions five and six had the same average degree of polymerization. Thus, from the large scale fractionation of the high viscosity cellulose nitrate, seven fractions ranging in average degree of polymerization from 520 to 165 were available for mechanical testing.

TABLE 1

SAMPLE OF FRACTIONS OBTAINED IN LARGE SCALE PROCEDURE

Fraction Number	Percent Obtained	Average D.P.
1	19.7	550
2	17.4	535
3	13.0	505
4	6.9	465
5	6.9	415
6	7.1	360
7	7.8	275
8	8.5	220
9	2.7	165

Total percent obtained 90.0

Fractionation of Low Viscosity Cellulose Nitrate

The purpose of fractionating the low viscosity cellulose nitrate, RS Type ½ second, with an average degree of polymerization of 60, was to obtain a quantity of material which had an average degree of polymerization of 50 or less. The procedure used did not need to be reproducible, since one large batch would supply enough material for mechanical testing and for use in the synthetic blends.

It was estimated that 100 grams of material, having an average degree of polymerization of 50 or slightly below, would suffice. Therefore, a quantity of 400 grams of the low viscosity blend was dissolved in 3600 grams of acetone and 650 grams of distilled water was added. This quantity of water was sufficient to produce a permanent turbidity in the mixture at 25 degrees Centigrade. Two distinct phases were obtained after the mixture had stood at 15 degrees Centigrade for 20 hours. The supernatant liquid was separated, placed under reduced pressure and evaporated to dryness. The soluble portion, thus recovered, was found by viscosity determination to have an average degree of polymerization of 55, and the weight of the dry material was 221 grams.

The precipitated phase was recovered by dissolving it in acetone and pouring the acetone solution into water. The average degree of polymerization of this portion was 75.

The soluble portion was again subjected to a similar fractionation procedure and separated into two fractions. Material weighing 80 grams and having an average degree of polymerization of 30 was obtained. The precipitated phase again had an average degree of polymerization of 71, and it was combined with the first precipitate. Thus, it was possible to

obtain from the low viscosity cellulose nitrate two fractions having average degrees of polymerization of 75 and 30, respectively.

Presentation of Data from Fractionation Procedure

The immediate outcome of any fractionation procedure is a table such as Table 1, which lists the weight percent and the corresponding average degree of polymerization of each fraction obtained. The simplest way to present such data is to convert this data into a curve, plotting the cumulative weight percent of the fractionated material against its average degree of polymerization. This leads to an integral distribution curve such as that presented in Graph 1, which represents the distribution in the high viscosity cellulose nitrate.

The differential distribution curve is obtained by a point by point graphical determination of the slope of the curve using a tangentometer. The resultant values in degrees are translated into tangents, and the values of the tangents are plotted against the corresponding degrees of polymerization. In this differential distribution curve, the shape is an indication of the heterogeneity of the sample with respect to the degree of polymerization. Thus, the shape of this particular differential curve indicates that the sample contains a preponderance of material having a degree of polymerization between 450 and 650 with a maximum of 500.
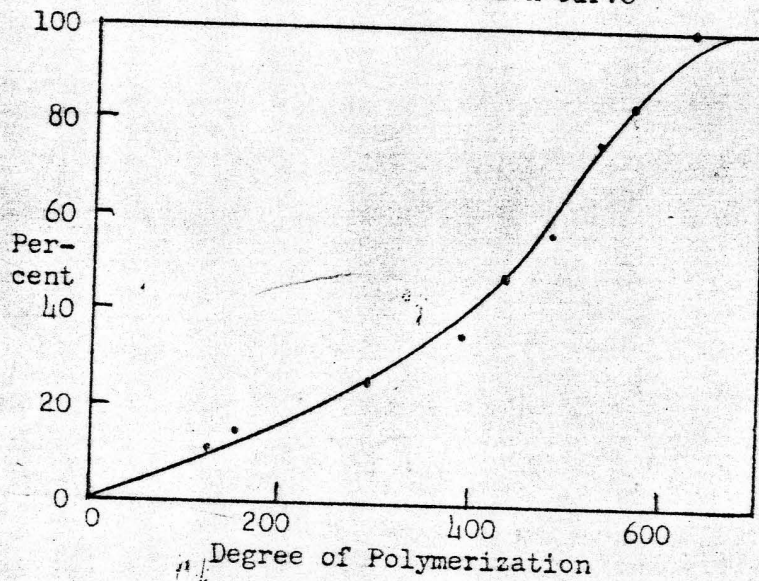
The differential distribution curve of the low viscosity cellulose nitrate (see Graph 2) was obtained by a similar method as described for the large scale fractionation of this material, and this method will be described more completely in the section "Preparation, Testing, and
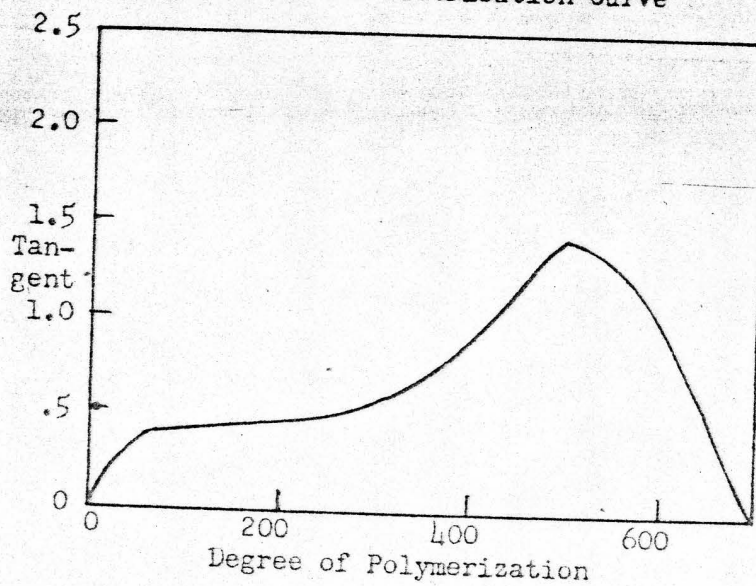
GRAPH 1

Original Blend

Average Degree of Polymerization 420
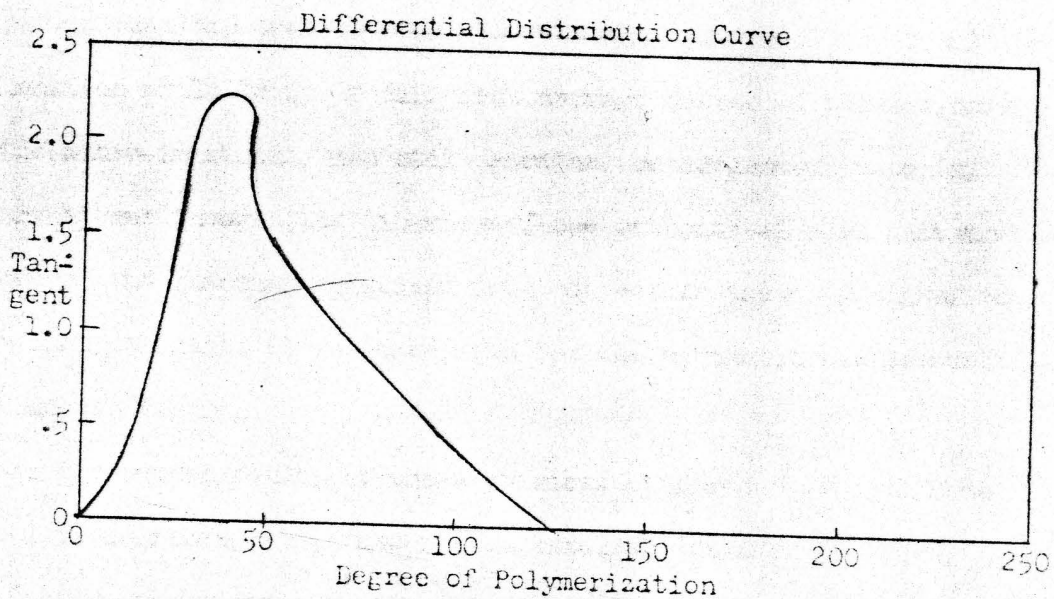
Integral Distribution Curve

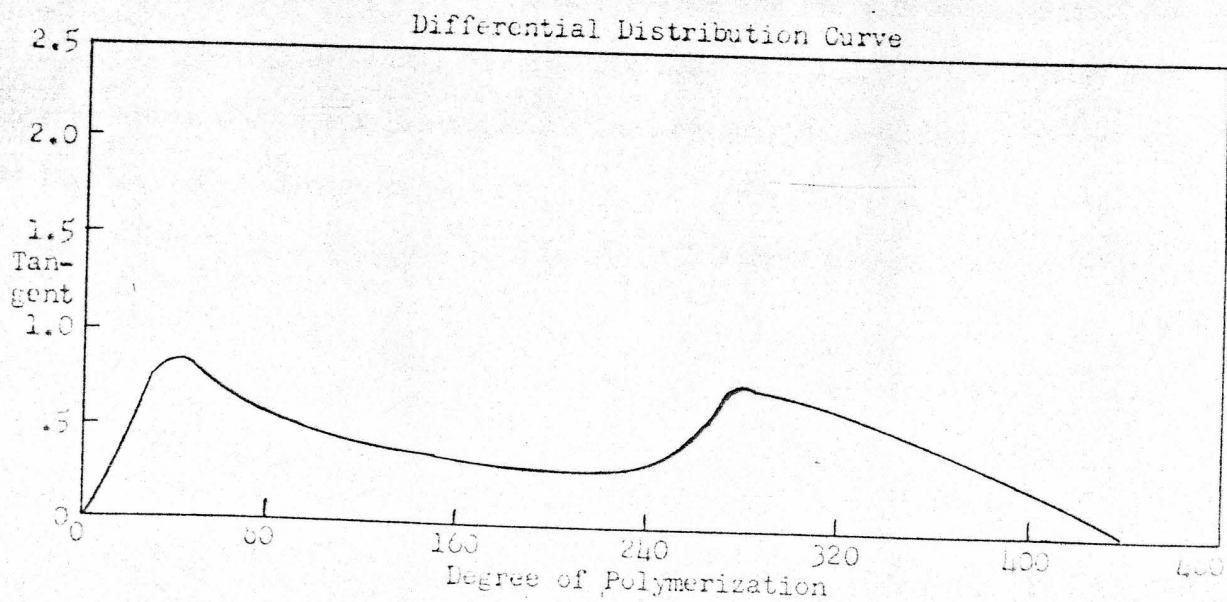#### Differential Distribution Curve

GRAPH 2

Original Blend

Average Degree of Polymerization 60

Differential Distribution Curve

GRAPH 4

Blend Number 1

Average Degree of Polymerization 210

Differential Distribution Curve

Analysis of Blends".

Formation of Films and Mechanical Testing of Fractions

It was realized that each of the fractions obtained by a single fractionation while having a different average degree of polymerization from the other fractions, was still a rather heterogeneous material. However, it was thought that in view of the scarcity of such data in the literature, the information gained from subjecting these fractions to the same mechanical tests as would be used for the synthetic blends would be of considerable value.

For the determination of the mechanical properties of cellulose nitrate, it is necessary to use the material in the form of films. Therefore, it was necessary to develop a suitable procedure for casting and drying the film samples.

In the development of a satisfactory procedure for film casting, several different solvents and solvent mixtures were used. It was only with the use of commercial ethyl acetate as the solvent and drying of the films at 45 degrees Centigrade for one hour that films suitable for testing were obtained. The films were obtained by pouring a quantity of the cellulose nitrate solution on a glass plate and spreading the solution to a uniform thickness by drawing a glass rod equipped with wire spacers at each end slowly along the glass plate.

Films cast in this manner were satisfactory in thickness and uniformity. The viscosity of the solutions was necessarily varied as the degree of polymerization of the different fractions changed, and different sizes of wire were used for the spacers in order to maintain a film thickness of

0.0025 inches. The films were removed from the glass plate by the use
of a water bead with the exception of the very low viscosity fraction.
This fraction having an average degree of polymerization of 30 was very
brittle, and in order not to tear the film, it was necessary to soak them
completely loose before any attempt was made to remove them from the glass
plate.

After removing the films from the glass plates, they were placed be-
tween sheets of paper toweling and pressed flat with a glass plate. This
removed the water clinging to the surface of the films and prevented
them from curling.

After pressing, the films were placed in the conditioning room for
at least 40 hours prior to testing, under conditions of constant tempera-
ture of 77 ± 1.8 degrees Fahrenheit and constant relative humidity of
50 ± 2 percent. These are the standard atmospheric conditions set forth
by the A.S.T.M. Designation: D 618-46T.

Mechanical Tests Applied to Films

The testing machines employed in the tests were the Schopper Type
Tensile Strength and Elongation Tester, the Schopper Type Folding En-
durance Tester, the Mullen Bursting Strength Tester, and the Elmendorf
Tearing Strength Tester. These machines were designed for the testing
of paper products, and in the tests the paper products were to be tested
in two principal directions: One direction parallel to the formation of
the paper sheet, and the other normal to the formation of the paper sheet.
The film samples were tested in accordance with this procedure. The
results obtained from samples cut with their length in the parallel

direction, the direction in which the films were spread, were designated "with values". Those obtained from specimens cut at right angles were designated as "cross values".

The Schopper Type Tensile Strength and Elongation Tester

The procedure used for testing was that set forth in A.S.T.M. Designation: D 822-46T. A total of forty samples, 0.0025 inches thick, twenty samples cut in each of the two principal directions, was tested in order to obtain a representative value for each fraction. The values given in Table 2 are the average values of these forty tests.

The averages of the corresponding values obtained for the elongation calculated in percent elongation based on a distance of 4 inches between the steel clamps are given in Table 2.

The Schopper Type Folding Endurance Tester

The procedure used for testing was that set forth in A.S.T.M. Designation: D 643-43. A total of forty samples 0.0025 inches thick, twenty samples cut in each of the two principal directions, was tested from each fraction. The average number of double folds required to break the film at the point of binding is given in Table 2.

The Mullen Bursting Strength Tester

A total of ten tests were carried out for each fraction according to the procedure set forth in A.S.T.M. Designation: D 774-46. Each sample was 0.0025 inches thick, and the average values from these tests are given in Table 2.

TABLE 2

SUMMARY OF AVERAGE VALUES FOR FRACTIONS

Average D.P. of Fraction	Tensile Strength psi	Percent Elongation	Schopper Folds	Bursting Strength psi	Tear Strength grams
520	10,900	4.2	50.7	78.9	27.8
465	10,900	7.2	55.1	65.1	27.8
390	11,550	6.7	42.1	63.0	26.2
345	12,000	7.1	36.9	77.0	26.9
265	10,600	7.3	59.2	75.5	26.2
215	10,450	5.5	57.5	71.8	28.6
165	10,950	7.4	54.6	79.8	25.8
75	10,300	7.4	29.9	62.8	22.5
30*	4,550	1.1	----	26.0	----

Values given for Tensile Strength, Elongation, and Schopper Folds are averages of 40 samples. Values given for Bursting Strength and Tear Strength are averages of 10 samples.

* A total of eight samples were used for Tensile Strength and Elongation; four samples were used for Burst Strength. Material was too brittle for further testing.

The Elmendorf Tearing Strength Tester

The procedure used for testing was that set forth in A.S.T.M. Designation: D 689-44. Five tests were made in each principal direction. Each test required 16 sheets of film 0.0025 inches thick. The average values obtained for the ten tests run on each fraction are given in Table 2.

To permit a graphical interpretation of the data obtained from these mechanical tests on the fractions, plots of the data were made and are given in Graphs 3a and 3b.

Preparation, Testing, and Analysis of Blends

In order to attack the problem of the effect of the shape of the distribution curve on the mechanical properties of cellulose nitrate films, it was necessary to place two restrictions on the blends to be synthetically prepared. First, the blends must be so prepared as to give a smooth integral distribution curve, from which a differential distribution curve could be graphically obtained, each different from the others. This could be accomplished only by trial and error methods of plotting the proposed percentage compositions against the average degree of polymerization.

Secondly, it was necessary to place a restriction on the average degree of polymerization for the blends so that while the shapes of the distribution curves were to be different, the average degrees of polymerization for the blends could be held within a narrow range of 10 to 20 units. This could be accomplished by calculating the weighted mean for each blend.
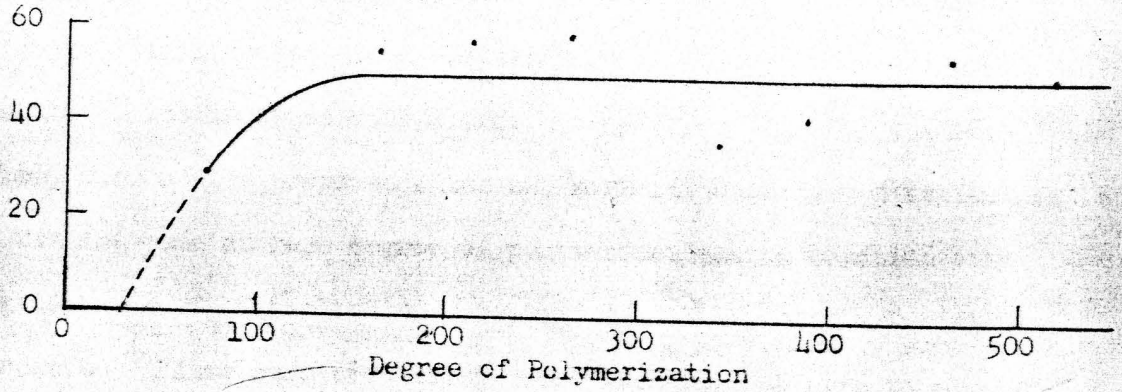
GRAPH 3a
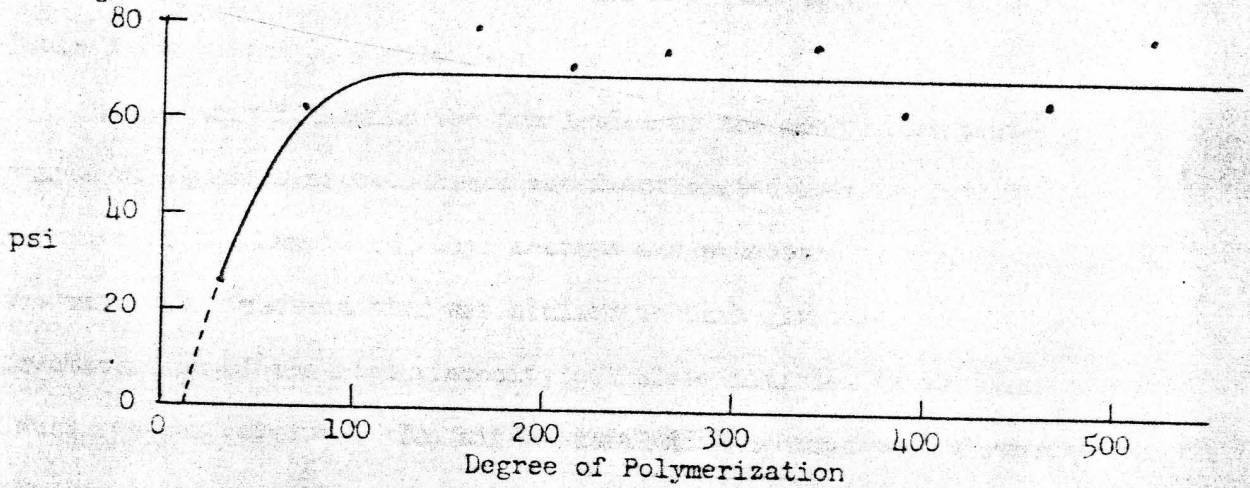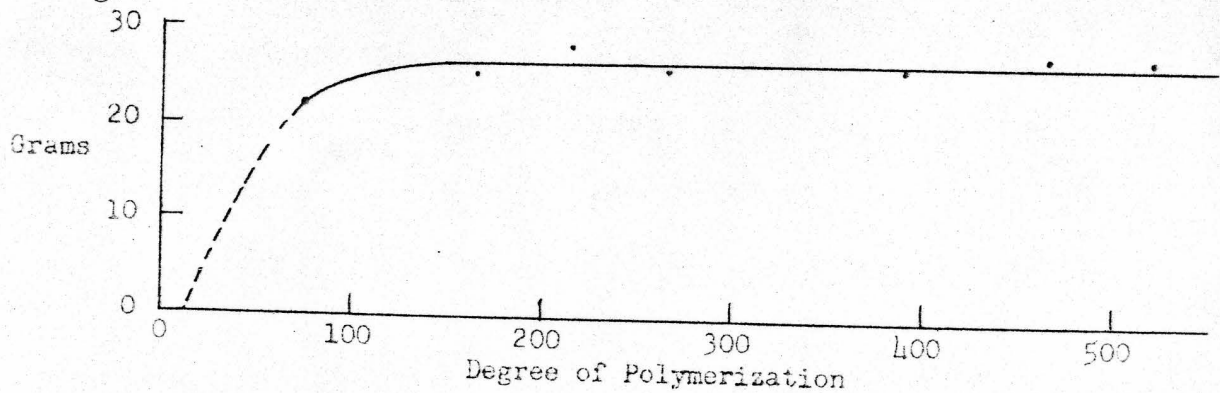
Results of Mechanical Tests on Fractions
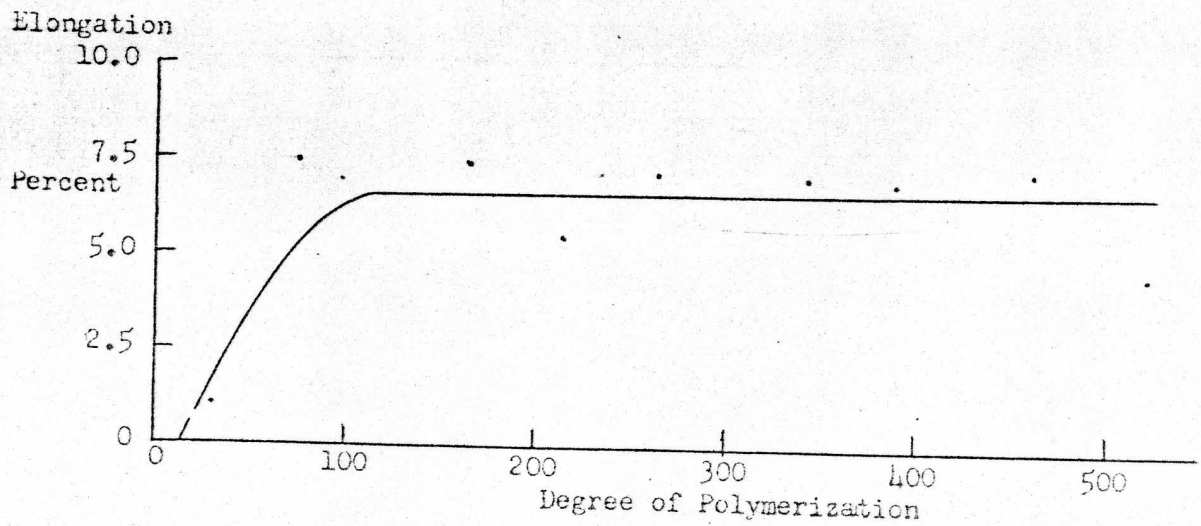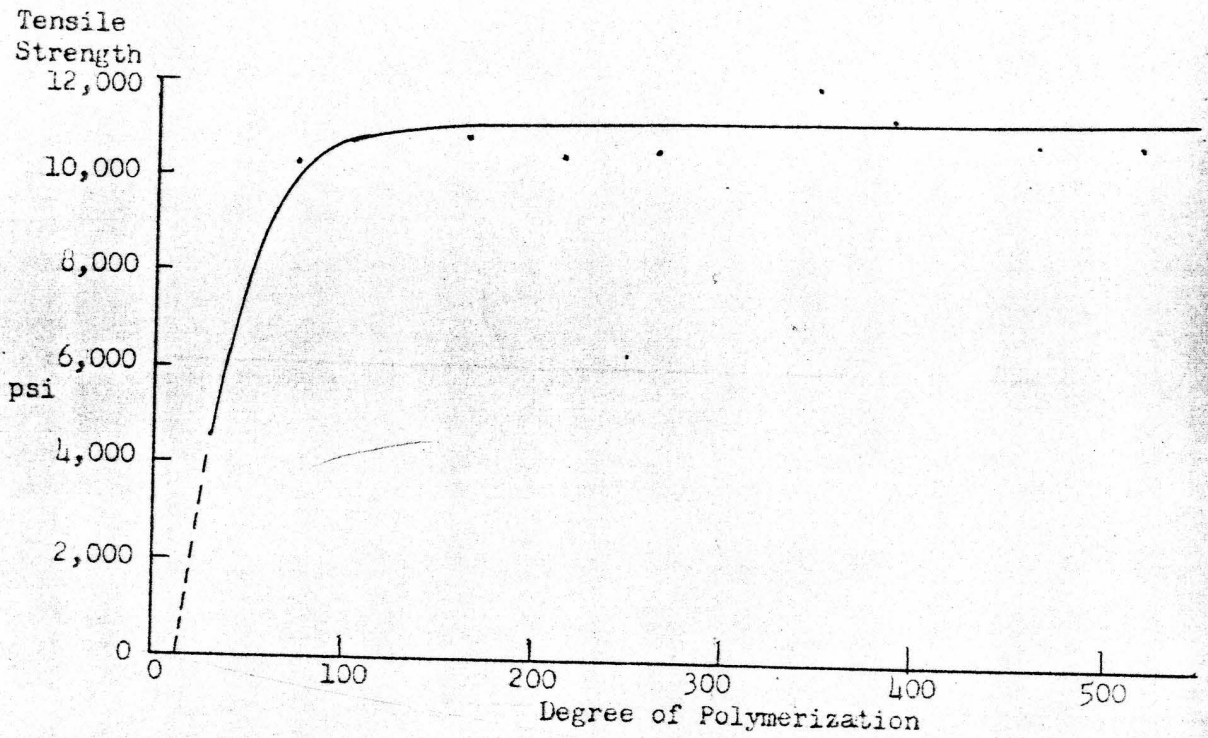
GRAPH 3b

Schopper Folds vs Degree of Polymerization

Burst Strength (psi) vs Degree of Polymerization

Tear Strength (Grams) vs Degree of Polymerization

The average degree of polymerization was chosen as 250 units in order to permit a considerable degree of freedom in the formulation of the synthetic blends. This value permitted the use of all fractions obtained from the fractionations of both high and low viscosity blends, and the use of the low viscosity blend.

Three blends were prepared which had markedly different distribution curves but the same average degree of polymerization. A solution containing 60 grams of each blend was prepared as a 10 percent solution in ethyl acetate. Films were cast using 0.064 inch wire spacers to obtain clear films 0.0025 inches thick according to the procedure previously given, and the resulting films were conditioned and tested in accordance with A.S.T.M. methods. The average values of the tests are given in Table 3 for Blends 1, 2, and 3.

Immediately following the completion of the mechanical tests, a sample of 20 grams of each blend was fractionated using a 2 percent solution of the sample in ethyl acetate and n-heptane as the precipitant. The method of fractionation was similar to that given for the large scale fractionation of the high viscosity cellulose nitrate. A total of eight fractions was obtained. The differential distribution curves representing the composition of Blends 1, 2, and 3 are given in Graphs 4, 5, and 6. From these plots it is evident that the fractions being used are not homogeneous fractions since two maxima were obtained. There is again evidence of degradation in the fractions of higher average D.P. since the calculated averages were 250 and the average D.P.'s obtained from viscosity measurements were in the range of 220. This large a deviation can hardly be attributed to experimental error.

A study of the results obtained from the mechanical testing of these

TABLE 3

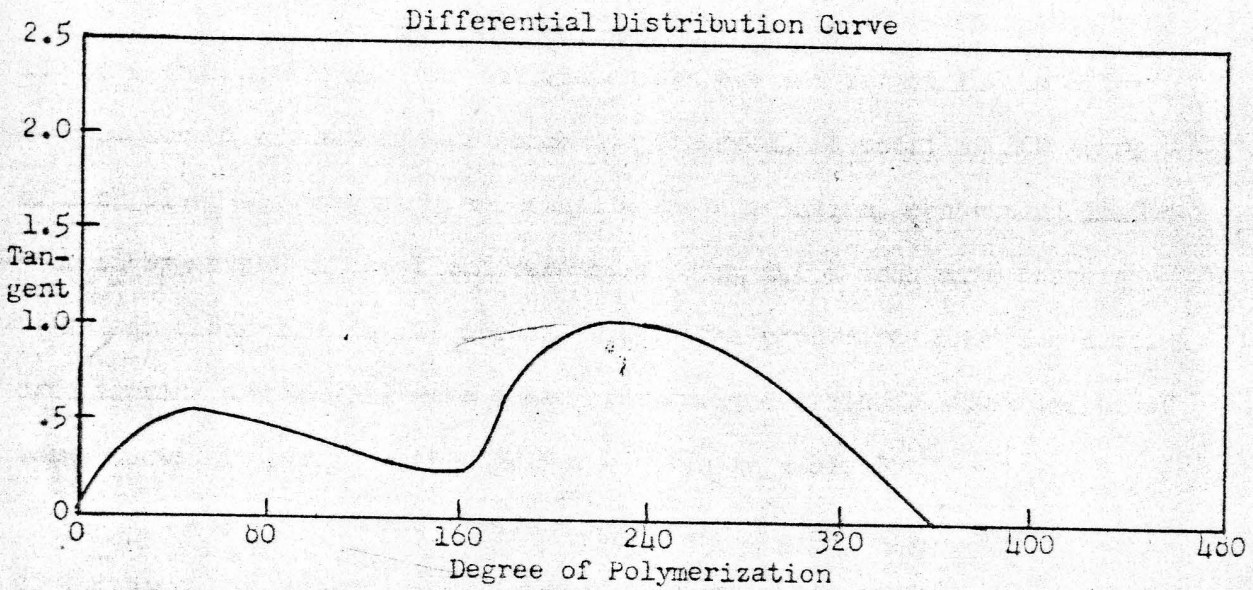### SUMMARY OF AVERAGE VALUES FOR BLENDS

Blend Number	Average D.P. of Blend	Tensile Strength psi	Percent Elongation	Schopper Folds	Bursting Strength psi	Tear Strength grams
Orig.	420	11,000	7.3	54.0	67.0	25.4
Orig.	60	9,600	5.1	36.4	58.0	21.9
1	218	10,250	8.7	57.6	69.9	25.1
2	222	10,350	5.7	43.6	78.3	26.4
3	216	10,900	7.4	43.8	78.3	26.3
4	106	9,200	5.3	31.9	44.5	21.5
5	103	10,400	8.9	37.1	64.8	24.5
6	106	10,650	8.2	41.1	61.0	24.2
7	101	10,850	9.2	42.8	59.3	24.7
8	100	11,000	8.9	44.5	69.0	25.5
9	106	10,700	9.2	50.5	66.0	24.6

Values given for Tensile Strength, Elongation, and Schopper Folds are averages of 40 samples. Values given for Bursting Strength and Tear Strength are averages of 10 samples.
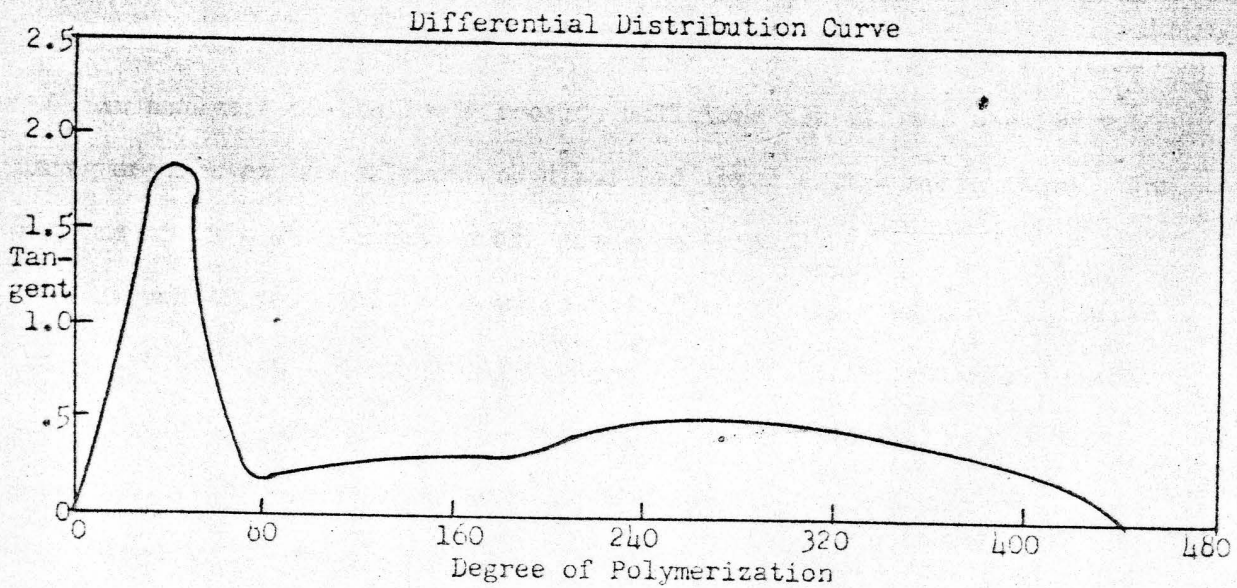
GRAPH 5

Blend Number 2

Average Degree of Polymerization 222

Differential Distribution Curve

GRAPH 6

Blend Number 3

Average Degree of Polymerization 215

Differential Distribution Curve

three blends revealed an indication that as long as the average degree of polymerization was as high as 220, the mechanical properties are not very sensitive to marked changes in the shape of the differential distribution curve.

A series of six blends having an average degree of polymerization of 100 were then prepared. The calculated average was set at 110 to allow for the amount of degradation which had occurred. A total of 100 grams of each blend was prepared, and ethyl acetate solutions containing 16.7 percent by weight of the blend were cast using 0.031 inch wire spacers to obtain clear film 0.0025 inches thick. The procedures used for casting, conditioning and testing were those previously described. The results of these tests for Blends 4 through 9 are given in Table 3.

The analysis of these blends was carried out using a 5 gram sample of the blend dissolved in 495 grams of acetone, and distilled water was used as the precipitant. The results obtained are shown in Graphs 7 through 12.

The mechanical tests for the original high viscosity and low viscosity cellulose nitrates were carried out by the use of the procedures previously described and the results are given in Table 3.

An analysis of the low viscosity cellulose nitrate was carried out using acetone as the solvent and distilled water as the precipitant. The results of this fractionation are given in Graph 2.

It was thought that if some method of correlation of the mechanical properties of the blends with the shape of the differential distribution could be found, it might be interesting to observe whether the results obtained from the testing of some of the fractions might also fit into the system of correlation. If the distributions of the fractions having
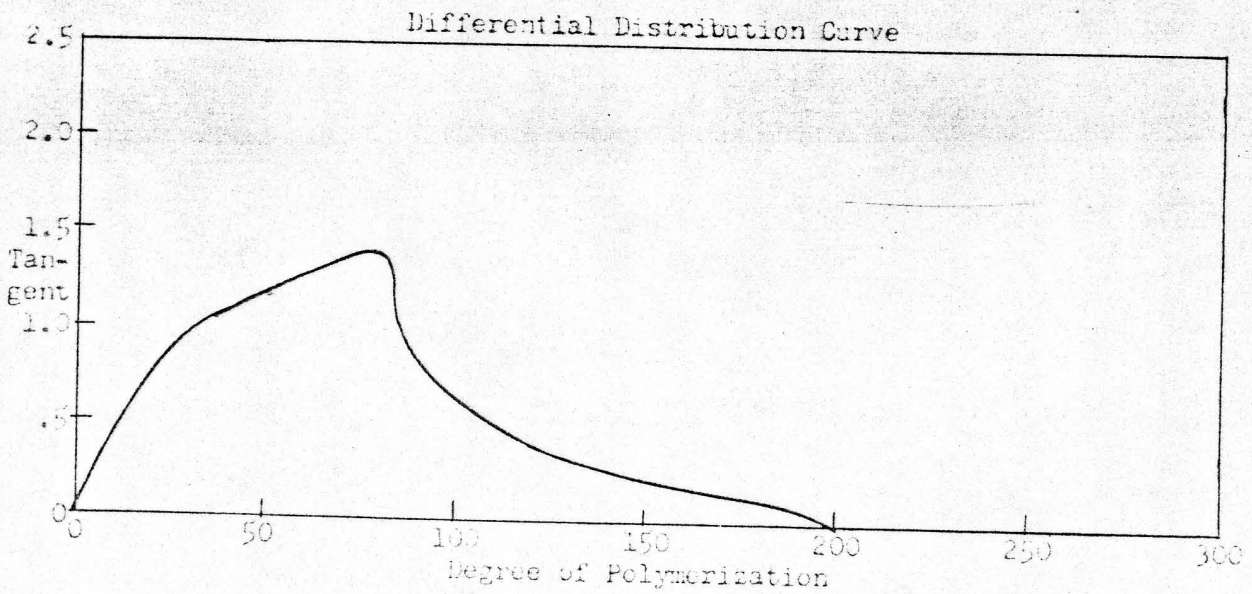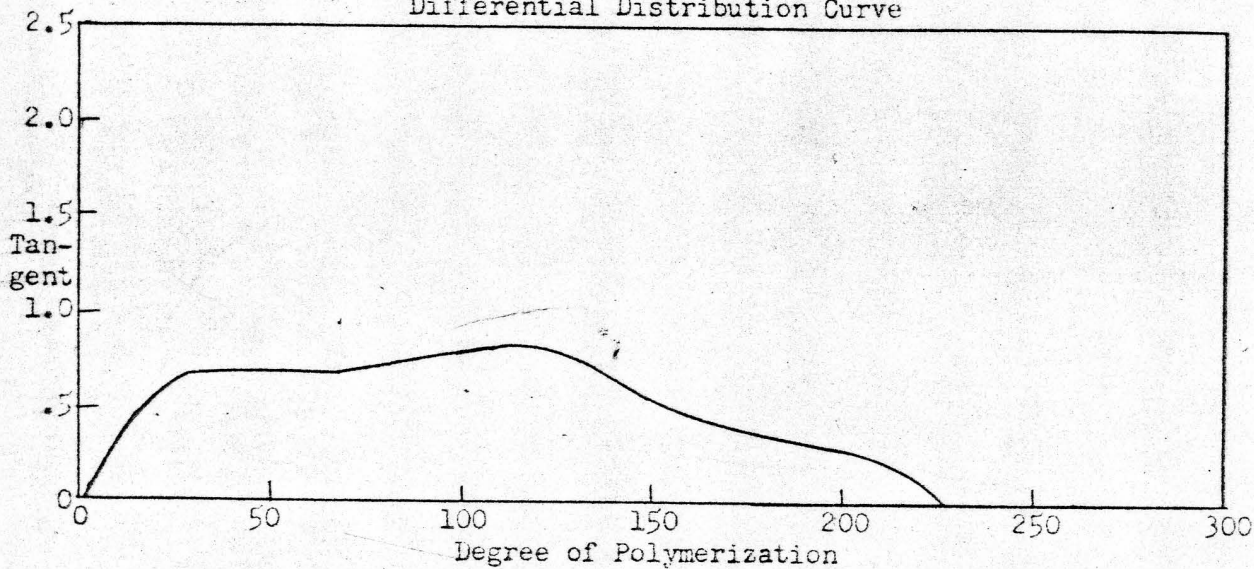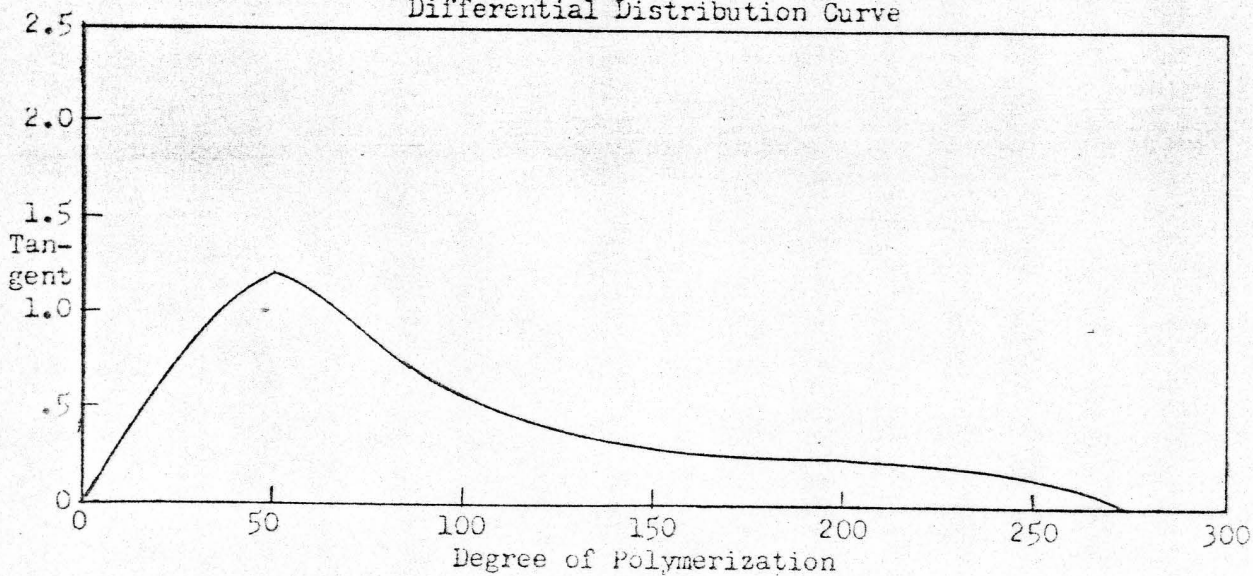
GRAPH 7

Blend Number 4

Average Degree of Polymerization 106

Differential Distribution Curve

GRAPH 8

Blend Number 5
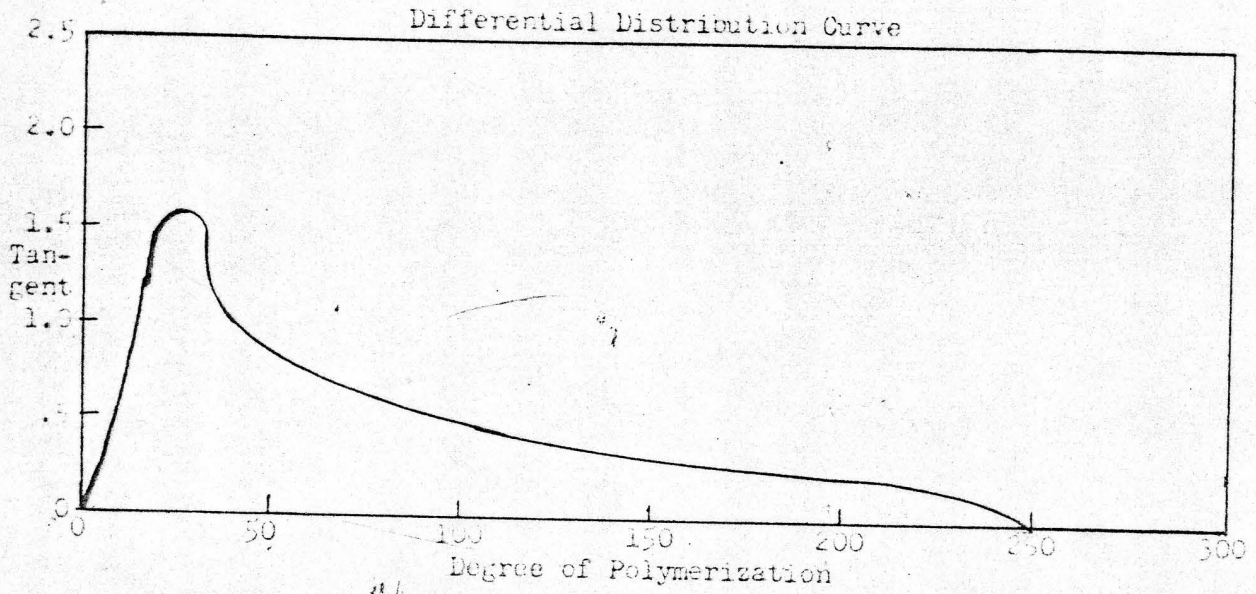
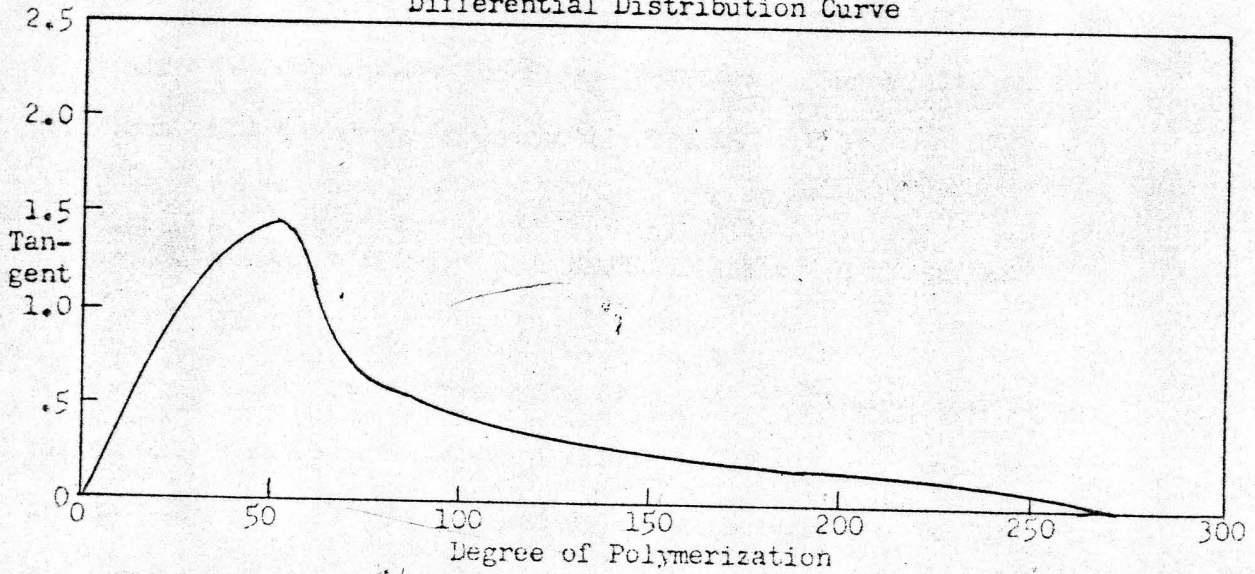Average Degree of Polymerization 103

Differential Distribution Curve

GRAPH 9

Blend Number 6

Average Degree of Polymerization 106

Differential Distribution Curve

GRAPH 10

Blend Number 7

Average Degree of Polymerization 101

Differential Distribution Curve

GRAPH 11

Blend Number 8

Average Degree of Polymerization 100

Differential Distribution Curve

GRAPH 12

Blend Number 9

Average Degree of Polymerization 106
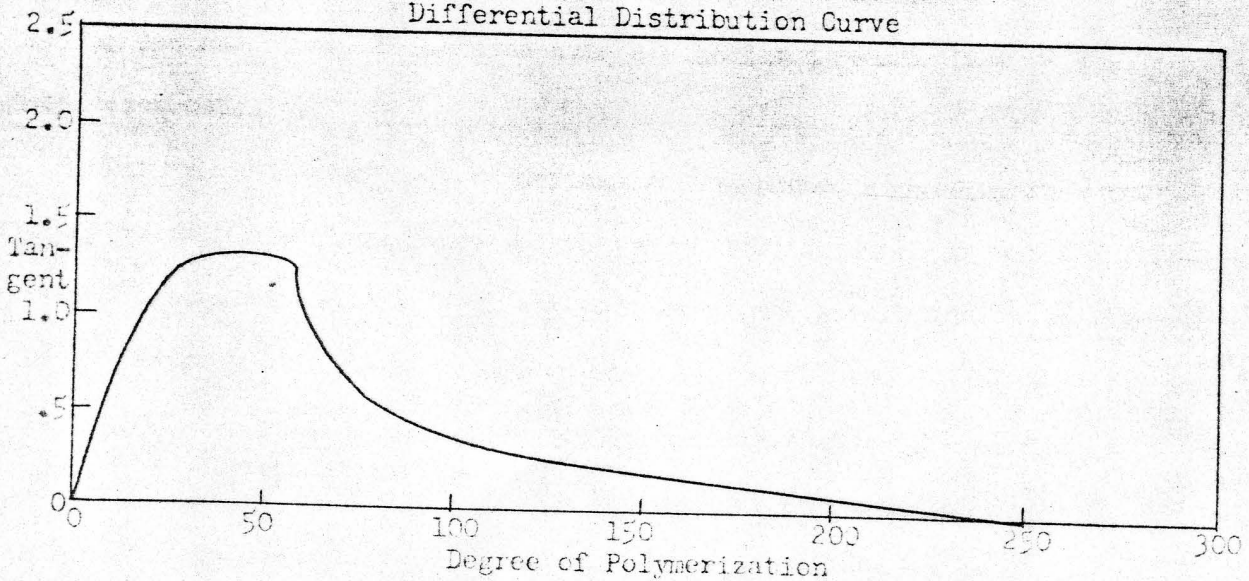
Differential Distribution Curve

average D.P.'s of 75, 165, 215, and 265 were determined, then these fractions could possibly be treated as blends of different average degrees of polymerization from the nine blends prepared synthetically. Therefore, the four fractions mentioned were fractionated using acetone and heptane as the solvent and precipitant. Even in a 1 percent solution it was necessary to refractionate the first fractions. The results of these fractionations are shown in Graphs 13, 14, 15, and 16.

CORRELATION OF DATA FROM MECHANICAL TESTING OF BLENDS

The problem of the correlation of the data obtained from such a series of blends having different distribution curves, including three blends and one fraction which had distribution curves with two maxima, had not been considered by those workers who had previously prepared blends of two fractions (2,10,11). Therefore, the solution to the problem was by no means readily apparent.

At the same time, work paralleling the work on cellulose nitrate was being carried out on ethyl cellulose (4), and a method of correlating the mechanical properties with a calculated "shape factor" was used successfully.

The "shape factor" may be defined as the number resulting from the division of the maximum degree of polymerization obtained from the differential distribution curve by the logarithm of the heterogeneity, a measure of the average width. It should be emphasized that the calculation is of an empirical nature, but it does permit the correlation of the data.
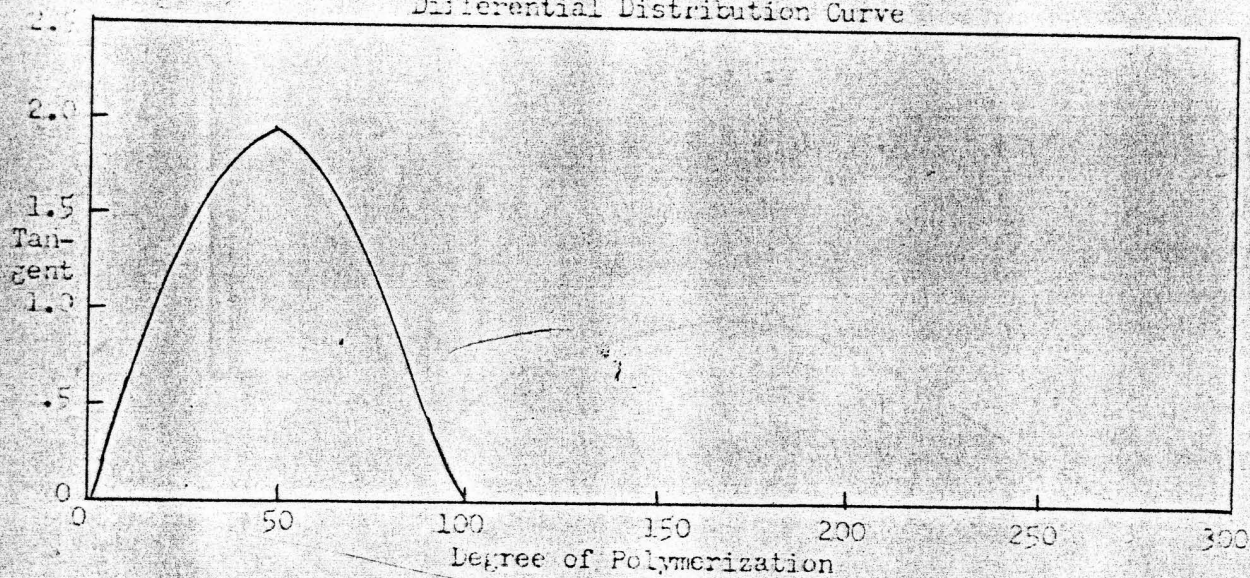
As a sample calculation of the "shape factor", the data given in Graph 7 on Blend 4 may be considered. In this particular blend, there

GRAPH 13

Fraction

Average Degree of Polymerization 75
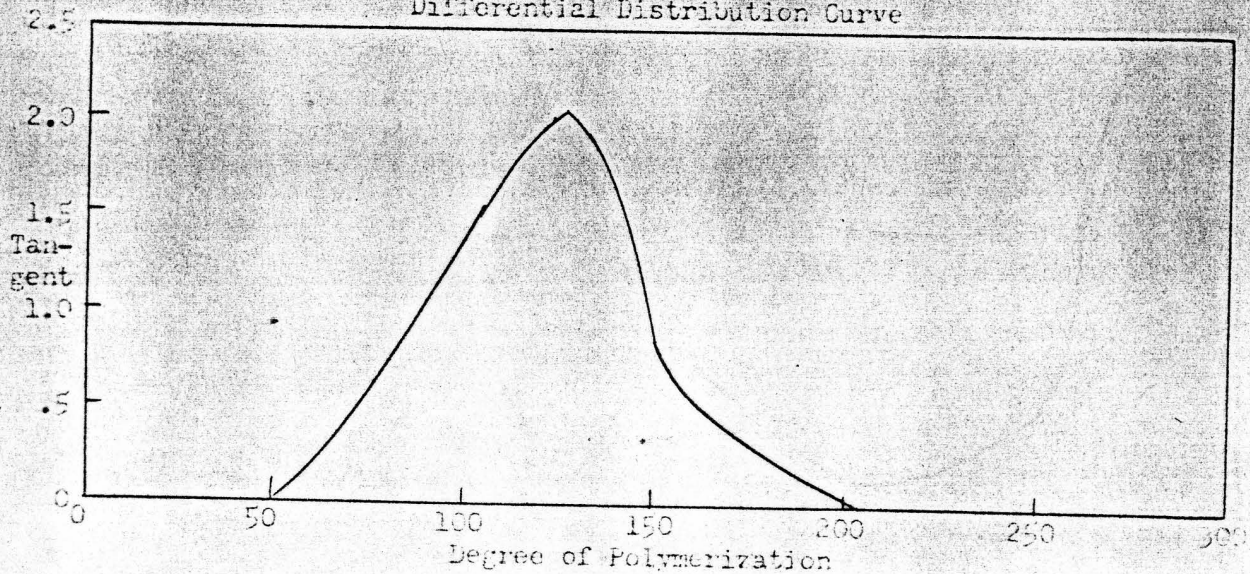
Differential Distribution Curve

Degree of Polymerization

GRAPH 14

Fraction

Average Degree of Polymerization 105

Differential Distribution Curve

Degree of Polymerization
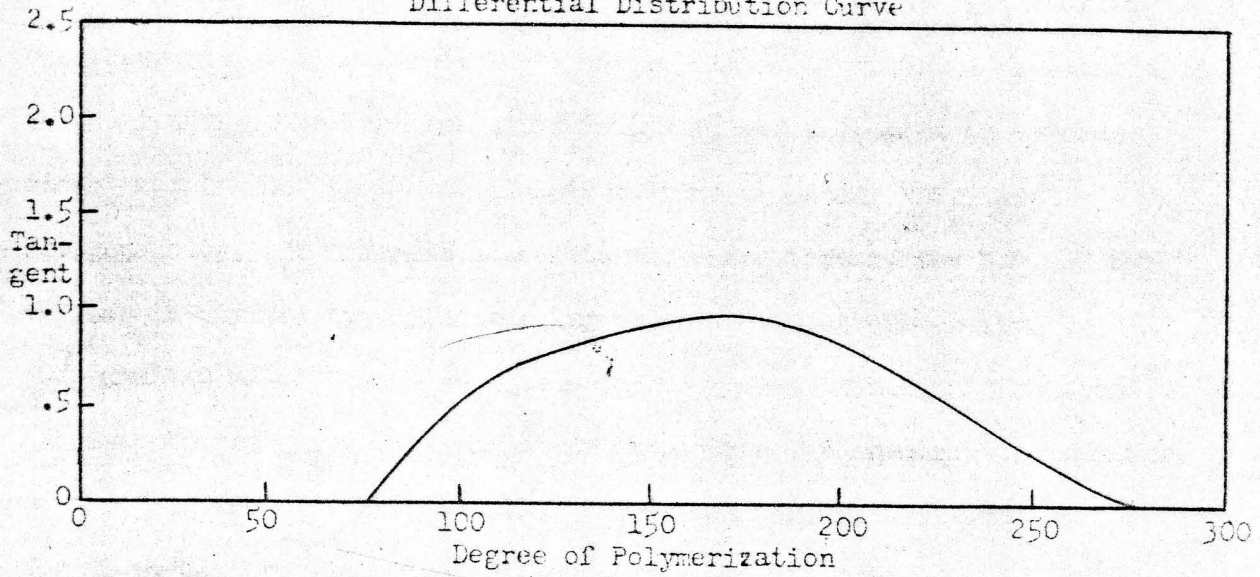
GRAPH 15

Fraction

Average Degree of Polymerization 215

Differential Distribution Curve

Degree of Polymerization

GRAPH 16

Fraction

Average Degree of Polymerization 265

Differential Distribution Curve
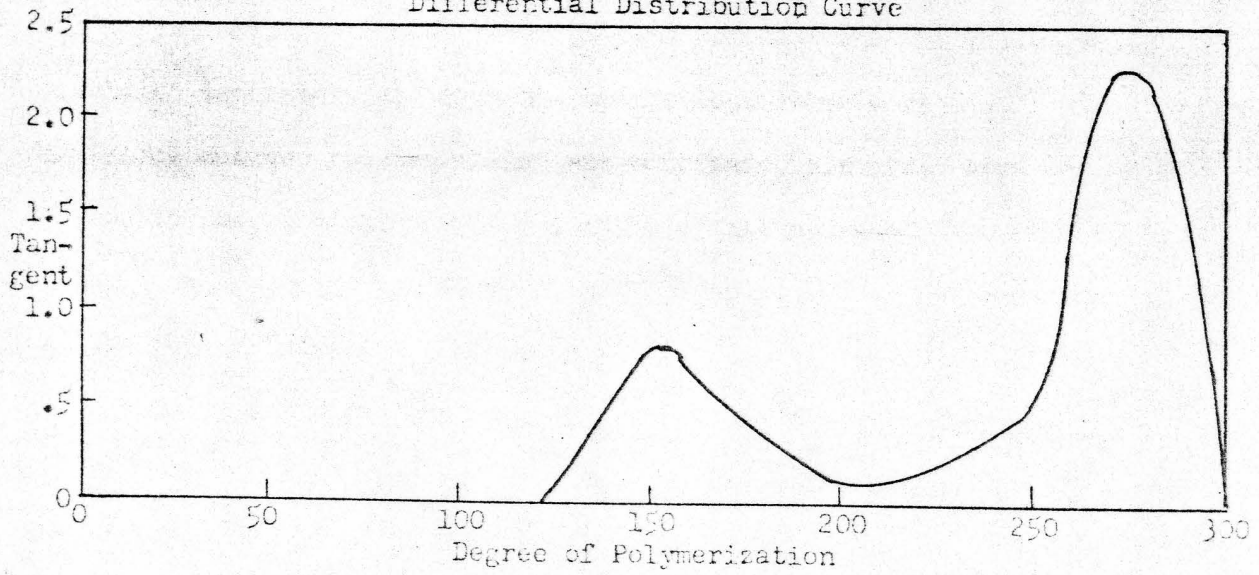
Degree of Polymerization

is one maximum which occurs at a D.P. of 25. The total height at this maximum in terms of the tangent values, the ordinate, is 1.55. The width of the curve is measured in terms of D.P. at five different points along the total height of the curve at the maximum. These points are 0.9, 0.8, 0.6, 0.4, and 0.2 of the total height. These values of the width are shown with the remainder of the calculations in Table 4. A mean value of these five readings was calculated, and this mean or "average width" was divided by the total height, thus obtaining "H", the heterogeneity. In order to calculate the shape factor, the D.P. of the maximum is divided by the common logarithm of the heterogeneity.

Similar calculations were made for the other blends and fractions which contained one maximum in their respective differential distribution curves. It was necessary to alter the calculation of the shape factor for those differential distribution curves which had two maxima. The calculation was made as follows: The measurements of the width were made in the same manner, and if the 0.2 measurement was below the curve, then that portion of the curve between the maxima was extrapolated to zero. This extrapolation indicated, then, that two separate distributions existed but overlapped each other at some points. The "H" values were calculated separately and then the common logarithms were added. The difference between the two maxima was obtained; this difference was divided by two, and entered in the table as the maximum. The values of log H, the D.P. at the maximum, and the shape factor for the blends and the four fractions are given in Table 5.

Plots of the mechanical properties and the shape factors are given in Graphs 17a and 17b for each of the properties determined in this investigation.

TABLE 4

CALCULATION OF SHAPE FACTOR
BLEND 4

Fraction of Total Height	Tangent Value	Width of Curve in D.P.	Difference
1.0	1.55	-	—
.9	1.41	30 - 20	10
.8	1.24	35 - 17	18
.6	0.93	45 - 12	33
.4	0.62	77 - 9	68
.2	0.31	154 - 5	149
		Total Width	278
		Average Width	55.6

$$H = \frac{55.6}{1.55} = 35.9$$

$$\log H = 1.555$$

Maximum D.P. = 25

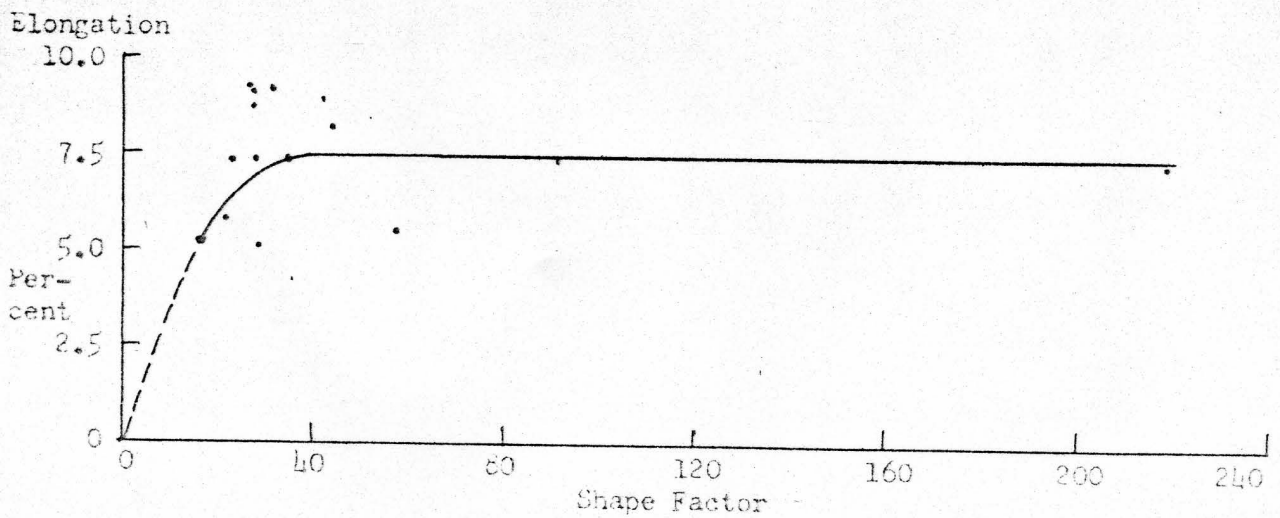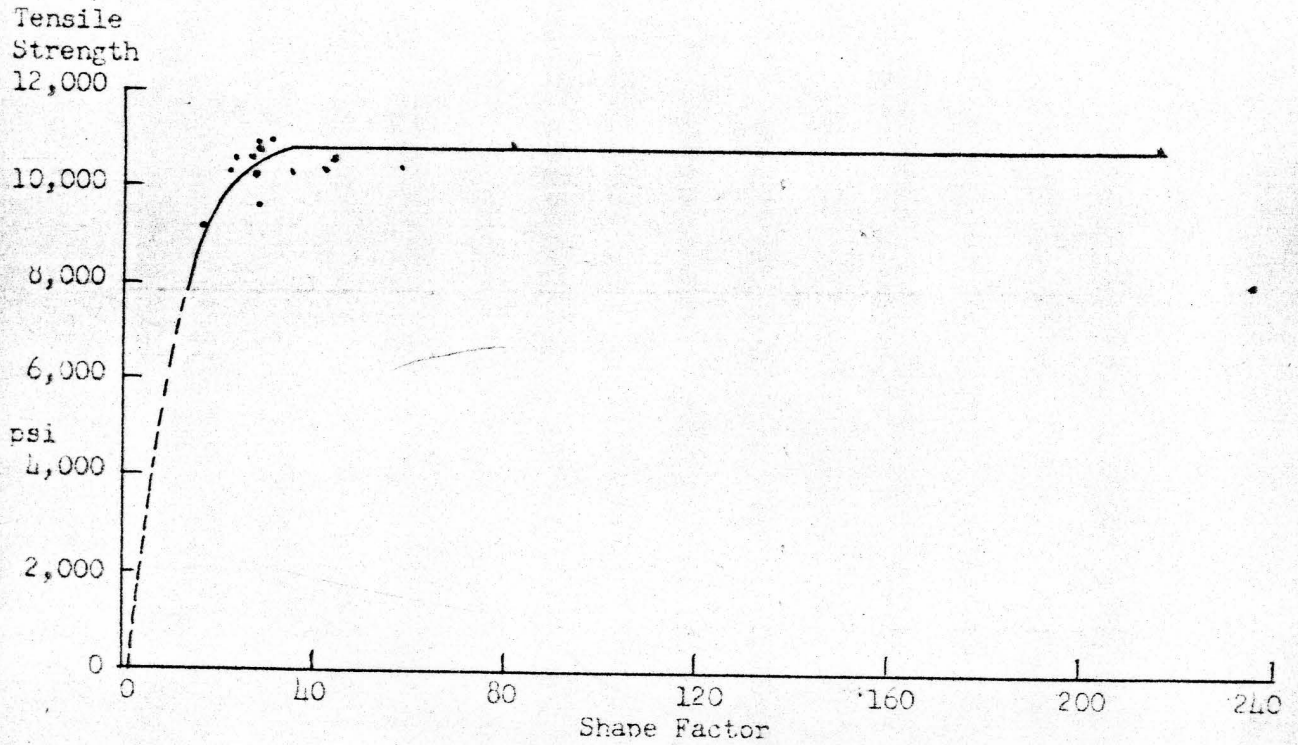$$\text{Shape Factor} = \frac{25}{1.555} = 16.1$$

TABLE 5

HETEROGENEITY AND SHAPE FACTORS

Blends	log H	D.P. at Maximum	Shape Factor
Orig.D.P.420	2.290	500	218.3
Orig.D.P.60	1.333	38	28.5
1*	4.365	120	27.5
2*	4.361	95	22.0
3*	3.912	110	26.1
4	1.555	25	16.1
5	1.739	73	42.0
6	2.263	100	44.2
7	1.810	50	23.6
8	1.646	50	30.4
9	1.703	45	26.4
D.P. of Fractions			
75	1.430	50	35.0
165	1.368	125	91.4
215	2.079	120	57.7
265*	2.728	63	22.9

* Differential distribution curves showed two maxima.
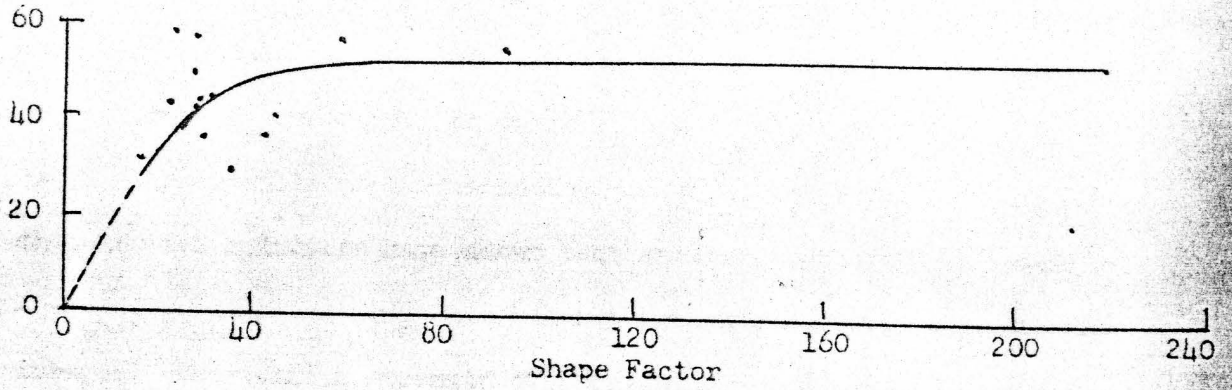
GRAPH 17a

Correlation of Results of Mechanical Tests on Synthetic Blends
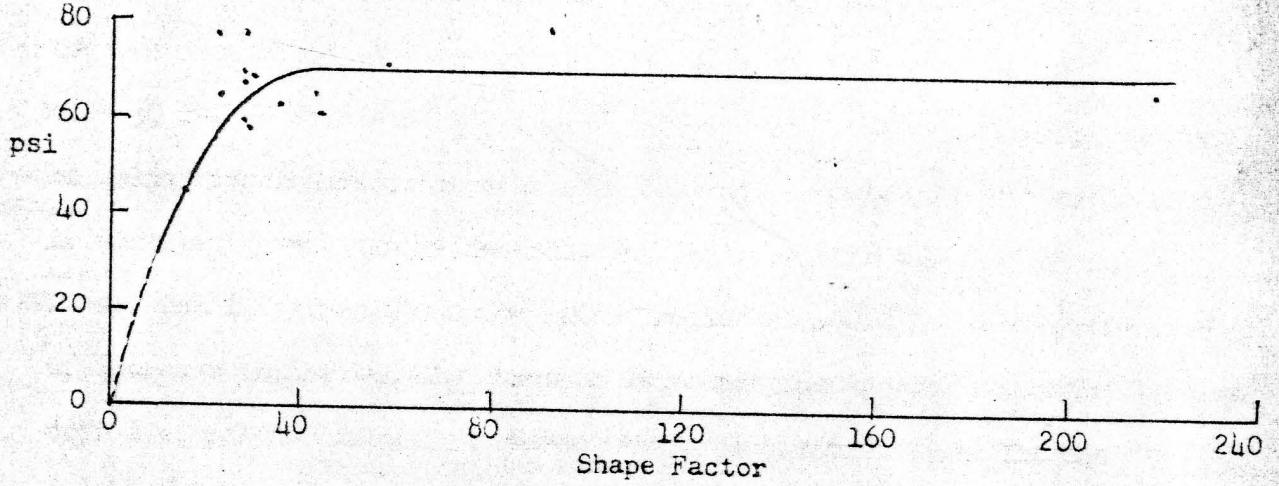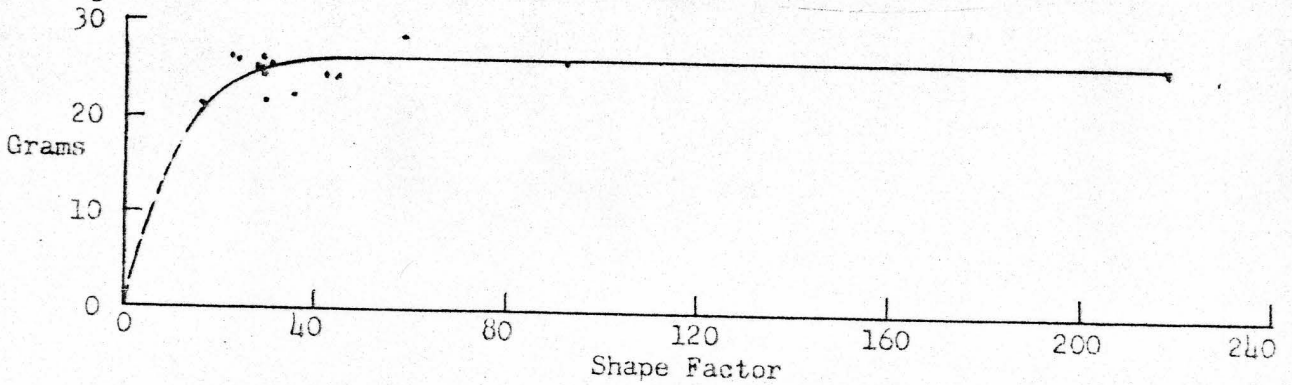with Shape Factor of Distribution Curve

GRAPH 17b

DISCUSSION OF RESULTS

The results of this investigation are discussed under five separate divisions in order to permit an orderliness in presenting the discussion and the conclusions derived therefrom.

1. The results of the mechanical tests on the films deposited from ethyl acetate solutions have shown that any fraction having an average degree of polymerization greater than 50 shows considerable mechanical strength. The tensile strength of a fraction which has an average degree of polymerization of 30 is not zero. This material in the form of films is very brittle, but with careful handling, test samples were prepared and an average tensile strength of 4,500 psi was calculated from the average results of eight samples. According to experimental results and theory, the tensile strength increases very rapidly as the average degree of polymerization is increased. The increase as determined by experiment is more rapid than theory demands, and the change in the rate of increase in the tensile strength occurs in the region of 100. Above 100, the rate of increase in the tensile strength decreases, and above 200 as the average degree of polymerization increases, there is practically no further increase in the tensile strength.

The results obtained for percentages of elongation follow very closely those obtained for the tensile strength. The rate of increase is again rapid up to an average degree of polymerization of 100, and the elongation does not increase appreciably above this value.

The values obtained for the Schopper Folding Endurance test show a wide variation which is apparently inherent in this type of test. It is a well established fact that unmodified cellulose nitrate films are brittle.

Conclusions drawn from Schopper Folding tests alone are subject to considerable doubt as to their accuracy. However, if the results of the Schopper Folding tests are in line with the results of other mechanical strength tests, then a more completely rounded picture is available for theoretical consideration. Therefore, it may be said that in spite of the large variability involved, similar conclusions as stated above for the tensile strength and elongation may be said to hold for the folding endurance tests.

The Mullen Bursting Strength tests show a considerable variation in the films tested from the various fractions. It should be remembered that this test was primarily designed for the testing of paper products, and a modification of this basic tester might prove to be more useful in determining the burst strength of such films as those prepared in this investigation.

It is still possible, however, to state that in view of the experimental results obtained from the burst test, a similar relation exists for this test as for those previously discussed.

The results obtained from the use of the Elmendorf Tearing Strength Tester indicate that this test is not very sensitive to changes in the average degree of polymerization throughout the range of polymerization studied. It is unfortunate that no materials having average degrees of polymerization between 75 and 165, and between 30 and 75, were available for testing. The tests do indicate what is believed to be a significant decrease for the sample which had an average degree of polymerization of 75. Since the value obtained for this test was 22.5 grams, this is an indication that any fraction having an average degree of polymerization between 50 and 75 should exhibit some tear strength. Only in fractions

having an average degree of polymerization below 50 should the tear strength value be close to zero.

From the experimental values obtained, it may be concluded that, as in the other mechanical tests, a certain minimum average degree of polymerization is necessary for a fraction to show any resistance to tearing. This minimum value is just above 30. The resistance to tearing increases rapidly as the average degree of polymerization increases to a value of about 75. Above an average value of 75, the resistance to tear increases more slowly and above 150, no appreciable increase is observed.

2. In the first series of synthetic blends prepared, Blends 1, 2, and 3, it was planned to have the blends skewed toward the low D.P. side in order to get an indication of the harmful effects caused by the presence of a large percentage of low D.P. material. From the plots of the analytical curves obtained by fractionation, Graphs 4, 5, and 6, each of the three blends contained at least 20 percent of material having an average degree of polymerization below 80, and Blend 3 had 37 percent of material having an average of 80 or below. Since all theoretical discussions on the subject of polymolecularity and the effect of low molecular weight material had presented the idea of the presence of this low D.P. material affecting adversely the mechanical properties, it was not expected that the mechanical properties should show almost no differences. For example, the average tensile strengths for the blends were 10,250 psi for Blend 1, 10,350 psi for Blend 2, and 10,900 for Blend 3. Similar results were obtained for each of the other properties tested, and in every case the values approximated those obtained for the fraction having an average D.P. of 215. (Refer to Tables 2 and 3.) It was readily seen from these results that any material having an average degree of

polymerization above 200 was not affected adversely by the presence of as much as 35 percent of material having a D.P. of 60 or below. This conclusion was again contrary to theory.

3. It was not intended that the three blends should contain two maxima in their differential distribution curves. Due to the unavoidable degradation during storage of the fractions, the distributions were such that upon analysis, two maxima were obtained. It had been stated by Douglas and Stoops (2) that if a mixture of fractions of vinyl ester resins was made such that the differential distribution curve should have two maxima, only one maximum was found upon fractionation of the mixture. This statement was made regarding vinyl esters, and no such information concerning cellulose esters has been found. Therefore, it was rather unexpected to obtain such results from the fractionations of these three blends.

Thus, despite the fact that the two-peak distributions were not planned, it is evident from the results of the fractionations that cellulose nitrate blends which have distributions resulting in two maxima in the differential distribution curves, can be fractionated in such a manner as to obtain two maxima in the differential distribution curve. It was necessary to carry out these fractionations in one percent solutions in order to decrease the amount of low D.P. material which might be occluded in the higher D.P. fractions. The refractionation of the first fractions was, however, still necessary in order to eliminate the low D.P. material that was occluded in the fractional precipitation even from the one percent solution.

4. The preparation of the second series of blends which had an average degree of polymerization of 100 was somewhat hindered by the

lack of fractions which had average D.P.'s in the range between 75 and 215. This deficiency could not be rectified since the highest D.P. material available from the low viscosity original blend was 75, and no material in this range was available from the high viscosity original blend in sufficient quantity for use. Since it was believed to be more important to investigate the effect of skewing the differential distribution curve to the right, thus placing the emphasis on the weight percentages of low D.P. material, this deficiency was not of any great consequence.

The results obtained from the mechanical tests of these six blends indicated that the shape of the distribution curve had a marked influence on the properties of these blends. For example, Blend 4 which had the same average degree of polymerization as the other five blends showed distinctly inferior properties in all of the mechanical tests. Furthermore, the distribution curves of Blends 4 and 8 can be superimposed one upon the other above a D.P. of 75. The difference in the mechanical properties were so marked that these differences could only be attributed to the differences in the shapes of the two distribution curves below 75 and the positions of the maxima. The mechanical properties of the other blends showed in some cases considerable variation, but the shapes of the differential distribution curves were so different that no simple correlation of the data was possible. No conclusion could be drawn except the presence of a considerable quantity of very low D.P. material exerted a harmful effect on the mechanical properties of films prepared from these blends.

5. It was realized that no simple relation was available which would permit the data to be correlated with the different shapes of the

differential distribution curves. The problem was to arrive at some method which would permit a simple plot of the data against some function which expressed the shape of the differential distribution curve. Such a function was the so-called "shape factor" which has been previously defined as the quotient of the D.P. of the maximum divided by the common logarithm of the heterogeneity.

By the use of this function as a measure of the shape of the differential distribution curve, it has been possible to prepare plots of the data obtained from the mechanical testing of the films prepared from nine synthetic blends, the two original commercially obtained blends and the four fractions analyzed. From these plots as given in Graphs 17a and 17b, it may be concluded that the value of a mechanical property increases as the shape factor increases up to a value of the "shape factor" of about 30. Above a "shape factor" of 30, very little increase is obtained in the mechanical property under consideration. It should be noted that, in general, a large value of the "shape factor" implies either a sharp maximum, that is a narrow range of heterogeneity in the polymeric material, and/or a high average degree of polymerization.

Each value of the "shape factor" defines a group of distributions, all of which have the same mechanical properties. High maximum D.P. can counterbalance the effect of wide heterogeneity in a curve, and the effect of a low maximum D.P. can be neutralized by the sharpness of the distribution curve, or low heterogeneity of distribution.

CONCLUSIONS

The results of this investigation on the effect of the shape of the differential distribution curve on the mechanical properties of cellulose nitrate films may be summarized in the following manner:

1. The results of mechanical tests on the films obtained from the fractions show that a minimum average degree of polymerization must be present before any mechanical strength is observed. Contrary to theory, this minimum is in the range of 30 for the cellulose nitrate used in this investigation and varies somewhat according to the particular strength property under consideration. The tensile strength and percent elongation increase quite rapidly as the average degree of polymerization is increased up to a certain value, which, contrary to the theoretically proposed value of 250, has been determined as being about 100. Above an average degree of polymerization of 100, these values do not increase markedly.

The Schopper Folding Endurance, Mullen Bursting Strength, and Elmendorf Tearing Strength Testers show similar results to a greater or lesser extent dependent upon the variability involved in the particular test and the overall sensitivity of the testing machine to the range in the polymerization studied.

It should be realized that the conclusions drawn from this work are the results obtained from films deposited from ethyl acetate solutions and should not be applied to films deposited from any and all other solvents and solvent mixtures. Furthermore, it is realized that the fractions used were non-homogeneous, but an improvement in the homogeneity would probably result in the shifting of the region of abrupt change in the mechanical

properties still farther from the theoretical values.

2. A study of the results obtained from the mechanical testing of Blends 1, 2, and 3 indicate that the influence of the presence of as much as 20 percent of material having an average degree of polymerization below 40 is very slight. In fact, according to these experiments, the effect of as much as 35 percent of low D.P. material is negligible provided the average degree of polymerization is maintained above 200. This is again contrary to the statements in the literature (5,8).

3. A second conclusion which can be drawn from Blends 1, 2, and 3, is that blends which contain two maxima in the plots of their differential distribution curves can be successfully analyzed. Such fractionations must be carried out in dilute solution and in even a one percent solution it may be necessary to refractionate the first and possibly the second fractions.

4. A study of the second series of synthetically prepared blends, those six having average degrees of polymerization of 100, has shown conclusively the harmful effects of the presence of a quantity of very low D.P. material on the mechanical properties of films prepared from such blends. The extent of decrease in the strength properties is easily shown by a comparison of Blends 4 and 6 (Graphs 7 and 11) which have distributions very similar above a D.P. of about 75. However, the differences in the distribution curves in the region below 75 are reflected markedly in the mechanical properties. For example, Blend 4 which has a maximum at 25 in the differential distribution curve shows a tensile strength of 9,200 psi. Blend 6, however, shows a maximum at a D.P. of 50, and has a tensile strength of 11,000 psi. The other mechanical properties exhibit similar results.

5. It has been shown that a correlation of the mechanical properties with the shapes of the differential distribution curves of the synthetic blends may be obtained by the use of the "shape factor". The calculation of the shape factor is admitted to be an empirical calculation. However, it permits some measure of the heterogeneity present in the blend sample and allows the correlation of blends not only of the same average degree of polymerization but also of different average degrees of polymerization, including the low viscosity original blend having an average D.P. of 60 and the high viscosity original blend having an average D.P. of 420.

The conclusions derived from this investigation may be applied only to cellulose nitrate having a nitrogen content of 12 percent. A cellulose nitrate having a different nitrogen content from 12 percent may show somewhat different mechanical properties in the same range of average polymerization degree due to the differences in the strength of the secondary valence forces. The change in the mechanical properties may be similar to that found for the solubility of cellulose nitrates of different degrees of substitution (3). Data to prove or disprove the reliability of this statement are not available at this time.

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