THE DEVELOPMENT OF A METHOD
FOR
PRECISION FRACTIONATION OF CELLULOSE ACETATE

by

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STATEMENT OF THE PROBLEM

The purpose of this investigation is to obtain a reproducible procedure for a large scale fractionation of cellulose acetate. The criteria for such a procedure may be briefly stated as:

(1) The volume of solution handled is to be kept to a minimum.

  (a) The original solution should have as high a concentration of cellulose acetate as is possible for clear-cut fractionation.

  (b) The precipitating agent used for fractional precipitation should have as high a precipitation value as is convenient.

(2) The number of operations necessary for producing fractions should be kept to a minimum. That is to say, there should be few, if any, refractionations.

(3) The original cellulose acetate should be separated into ten approximately equal fractions.

(4) The fractionation should be according to degree of polymerization (molecular weight) and not according to degree of substitution (amount of combined acetic acid).

(5) The procedure should be reproducible as to weight of the fractions, and as to the average degree of polymerization of the fractions.

(6) Both the solvent and the precipitating agent should be recoverable.

REVIEW OF THE LITERATURE

The Structure of Cellulose

According to the generally accepted concept, cellulose consists of long chains of B-anhydroglucose units. These units are connected by oxygen bridges from the number one carbon atom of one unit to the number four carbon atom of the next unit. The details of the proof of this structure may be found in most standard works on cellulose (22, 44). The present-day accepted version of the structure of the cellulose molecule is diagramed in figure 1.

Naturally occurring cellulose possesses a degree of crystallinity. Evidence indicates that the cellulose fibers alternate between crystalline regions and amorphous regions. Each chain may pass through several of these regions. The regions of crystallinity are said to measure, on the average, about 600 Å along the fiber axis and about 50 by 60 Å across this direction. The unit crystal is monoclinic. The dimensions and the structure of the unit are shown in figures 2 and 3. Detailed discussion of the cellulose crystal may be found in most standard works on cellulose (1, 22, 44, 36, 53).

Acetylation of Cellulose

Since cellulose is a polyalcohol, it undergoes most of the reactions of alcohols. Thus, it is not surprising to find that cellulose may be esterified.

There are a great many acetylation methods in use today. The

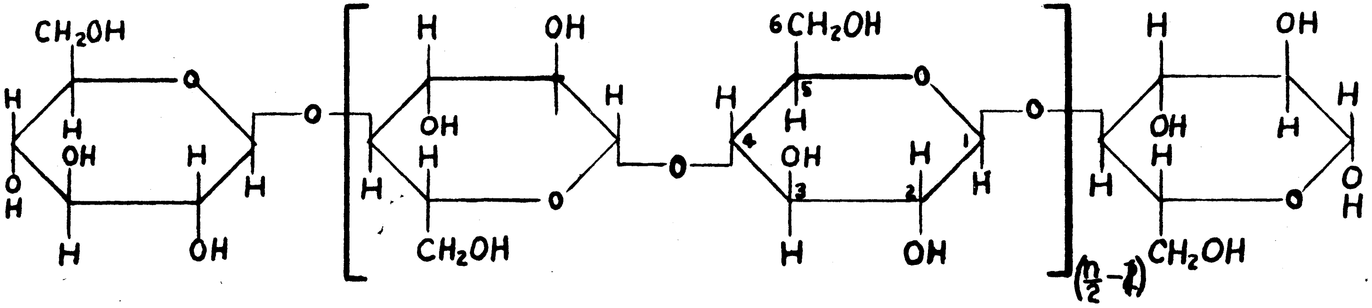

Figure I. Accepted Structure of Cellulose

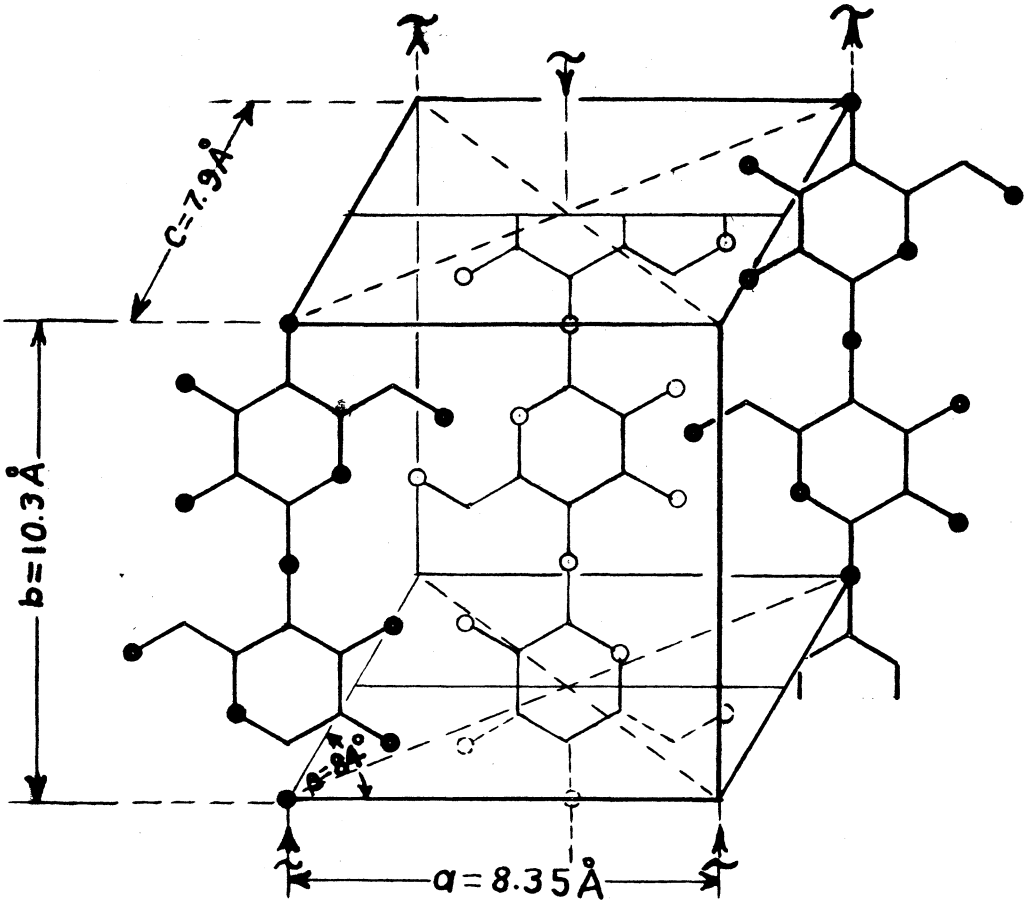

Figure 2. Unit Cell of Native Cellulose (from Ott, High Polymers, Vol. V, Cellulose and Cellulose Derivatives, Interscience Publishers, Inc., New York (1946)

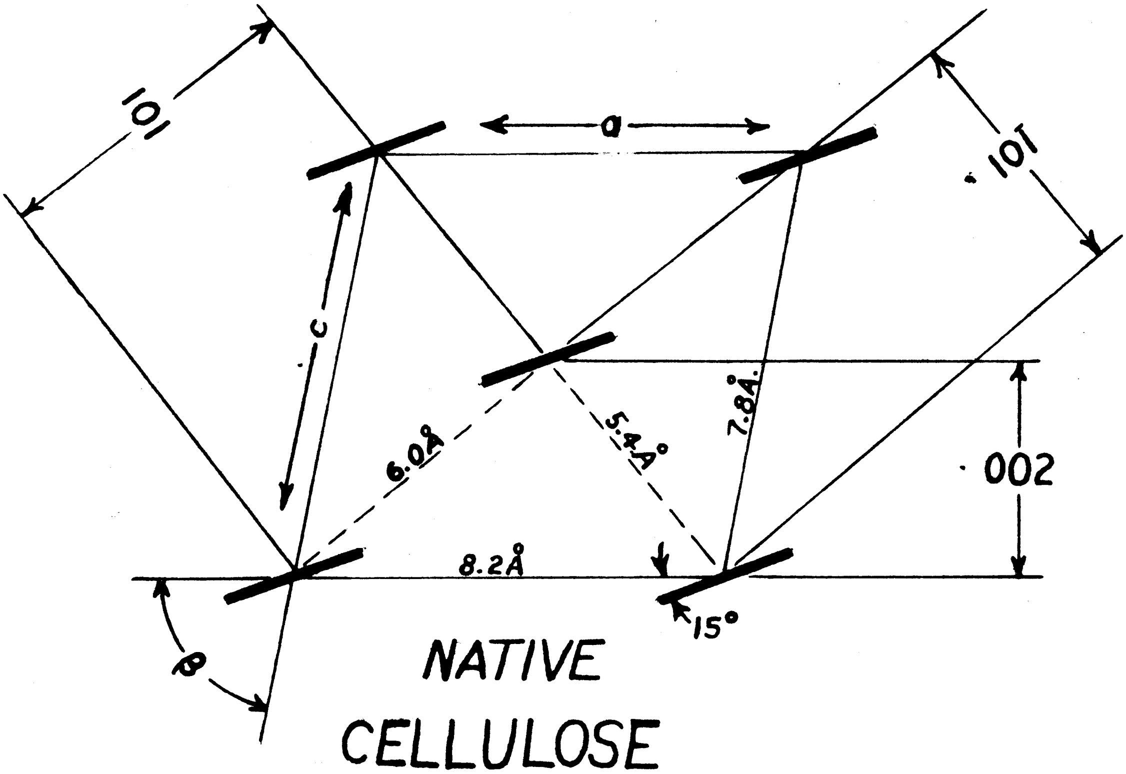

Figure 3. View Down b Axis of Unit Cell of Native Cellulose (from Ott, High Polymers, Vol. V, Cellulose and Cellulose Derivatives, Interscience Publishers, Inc., New York (1946)

following generalized procedure will, however, give an idea as to the process. After suitable drying, 100 parts of cotton linters are pretreated with 700 parts of glacial acetic acid for 4 hours at 38°C. The mixture is then cooled to 21°C and to it is added a solution, previously prepared and cooled to -18°C, of 310 parts of 85% acetic anhydride and 7.2 parts of sulfuric acid. The reaction temperature is kept between 21° and 27°C until the reaction is complete, 7 to 8 hours. It is during this period that the cellulose is acetylated; the product of this reaction is essentially the triacetate, and is generally called primary cellulose acetate. The primary acetate is then hydrolyzed by the addition of 220 parts of 50% acetic acid. The temperature is allowed to rise to 38°C and is held there until the desired degree of hydrolysis is obtained (usually between 50 and 58% combined acetic acid). The product at this point is called secondary cellulose acetate and contains between 2 and 2.5 acetyl groups per glucose residue. The acetate is then precipitated by pouring the solution into a large volume of water. This is followed by stabilizing (removal of excess acid), thorough washing, and finally drying. There are numerous variations in the acetylation procedure, including the use of different catalysts (sulfuric acid), the use of different solvents (acetic acid), and the use of different temperatures. Thorough discussions of this process are given in standard works on cellulose (22, 44).

The Structure of Cellulose Acetate

As was indicated in the preceding section, there are two general classifications of cellulose acetate; namely, primary and secondary cellulose acetate. The primary cellulose acetate, or the triacetate, is soluble in chloroform, but it is not soluble in acetone; in fact, chloroform seems to be the only good solvent for the triacetate. The secondary cellulose acetate is the partially hydrolyzed product of the primary acetate. Secondary acetates, having a combined acetic acid content of between 50 and 58%, are acetone soluble. Below 50% combined acetic acid, the secondary acetate is acetone insoluble.

There have been considerable studies on the effect of partial hydrolysis upon the distribution of the hydroxyl groups in the cellulose chain (8, 9, 17). The latest work is summarized by the investigation of Gardner and Purves (17). In this investigation, it was concluded that in a sample of secondary cellulose acetate averaging 2.44 acyl groups and 0.56 hydroxyl group per monomeric unit, that, on the average, there were 0.196 hydroxyl group on the sixth carbon atom, 0.139 on the second carbon atom, and 0.223 on the third carbon atom of the glucose unit. Furthermore, the investigation indicated there were 0.0074 moles of unsubstituted 2,3 glycol groups per glucose residue. The amount of unsubstituted 2,3 glycol groups per glucose residue, calculated on the basis of random hydrolysis of the second and the third positions was 0.031 moles per glucose residue. It is therefore concluded that deacetylation in either the second or the third position stabilizes the adjacent acyl group.

Fractionation and Distribution Curves

Like all polymers, natural or synthetic, cellulose derivatives exhibit a high degree of heterogeneity with respect to molecular weight, or degree of polymerization. For the most part, the cellulose derivatives are homogeneous with respect to the degree of substitution, or in other words, one molecule has the same per cent composition as another (neglecting the effect of the end groups) (22, 23, 26, 35, 43, 44, 46, 47, 52).

The purpose of fractionation is to obtain an idea of the degree of heterogeneity of the polymer and to study the effects of heterogeneity. In fractionation, one strives to separate the heterogeneous polymer into groups, or fractions, which are homogeneous as to molecular weight. Actually, this is never accomplished, and it has been shown mathematically that with one of the best procedures, fractional precipitation, the best that can be hoped for is fractions no sharper than ±5% variation from the mean by repeated fractionation (44, 49). Actually, no valid claim to such sharp fractionation has ever been made.

After obtaining the fractions by one of the methods described in the next section and determining the average D. P. (degree of polymerization), an "integral distribution curve" may be plotted. This curve is obtained by plotting I_p versus the average degree of polymerization (22, 50, 52). The values of I_p are obtained by the following method: To one-half of the weight percentage of each fraction is added the sum of the weight percentages of each preceding fraction, starting with the fraction of the lowest D. P. The value of I_p so obtained represents the total weight percentage of the entire material with D. P. values between unity and the D. P. considered. This procedure involves the assumption that the chain lengths in any fraction are symmetrically distributed about the average chain length of the fraction, and the curve thus obtained will resemble the curve of a Gompertz, or of a modified Gompertz equation (10, 37).

If this curve is differentiated, either by determining the equation for the curve and mathematically differentiating, or by taking the slope of the curve at various points, and if the slope, at various points, is plotted versus the D. P., a probability curve will be obtained. This curve is known as the "differential distribution curve", and the area under this curve should be 100%. If the area under the curve is not 100%, it may easily be normalized. The curve thus obtained represents the probability (in per cent) of finding a chain of a given length in a sample of the unfractionated polymer. The shape of the curve may be a normal probability curve; it may be skewed to the right, or to the left; it will contain one or more peaks. With respect to the last statement, we do not expect naturally occurring polymers, or even those made synthetically, to have more than one peak unless it is a blend of some sort.

Methods of Fractionation.

There are several methods available for fractionating high polymers. Due to the homogeneity, with respect to D. S. (degree of substitution), of cellulose acetate, all of the methods give fractionation with respect to D. P. The methods of fractionation of high polymeric substances, which have been used with varying degrees of success are: (1) ultrafiltration, (2) diffusion, (3) fractional solution, (4) fractional precipitation, (5) chromatographic adsorption, (6) molecular distillation, and (7) ultracentrifugation.

In fractionation, probably the first method that comes to mind is a process of filtering out the larger particles and allowing the smaller particles to pass through, which is the principle of the ultrafiltration process. Duclaux and Wollman (12) fractionated cellulose nitrate by this process, using filters of varying pore size. This method is, for the most part, unsatisfactory for long chain polymers, since the diameter of the various chain lengths is approximately the same, the greatest variation appearing in the length of the chain. Thus, when a filter is used, the long chains may pass through the pores almost as easily as the short chains, provided they strike the pores endwise. If, however, the chains strike the pores broadside, then the shorter chains, as well as the longer chains, will be retained. Thus, the surprising fact is not that poor fraction was obtained by this method, but rather that fractionation was obtained at all. The explanation evidently lies in the fact that the higher molecular weight molecules do have a larger diameter than the lower molecular weight molecules (2, 3, 20, 21).

The second method that might come to mind is that of diffusion. The rate of diffusion, D, of a particle has been shown by Einstein (13) to be

$$D = \frac{RT}{Nf}$$

where R is the gas constant; T is the absolute temperature; N is Avogadro's number; and f is the frictional force opposing a particle which is moving with a velocity of one centimeter per second. The value of f is obviously some direct function of the size of the particle. Thus, as the molecular weight increases, the rate of diffusion decreases. By carefully placing a layer of solvent over a solution of the polymer, and allowing this to stand for a period of time, one can separate the polymer into two fractions. The upper layer would contain the lower D. P. material, while the lower would contain the higher D. P. material. This method has been attempted by Krüger (29), and by Herzog, Krüger, and Yamaga (24).

The third method that might be considered is fractional solution. This method depends upon the fact that the solubility of long chain molecules in a solvent, in which they are only slightly soluble, is an inverse exponential function of the length of the chain (49,51). That is to say, the longer chains are less soluble than the shorter chains. Thus, by extraction of a polymer with a series of solvents or solvent mixtures, it is possible to obtain a number of fractions of varying average D. P. This type of fractionation has been accomplished by a number of investigators (11, 12, 33, 45, 47, 48).

By far, the easiest and the most widely-used method of fractionation is fractional precipitation. This was probably first applied by Goebel and Stepanow (19), and was first applied to cellulose acetate by Mardles (32). It has since been applied to a number of polymeric materials (23, 35, 42, 46, 52, 54, 59). The theory of fractional precipitation closely parallels that of fractional solution and will be discussed in the next section. The method consists of adding a nonsolvent or precipitating agent to a solution of the polymer until the solution becomes hazy or cloudy. The solution is then allowed to stand for a period of time, or it is centrifuged until there is a layer of undissolved polymer on the bottom of the container. The supernatant liquid is poured off and more nonsolvent is added to the solution. The process is repeated until complete precipitation is obtained. In this method, the highest molecular weight precipitates first, then the next highest, and so forth until the last fraction, which is the lowest molecular weight substance, is precipitated.

The fifth method of fractionation is by chromatographic adsorption. The relation between chain length and adsorption equilibrium results from different heats of adsorption. This effect in the case of displacement equilibrium could lead to either an increase or decrease in amount adsorbed with increase in chain length, as shown by the heats of adsorption. The quantum calculation yields a supplementary member, which is brought about by the increase in phase volume of the free molecules by adsorption of the small molecules. This leads to a preferential adsorption of the long chains (5). Fractionation of cellulose acetate has been carried out by this method by Mark and Saito (34), using a column packed with powdered blood charcoal.

The sixth method of fractionation is by molecular distillation (25). In this process, a vacuum is applied such that the mean free path of the vaporized molecules is longer than the distance from the evaporating surface to the condensing surface. Thus, the shorter chain lengths would come off first, followed by the longer chain lengths. The limitations of this method are that only a small amount may be fractionated at a time and that the temperatures required are so high that the polymer may degrade before it is melted or vaporized. This method has been used mainly to remove the very shortest chains of synthetic polymers.

The seventh, and last, method of fractionation to be considered in this discussion is fractionation by means of the ultracentrifuge.. This method is valuable in determining the distribution curve, but is inadequate for obtaining usuable fractions. The process depends upon the fact that the heavier molecules settle faster than the lighter molecules. This is the only method of simultaneously obtaining not only the average molecular weight, but also the distribution curve of the polymer (6, 30, 33, 57). Kraemer (22, 28) has listed the advantages of the ultracentrifugal method as follows: (1) It has the same thermodynamic foundation as osmotic pressure or vapor pressure methods; (2) it is, accordingly, not influenced by particle shape; (3) in general, it is not affected by solvation; (4) its sensitivity increases with particle size; (5) it may be used with complex solvents, such as cupra ammonium hydroxide, with which osmotic pressure measurements would be very difficult; (6) it avoids difficulties associated with the use of semi-permeable membranes; (7) it permits recognition of the uniformity or non-uniformity of particle size and it can give a quantitative rating of the degree of non-uniformity (30); and (8) for solutes containing relatively small molecular weight contaminants, it is much less adversely affected than osmotic pressure and other methods.

Theory of Fractional Precipitation (44)

As has been stated previously, the theory of fractional precipitation rests on the fact that the solubility of long chain molecules in a solvent in which they are slightly soluble decreases exponentially as the chain length increases. Using the concept that the attraction between chains is proportional to their length, but neglecting the entropy of dilution, Schulz (40, 49, 51) calculated the degree of fractionation for various conditions of fractionation which are in agreement with the more theoretically exact one of Huggins (27) and others (7, 14, 15, 16, 18, 40).

Schulz's explanation may be briefly described by the following discussion. If a solvent is powerful enough to dissolve the smaller chains, the remainder is usually present as a highly swollen mass which shows all the properties of a liquid phase. The process may, therefore, be treated as one of distribution of a solute between two immiscible liquids. By letting E represent the energy difference per molecule of material on passing from the supernatant phase, and a_1 represent the activity of the polymer molecule in the precipitated phase, and a_2 represent the activity of the polymer molecule in the supernatant phase, then equation 1 evolves.

$$\frac{a_2}{a_1} = K' e^{-E/kT}$$

eq. 1

Schulz then assumed that concentrations may be substituted for activities and that the two phases may be considered as two immiscible liquids. If, then, we define E as proportional to the molecular weight, M, and the proportionality constant is a linear function of the per cent precipitant added, P,

$$E = (A + BP)M$$

eq. 2

then equation 1 becomes

$$\frac{c_2}{c_1} = K'' e^{-(A+BP)M/kT}$$

eq. 3

The concentration of the polymer in solution which produces saturation is designated by C_s and the per cent of precipitant by P_s. Schulz made one more assumption and that is that the concentration of the polymer in the precipitated phase, c_1, is constant. This introduces an error which counterbalances the error in the substitution of concentrations for activities. We thus obtain equation 4.

$$C_s = K e^{-(A+BP_s)M/kT}$$

eq. 4

In this equation K, A, and B are constants.

The results of Schulz may be graphically represented by figures 4, 5, and 6. Figure 4 shows that as the chain length of the polymer increases, other conditions being constant, an increasing volume of the supernatant liquid is necessary in order to dissolve the polymer.

Figure 5 shows that for a given ratio of volumes, an increase in

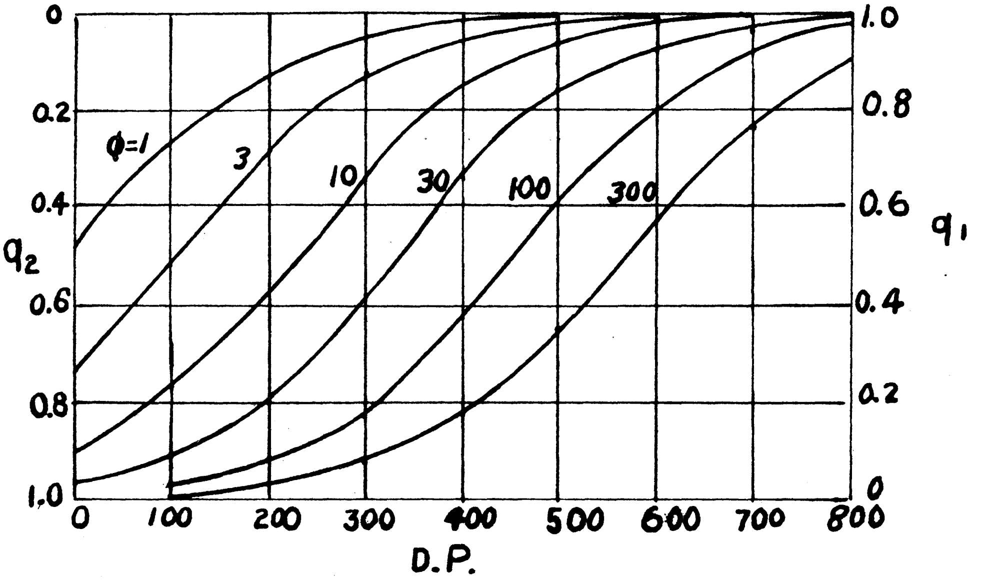

Figure 4. Dependence of Distribution of Polymer Fractions between Two Phases, as a Function of the Volumes of the Phases.

Energy difference per monomer unit (E_o) between phases assumed to be 6 cal.

Temperature = 300°K

q_1 = Grams of material of a given D. P. in phase 1 (precipitate phase).

q_2 = Grams of material of a given D. P. in phase 2 (supernatant phase).

$\phi = \frac{V_2}{V_1}$ = Ratio of volumes of phases 2 and 1.

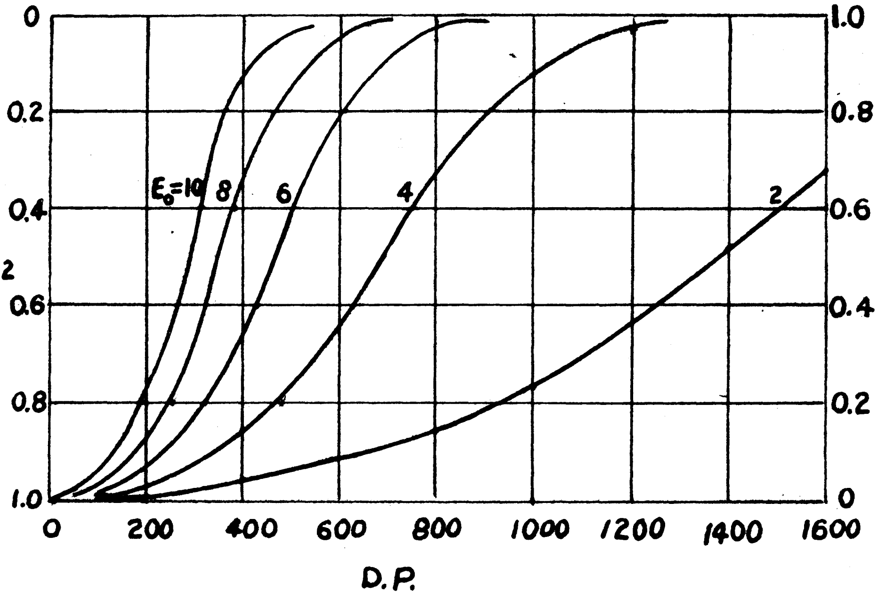

Figure 5. Dependence of Distribution of Polymer Fractions between Two Phases, as a Function of the Energy Difference between the Phases.

Ratio of volumes of phases = 100

Temperature = 300°K

q_1 = Grams of material of a given D. P. in phase 1 (precipitate phase)

q_2 = Grams of materila of a given D. P. in phase 2 (supernatant phase)

E_0 = Energy difference per monomer unit between phases.

precipitant (an increase in E_0) tends to throw the polymer into the precipitate phase. Thus, the ratio of volumes and the amount of diluent may be varied independently to obtain the desired proportion of polymer of a given D. P. in solution. It is necessary to compare the separation curves for different combinations of E_0 and ϕ (ratio of volume of supernatant phase to the volume of precipitated phase) so chosen that material of a given D. P. has a constant separation ratio.

In figure 6, conditions have been chosen so that half of the polymer of D. P. = 600 is in each phase. Thus, it is seen that the greater the volume ratio and the greater the concentration of precipitant, the sharper will be the fractionation.

In practical terms, Schulz's work concludes that the sharpest fractionations are obtained by (1) the most dilute solution, (2) the greatest amount of diluent or precipitant, and (3) the smallest increments of precipitate. Further conclusions may be drawn from Schulz's work. First, the shape of the distribution curve can be determined with about as much accuracy after refractionating the fractions once as is possible after many more refractionations. Second, the ease of obtaining fractions of the same percentage uniformity is the same for large polymers as for small. Third, there is little hope of securing fractions sharper than ±5% variation from the mean by repeated refractionation.

Morey and Tamblyn (39, 40) discuss cases of reverse order precipitation in which the lower molecular weights precipitate before the higher molecular weights. They present evidence for the occurrence

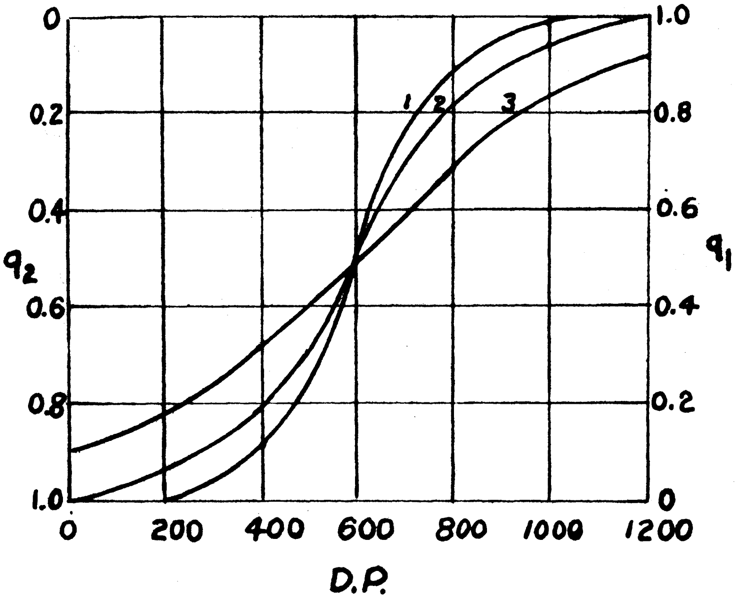

Figure 6. Dependence of Distribution of Polymer Fractions on Phase Volumes and on Energy Differences when One-Half of Material of D. P. 600 is in each Phase.

Curve 1: ϕ = 1000; E_0 = 6.9 cal.

Curve 2; ϕ = 100; E_0 = 4.6 cal.

Curve 3: ϕ = 10; E_0 = 2.3 cal.

q_1 = Grams of material of a given D. P. in phase 1.

q_2 = Grams of material of a given D. P. in phase 2.

$\phi = \frac{V_2}{V_1}$ = Ratio of volumes of phases 2 and 1.

E_0 = Energy difference per monomer unit between phases.

of this phenomenon and a thermodynamic approach to the subject. It is pointed out that this phenomenon is independent of the temperature, but dependent on the concentration of solution and the choice of solvent and precipitant. Their theory does not adequately explain the effect of variations in concentration.

Methods of Determining the Degree of Polymerization

There are many ways of determining molecular weights; some of these are applicable only to low molecular weight substances, others are applicable only to high molecular weight substances, and some may be used, within limits, both for high polymers and for ordinary organic substances. Some of the methods may be listed as: (1) Victor-Meyer, (2) boiling point elevation, (3) freezing point depression, (4) osmotic pressure, (5) end group determinations, (6) viscosity, and (7) ultra-centrifugation.

The Victor-Meyer method depends upon the vaporization of the substance, and upon the condition that the vapors will obey the perfect gas laws. It is immediately apparent that it would be absurd to attempt to apply this method to high polymers as many decompose before reaching the melting point.

The boiling point is as absurd as the Victor-Meyer, but the reason is not quite as apparent. In order to obtain a boiling point elevation of $0.01^{\circ}C$ from a solution of cellulose acetate, whose D. P. is 200 and whose D. S. is 2.0, the solution must have a concentration of 260 grams of cellulose acetate for each kilogram of acetone (assuming solution laws hold). This concentration is unreasonable and furthermore, the classical laws of solutions would not be valid for a solution of such high concentration.

That which has been said for the boiling point method applies, in principle, to the freezing point method.

The osmotic pressure method has been applied with reasonable degree of success. This method depends upon the validity of the classical equation:

$$PV = \frac{g}{M} RT$$

It is readily apparent that this method will give a number average molecular weight. A good review of this subject has been written by Spurlin (44).

In the cellulose molecule, there is one reducing end group (the hemiacetal group). Thus, by applying suitable reactions, such as the copper number determination, it is possible to determine how many end groups are present in a given solution. The number of end groups is obviously the same as the number of molecules, and thus, a number average molecular weight is obtained.

The viscosity method originally developed by Staudinger (22, 44, 51, 55, 56, 58) stated that at low concentrations of solutions of polymeric substances, whose molecules had the configuration of a rod, the degree of polymerization was proportional to the specific viscosity. The viscosity method presents the most rapid method of determining molecular weights, is probably the most widely used, and leads to approximately a weight average molecular weight. The method has no firm theoretical background, but by comparison with results from the ultracentrifuge on dilute solutions, the relation developed by Staudinger seems to hold with a considerable degree of accuracy (28). The original equation has been modified by many investigators (2, 3, 4, 20, 22, 28, 31, 38, 44) in the field. This will be more fully discussed in the next section.

The ultracentrifuge method was discussed in the section on fractionation. This method is by far the most accurate method. The main difficulty with this method is the cost and the bulk of the equipment. It gives a weight average molecular weight.

Viscosity and Molecular Weight Relations

Staudinger (22, 44, 52, 55, 56, 58) has developed the following equation for the relationship between the viscosity of long chain polymers and their average molecular weight.

$$\frac{\eta_{sp}}{c} = K_m M$$

eq. 1

In this equation, η_{sp} is the specific viscosity (the viscosity increase over the viscosity of the solvent); c is the concentration expressed in grams per liter of solution; M is the molecular weight; and K_m is the associated constant. Of course, this equation may be expressed in terms of the degree of polymerization, P, thus:

$$\frac{\eta_{sp}}{c} = K_p P$$

eq. 2

To establish the constant, it is necessary to determine the molecular weight of a substance by some method such as the ultracentrifuge and substituting back in the equation and solving for the constant. This relation seems to hold for long chain polymers as confirmed by the ultracentrifuge (22).

Kreamer (28) modified the method by stating that a more exact relation may be obtained by substituting intrinsic viscosity $[\eta]$ for specific viscosity over concentration, η_{sp}/c . The intrinsic viscosity is defined by the equation

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

eq. 3

This leads to equation 4

$$[\eta] = K_p P$$

eq. 4

It has been found, however, though not stated, that for solutions as dilute as 1 gram/liter, equation 2 is sufficiently accurate, especially in the low molecular weight ranges (3).

It has been indicated by several investigators that a more general equation is required due to the curling or kinking of the longer chains (2, 3, 4, 20, 38).

Bartovics and Mark (4) indicated that a more general equation such as equation 5 was applicable.

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

eq. 5

In this equation, a is a constant.

The discussion by Huggins (44) proposes some theoretical background for the viscosity-molecular weight relationship. He has shown that the Staudinger relationship holds when the kinking of the molecule is perfectly random. From this discussion, two other relationships are evolved:

$$[\eta] = K_0 + K_1 M^{\nu}$$

eq. 6

$$\frac{\eta_{sp}}{c} = K_m M + k K_m M^2 c + \text{further terms}$$

eq. 7

Of these two equations, equation 6 should hold for the infinitely dilute solutions, and equation 7 should hold for the solutions which have a finite but not a too high concentration (c ≦ 5 grams/liter).

In the discussion by Badgley and Mark (3), they give the following relationship:

$$[\eta] = KM^a - K'M^{2a}$$

eq. 8

and give the constants as $a = 1$, $K = 2.09 \times 10^{-5}$, and $K' = 3.15 \times 10^{-11}$ for cellulose acetate. They, however, recommend that the investigator develop his own constants for the material with which he is working.

EXPERIMENTAL

Chemicals Used

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

The cellulose acetate was 140 second, PH-1, lot #3681 from Hercules Powder Company, Parlin, New Jersey. It analyzed 52.8% combined acetic acid and had an average degree of polymerization of 178.

The n-heptane was pure grade, 99 mole per cent minimum, from Phillips Petroleum Company, Bartlesville, Oklahoma.

The methyl cellosolve (ethylene glycol monomethyl ether) was obtained from Carbide and Carbon Chemicals Corporation, South Charleston, West Virginia. This reagent was dried over calcium oxide and twice distilled through a fractionating column. The boiling point was 122°C at 720 mm.

Introduction

Work by various investigators indicated that the proper procedure for fractionation was to add a nonsolvent to a solution of a polymer until the first haziness or cloudiness appeared. Preliminary experimental work showed that this haziness was not a good indication of the true end point, since, depending upon the solution used, the addition of a nonsolvent, until this end point was reached, either gave no precipitate, or if it gave a precipitate, the weight of the precipitate was not reproducible. It therefore seemed advantageous to devise a method by which it would be possible to determine when enough nonsolvent had been added to produce a predetermined weight of fraction.

Experiments with Nephelometry

It seemed reasonable that the degree of turbidity would be a function of the amount of suspended, but not dissolved, particles. Therefore, if nonsolvent were added to a solution of acetate and the degree of turbidity were measured with a nephelometer, it would seem that there should be some correlation between the readings of the nephelometer and the weight of precipitate which would be obtained on long standing. A Klett-Summerson Photoelectric Colorimeter was chosen to investigate this.

The first experiment using nephelometry to measure the end point was made on a 4% solution of cellulose acetate, using as a solvent 80% acetone and 20% ethyl alcohol (95%). Ten samples of 150 ml each were taken from the solution and to each was added varying amounts of n-heptane. The turbidity was measured one minute after the addition of the heptane, and again at 30 minutes after the addition of the heptane. In each case, the heptane was added in a fine stream from a burette and the solution was agitated during the addition, and for 30 seconds thereafter. No correlation was found between the amount of heptane added and the turbidity, nor was there any correlation between the amount of precipitate obtained and turbidity.

The second experiment was made on a solution of 4% cellulose acetate in acetone. Again, the solution was divided into 10 parts of 150 ml each. Heptane was added in the manner described before. This time, there was some apparent relation between turbidity and volume of heptane added, and also between turbidity and weight of fraction obtained, as shown by Table 1.

TABLE 1

Relation between Volume of N-Heptane Added to 150 ml of 4% Cellulose Acetate Solution and Turbidity and Per cent Fraction Obtained

Vol. n-heptane (ml)	16.0	17.0	18.0	19.0	20.0	21.0	22.0	23.0
Turbidity	325	343	350	382	382	412	434	425
Per cent fraction	0.0	51.4	51.4	53.0	53.0	55.0	58.0	59.0

From Table 1, it is clear that this choice of solvent and precipitant was poor since a difference of one milliter in volume of precipitant made the difference between no fraction, and a fraction containing approximately 51% of the total cellulose acetate.

Other experiments were run in the hope that a more satisfactory correlation could be found between turbidity and weight of fraction. The results of these experiments varied from those of the first experiment to those of the second experiment.

The final experiment in nephelometry confirmed the opinion that there was no accurate correlation between turbidity and weight of fraction obtained. A 4% solution of cellulose acetate was made, using a solvent of 90% acetone and 10% methyl alcohol. N-heptane was added from a burette to ten samples of 200 ml each. The samples were agitated during the addition and for 30 seconds thereafter. The turbidity was measured one minute after the addition of the heptane, and at intervals thereafter up to 7 hours. The solutions were then placed in a 15°C constant temperature box for 24 hours. After 24 hours, the supernatant liquid was poured off; the precipitate was dissolved in acetone, reprecipitated in distilled water, dried, and weighed. The results are tabulated in Table 2.

It may be seen from these results that there was an initial increase in turbidity of each sample followed by a slow decrease in turbidity with time. In general, the greater the amount of precipitating agent, the more turbid was the solution. However, it becomes immediately apparent that it is not possible to use this method as a means of determining the amount of precipitate that will be obtained. The results of this experiment indicate that there is a closer relation between the amount heptane added and the weight of fraction obtained.

Experiments with Dielectric Constant

It was thought that there might exist a relation between the dielectric constant and the amount of precipitate obtained by adding a nonsolvent to a solution of cellulose acetate. An apparatus was available which could give a measure of this property, but the results obtained from experiments with this equipment were erratic and inconsistent. This may have been due to lack of accuracy in the equipment, but the method did not promise a satisfactory correlation, and further work was dropped.

Experiments with Acetone - Water - N-Heptane - Cellulose Acetate System

From the results obtained with turbidity and with dielectric constant

TABLE 2

Correlation between Volume of N-Heptane, Turbidity, Time, and Weight of Fraction obtained on 24 Hours Standing at 15°C.

Vol C_7H_{16} (ml)	Relative Turbidity at Time (hours) Indicated											Weight Fract. (gms)
	0.0	0.5	1.0	1.5	2.0	2.5	3.0	4.0	5.0	6.0	7.0	
18.0	44.0	103	102	104	104	104	103	101	102	102	-	0.00
19.0	44.5	174	163	-	156	-	157	146	144	140	143	0.52
20.0	43.5	187	175	170	165	160	156	151	145	145	-	1.26
20.5	44.3	230	195	-	178	-	166	158	157	151	152	1.30
21.0	42.5	218	200	189	182	178	172	166	162	158	-	1.37
21.5	44.2	270	229	-	197	-	183	172	167	164	165	1.37
22.0	45.3	243	214	199	192	185	179	171	168	164	-	1.42
22.5	44.9	293	242	-	200	-	192	184	176	170	170	1.46
23.0	45.0	256	224	205	198	190	183	175	171	168	-	1.48
25.0	45.2	308	263	-	206	-	204	198	185	181	176	1.86

measurements, it was concluded that the best correlation that could be found for the weight of precipitate was that between the volume of heptane added and the weight of fraction obtained. It was noticed that there was some discrepancy in this relationship and that possibly this could be due to varying amounts of water absorbed by the acetone. Rather than trying to obtain absolutely dry acetone, it seemed better to purposely add water to the acetone so that small variations in the water content of the acetone would be far overshadowed by the water added. Also, this addition of water would tend to decrease the amount of extra water absorbed by the acetone.

The phase diagram for acetone, water, and n-heptane was determined. From this diagram, it was seen that 5% water by volume, or that 5% water by weight, could be used in the solvent and that enough heptane could then be added to bring down the fractions without having the supernatant liquid separate into two layers.

Using a solvent of 95% by volume acetone and 5% by volume water, a solution was prepared that contained 4% cellulose acetate. To five samples of 200 ml each, varying amounts of heptane were added in order to determine the point where 10% of the cellulose acetate would precipitate. The result of this experiment was that 25.6 ml of heptane precipitated 6.8% of the cellulose acetate, while 26.0 ml of heptane precipitated 14.9% of the material. Thus, only 0.4 ml difference of heptane gave 8.1% difference in the per cent of the fraction. It was obvious that the precipitating power of the heptane was too great, and that some modification would have to be made.

Experiments with Various Solvent-Nonsolvent Systems

In order to obtain a curve of lower slope than that found with heptane as a precipitating agent, various solvent and nonsolvent systems were tried. The results are tabulated in Table 3. A sample of 200 ml of 4% cellulose acetate was used in each case, and the precipitating agent was added until the first sign of cloudiness appeared.

Location of the Precipitation Point of the Various Fractions

When the results with various solvent-nonsolvent systems were considered, it seemed that the best system was the one which used a solvent of 95% by volume acetone and 5% by volume water, and which used 75% by volume n-heptane and 25% by volume acetone.

The next step in the procedure was to use the above-mentioned system and determine the amount of precipitant required to bring down the first 10% fraction, then the next 10% fraction, and so forth until all, or nearly all, the cellulose acetate had been precipitated. In order to accomplish this, a 4% solution of cellulose acetate was prepared, using this solvent. The solution was thoroughly agitated and allowed to stand for 24 hours at 25°C to insure complete solution. The solution was then divided into five parts of 160 grams each. Varying amounts of precipitant were added to the flasks, and the flasks were then placed in a 15°C constant temperature box. After 24 hours, the solutions were decanted; the fractions were dissolved in acetone, reprecipitated in a large volume of distilled water, dried at 105°C, and weighed to the

TABLE 3

Results from Experiments with Various Solvents and Various Precipitants

Solvent	Precipitant	Results
90% acetone 10% water	water	flocculant precipitate unable to decant or filter
90% acetone 10% water	50% water 50% acetone	226 ml gave no precipitate
40% ethyl alcohol 60% acetone	ethyl alcohol	115 ml gave 4.17 grams of precipitate
70% ethyl acetate 30% ethyl alcohol	- - -	incomplete solution
acetone	ethylene glycol	190 ml gave 3.23 grams of precipitate
acetone	n-butyl alcohol	140 ml gave 1.92 grams of precipitate 22 ml gave flocculant precipitate
acetone	isobutyl alcohol	soft and flocculant precipitate
acetone	ethylene chloride	115 ml gave no precipitate
acetone	ethyl acetate	gave no precipitate
95% (vol.) acetone 5% (vol.) water	n-heptane	slope = 20.3 %/ml
95% (vol.) acetone 5% (vol.) water	90% (vol.) n-heptane 10% (vol.) acetone	slope = 6.5 %/ml

TABLE 3 - Continued

Solvent	Precipitant	Results
95% (vol.) acetone 5% (vol.) water	85% (vol.) n-heptane 15% (vol.) acetone	slope = 5.8 %/ml
95% (vol.) acetone 5% (vol.) water	75% (vol.) n-heptane 25% (vol.) acetone	slope = 4.1 %/ml

nearest milligram. The per cent fraction obtained was plotted against the volume of precipitant required, and by interpolation, the volume of precipitant required for a 10% fraction was determined.

In determining the precipitation point for the succeeding fractions, a similar procedure was followed. To five flasks containing 160 grams of solution was added the required amount of precipitant to bring down the preceding fractions one at a time. These fractions were treated the same as the first fraction and were used as confirmation of the previous calculations. Then, in order to determine the precipitation point of the fraction in question, varying amounts of the precipitant were added to the supernatant liquid from the previous fractions (at 25°C). The solutions were again placed in the 15°C box for 24 hours, decanted, and the precipitate treated as before.

After precipitating 90% of the total cellulose acetate by this method, the procedure was transferred to the basis of 800 grams of solution. The tenth fraction was obtained by adding 200 ml of pure heptane and the eleventh fraction was obtained by distilling off the solvent under vacuum, and over a water bath.

The fractions obtained from two samples of 800 grams of solution were collected and analyzed for per cent combined acetic acid and for average degree of polymerization.

The procedure followed in the determination of combined acetic acid was the one described by Murray, Staud, and Gray (41). Twenty milliters of acetone was pipetted into a 300 ml wide-mouth Erlenmeyer flask, and

0.5 grams of cellulose acetate (weighed to the nearest tenth milligram) was added. The flasks were loosely stoppered, and placed in a 50°C constant temperature box for one hour, with occasional shaking. At the end of this period, 20 ml of standardized 0.5 N NaOH was added, and the flasks were again loosely stoppered and placed in the 50°C box for one hour. The sides of the flasks were then washed down with distilled water and the solution was back titrated with standardized 0.5 N HCl, using phenolphthalein as an indicator. The per cent combined acetic acid was calculated on the basis of the amount of NaOH required to hydrolyze the cellulose acetate, and the results are tabulated in Table 4.

The degree of polymerization of the samples was determined by the viscosity method of Staudinger, as described by Sookne, Rutherford, Mark and Harris (52). The constant K_p used was 9.8×10^{-4} at 25.0°C for cellulose acetate in methyl cellosolve. In this procedure, 0.05 gram of sample was weighed to the nearest tenth milligram, placed in a 25 x 200 mm test tube, and 50 ml of methyl cellosolve was pipetted into each. The solutions were shaken and allowed to stand for 24 hours to insure complete solution. The viscosity determinations were made with Oswald viscosimeters at 25.0°C ± 0.05°C.

The results of this fractionation are tabulated in Table 4, and may be summarized as follows.

1. The precipitation points had been located with a reasonable degree of accuracy.

2. The amount of combined acetic acid increased slightly from the

TABLE 4

Results of the First Fractionation Procedure

Fract #	Volume Pptant. (ml)	Avg. % Fract.	% Comb. CH_3COOH	Avg. D. P.
1	161.0	9.98	51.1	218
2	13.0	10.26	51.2	231
3	10.6	10.07	51.8	212
4	10.4	9.85	51.6	---
5	12.1	10.46	52.6	---
6	14.5	10.13	52.3	---
7	18.9	9.67	52.9	---
8	26.9	9.68	53.8	---
9	66.5	9.75	54.0	---
10	200.0 (n-heptane)	7.10	54.9	---
11	evap.	1.57	---	---
Original Cellulose acetate -			53.2	177
Original Cell. Ac. Reprecipitated - - - - - - - - - - - - - - - - -			52.8	

first fraction to the last. This, however, may be explained on the basis that there is an extra esterifiable alcohol group on each chain, and that as the degree of polymerization decreases, the effect of an acetyl group in this position increases, thus giving rise to an increase in the per cent combined acetic acid. Furthermore, the original cellulose acetate gave a higher acetate content than was found for it, if it were dissolved in acetone and reprecipitated in water. This reprecipitation process evidently washed out acetate salts which were held to the cellulose acetate. It was found by Sookne and co-workers (52) that the lower D. P. material does have a higher concentration of ash and a higher per cent of combined acetic acid.

3. There is an inversion in the molecular weights. That is to say, the first fraction has a lower D. P. than the second fraction, but the third has a lower D. P. than the second. It was thought that this may be accounted for by reverse order precipitation, by the occlusion of lower D. P. material, or by a high ash content. It was noticed that the original solution made for fractionation had undissolved material in it.

Verification of Inversion in Degree of Polymerization of First Fraction

In an effort to correct the inversion of the first fraction which might have been due to high ash content, it was thought that it might be desirable to include a purification step. The step decided upon was the bringing down of an initial fraction which would contain only 1% of the total original cellulose acetate. It was thought that this would be superior to filtration as the gel would have a better chance of trapping colloidal particles than would a filtering medium. Furthermore, the gel would be able to adsorb dissolved ionic impurities. The rest of the fractions were obtained by the same manner as described before.

The results from four different sets of fractionations, and ten determinations of D. P., are shown in Table 5. It is readily apparent that these results agree with the previous results, and that there is an inversion in the first fraction. This could mean only that the difficulty lay not in the technique of fractionation nor in the technique of determining the degrees of polymerization, but rather in some fundamental property of the system on which the work was carried out.

It was then decided that a closer study of the system was in order. The first fraction containing about 1% of the total was obtained as before. The next fraction was designed to contain 37% of the total cellulose acetate and thus contain all of the very high D. P. material. The remaining fractions were taken to contain about 10% each of the total cellulose acetate. Two simultaneous fractionations were carried out following this scheme. In this case, there were no inversions. The 37% fraction had a D. P. of 232, the next 218, and the rest had decreasing D. P. 's in order.

Upon refractionation of the 37% fraction, subfractions were obtained having average D. P.'s ranging from 279 to 137. In order to obtain sharper fractionation, it was decided that 37% was too large a fraction to accept. Thus, a change in procedure was indicated.

TABLE 5

Verification of Inversion in D. P.'s

Fract. #	% Fract.	Avg. D.P.	No of D. P. Determ.
1	0.91	---	---
2	9.99	222	12
3	9.50	230	11
4	10.40	226	7
5	10.28	222	9
6	10.21	194	10
7	10.37	182	8
8	10.72	169	5
9	9.73	143	4
10	10.08	102	4
11	5.78	45	4
12	2.02	33	4

Determination of a Precise Method of Fractionation

Results from preceding experiments indicated that a precise method of fractionation could be obtained, but the method would have to include either resorting to a lower concentration of solution, or a refractionation of one or more fractions. The easiest procedure seemed to lie in perfecting some method of refractionation of a first large fraction without resorting to drying and redissolving this fraction. Previous work indicated that the precision of the fractionation procedure was great, with respect to obtaining reproducible weights of fractions. If then, a fraction containing say, 40% of the total weight could be obtained with precision, then it could be assumed that under identical conditions, the same weight of fraction would be obtained every time. Then, without drying and weighing the fraction, enough solvent could be added to the swollen precipitate to make up a solution of any desired concentration, followed by precise fractionation of this solution. All of the following fractionations were based on this premise.

Since the procedure of fractionation had to be changed, it was deemed that this would be a good place to change from preparing the solvent and the nonsolvent on a volume basis to preparing them on a weight basis. This change was thought advisable due to the wide variations in room temperature. This change, of course, necessitated the relocation of the purification fraction, and the 40% fraction. This was considered to be a small sacrifice, when it was realized that all other fractions would have to be relocated in any event.

The new solvent chosen was 95% by weight acetone and 5% by weight water. The new precipitant chosen was 75% by weight n-heptane and 25% by weight acetone. The solution was prepared as before, by adding to the solvent, with continuous agitation, enough cellulose acetate to make a 4% solution. The solution was then allowed to stand for 24 hours to insure complete solution. The purification fraction and the 40% fraction were located by the same method used before.

After the location of these fractions, two 800 gram solutions of cellulose acetate were prepared. The purification fraction was removed, and then the 40% fraction was obtained. The supernatant liquid from this fraction was stoppered and placed in the 25°C constant temperature box. Assuming that a 40% fraction was obtained, enough solvent was added to the precipitated gel to make a 2% solution of cellulose acetate. It was deemed that greater precision would be found if a constant weight of solution were prepared from this fraction, than if the weight of solvent were calculated on the basis of the weight of the swollen gel. The resultant mixture of solvent and gel were agitated and brought to a temperature of 25°C. The solutions were allowed to stand until one hour had elapsed from the time of decanting. It was later shown that this was insufficient time to obtain complete solution of the swollen cellulose acetate. Varying amounts of precipitant were added to this solution and fractions were obtained by placing the solutions in the 15°C box. The solutions were decanted and the supernatant liquid was combined with the supernatant liquid from the 40% fraction. The combined solutions were brought to 25°C, precipitant was added, and a fraction was obtained by placing the solutions in the 15°C box. By the continuation of this procedure, the remaining fractions were obtained. The last two fractions, however, were obtained by the addition of n-heptane and by the distillation of the solvent (under vacuum and over a water bath) respectively. From the curve obtained by plotting the accumulative per cent of fraction versus the volume of precipitant added, it was possible to determine, with a fair degree of accuracy, the location of the various fractions.

Succeeding experiments showed that any attempt to bring down less than a 20% fraction in the refractionation procedure resulted in a gel which was too soft to decant. Preliminary determinations of D. P. indicated that there were no inversions in this procedure, and that the first fraction had a D. P. higher than any previously obtained by ordinary fractionation procedures.

Procedure Followed for Precise Fractionation of Cellulose Acetate

By combining the information obtained from the preceding experiments, the following procedure was developed, and followed in the remaining fractionations.

First Day. Solutions of cellulose acetate were prepared as follows:

Solvent:	95% acetone	729.6 grams
	5% water	38.4 grams
		768.0 grams
Solute:	cellulose acetate	32.0 grams
Solution:		800.0 grams

The solution was prepared by mixing the acetone and the water in a 2 liter Erlenmeyer flask, then slowly pouring in a steady stream of cellulose acetate while whirling the flask. The solution was allowed to stand overnight at 25°C with occasional shaking.

The precipitating agent was prepared as follows:

75% n-heptane	300 grams
25% acetone	100 grams
total	400 grams

This was sufficient precipitant for the fractionation of one 800 gram solution of cellulose acetate.

Second Day. After the cellulose acetate solution had been allowed to stand overnight, enough precipitant was added to bring down an approximately 1% fraction. This fraction was known as the purifying fraction and was designated as fraction 1-a. The solution was agitated during the addition of the precipitant and then placed in the 25°C constant temperature box. After standing in the 25°C box for one hour, the flask was then transferred to the 15°C constant temperature box, and tilted so as to collect the precipitate on one side.

Third Day. After the solution had been in the 15°C box for 22 hours, the supernatant liquid was carefully poured off, stoppered, and placed in the 50°C constant temperature box until the solution temperature had reached 25°C, at which time it was placed in the 25°C box. When one hour had elapsed from the time of decanting, enough precipitating agent was added, with agitation, to bring down 40% of the total cellulose acetate, and the solution was again placed in the 25°C box for one hour. This was followed by a 22-hour period in the 15°C box as before.

In the meantime, the precipitate obtained was redissolved in enough acetone to make a very viscous solution and a little distilled water was added to decrease the viscosity. This solution was allowed to stand overnight with occasional agitation in order to insure homogeneity of the solution. The solution was then poured rapidly into about 2 or 3 liters of violently agitated distilled water. The precipitate so obtained was filtered, washed with distilled water, dried overnight at 50°C, and finally dried at 105° - 110°C for 2 hours. The fraction was then weighed and stored.

Fourth Day. The supernatant liquid was decanted into a 3 liter Erlenmeyer flask, stoppered, and placed in the 25°C box. To the precipitate, designated as fraction 1-b and containing approximately 40% of the total cellulose acetate, was added enough solvent (95% acetone and 5% water) to make 640 grams of solution. The flask was then agitated by a slow but constant end-over-end rotation for 4 hours. The solution was then placed in the 25°C box for one hour. Enough precipitant was added, as before, to produce a fraction containing 20% of the original cellulose acetate. The flask was returned to the 25°C box for one hour and then transferred to the 15°C box, tilted, and allowed to stand for 42 hours.

Sixth Day. At the end of this period, the supernatant liquid was decanted into the supernatant liquid from the fourth day, and the solution was then placed in the 50°C box long enough to bring the temperature of the solution to 25°C, then transferred to the 25°C box. When one hour had expired from the time of decanting, enough precipitant was added to bring down a 10% fraction; the flask was returned to the 25°C box for one hour, then transferred to the 15°C box, tilted, and allowed to stand for 22 hours. The precipitate obtained on this day was designated as fraction 1 and was treated exactly the same as was the precipitate obtained on the third day.

Seventh through Eleventh Day. The supernatant liquid was poured into a 3 liter Erlenmeyer flask and the temperature of the solution was brought to 25°C. The flask was then transferred to the 25°C box until one hour had elapsed from the time of decanting. Enough precipitant was added to bring down a 10% fraction and the flask was returned to the 25°C box for one hour, then transferred to the 15°C box, tilted, and allowed to stand for 22 hours. The precipitates obtained were designated successively as fraction 2, fraction 3, ..., fraction 7, and in each case, the precipitate was treated according to the method described on the third day.

Twelfth Day. The procedure followed on this day was the same as before, except it was found to be convenient to change the precipitating agent at this point to pure n-heptane.

Thirteenth Day. The preceding days had produced a total of 90% of the cellulose acetate as fractions. The procedure followed was the same as before, except in this case, a large excess of n-heptane (500 ml) was added to precipitate as much of the remaining cellulose acetate as possible by nonsolvent addition.

Fourteenth Day. The supernatant liquid was decanted as before and the fraction obtained was treated in the same manner as were all the previous fractions. The supernatant liquid was placed in a vacuum distillation apparatus and the liquid was distilled under vacuum. The heat was supplied by a water bath to prevent charring of any remaining cellulose acetate. The solid material was recovered, dried, weighed, and stored.

RESULTS AND DISCUSSION OF RESULTS

By following the procedure outlined in the previous section, a precise fractionation was accomplished. There were no inversions of D. P.; the weights of the fractions were reproducible; and the D. P.'s were reproducible.

Table 6 shows in tabular form the results of three different fractionations. The percentage of the fractions is based on the total amount of cellulose acetate recovered, neglecting fraction 1-a. The degrees of polymerization were determined by the Staudinger equation as was described before.

Table 7 shows the statistical analysis of variance on the D. P.'s. This table shows that variations as great as those between fractions would occur less than 1% of the time by chance alone, and that the variations within a given fraction could be accounted for by chance alone.

No attempt has been made to analyze statistically the weight per cent of the fractions. Any such analysis on percentage would be futile since the sums were purposely made to be 100%. However, it will be noticed that the maximum variation in per cent of any given fraction from the mean of that fraction is 0.468% or less, and that the average variation is considerably below this value. This greatest variation, which was found in run X, fraction 8 may be explained in that this fraction was dissolved in too much acetone, and thus, when it was re-precipitated in water, it came down as a very finely divided, partially

TABLE 6

RESULTS OF FRACTIONATION PROCEDURE AND DEGREES OF POLYMERIZATION OF THE FRACTIONS
(D. P. of original = 178)

Fract.	Run	Wt.Soln. (gms)	Vol.Precipitant (ml)	Wt. Fract. (gms)	% Fract.	I_p *	D. P.
1-a	X	800.0	123.1	0.186	----	-----	-----
	Y	800.0	123.1	0.277	----	-----	-----
	Z	800.0	123.1	0.304	----	-----	-----
1-b	X	879.4	59.0	---	----	-----	-----
	Y	877.8	59.0	---	----	-----	-----
	Z	876.7	59.0	---	----	-----	-----
1	X	640.0	118.0	6.467	21.577	89.212	258, 258
	Y	640.0	118.0	6.479	21.291	89.353	250, 256
	Z	640.0	118.0	6.303	20.767	89.615	253, 249
	average	- - -	- - -	- - -	21.212	89.393	254
2	X	1482.7	16.7	3.047	10.166	73.340	234, 242
	Y	1484.4	16.7	3.051	10.026	73.694	246, 238
	Z	1478.2	16.7	3.125	10.296	73.772	243, 248
	average	- - -	- - -	- - -	10.163	73.706	242

TABLE 6 - Continued

Fract.	Run	Wt.Soln. (gms)	Vol.Precip-itant (ml)	Wt. Fract. (gms)	%Fract.	I_p*	D.P.
3	X	1468.8	23.2	2.881	9.612	63.451	231, 229
	Y	1470.3	23.2	2.905	9.547	63.908	229, 227
	Z	1463.6	23.2	3.042	10.023	63.924	232, 230
	average -				9.727	63.761	230
4	X	1459.3	26.0	2.927	9.766	53.762	211, 207
	Y	1461.0	26.0	2.884	9.477	54.396	202, 202
	Z	1455.2	26.0	2.946	9.706	54.059	206, 204
	average -				9.650	54.072	205
5	X	1454.5	35.0	3.292	10.984	43.387	174, 180
	Y	1456.4	35.0	3.320	10.910	44.202	183, 173
	Z	1449.7	35.0	3.173	10.454	43.974	188, 183
	average -				10.783	43.862	180
6	X	1454.7	42.0	2.782	9.282	33.254	160, 158
	Y	1457.5	42.0	2.853	9.376	34.059	161, 160
	Z	1451.3	42.0	2.921	9.624	33.940	151, 161
	average -				9.427	33.749	159

TABLE 6 - Continued

Fract.	Run	Wt. Soln. (gms)	Vol. Precipitant (ml)	Wt. Fract. (gms)	% Fract.	I_p*	D. P.
7	X	1465.2	59.0	2.677	8.932	24.147	157, 150
	Y	1467.6	59.0	2.695	8.856	24.943	151, 151
	Z	1460.5	59.0	2.695	8.879	24.689	156, 148
	average -				8.889	24.593	152
8	X	1487.7	100.0 heptane	2.835**	9.459	14.952	98, 102
	Y	1491.0	100.0 heptane	3.118	10.246	15.392	104, 94
	Z	1484.2	100.0	3.058	10.075	15.212	103, 102
	average -				9.927	15.186	101
9	X	1540.3	500.0 heptane	1.657	5.528	7.458	53, 38
	Y	1543.1	500.0 heptane	1.734	5.698	7.420	42, 54
	Z	1535.6	500.0	1.710	5.634	7.357	52, 53
	average -				5.620	7.409	49

TABLE 6 - Continued

Fract.	Run	Wt. Soln. (gms)	Vol. Precipitant (ml)	Wt. Fract. (gms)	% Fract.	I_p*	D. P.
10	X	--	evap.	1.407	4.694	2.347	37, 40
	Y	--	evap.	1.391	4.571	2.286	33, 39
	Z	1865.4	evap.	1.378	4.540	2.270	35, 36
	average				4.602	2.301	31

* I_p, for a given fraction is defined as one-half of the per cent of that fraction plus the sum of the perdentages of all fractions of lower D. P.

**Fraction 8-X, when reprecipitated into water, came down as a finely divided, partially colloidal, precipitate which was difficult to filter, and to remove from the filter paper.

TABLE 7

Analysis of Variance among the Degrees of Polymerization

Source	Degrees of Freedom	Sum of Squares	Mean Squares	F
1. Among Runs	2	324,314.42	162,157.21	9531.37**
2. Among Fractions	9	48.10	5.34	0.31
3. Sampling Error	30	574.50	19.15	1.13
4. Experimental Error	18	306.23	17.01	----
5. Total	59	325,243.25	------	----

** This is significant at the 1% level.

The rest are not significant.

colloidal, precipitate which was difficult to filter and to remove from the filter paper. This mishap caused the weight of this fraction to be low and consequently, the percentages of the other fractions in run X to be slightly higher.

Figure 7 shows the average differential distribution curve by this method of fractionating this particular sample of cellulose acetate. Figure 8 shows the average differential distribution curve obtained by graphically differentiating the curve in Figure 7. These two curves are weight average curves. It was necessary to minimize the breaks and peaks of the curves as this method of fractionation is not sufficiently accurate to locate very sharp, narrow peaks. The reason for the differential curve showing two peaks is obscure, but the cause could have been that a blend of cellulose was used in the acetylating bath by the manufacturer. In order to determine accurately the true distribution curve, it would be necessary to produce as many fractions as possible, and to refractionate these. It will be remembered, however, that the purpose of this investigation was to produce a given number of fractions of a given weight and not to determine the distribution curve of the material.

The materials used have been recovered by a relatively simple process. The distillate from the last fraction was treated with water in order to separate the heptane from the acetone. The acetone-water layer was fractionally distilled by the Chemical Engineering Department of the Virginia Polytechnic Institute and a product claimed to be pure acetone

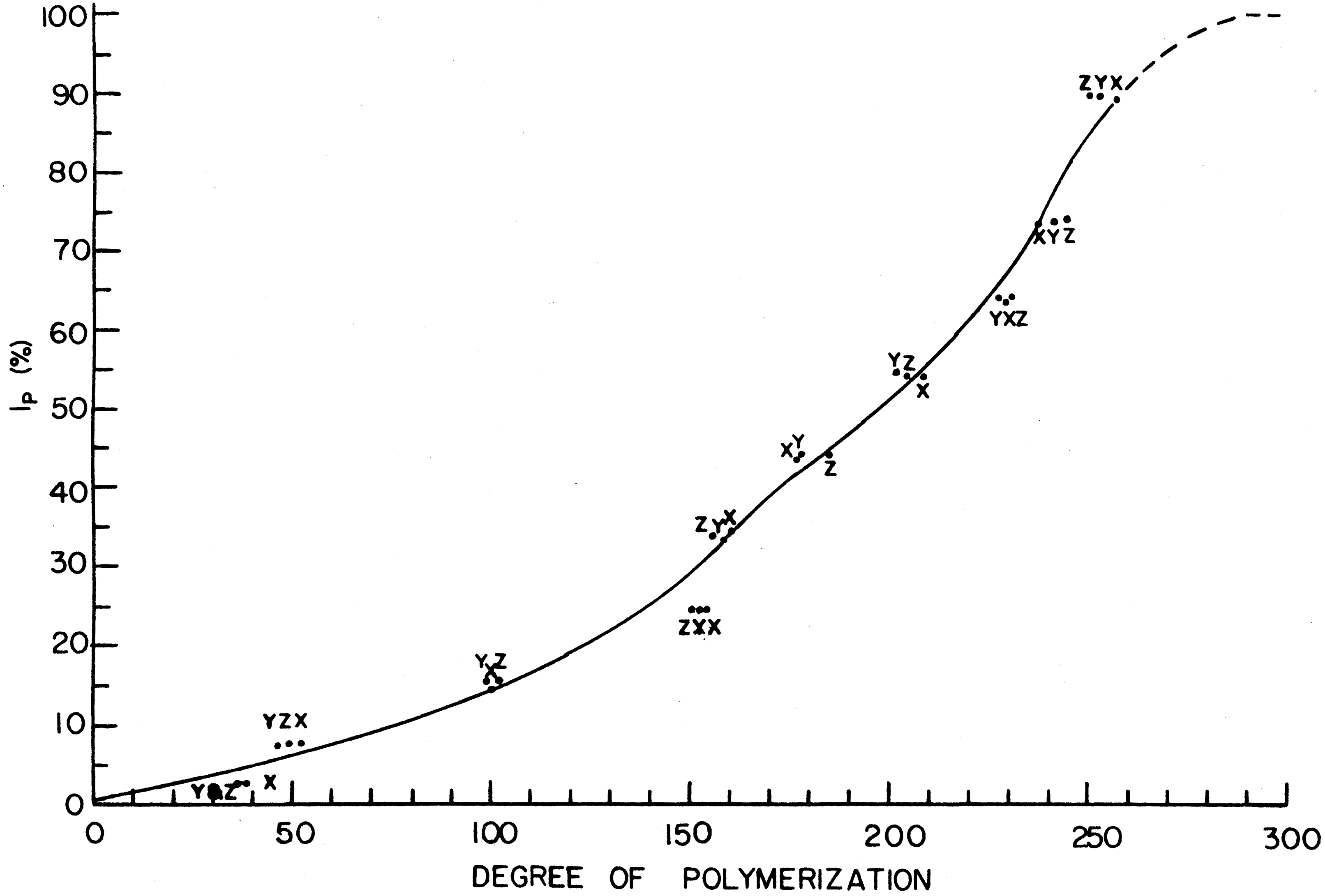

FIGURE 7. INTEGRAL DISTRIBUTION CURVE

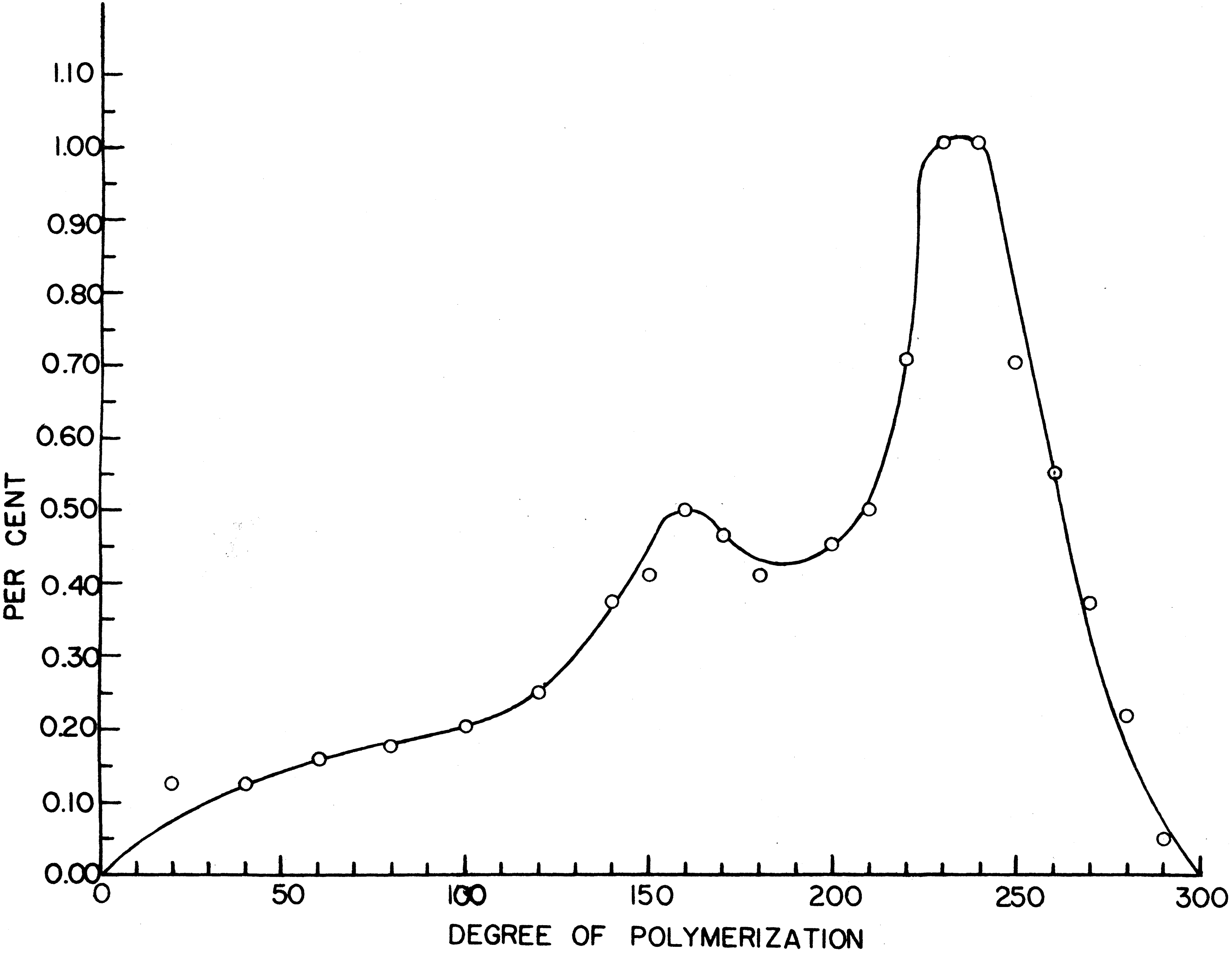

FIGURE 8. NORMALIZED DIFFERENTIAL DISTRIBUTION CURVE

was obtained. The heptane layer was washed several times with water, dried over anhydrous calcium chloride, and distilled in a small batch, fractionating still. The product recovered was essentially pure n-heptane.

CONCLUSIONS

1. By following the procedure outlined under the subheading Procedure Followed for Precise Fractionation of Cellulose Acetate, it was possible to precisely fractionate the sample of cellulose acetate described under the subheading Chemicals Used.

2. The method of fractionation was capable of a high degree of reproducibility, both as to per cent fraction obtained, and as to degree of polymerization of the fractions.

3. The method of fractionation gave no inversions of degrees of polymerization.

4. The method can be altered so as to carry out a large scale fractionation.

5. The acetone and n-heptane could be recovered in the pure form.

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