THE EFFECT OF DEGREE OF SUBSTITUTION ON THE FRACTIONAL PRECIPITATION OF CELLULOSE NITRATES

A Thesis

by

Clifton Francis Bennett

Submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Doctor of Philosophy

McGill University

May 1956

ACKNOWLEDGMENTS

The author wishes to express his sincere gratitude to Dr. T. E. Timell for his encouragement and guidance throughout the course of this work.

Grateful acknowledgments are also made to Spruce Falls Power and Paper Company, Limited, and to Allied Chemical and Dye Corporation for the awarding of fellowships; and to the Pulp and Paper Research Institute of Canada for a scholarship.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

GENERAL INTRODUCTION

High polymers, such as cellulose, are polymolecular, i.e., their component molecules exhibit a usually widely varying molecular weight. Being non-uniform, they are infinitely variable and the molecular weight distribution may vary from sample to sample of one and the same high polymer. Although of the same average molecular weight and chemical constitution, two polymeric specimens might accordingly show quite different properties depending on their particular molecular weight distribution, which will affect its behavior both in the solid and the dissolved state.

Determination of the molecular-weight distribution of high polymers therefore gives valuable information concerning many important properties of such materials, and it is thus highly important that methods be available for ascertaining this distribution. Such an evaluation of the polymolecularity could conceivably be carried out by any one of a number of methods, for example by comparison between osmotic and viscometric molecular weights, by ultracentrifugal techniques, by light-scattering, chromatographic adsorption, ultrafiltration, dielectric dispersion, electron microscopy, etc.

In the case of cellulose, most results have so far been obtained by application of solubility methods, which are based on the fact that the solubility of a polymer molecule increases exponentially with decreasing molecular weight.

Various techniques have been employed in this connection such as fractional precipitation and solution, summative methods and precipitation titration. The solubility of a polymer depends, however, not only on its molecular weight but also, and generally to a much higher degree, upon its chemical constitution. Direct fractionation of cellulose has proven difficult because of its instability in solutions, all of which are either strongly basic or acidic in nature. Derivatives such as the acetate or nitrate are more suitable in this respect and at least the latter can easily be prepared from any cellulose without accompanying degradation. Nitrates have also been more widely used for molecular weight and polymolecularity studies than any other cellulose derivative. Unfortunately, complete substitution is very difficult to achieve in this case without simultaneous depolymerization.

All partially substituted derivatives of cellulose are more or less non-uniform as far as the distribution of the substituents is concerned, i.e., some chain molecules are likely to contain more substituent groups than others. This fact will influence their solubility behavior and if such a material is fractionated by a solubility method, separation will occur according to both the length and the chemical nature of the chain molecules.

Recent investigations have shown that such a dual fractionation does indeed take place when cellulose nitrates are fractionated. It was the object of the present study to ascertain the extent of this undesirable influence of the chemical non-uniformity of the cellulose derivative on the results obtained by subjecting it to accepted fractionation procedures. For comparative purposes, a completely substituted, undegraded trinitrate was essential, and the first part of the present investigation hence had to be devoted to developing a method for preparing such a compound * . In the second part, comparative fractionations could then be carried out by different procedures.

---

* Published in Svensk Papperstidn. 58, 281 (1955).

HISTORICAL INTRODUCTION

The literature on fractionation of high polymers has been adequately reviewed by Cragg and Hammerschlag (1) and will therefore not be discussed here. Conrad (2) has recently summarized the literature on the polymolecularity of cellulose and cellulose derivatives up to and including the year 1952 and the following brief review will accordingly deal only with the more important contributions particularly pertinent to the present research. Less comprehensive reviews have also been presented by Sihtola (3), Wannow (4) and Broughton (5).

Fractionation of cellulose nitrate was for a long time almost invariably carried out by the solution method, i.e., the derivative was successively extracted in the solid state with solvent-nonsolvent mixtures of increasing solution capacity. This procedure seems especially to have been favored in the case of wood cellulose as witnessed by the large number of investigations in the field, e.g., those of Schieber (6), Atchison (7), Mitchell (8) and Heuser and coworkers (9) to mention only a few.

The last major investigation in which the solution method was used was reported in 1950 by Heuser (9), and in the same year Jörgensen (10) published an important comparative study of the solution and precipitation procedures as applied to cellulose nitrates (cf. Heuser and Jörgensen, 11). It was shown conclusively that the precipitation method, which involves gradual precipitation of a solution of the nitrate with a suitable nonsolvent, was widely superior to the solution process. The latter was, as could be expected, considerably influenced not only by the physical and chemical properties of the chain molecules but also by their location in the fiber. Jörgensen could show that the material first removed during fractional solution consisted of short-chain material located on the surface of the microfibrils of the cellulose, after which similar material within the more disordered regions was dissolved. With beginning swelling shorter chains inside the microfibril became accessible and was leached out until, during the final stages, chains of all different sizes were extracted. The main result of this complicated process was a molecular weight distribution that was largely an artifact and which especially failed to account for the polymolecularity of the high-molecular weight region. Fractional precipitation, particularly when applied in two stages instead of one, gave satisfactory results, which were also closely reproducible.

Since Jörgensen's comprehensive studies, all fractionations of cellulose or cellulose derivatives for evaluating the polymolecularity of these products have been performed by the precipitation method, acetone usually being chosen as the solvent and water or a hydrocarbon such as hexane as the nonsolvent. In those cases, however, where chief interest has been centered on the location of the various chains within the fibrillar cellulose framework or where variations in chemical constitution have been investigated, the solution procedure has still found extensive use, e.g., in studies on the methylation (12) and carboxymethylation (13) of cellulose or on the formation and properties of cellulose nitrates (14, 15).

Most earlier investigations on the fractional precipitation of cellulose nitrates dealt with rather low-molecular weight products. Wannow and Thormann (16), for example, studied a hydrolyzed cotton cellulose and concluded that identical results were obtained irrespective of whether a refractionation of the primary fractions was carried out or not. A similar conclusion was drawn by Roseveare and Poore (17), who worked with a rayon cellulose. Timell and Jahn (18) tried to ascertain the reproducibility of a two-stage precipitation method by subjecting a sample of cotton linters to a triplicate fractionation. Two series of the data obtained checked very well but the third did not. More difficulties were encountered by Timell (19) when dealing with high-molecular weight celluloses such as ramie nitrates. These materials were found to be rather unstable in acetone solution, resulting in a degradation that was more severe the longer the period of contact between the polymer and the solvent. When the intrinsic viscosity of the fractions was estimated it was found necessary to account for the influence of the rate of shear on the former, chain-length distributions that were too narrow otherwise being obtained. The necessity of repeated refractionation for obtaining reasonably sharp fractions was also stressed. In a later investigation it was actually shown (20) that even 11 refractionations failed to produce a uniform material. Recently Meffroy-Biget (21) devised a fractionation procedure aimed at overcoming a part of these difficulties.

Few data are available concerning the influence of the chemical non-uniformity of cellulose derivatives on their behavior when subjected to either fractional solution or precipitation. Earlier studies (22, 23, 24) indicated that the nitrogen content of the fractions did not remain constant. Smith (14) recently studied the chemical uniformity of various technical cellulose nitrates by a fractional solution procedure and found that nitrate substitution decreased with decreasing average D.P. of the fractions. A similar trend was noticed by Timell (20) when fractionally precipitating nitrated cotton linters. Miller and Timell (15) studied the distribution of nitrate groups in various nitrates from cotton linters, prepared both in rate-controlled reactions and under equilibrium conditions. The products were separated into a number of fractions by a successive extraction that was continued until the fibers began to swell. The first material to be removed, which was also that of lowest molecular weight, contained less nitrate groups than the remainder and the nitrate substitution as a rule increased with increasing D.P. This non-uniformity was less pronounced in specimens prepared under equilibrium as compared to those made under rate-controlled conditions but persisted even at high degrees of substitution. The authors tentatively suggested that the accessible and short-chain portions of the fibrils had been less highly nitrated because of the ability of the nitric acid molecules to enter the crystalline portions. Another interpretation of the same phenomenon was offered by Smith (14), who postulated a preferential hydrolysis and denitration within the highly organized localities. As a non-degrading acid mixture had been used in the former investigation, this explanation could not, however, apply generally.

One of the most important contributions in this connection has been made by Rosenthal and White (25), who studied the fractionation of cellulose acetate. These investigators were able to show that the nature of the solvent-nonsolvent system used for fractionation sometimes strongly influenced the results obtained. A system of acetone-aqueous ethanol, for example, was found to be especially more sensitive than others to variations in acetyl content of the material. Other systems effected fractionation more according to the chain-length and by a proper combination of two widely different solvent combinations the authors were able to effect a so-called "cross-fractionation". In this way fractions with narrow acetate and D.P. distributions could be produced.

In earlier investigations the nitrogen content of the fractions obtained from cellulose nitrates were seldom if ever determined. Only gradually was it realized that the intrinsic viscosity of cellulose nitrates must depend not only on the molecular weight but also on the degree of substitution of the material. Intrinsic viscosity, which is now usually given in dl/g, is a measure of the effective hydrodynamic volume of the molecular coil in solution. It has been conclusively shown (26) that in acetone or similar solutions of cellulose nitrate only the nitrate groups are solvated. The degree of solvation is therefore directly related to the degree of substitution, and the latter accordingly is one of the factors determining the volume and thus the viscosity of the chain molecule in solution. One of the first to realize the importance of this was Wannow (27) but it was not until 1953, when Lindsley and Frank (28) developed a quantitative relationship, that it became possible to recalculate the intrinsic viscosity for any nitrate substitution. The increase in viscosity is particularly pronounced at high degrees of substitution, the maximum level being attained at the theoretical trisubstitution.

Using the equation of Lindsley and Frank, Timell (20) could show that failure to correct the viscometrically determined degrees of polymerization of fractions obtained in a one-stage precipitation of a cellulose nitrate led to a chain-length distribution that was more narrow than the true one.

Similarly, even more pronounced differences were noticed in a subsequent study on the polymolecularity of a white spruce cellulose (29). In spite of recent statements to the contrary (30) it appears necessary therefore to apply the equation of Lindsley and Frank when measuring the D.P. of cellulose nitrates by viscometric means. An indication of the interest this question has recently aroused can be seen in the fact that since the above equation was developed, three other investigations have appeared dealing with the same subject (31, 32, 33).

Application of a correction to the viscosity values is not enough, of course, to eliminate the dual influence on the fractionation referred to above. This can be achieved only by working with a completely substituted derivative and although the importance of this has been pointed out, no such fractionation seems ever to have been undertaken. In a suggested standard method for evaluating the polymolecularity of celluloses, Mitchell (34) recommended the use of a one-stage fractional precipitation of cellulose nitrates by gradual addition of water to its acetone solution. The effect of the average nitrate substitution was not mentioned but it was specifically stated that the nitrogen content of the material to be investigated must not be below 13.6%. The method selected by Mitchell, which is well known and essentially the same as that used by Jörgensen (10) and many other investigators, was also the one chosen for the present study, although in a few cases acetone-hexane was also used as the solvent-nonsolvent system.

EXPERIMENTAL PROCEDURES

MATERIALS

The cotton linters used throughout the present work were of an acetate-grade quality, and had been obtained through the courtesy of Hercules Powder Company, Wilmington, Delaware. This material was the same as that used previously by Timell (20) and by Miller and Timell (15). It had an average D.P. of 1,700 and exhibited a Gaussian chain-length distribution. The untreated cotton used was of a raw Coastland variety with an average D.P. of 4,700 (35) and the ramie was a commercial sample which had been kier-boiled and bleached. All materials were extracted with benzene-ethanol (2:1) and air-dried.

The nitrating mixture of Alexander and Mitchell (36) was prepared from purified, 90% fuming nitric acid and reagent grade phosphorus pentoxide. Its composition was 64% nitric acid, 26% phosphoric acid, and 10% phosphorus pentoxide. Anhydrous, 100% nitric acid was prepared from the decolorized fuming acid by distillation from sulfuric acid in an all-glass apparatus. Nitrogen pentoxide was distilled from a mixture of 100% nitric acid and reagent grade phosphorus pentoxide under vacuum at a temperature ranging from 20°C to 30°C. The boron trifluoride was of a commercial quality, about 99% pure, supplied from a cylinder. All solvents and reagents used were of a reagent quality with the exception that technical acetone was used for fractionations.

For stabilization of the cellulose nitrates by methanol extraction the Soxhlet apparatus was used as suggested by Roseveare and Poore (17); the alcoholic vapor entered the top of the condenser, thus was cooled so that the condensate was at approximately room temperature by the time it reached the sample.

The viscometer was of the Cannon-Fenske type, with a capillary radius of approximately 0.02 cm and an efflux volume of 3 ml. Semi-micro Kjeldahl analyses were carried out, using a micro balance for weighing samples to 10^{-5} g; 30 ml flasks for digestion, and an all-glass still for collection of the liberated ammonia.

METHODS

Nitrations With the Standard Mixture

The well-known nitration procedure of Alexander and Mitchell (36), whichis also the suggested standard method of the American Chemical Society (34), is generally assumed to convert cellulose into the nitrate derivative without any appreciable degradation (37, 38, 39, 40, 41; cf. 42, 43). The nitrating mixture was prepared by adding phosphorus pentoxide to purified fuming nitric acid to achieve the desired composition. Nitration was carried out using a weight ratio of acid mixture to cellulose of 100:1, and the reactions were allowed to proceed, with occasional shaking, for periods of four to five hours, at 0°C. The nitrate was separated from the excess acid by filtration, drowned in distilled water at 0°C, washed with 4 to 6 l of distilled water, and stabilized by boiling in three portions of 50% aqueous methanol, each for five minutes. Drying was accomplished by heating at 55°C in vacuo, for one to two hours, and standing at room temperature for one to two days in a vacuum desiccator. The products thus obtained usually averaged 13.90 to 14.00% nitrogen.

Determination of Nitrogen Content

All nitrogen determinations were carried out by a semimicro Kjeldahl procedure as described in detail by Timell and Purves (12) although with some modifications. Methyl purple was the preferred indicator and all values were referred to a sample of potassium nitrate which had been recrystallized twice from ethanol and separately analyzed by the nitron method (44). The accuracy was ± 0.02%. The Dumas and the Du Pont nitrometer procedures were also tried but found to be inferior to the Kjeldahl method, which also required less amounts of material, usually only 10-20 mg.

Data from one series of analyses are given in Table I.

TABLE I

Nitrogen content as determined by the semi-micro Kjeldahl procedure of five cellulose nitrates, prepared separately but under identical conditions by means of the 43:32:25 mixture.

Sample No.	Nitrogen Content, %
1	14.08, 14.09
2	14.10, 14.13
3	14.12, 14.14
4	14.12, 14.15
5	14.16, 14.18

Determination of Degree of Polymerization

Degrees of polymerization were throughout estimated viscometrically. Reduced viscosities were measured at 25°C in the Cannon-Fenske viscometer with acetone as the solvent and flow times adjusted to 350-550 sec. Extrapolation to zero concentration was carried out with Huggins' equation (45)

$$[\eta] = \frac{\eta_{sp} / C}{1 + K' \eta_{sp}}$$

where K' was assumed to equal 0.35. The intrinsic viscosity values thus obtained were adjusted to a theoretical trisubstitution with the aid of the equations developed by Lindsley and Frank (28):

$$\log \frac{[\eta]_T}{[\eta]} = \log f(x) \quad (14.15-x) \quad B$$

$$f(x) = \frac{297}{162} \left(1 - \frac{45.00}{14.01} \cdot \frac{x}{100} \right)$$

$[\eta]_T$ = i.v. at trisubstitution

x = nitrogen content in %

B = 0.114

The corrected intrinsic viscosities were finally converted to corresponding degrees of polymerization according to the relationship of Newman, Loeb and Conrad (46):

$$\text{D.P.} = K[\eta]$$

The value of the constant K in the equation had been determined by the above investigators to be 80 __ 3 for ethyl acetate solutions of cellulose nitrares containing an average of 13.60% nitrogen. The corresponding value for acetone solutions was approximately 100 (8, cf. 10); this when corrected according to Lindsley and Frank (28) gave another constant, K', which equalled 84.0 in the relationship

$$\text{D.P.} = K'[\eta]_T$$

Due to the relatively low average molecular weight of the nitrates no correction had to be applied for shear rate influence (47).

Various Analytical Procedures

Analyses for phosphorus in the nitrated celluloses were carried out according to the method described by Niederl and Niederl (48) and also by the colorimetric procedure of Fontaine (49). Both methods failed to indicate the presence of any phosphorus in the samples.

The carboxyl content of the purified cotton linters was estimated by the silver o- nitrophenolate procedure of Sookne and Harris (50). The data obtained suggested the presence of only 0.025 meq. per gram of carboxyl groups.

Nitration With Gaseous Nitrogen Pentoxide

The method of Vollmert (51) was used, involving direct distillation of nitrogen pentoxide from a mixture of nitric acid and phosphorus pentoxide. The apparatus consisted of two connected flasks as described by the above investigator, and distillation from one to the other was carried out for 24 hours by immersing one in a freezing mixture, and keeping the other at a temperature ranging from -5°C to +17°C. Purified cellulose, 500 mg, either cotton linters or kier-boiled ramie, was thus nitrated using 10 ml of 100% colorless nitric acid and 15 g of phosphorus pentoxide. After washing with 8 l of distilled water at 0°C, stabilization of the product was effected by boiling in three successive portions of aqueous 50% methanol, each for five minutes.

Nitration With a Solution of Nitrogen Pentoxide in Carbon Tetrachloride

The method of Dalmon, Chedin and Brissaud (52) was used. Samples of cellulose, 250 mg, were added to 30 ml of a 12.5% solution of nitrogen pentoxide in carbon tetrachloride and the reaction was allowed to proceed at +5°C for various lengths of time. In one experiment, 2% phosphorus pentoxide was also added to the carbon tetrachloride solution.

Various Nitrations

The mixture of Alexander and Mitchell was used in several experiments with additional reagents incorporated. In one series of experiments 2 to 15% of nitrogen pentoxide was added, and in another 15 to 20% of the same compound was used together with an anhydrous nitric acid containing 10% of phosphorus pentoxide.

In a third series of nitrations boron trifluoride was introduced in amounts ranging from 6 to 20% into the nitrating mixture of Alexander and Mitchell. All reactions were allowed to proceed for four hours at +5°C and isolations of the products were carried out as described above. None of the various procedures gave a completely substituted compound.

Nitration With Mixtures of Nitric Acid, Acetic Acid and Acetic Anhydride

Three different nitration mixtures were investigated, including two developed by Bouchonnet et al (53) and by Roseveare and Poore, respectively. The composition of these mixtures was in proportion by weight of nitric acid, acetic acid and acetic anhydride 50:25:25 and 52:38:10, respectively. In addition to these, a third mixture was also tested, containing the above reagents in a ratio of 43:32:25. The first mixture was prepared from 100%, anhydrous nitric acid, reagent grade acetic acid and acetic anhydride, whereas 90% fuming nitric acid was used for the other two.

In a typical experiment, acetic anhydride, 100 ml (108 g) was slowly added to 67 ml (100 g) of 90% purified nitric acid at a temperature of -20 to -30°C. To 40 ml of this mixture 250 mg of air-dried cotton linters was added at the same temperature and the reaction mixture was immediately transferred to an ice-bath where it was kept with occasional shaking for three hours. The nitrated material was poured into 2 l of ice-water and washed repeatedly on a sintered-glass filter funnel with cold distilled water until neutral. Stabilization was effected by extraction with cold methanol over-night in a Sohxlet extractor. Alternative methods of stabilization included extraction with cold water, boiling with 50% aqueous methanol or repeated washing with cold water. The nature of the stabilization procedure was found to have no influence on the final nitrogen content of the product.

Preparation of Cellulose Nitrates for Subsequent Fractionations

For preparation of a series of cellulose nitrates of the same degree of polymerization but varying in average nitrogen content from 13.5 up to and including the trinitrate, two different methods were applied.

The trinitrate was prepared as outlined above with the 43:32:25 mixture of nitric acid, acetic acid and acetic anhydride. All other specimens were obtained with the aid of the acid mixture of Alexander and Mitchell, either alone or diluted with successive amounts of 85% phosphoric acid as described by Lindsley and Frank (28) and by Timell (54). The reaction time was in all cases four hours at 0°C and the products were purified and stabilized as described previously. Eight different cellulose nitrates were obtained in this way averaging 13.52, 13.64, 13.70, 13.76, 13.82, 13.86, 13.94 and 14.14%, respectively, all of which exhibited the same, or nearly the same, degree of polymerization.

Fractional Precipitations With the System Acetone-Water

Cellulose nitrate, 1.5 g, was dissolved in 1,000 ml of 92% aqueous acetone with the aid of a Waring Blendor. Fractionation was effected at a constant temperature of 25 ± 0.05°C with constant stirring by gradually removing the solvent with a slow current of air. When a suitable amount of material had precipitated as judged from the intensity of the opalescence, the current of air was stopped and the two phases allowed to come to equilibrium over a period of ten minutes. The precipitate was separated from the solution by centrifuging, converted into a fibrous form by addition of methanol, dried and weighed. The clear, supernatent solution was used for collecting another fraction in the same manner. The last two fractions were obtained by concentrating the solution to half of its final volume and to dryness, respectively. Usually, a total number of 12 to 15 fractions were isolated in this way.

All of the above preparations were subjected once to this type of fractionation except the trinitrate which was fractionated in duplicate.

Analyses for nitrate substitution and intrinsic viscosity (degree of polymerization) were carried out as described above.

Fractionation With the System Acetone-Hexane

Cellulose nitrate, 1.5 g, was dissolved in 300 ml of acetone to which the same volume of hexane was added at once. Fractionation was effected by gradual addition of further quantities of hexane except for the last fraction which was obtained by evaporation to dryness. The number of fractions obtainable in this manner was usually 7 to 8, all of which were weighed and analyzed as before.

RESULTS

Preparation of Cellulose Trinitrate

Although the preparation of an undegraded cellulose trinitrate had not been achieved by the time the present study was initiated, several investigators had reported the formation of completely substituted products of unknown degree of polymerization. Dalmon (55), using nitrogen pentoxide in the vapor phase, obtained a product with a content of 14.12% nitrogen and Dalmon, Chédin and Brissaud (52), who applied the same reagent dissolved in carbon tetrachloride, were able to prepare a nitrate containing the theoretical amount of nitrogen corresponding to trisubstitution, namely 14.14%.

In the present attempt to prepare an undegraded cellulose trinitrate, nitrogen pentoxide, which is an extremely powerful nitrating agent, particularly for oligosaccharides, was accordingly first employed. Vollmert (51), trying to prepare a nitrated pectin, devised a method involving direct distillation of a mixture of nitrogen pentoxide and nitric acid formed by heating a mixture of nitric acid and phosphorus pentoxide, onto the polysaccharide. Application of this technique gave the results summarized in Table II, from which it is immediately seen that considerable degradation occurred, which was not entirely unexpected, and that the nitrogen level attained was not higher than that attained by the standard method of Alexander and Mitchell.

TABLE II

Vapor phase nitration (Vollmert) compared with the nitration of Alexander and Mitchell.

Material	Method	D.P.	Nitrogen, %
Hydrolyzed Ramie	A & M	770	13.9
Hydrolyzed Ramie	Vollmert	610	13.6
Hydrolyzed Linters	A & M	1100	14.0
Hydrolyzed Linters	Vollmert	600	13.9

When the procedure of Dalmon, Chédin and Brissaud was used, involving the nitration with 12.5% solution of nitrogen pentoxide in carbon tetrachloride, similar results were noticed, as may be seen from Table III. Trisubstitution was not achieved; and a continuously progressing depolymerization evidently occurred, indications for which had already been obtained previously by Jullander (40).

TABLE III

Nitration of purified linters at 5°C with a 12.5% solution of nitrogen pentoxide in carbon tetrachloride.

Time, hr	Nitrogen, %	$[\eta]$
7	-	18.4
8	-	16.7
9	13.98	15.7
22	-	12.2

A portion of the nitric acid in the standard nitrating mixture of nitric acid, phosphoric acid and phosphorus pentoxide is probably present in the form of nitrogen pentoxide; it therefore was thought to be of interest to investigate how this compound would affect the extent of nitration. Various quantities of nitrogen pentoxide, ranging from 2 to 15% by weight, were accordingly added to the above nitration mixture and the reaction allowed to proceed for four hours at 5°C. The results reported in Table IV indicate that, although no degradation occurred, the nitrate substitution was independent of the amount of nitrogen pentoxide present and only slightly higher than those generally noted with the original mixture. Elimination of the phosphoric acid component by using 100% nitric acid containing 10% of phosphorus pentoxide and varying quantities of nitrogen pentoxide, lowered rather than increased the nitration level, as is seen in Table V. The same was evidently the case, as is evident from Table VI, when boron trifluoride was incorporated in the standard nitration mixture in an attempt to facilitate the formation of the nitronium ion (NO_2^+).

TABLE IV

Nitration for four hours at 5°C with the nitrating mixture of Alexander and Mitchell, containing additional amounts of nitrogen pentoxide.

Additional N_2O_5, %	Nitrogen, %	D.P.
2	13.89	1690
4	14.00	1680
6	13.98	1690
8	14.04	1660
10	13.88	1710
15	14.00	1620

TABLE V

Nitration for four hours at 5°C with 100% nitric acid containing 10% by weight of phosphorus pentoxide and various amounts of nitrogen pentoxide.

Additional N_2O_5, %	Nitrogen, %	D.P.
15	13.96	1710
20	13.76	1820
25	13.82	1780

TABLE VI

Effect of the addition of various amounts of boron trifluoride to the nitrating mixture of Alexander and Mitchell.

BF_3, %	Nitrogen, %	D.P.
0	13.86	1680
6	13.95	1700
10	13.93	-
15	13.86	-
20	13.91	1700

At this point it was shown in separate experiments that the impossibility of obtaining a trinitrate was due neither to the presence of carboxyl groups in the original cellulose, nor to the introduction of phosphate groups in the nitrate derivative, very few of such groups being detected by sensitive analytical techniques.

It was apparent from the above that nitrogen pentoxide, used either alone or in the standard acid mixture, was not capable of producing the desired result. Therefore, attention was directed toward other nitrating agents. Bouchonnet, Trombe and Petitpas (53) have been able to prepare nitrates from cotton containing 14.04 to 14.08% nitrogen by using a mixture of nitric acid, acetic acid, and acetic anhydride, in the proportion 50:25:25. Exhaustive extraction with methanol increased the nitrogen content to 14.12%, and also, in some cases to 14.15%. With ramie, lower degrees of substitution were noticed. Mixtures of nitric acid and acetic anhydride have been studied by Chedin and his co-workers. Raman spectra (56) indicated the following equilibris to be valid at -10°C:

$$2\ HNO_3 + Ac_2O \rightleftarrows N_2O_5 + 2\ HOAc$$

$$N_2O_5 + Ac_2O \rightleftarrows 2\ AcONO_2$$

With an excess of acetic anhydride the only products formed were acetic acid and acetyl nitrate but with an excess of nitric acid, nitrogen pentoxide (as NO_2^+ and NO_3^-) was also present. Addition of acetic acid to this nitration mixture appears to increase its swelling power, lower substituted products being obtained without it (57). Pure acetyl nitrate itself, which is an extremely powerful nitrating agent, effects very little nitration when applied directly to cellulose, but this has been shown to be due entirely to poor penetration of the unswollen fiber (57, 58, 59) and can be overcome by proper pretreatment.

Three nitration mixtures of the type referred to above were tested in the present study. The first was identical with that used previously by Alexander and Mitchell (36) and, later, by Roseveare and Poore (17). The viscosity value obtained by the former investigators suggested little degradation but the nitrogen content reported by the latter was only 13.8%. The second mixture was that employed by Bouchonnet, Trombe and Petitpas and the third was one originating in the present investigation and having the advantage of being easily prepared from commercially available fuming nitric acid. A summary of the composition of and the results obtained with the three nitration mixtures when applied to purified cotton linters is given in Table VII. All mixtures apparently gave nitrates of high nitrogen substitution but, unlike the first and the third, the second one appeared to have caused some degradation. This result was corroborated by the data in Table VIII, which indicated a definite degradative effect, probably caused by the gradual decomposition of the unstable reagent. The third mixture, which affected the highest degree of nitration, seemed to be superior to the second as far as stability was concerned. Application of this nitrating mixture for three hours at 0°C to three celluloses from different sources gave the results summarized in Table IX. The purified cotton linters and the ramie were both nitrated to the theoretical trisubstitution and both had exactly the same D.P. as had been obtained earlier with the standard mixture. There exists no rigid proof that cellulose is not degraded by the latter nitration mixture, but the very fact that two so different nitration procedures as those applied here resulted in products exhibiting the same molecular weight would seem to constitute a good indirect proof that no degradation occurred in either case. A similar conclusion was also reached by Harland (41) who, after the present investigation was terminated, reported the preparation of undegraded cellulose trinitrates from rayon by the use of a similar nitration mixture. The results obtained also indicated the correctness of the relationship between intrinsic viscosity and nitrate substitution recently developed by Lindsley and Frank (28). The untreated cotton, finally, was not quite as highly nitrated as the other two specimens and was also severely degraded. Duplicate experiments gave similar results but no further attempts were made to elucidate this phenomenon.

TABLE VII

Nitration at -5 to 0°C for seven hours with three nitration mixtures containing nitric acid, acetic acid and acetic anhydride.

Nitration Mixture Weight, %	Nitrogen, %	D.P.
52:38:10	14.04	1730
50:25:25	14.07	1400
43:32:25	14.12	1680

TABLE VIII

Nitration at 0°C with a 50:25:25 nitration mixture according to Bouchonnet and coworkers.

Time, hr	Nitrogen, %	D.P.
3	14.10	1660
4	14.16	1520
5.5	14.17	1430
6.5	14.07	1400

TABLE IX

Nitration of three celluloses of different origin at 0°C for three hours with the 43:32:25 nitrating mixture; and comparison with the nitration according to Alexander and Mitchell.

Material	Nitrogen, %	D.P. (A & M)	D.P. (43:32:25)
Untreated Raw Cotton	14.10	4720	3700
Purified Cotton Linters	14.14	1680	1680
Purified Ramie	14.13	2050	2050

According to Bouchonnet, Trombe and Petitpas (53), the nitrogen content for trisubstitution was reached only after extraction of the crude nitrates with methanol. This experience was not encountered in the present study. In a specific case, a sample prepared by the 43:32:25 nitration mixture and containing 14.10% nitrogen was extracted with cold methanol for 24 hours. The nitration content after extraction was substantially the same, namely 14.11%, and only 0.6% of the material was removed. The latter had a nitrogen content of 16.5%. Application of various stabilization procedures also had no noticeable effect on the degree of substitution as is evident from Table X, and all nitrates were accordingly henceforth stabilized by extraction with methanol.

TABLE X

Effect of stabilization procedure on nitrogen content.

Treatment	Time	Nitrogen, %
Extraction with cold methanol	14 hr.	14.13
Extraction with cold water	14 hr.	14.12
Boiling with 50% aqueous methanol	10 min.	14.17
Repeated washing with cold water	3 da.	14.14

Unlike the nitration mixture of Harland (41) mentioned above, the mixture used here nitrated cellulose only slowly, as may be seen from Table XI, valid for cotton linters and 0°C. After the first 15 minutes the reaction proceeded only slowly, and trisubstitution was reached only after three hours at this temperature. Complete solubility in acetone or ethyl acetate was not achieved until a nitrogen content of 14.0% had been attained. Corresponding nitrates prepared by the standard procedure, on the other hand, became soluble at a nitrogen level of 13.0 to 13.5% (60).

TABLE XI

Nitration at 0°C with a 43:32:25 nitration mixture.

Time, hr	Nitrogen, %	D.P.
0.25	9.87	-
0.50	11.01	-
1	12.66	-
1.75	13.86	-
2	14.05	1680
3	14.12	1650
4	14.15	1660
5	14.13	1640
6	-	1590
8	14.12	1500
10	14.12	1540
15	-	1440
24	14.10	1470
48	14.16	1180
74	14.14	1160
96	-	1100
120	14.13	1090

All these facts suggested a reaction governed by the rate of diffusion of the reagents from the surface into the interior of the cellulose fibrils, caused primarily by the limited swelling ability of the nitrating mixture. A reaction of this type would be expected to produce a product with good solubility properties only at a very high degree of conversion when even the hydrogen bonds holding the chain molecules in the middle of the microfibril together had been broken. The data in Table X show that the degree of substitution remained, within the limits of experimental errors, unchanged throughout the time the esterification was followed but that the degree of polymerization decreased after the first four to five hours.

Fractionations

For the subsequent study of the influence of the average degree of substitution and thus also the chemical non-uniformity on the results obtained when fractionally precipitating cellulose nitrates, a series of such saples had to be prepared, varying in nitrogen content but of the same average degree of polymerization. It was shown above that a trisubstituted cellulose could be made without simultaneous degradation by using a nitric acid, acetic acid, acetic anhydride mixture. This reagent, however, was not suitable for preparing lower substituted products as these apparently would have only limited solubility in acetone. Recourse was therefore to be had to some other procedure and fortunately such a method was readily available, having recently been developed by Lindsley and Frank (28). These investigators found that addition of various amounts of 85% phosphoric acid to the mixture of Alexander and Mitchell greatly reduced the nitrating power of the latter and made it possible to obtain products of intermediate degrees of substitution, the lower the more phosphoric acid was added. This result was somewhat later corroborated by Timell (60), who also confirmed the non-degrading action of the mixtures reported by the above workers.

A series of eight cellulose nitrates ranging in nitrogen content from 13.52 to 14.14% was prepared by the above methods. Their intrinsic viscosities, when corrected for their various nitrate substitutions, indicated the same average degree of polymerization for them all, thus again showing the correctness of the equation of Lindsley and Frank (28).

The cellulose nitrates were subdivided into approximately 15 fractions, essentially according to the suggested standard method of the American Chemical Society as described by Mitchell (34). Two different solvent-nonsolvent systems were used, however, namely, acetone-water and acetone-hexane. Approximately 15 fractions could be isolated by the former and 7-8 by the later technique. To improve fractionation efficiency, concentrations were throughout kept between 0.15 and 0.20%. In the former case the nitrates were dissolved in 92% aqueous acetone and precipitation effected by slow removal of the acetone; in the latter fractions were isolated by gradual addition of hexane. Much larger quantities of this precipitant were necessary as compared to the other system because of its inferior ability to remove the solvated acetone molecules from the nitrate groups in the chain molecules.

All eight of the above-mentioned specimens were fractionated using water as the precipitant. Duplicate fractionations were carried out with the trinitrate in an attempt to check the reproducibility of the procedure. Five samples, including the trinitrate, were subjected to a similar fractionation involving hexane as the nonsolvent. The fractions were analyzed for nitrogen contents and intrinsic viscosities and the latter adjusted to the trinitrate level and converted to degrees of polymerization. The average nitrogen content of the fractions was calculated and compared to the original one. Similarly, weight average degrees of polymerization were also computed and compared to the original, viscosity-average value for each specimen, weight- and viscosity-average molecular weights being identical in the case of cellulose nitrates.

All numerical data obtained are summarized in Tables XII-XXV. Integral weight distribution curves were constructed according to the directions of Mitchell (34) and Hermans (61), the procedure employed being that originally suggested by Schulz (62). The results are presented in Figs. 1-14. A summary of the nitrogen contents and degrees of polymerization of all samples finally is given in Table XXVI.

TABLE XII

Fractionation of cellulose nitrate sample No. 1, containing 13.52% N, acetone-water system.

Fraction No.	Weight, %	Nitrogen, %	$[\eta]$, dl/g	$[\eta]_T$, dl/g	D.P.	Weighted D.P.	Weighted Nitrogen
1	6.8	13.43	22.5	28.4	2390	163	0.91
2	13.6	13.49	23.3	28.8	2420	329	1.83
3	15.2	13.43	22.3	28.7	2420	368	2.04
4	7.3	13.55	22.9	27.7	2330	170	0.99
5	6.1	13.45	20.0	25.0	2100	128	0.82
6	9.6	13.58	16.6	19.9	1670	160	1.30
7	6.0	13.48	16.0	19.8	1670	100	0.81
8	9.9	13.48	10.4	12.6	1060	105	1.34
9	6.4	13.55	11.9	14.5	1220	78	0.86
10	6.7	13.52	11.3	14.0	1180	79	0.90
11	9.0	12.30	5.1	9.2	770	69	1.11
12	3.4	11.32	3.5	8.6	720	25	0.38
						1774	13.29

TABLE XIII

Fractionation of cellulose nitrate sample No. 2, containing 13.64% N, acetone-water system.

Fraction No.	Weight, %	Nitrogen, %	$[\eta]$, dl/g	$[\eta]_T$, dl/g	D.P.	Weighted D.P.	Weighted Nitrogen
1	12.1	13.48	24.3	30.1	2530	306	1.63
2	8.6	13.60	24.0	28.6	2400	206	1.17
3	9.7	13.54	23.4	28.2	2370	230	1.31
4	10.3	13.67	21.0	24.4	2050	211	1.41
5	10.1	13.64	19.8	23.2	1950	197	1.38
6	5.4	13.58	18.9	22.4	1880	101	0.73
7	9.9	13.65	15.8	18.5	1550	153	1.53
8	8.0	13.66	14.9	17.3	1450	116	1.16
9	8.1	13.65	11.7	13.7	1150	93	1.10
10	11.5	13.47	9.8	12.1	1020	117	1.55
11	6.3	12.80	3.2	4.9	410	26	0.80
						1756	13.77

TABLE XIV

Fractionation of cellulose nitrate sample No. 3, containing 13.70% N, acetone-water system.

Fraction No.	Weight, %	Nitrogen, %	$[\eta]$ dl/g	$[\eta]_T$ dl/g	D.P.	Weighted D.P.	Weighted Nitrogen
1	6.5	13.58	24.4	29.3	2460	160	0.88
2	11.7	13.70	23.2	26.9	2260	262	1.60
3	4.5	13.67	22.6	26.4	2220	100	0.62
4	10.1	13.75	22.5	25.4	2130	215	1.39
5	14.4	13.88	20.8	22.7	1910	275	2.00
6	12.6	13.80	15.8	17.7	1490	188	1.74
7	9.1	13.79	14.6	16.4	1380	126	1.26
8	8.6	13.72	13.7	15.8	1330	114	1.18
9	8.0	13.69	12.4	14.4	1210	97	1.10
10	8.9	13.49	6.1	7.5	630	56	1.20
11	5.6	11.80	3.5	7.4	620	35	0.66
						1628	13.63

TABLE XV

Fractionation of cellulose nitrate sample No. 4, containing 13.76% N, acetone-water system.

Fraction No.	Weight, %	Nitrogen, %	$[\eta]$ dl/g	$[\eta]_T$ dl/g	D.P.	Weighted D.P.	Weighted Nitrogen
1	2.8	13.52	24.9	30.4	2550	71	0.38
2	8.8	13.54	25.8	31.2	2620	231	1.19
3	7.7	13.80	24.7	27.6	2320	179	1.06
4	11.8	13.72	22.8	26.0	2180	257	1.62
5	8.7	13.69	22.3	25.9	2180	190	1.19
6	15.0	13.74	19.3	21.8	1830	274	2.06
7	9.9	13.79	16.0	17.9	1500	148	1.37
8	9.1	13.59	14.2	16.9	1420	130	1.24
9	5.3	13.53	14.0	16.9	1420	75	0.72
10	6.8	13.60	12.7	15.1	1270	86	0.92
11	5.3	13.51	10.8	13.2	1110	59	0.72
12	6.4	12.35	5.1	9.1	760	49	0.79
13	2.4	9.01	1.6	8.2	690	17	0.22
						1766	13.48

TABLE XVI

Fractionation of cellulose nitrate sample No. 5, containing 13.82% N, acetone-water system.

Fraction No.	Weight, %	Nitrogen, %	$[\eta]$ dl/g	$[\eta]_T$ dl/g	D.P.	Weighted D.P.	Weighted Nitrogen
1	4.7	13.43	24.2	30.5	2560	120	0.63
2	7.6	13.59	25.5	30.6	2570	195	1.03
3	8.3	13.62	25.9	30.6	2570	215	1.13
4	8.0	13.80	24.4	27.3	2290	183	1.01
5	6.8	13.91	23.9	25.6	2150	146	0.95
6	8.1	13.83	22.1	24.3	2030	165	1.12
7	5.6	13.92	20.4	21.8	1830	102	0.78
8	7.6	13.87	17.1	18.5	1550	118	1.05
9	9.4	13.83	16.7	18.3	1540	145	1.30
10	8.6	13.67	14.8	17.2	1450	125	1.18
11	6.0	13.58	12.7	15.2	1280	77	0.82
12	10.9	13.50	8.2	10.1	850	93	1.47
13	8.4	9.35	1.9	8.6	720	60	0.79
						1744	13.26

TABLE XVII

Fractionation of cellulose nitrate sample No. 6, containing 13.86% N, acetone-water system.

Fraction No.	Weight, %	Nitrogen, %	$[\eta]$ dl/g	$[\eta]_T$ dl/g	D.P.	Weighted D.P.	Weighted Nitrogen
1	3.7	13.55	25.2	30.4	2550	94	0.50
2	6.7	13.65	26.2	30.7	2580	173	0.92
3	6.1	13.72	24.6	28.0	2350	143	0.84
4	6.2	13.75	24.7	27.9	2340	146	0.85
5	5.3	13.79	23.5	26.2	2200	117	0.73
6	6.6	13.82	23.0	25.5	2140	141	0.91
7	12.9	13.88	21.6	23.4	1970	254	1.79
8	6.8	13.82	19.3	21.4	1800	122	0.94
9	8.3	13.89	16.9	18.2	1530	127	1.15
10	6.1	13.82	17.4	19.3	1620	99	0.84
11	6.3	13.74	14.8	16.9	1420	89	0.87
12	7.4	13.58	13.5	16.1	1350	100	1.00
13	6.2	13.50	9.7	11.9	1000	62	0.84
14	7.2	13.44	6.5	8.1	680	49	0.28
15	4.2	6.82	1.0	9.2	770	32	0.97
						1748	13.43

TABLE XVIII

Fractionation of cellulose nitrate sample No. 7, containing 13.94% N, acetone-water system.

Fraction No.	Weight, %	Nitrogen, %	$[\eta]$ dl/g	$[\eta]_T$ dl/g	D.P.	Weighted D.P.	Weighted Nitrogen
1	6.9	13.83	27.5	30.2	2540	175	0.96
2	5.3	13.98	26.2	27.6	2320	123	0.74
3	7.6	14.02	23.3	24.2	2030	155	1.07
4	8.6	14.02	22.5	23.4	1970	170	1.21
5	10.0	14.04	21.2	22.0	1840	184	1.40
6	10.7	13.97	19.4	20.6	1730	185	1.49
7	11.2	13.94	17.3	18.5	1560	175	1.56
8	8.5	13.90	18.3	19.7	1660	141	1.19
9	10.3	13.81	16.1	17.9	1500	155	1.39
10	6.7	13.50	15.0	18.4	1550	104	0.93
11	6.0	13.32	10.2	13.3	1110	67	0.80
12	5.5	13.07	6.5	9.1	760	42	0.72
13	2.7	8.33	0.9	5.7	480	13	0.23
						1689	13.69

TABLE XIX

Fractionation of cellulose nitrate sample No. 9, containing 14.14% N, acetone-water system.

Fraction No.	Weight, %	Nitrogen, %	$[\eta]$ dl/g	$[\eta]_T$ dl/g	D.P.	Weighted D.P.	Weighted Nitrogen
1	13.2	14.03	28.5	29.3	2460	325	1.85
2	10.9	14.02	26.1	26.9	2260	246	1.53
3	9.0	14.10	23.8	24.2	2030	183	1.27
4	9.2	14.12	22.4	22.6	1900	175	1.30
5	10.0	14.13	20.5	20.5	1720	172	1.41
6	6.9	14.14	19.1	19.1	1600	110	0.98
7	7.1	14.09	18.0	18.3	1540	109	1.00
8	9.3	14.05	15.6	16.0	1350	126	1.31
9	7.2	14.06	13.8	14.2	1200	86	1.01
10	6.9	14.01	9.3	9.7	810	56	0.97
11	6.6	14.03	7.7	7.9	660	44	0.93
12	3.7	10.80	1.7	4.9	410	15	0.40
						1647	13.96

TABLE XX

Fractionation of cellulose nitrate sample No. 9, containing 14.14% N, acetone-water system, duplicate of fractionation, Table XIX.

Fraction No.	Weight, %	Nitrogen, %	$[\eta]$ dl/g	$[\eta]_T$ dl/g	D.P.	Weighted D.P.	Weighted Nitrogen
1	8.0	13.99	28.2	29.6	2490	199	1.12
2	10.4	14.04	25.4	26.4	2220	231	1.46
3	10.5	14.05	23.9	24.6	2060	216	1.48
4	8.8	14.04	22.0	22.8	1920	169	1.24
5	10.7	14.11	21.4	21.6	1820	195	1.51
6	7.8	14.12	20.0	20.2	1700	133	1.10
7	12.0	14.12	19.4	19.6	1650	198	1.70
8	7.5	14.10	17.3	17.6	1480	111	1.06
9	9.7	14.07	13.8	14.1	1180	115	1.37
10	8.4	13.97	8.5	9.0	760	64	1.17
11	6.2	13.05	4.8	6.9	580	36	0.81
						1667	14.02

TABLE XXI

Fractionation of cellulose nitrate sample No. 1, containing 13.52% N, acetone-hexane system.

Fraction No.	Weight, %	Nitrogen, %	$[\eta]$ dl/g	$[\eta]_T$ dl/g	D.P.	Weighted D.P.	Weighted Nitrogen
1	12.9	13.34	20.0	25.8	2170	280	1.72
2	13.2	13.37	22.2	28.4	2390	315	1.76
3	7.2	13.44	21.5	27.1	2280	164	0.97
4	19.3	13.51	20.2	24.6	2070	400	2.61
5	19.3	13.56	17.5	21.0	1760	340	2.62
6	10.9	13.49	14.2	17.5	1470	160	1.47
7	6.7	13.43	9.5	12.0	1010	68	0.90
8	10.5	12.62	5.6	9.1	760	80	1.32
						1807	13.37

TABLE XXII

Fractionation of cellulose nitrate sample No. 5, containing 13.82% N, acetone-hexane system.

Fraction No.	Weight, %	Nitrogen, %	$[\eta]$ dl/g	$[\eta]_T$ dl/g	D.P.	Weighted D.P.	Weighted Nitrogen
1	12.2	13.76	21.4	24.2	2030	248	1.68
2	12.9	13.74	24.3	27.7	2330	300	1.77
3	7.9	13.72	23.5	27.0	2270	179	1.08
4	8.1	13.65	23.6	27.6	2320	188	1.11
5	6.8	13.60	22.0	26.2	2200	150	0.92
6	15.1	13.72	23.8	27.4	2300	347	2.08
7	16.6	13.87	17.3	18.7	1570	260	2.30
8	12.9	13.87	11.2	12.1	1020	131	1.55
9	7.5	12.04	6.8	13.3	1120	84	1.04
						1887	13.53

TABLE XXIII

Fractionation of cellulose nitrate sample No. 6, containing 13.86% N, acetone-hexane system.

Fraction No.	Weight, %	Nitrogen, %	$[\eta]$ dl/g	$[\eta]_T$ dl/g	D.P.	Weighted D.P.	Weighted Nitrogen
1	9.8	13.66	19.9	23.2	1950	191	1.34
2	9.8	13.69	20.0	23.6	1980	194	1.34
3	11.4	13.66	21.5	25.2	2120	240	1.56
4	12.6	13.72	22.2	25.5	2140	270	1.73
5	25.0	13.73	23.8	27.0	2270	568	3.43
6	12.2	13.94	17.0	18.2	1530	187	1.70
7	10.2	13.83	12.6	14.5	1220	124	1.41
8	9.0	13.57	13.8	16.5	1390	125	1.22
						1899	13.73

TABLE XXIV

Fractionation of cellulose nitrate sample No. 7, containing 13.94% N, acetone-hexane system.

Fraction No.	Weight, %	Nitrogen, %	$[\eta]$ dl/g	$[\eta]_T$ dl/g	D.P.	Weighted D.P.	Weighted Nitrogen
1	6.8	13.54	21.0	25.4	2130	145	0.92
2	10.3	13.63	22.4	26.4	2220	229	1.68
3	21.3	13.70	23.7	27.2	2290	488	2.92
4	17.4	13.88	22.9	24.7	2080	362	2.42
5	21.0	13.94	19.7	21.1	1770	372	2.93
6	8.3	13.90	13.6	14.7	1240	103	1.16
7	9.4	13.87	13.9	15.2	1280	120	1.30
8	5.5	9.71	2.4	9.7	820	45	0.54
						1864	13.87

TABLE XXV

Fractionation of cellulose nitrate sample No. 8, containing 14.14% N, acetone-hexane system.

Fraction No.	Weight, %	Nitrogen, %	$[\eta]$ dl/g	$[\eta]_T$ dl/g	D.P.	Weighted D.P.	Weighted Nitrogen
1	15.0	13.94	24.2	25.9	2180	327	2.09
2	16.8	14.04	27.2	28.3	2380	400	2.36
3	22.0	14.16	25.0	25.0	2100	462	3.16
4	18.3	14.13	19.8	19.8	1660	306	2.59
5	13.8	14.10	13.2	13.3	1120	155	1.95
6	8.8	14.08	10.2	10.4	870	77	1.24
7	5.3	12.52	5.7	9.6	810	43	0.66
						1770	14.05

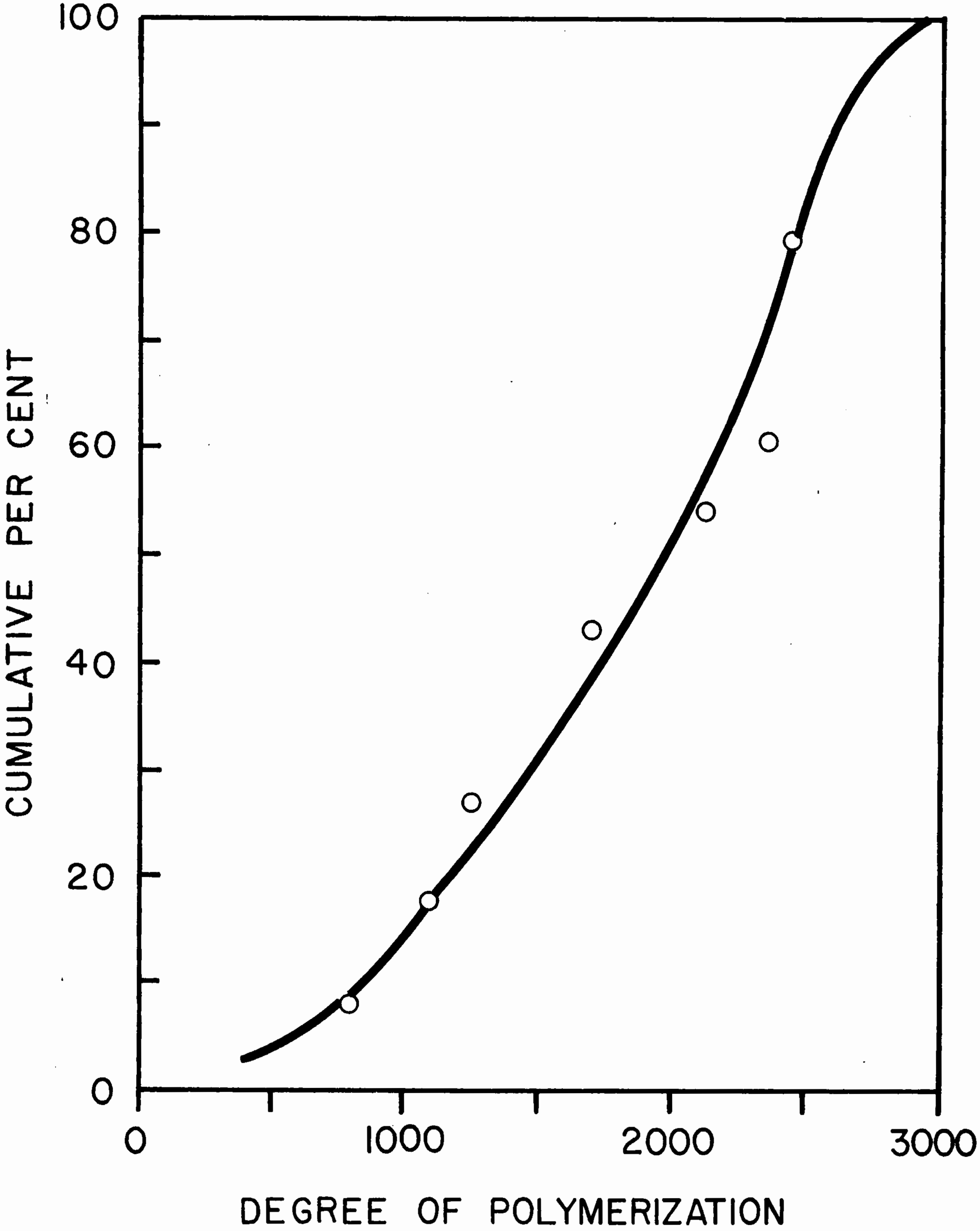

Fig. 1. Acetone-water system. Sample No. 1, containing 13.52% nitrogen.

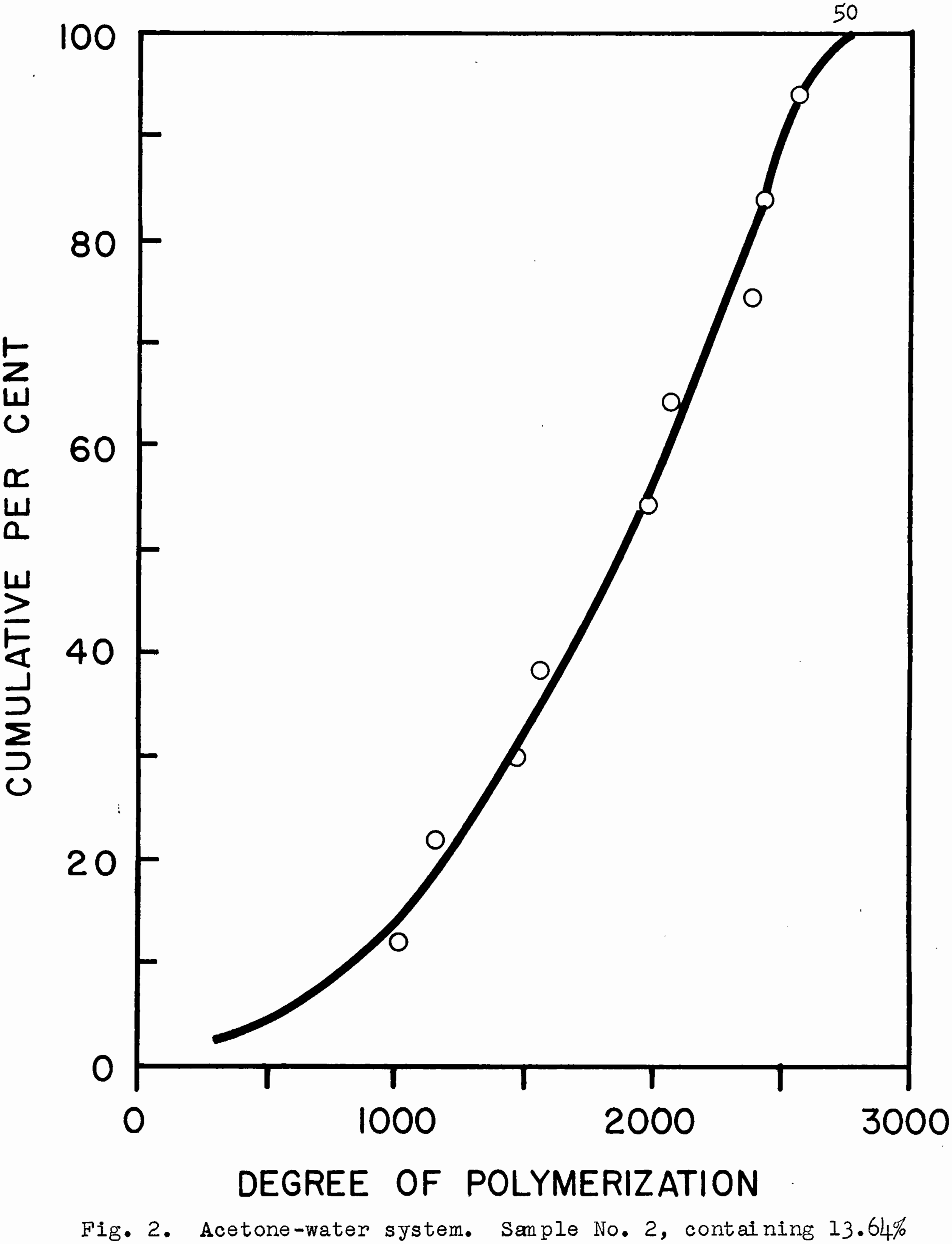

Fig. 2. Acetone-water system. Sample No. 2, containing 13.64% nitrogen.

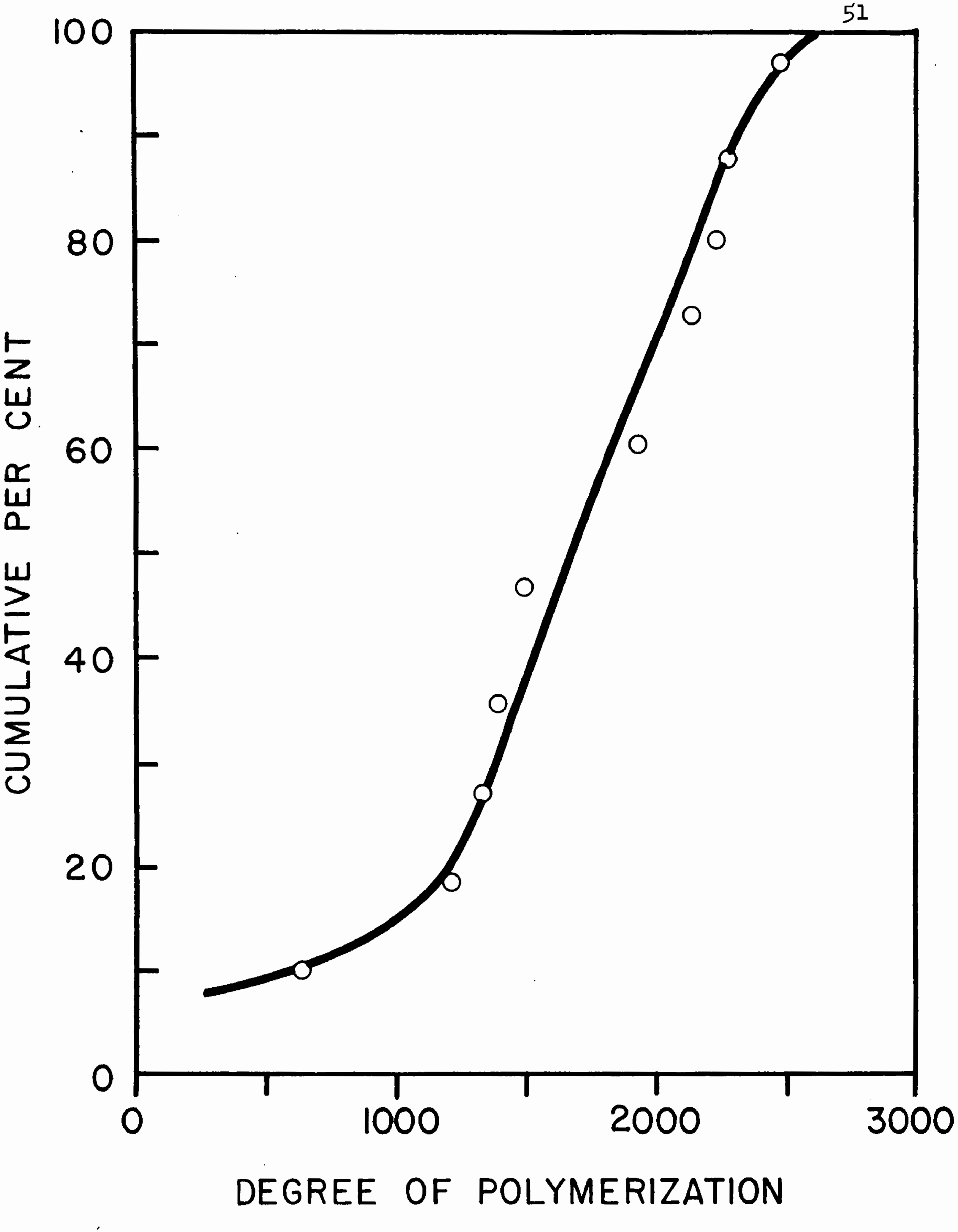

Fig. 3. Acetone-water system. Sample No. 3, containing 13.70% nitrogen.

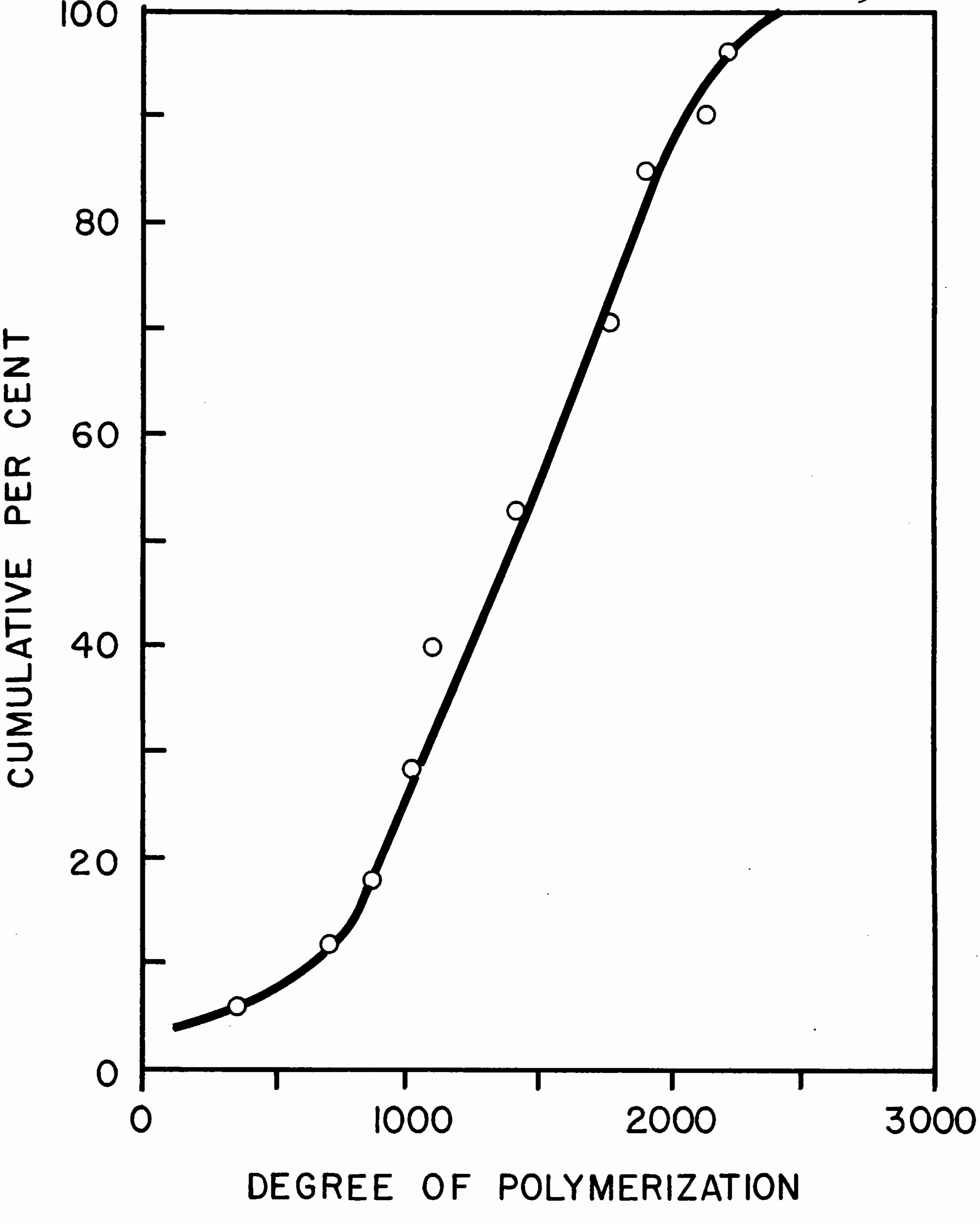

Fig. 4. Acetone-water system. Sample No. 4, containing 13.76% nitrogen.

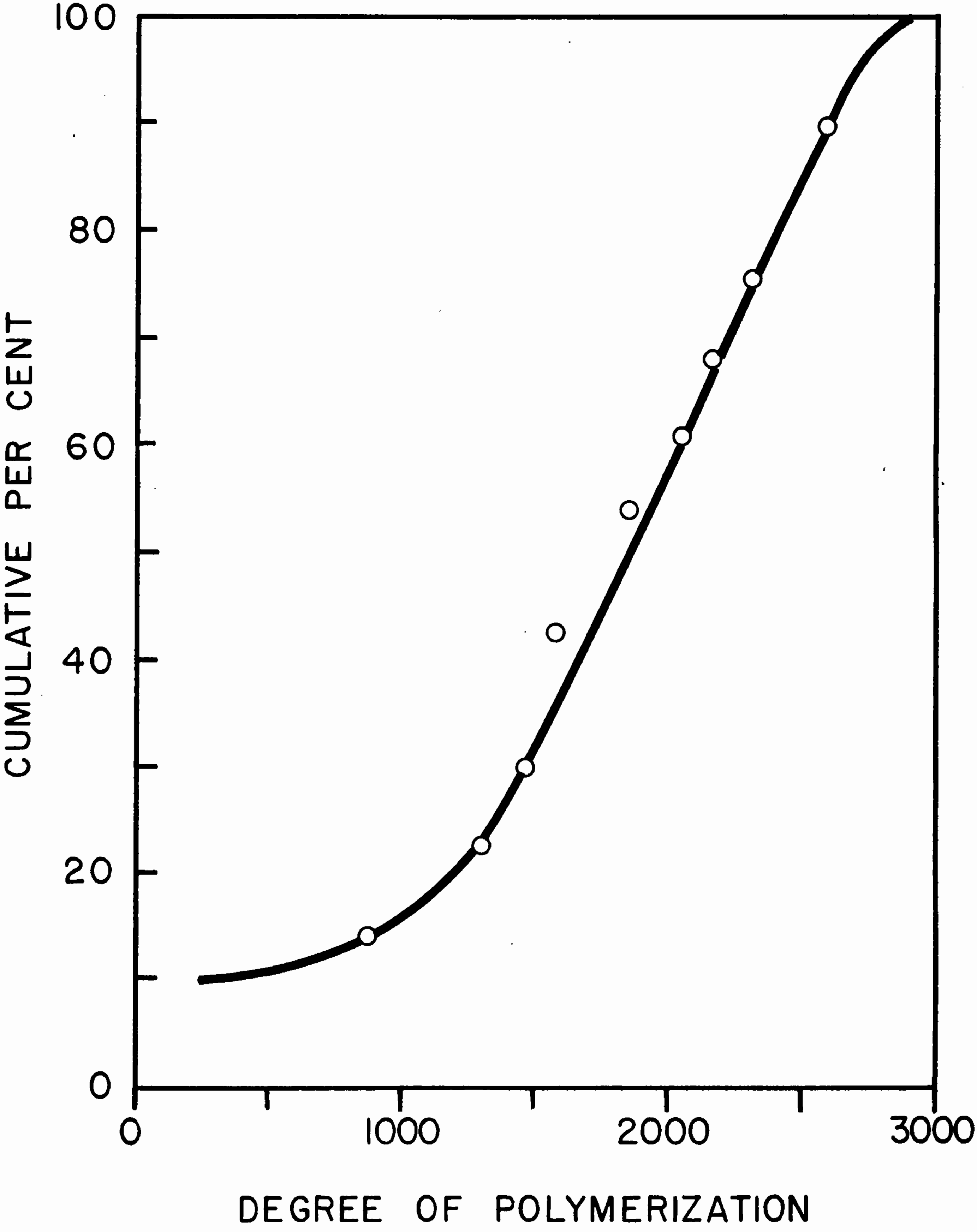

Fig. 5. Acetone-water system. Sample No. 5, containing 13.82% nitrogen.

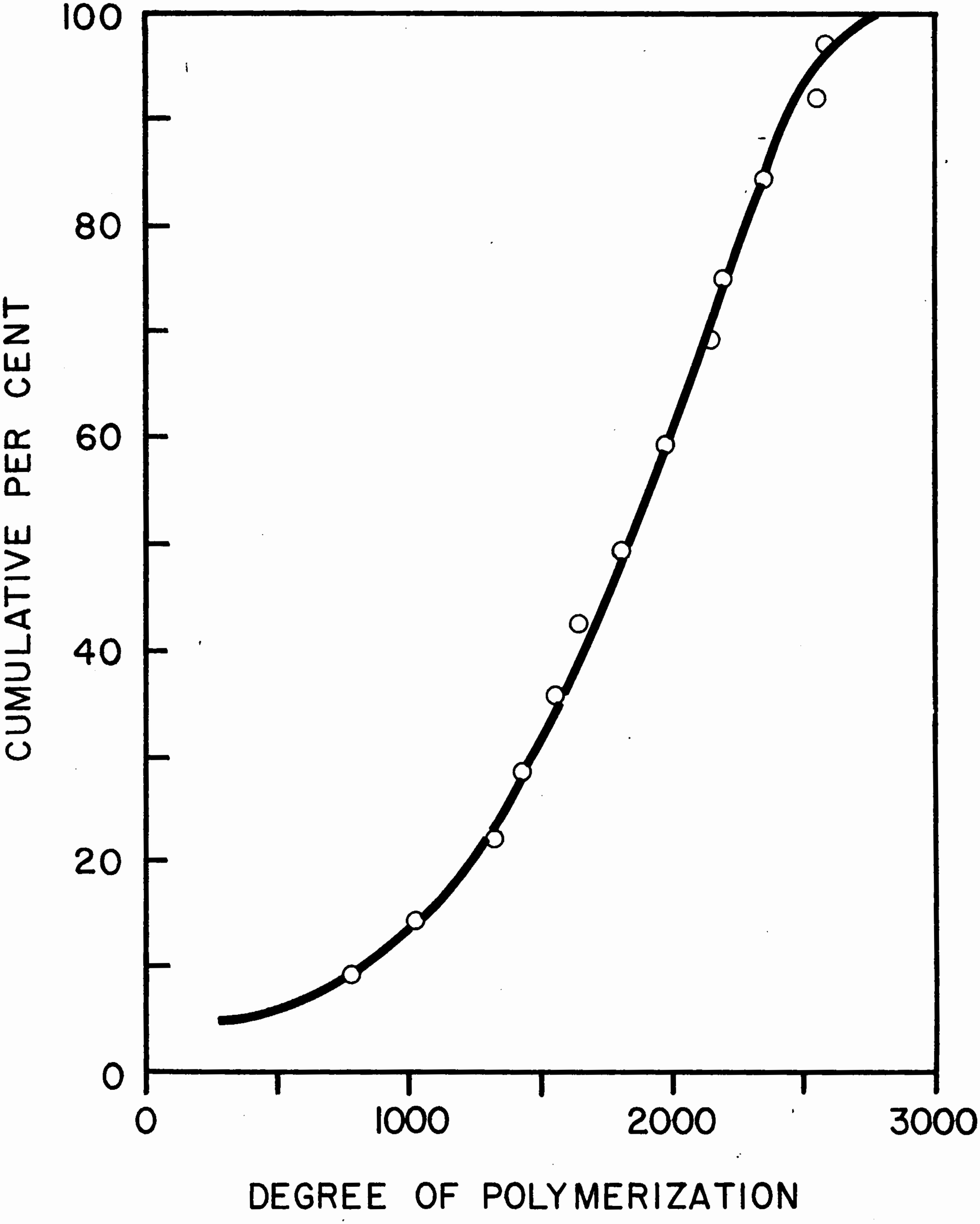

Fig. 6. Acetone-water system. Sample No. 6, containing 13.86% nitrogen.

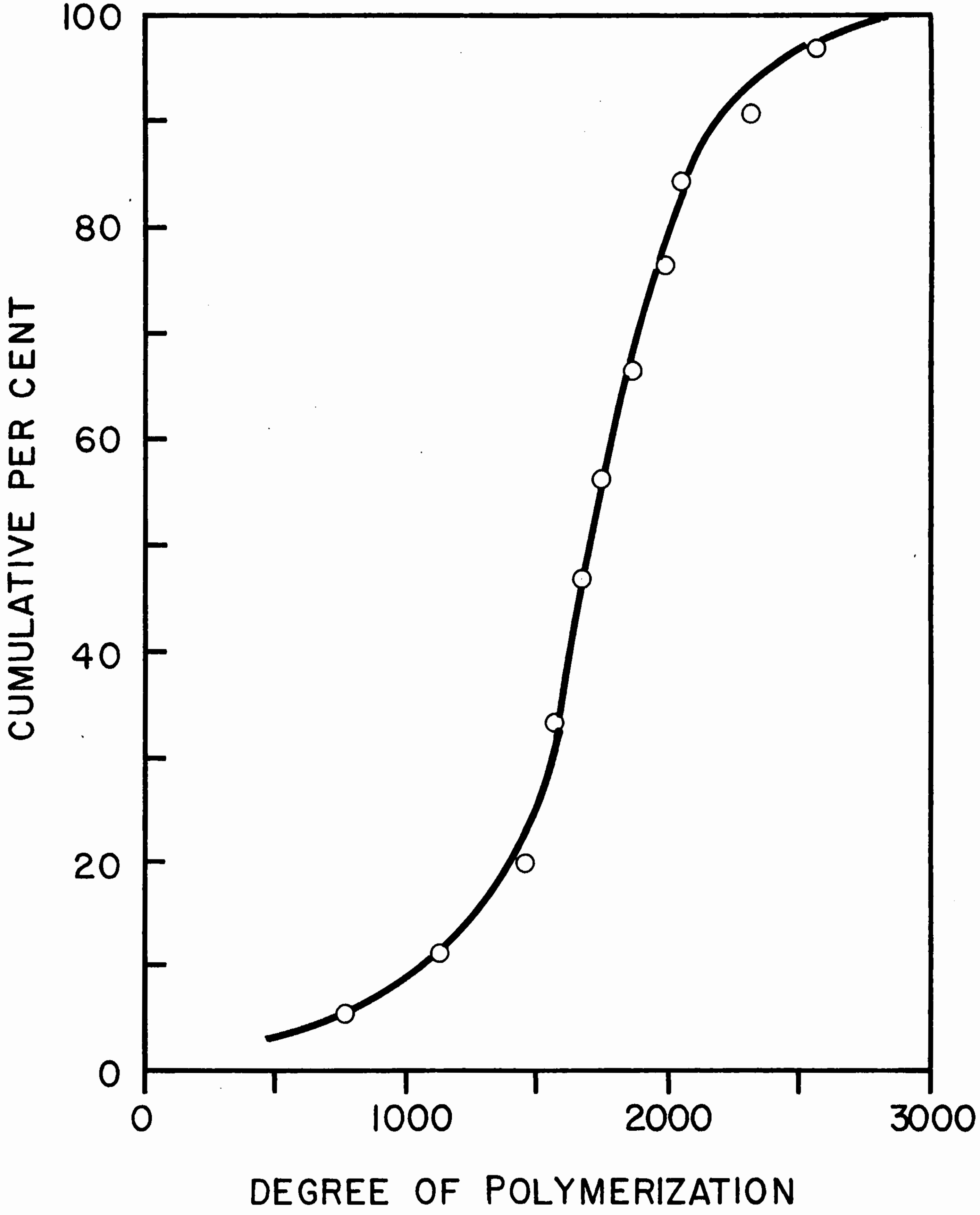

Fig. 7. Acetone-water system. Sample No. 7, containing 13.94% nitrogen.

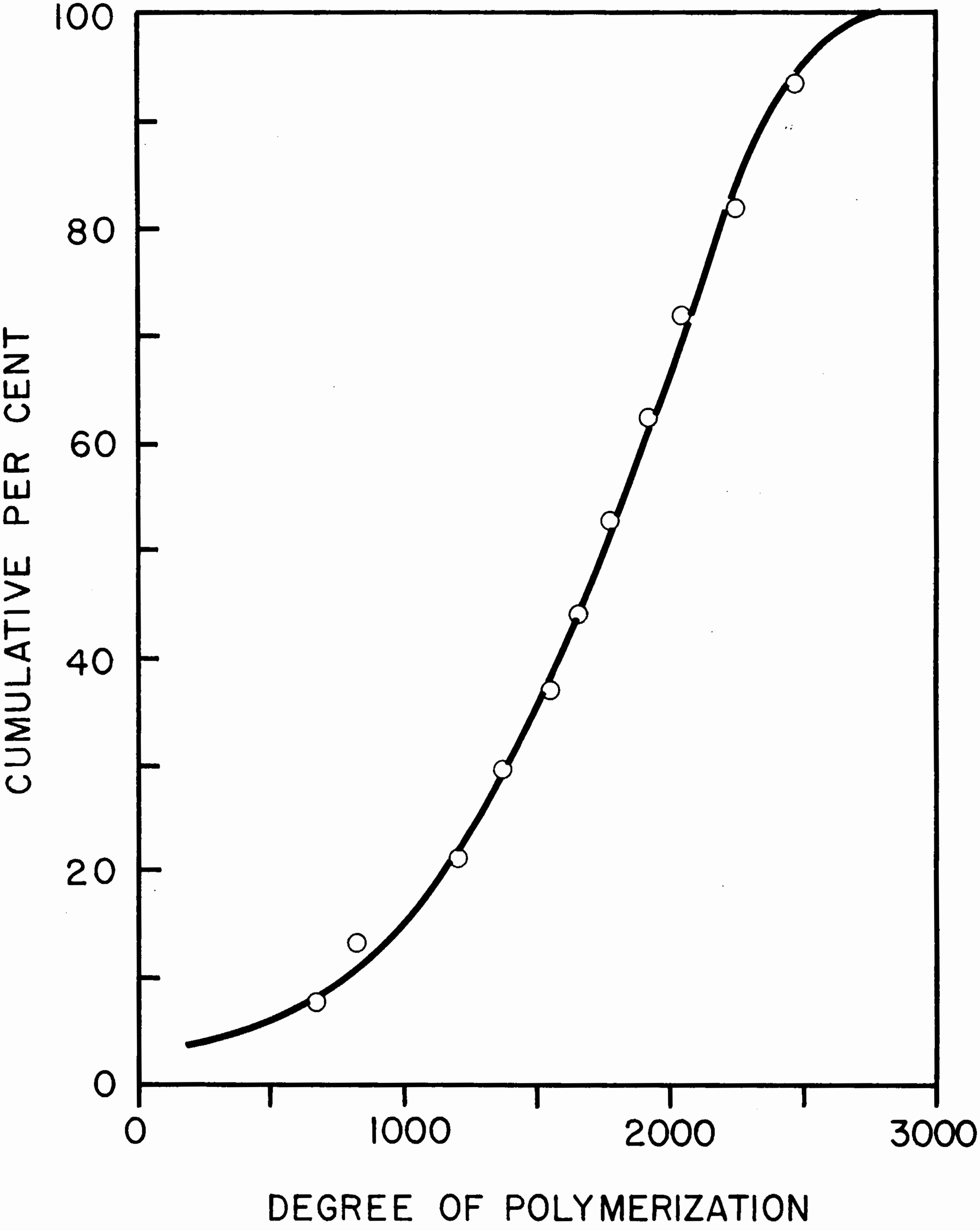

Fig. 8. Acetone-water system. Sample No. 9a, containing 14.14% nitrogen.

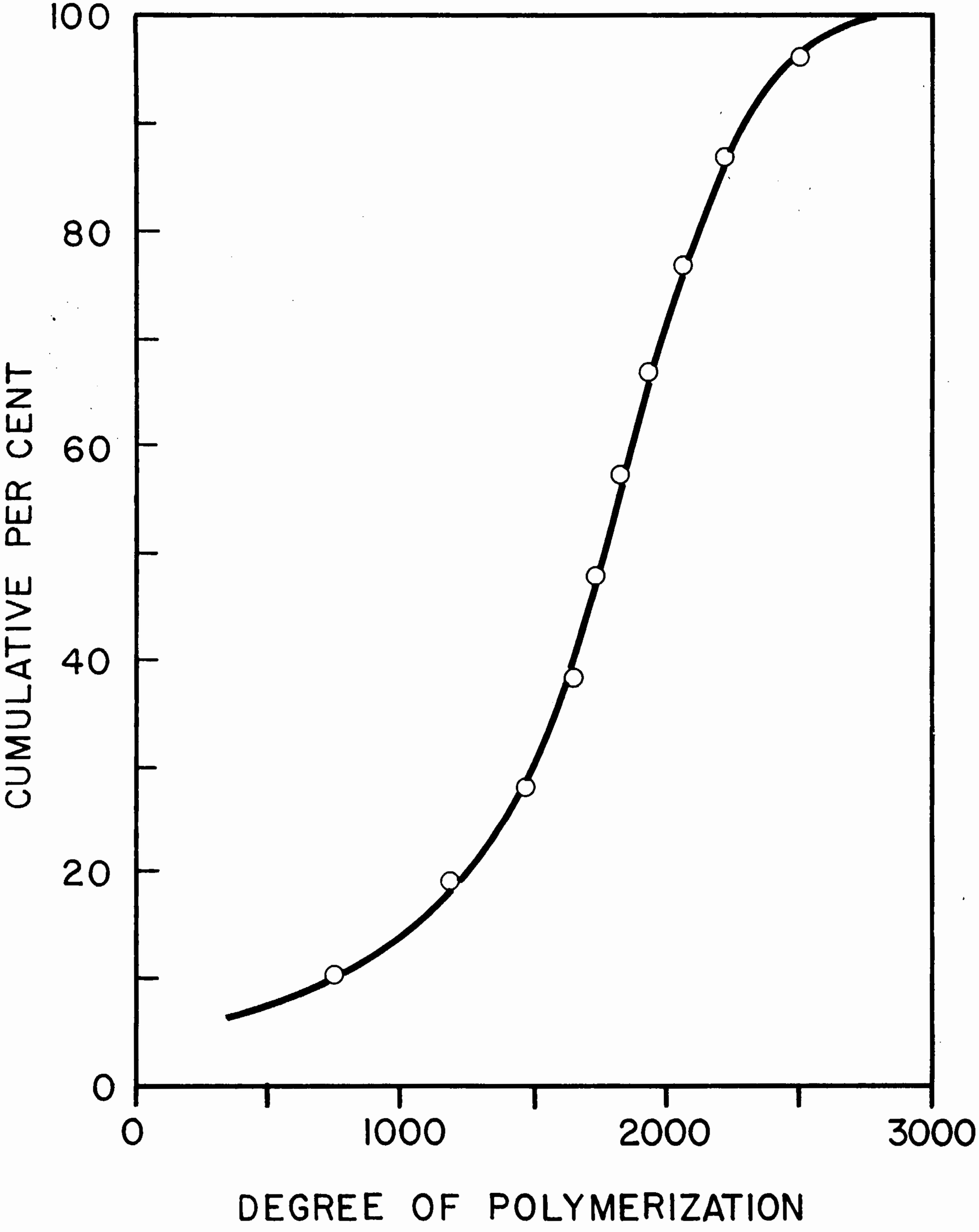

Fig. 9. Acetone-water system. Sample No. 9b, containing 14.14% nitrogen.

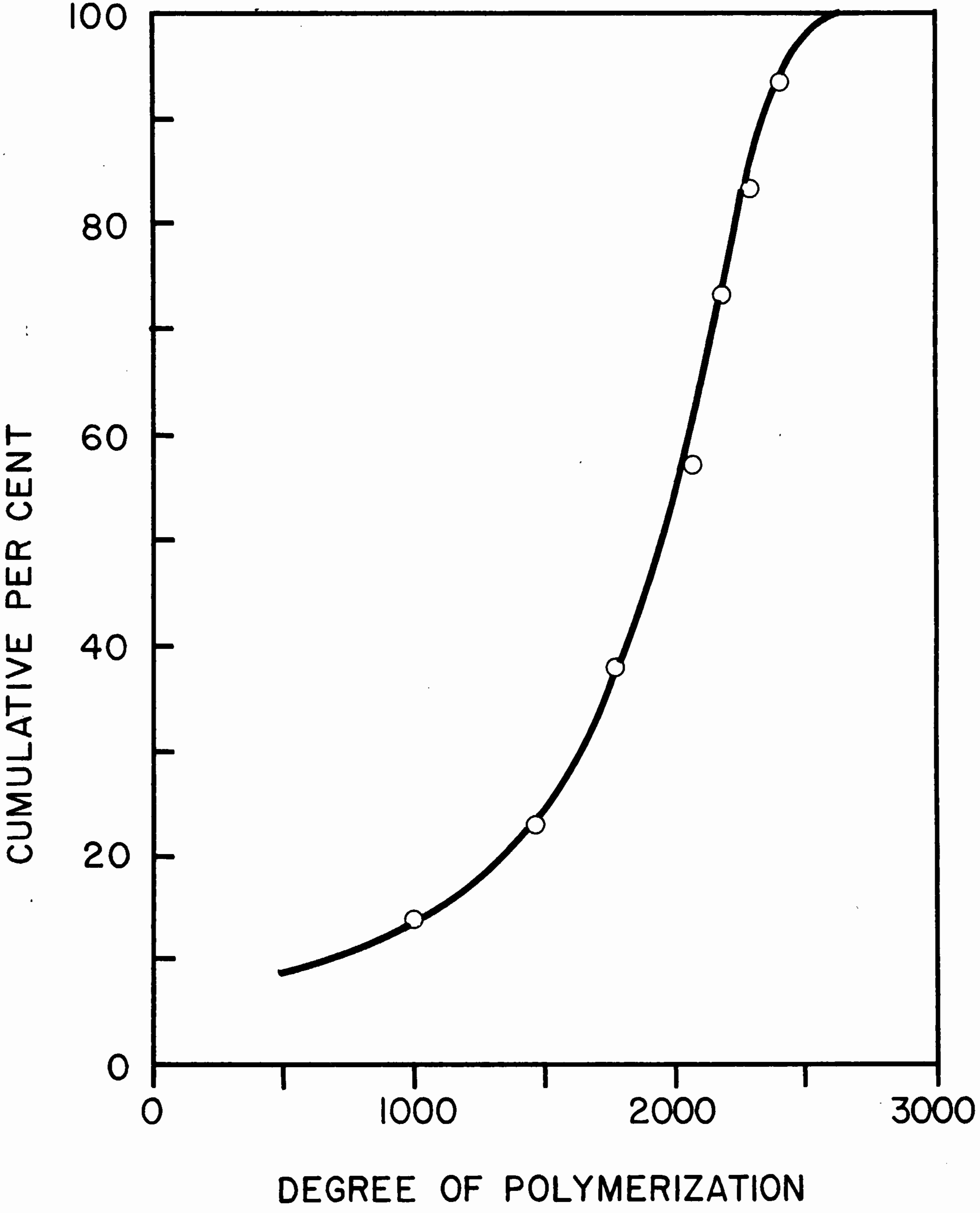

Fig. 10. Acetone-hexane system. Sample No. 1, containing 13.52% nitrogen.

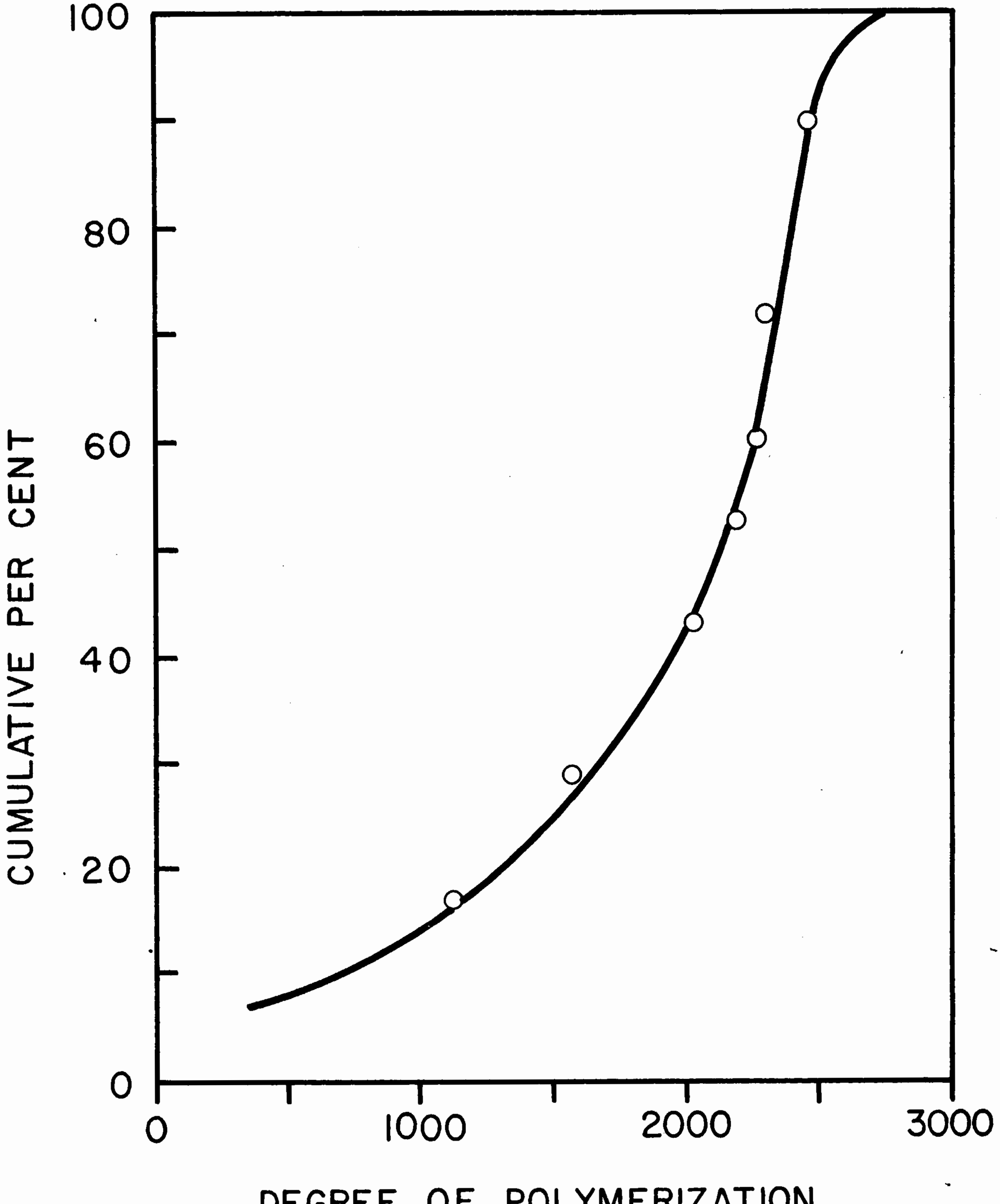

Fig. 11. Acetone-hexane system. Sample No. 5, containing 13.82% nitrogen.

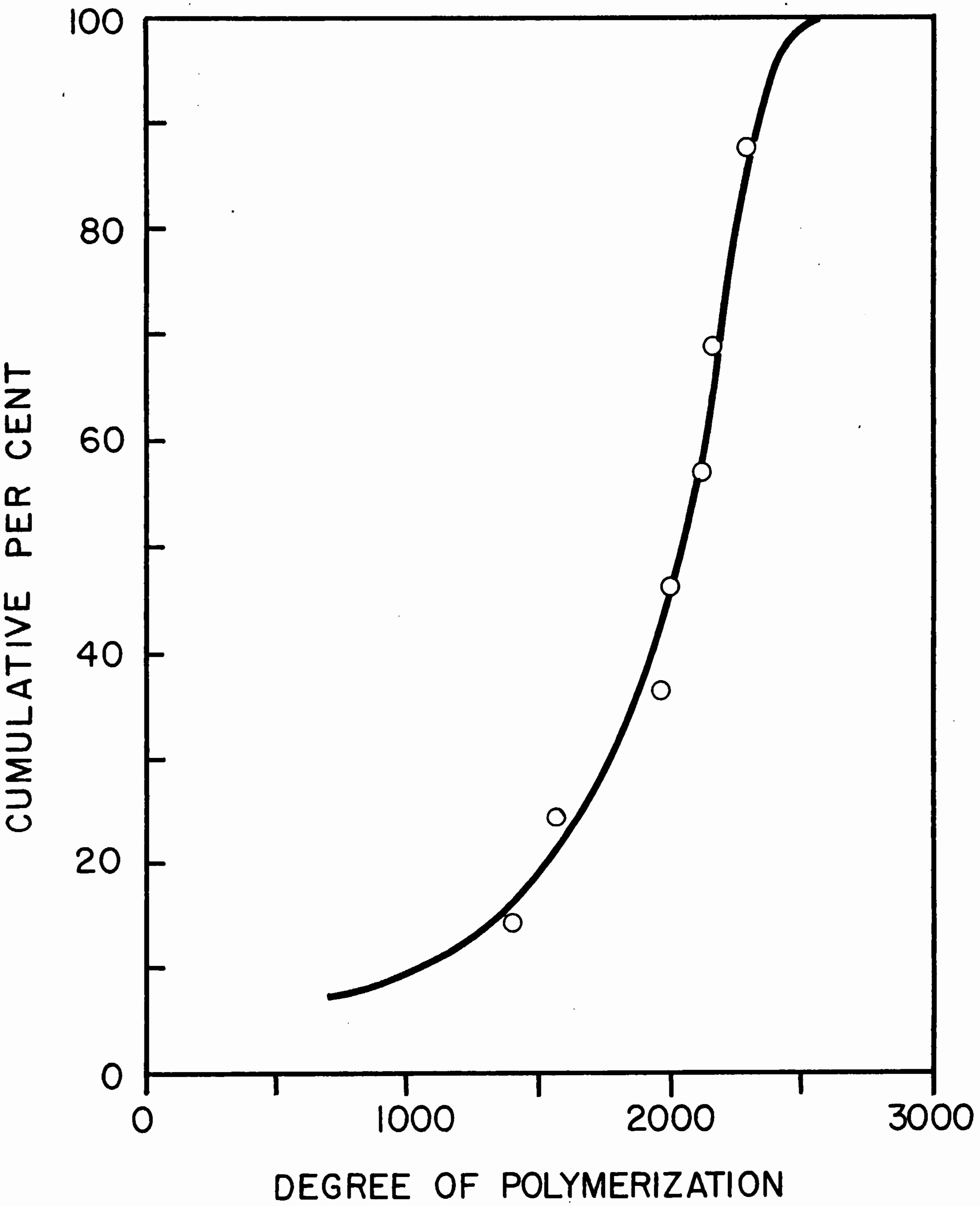

Fig. 12. Acetone-hexane system. Sample No. 6, 13.86% nitrogen.

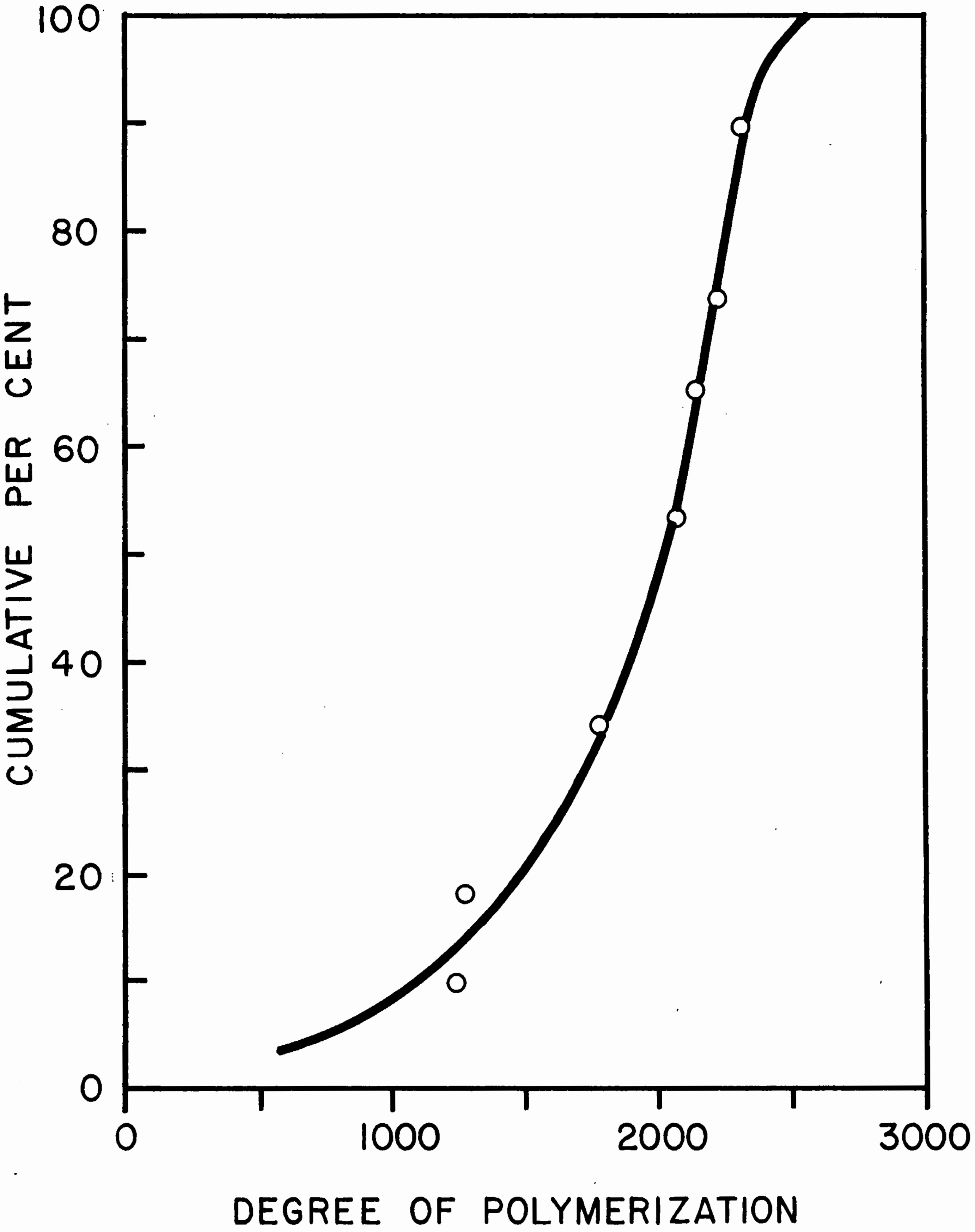

Fig. 13. Acetone-hexane system. Sample No. 7, containing 13.94% nitrogen.

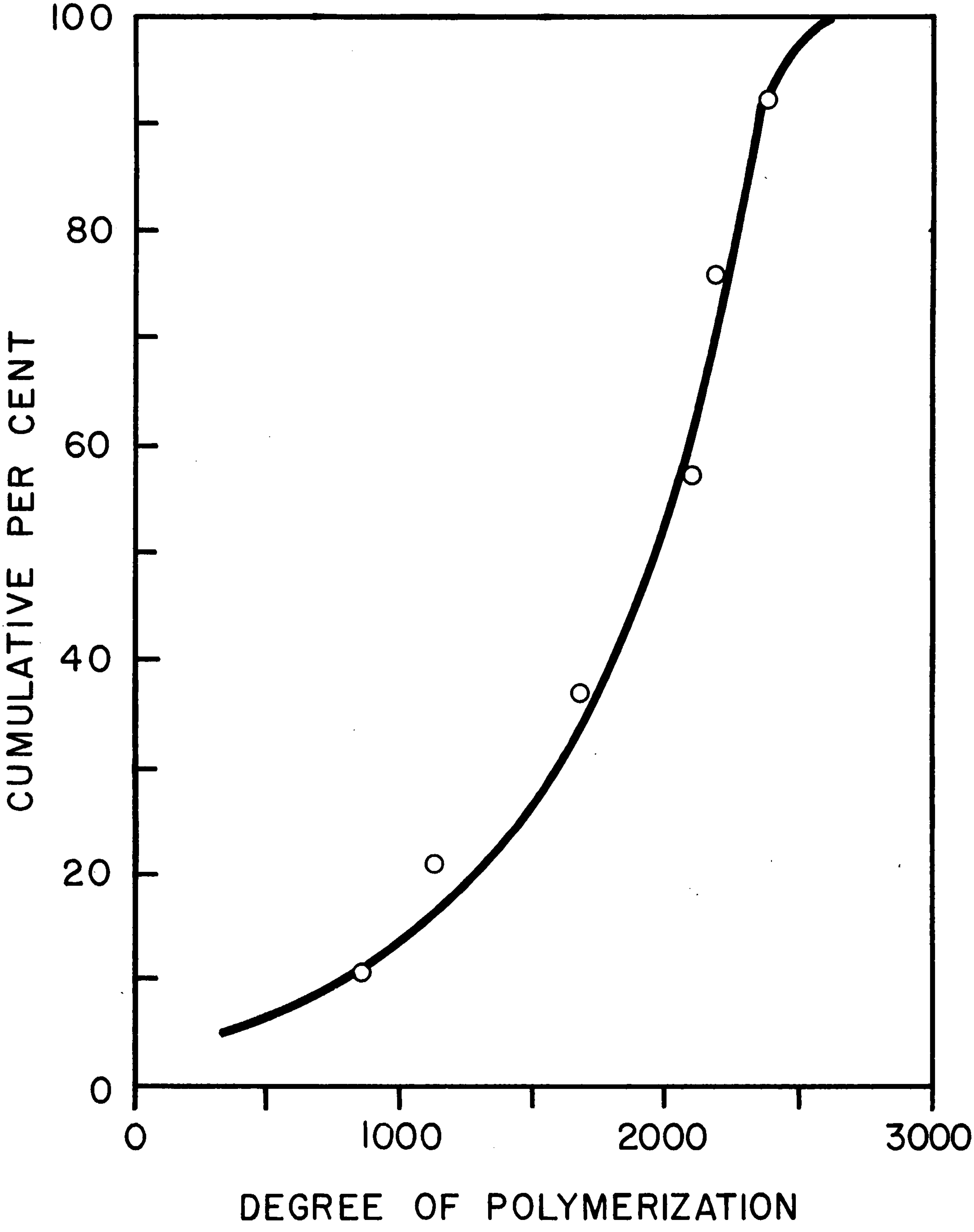

Fig. 14. Acetone-hexane system. Sample No. 8, containing 14.14% nitrogen.

DISCUSSION

The conversion of highly purified celluloses into nitrate derivatives exhibiting a maximum degree of substitution and a degree of polymerization identical with that of the original material is evidently possible by means of the particular nitric acid, acetic acid, acetic anhydride mixture used in the present investigation. Untreated cellulose materials such as raw cotton do not appear to be amenable to this treatment nor can products such as wood meal be successfully nitrated in this way, as is apparent from the study of Brissaud and Ronssin (13). Even a nitrating agent with a much greater swelling action such as the mixture of Alexander and Mitchell requires prolonged time of contact to effect a complete penetration of untreated wood meal (10, 29, 64, 65). The present mixture would accordingly seem very little suited for these specific purposes.

While accordingly limited in application, the nitrating mixture should prove useful in those instances where pure celluloses are studied. The dangerous nature of reagents of this type has probably been much exaggerated in the past. Provided it is made up and applied at a lower temperature, preferably not above 0°C, this mixture, when used fresh, does not seem to involve any special hazards. The preparation of this mixture is both more convenient and more rapid than that of the standard mixture and it also eliminates the possibility of any formation of cross-links through phosphate groups.

The possible influence of the chemical non-uniformity of cellulose nitrates on the results obtained by fractionation of these derivatives has often been mentioned in previous studies (14, 19, 20, 31). Such an influence is to be expected because of the fact that even high-substituted cellulose nitrates seldom if ever possess a distribution of substituent groups that is exactly uniform, that is, the same as that predicted from statistical considerations (66, 67, 68). Such a non-uniformity was found by Cherubin (69) and Smith (14), but was particularly evident from the results obtained by Miller and Timell (15) referred to above. It is apparent from the last-mentioned investigation that when fractionating a cellulose nitrate one should expect the high molecular weight fractions to contain more, and the low molecular weight ones less nitrate groups than the average. Such a trend has indeed often been observed, e.g., by Brown and Purves (22), by Smith (14) and by Timell (20).

The inherent properties of the cellulose nitrate are not the only factors, however, that will determine the course of the fractionation, the nature of the solvent-nonsolvent system applied also being of importance. In the case of the system acetone-water, for example, the solubility of the highly substituted chain molecules decreases with increasing water content at a more rapid rate than is the case with less nitrated molecules, which are more compatible with the water because of their larger content of hydroxyl groups. With water as the precipitant, the first fractions would accordingly be expected to exhibit a higher average degree of substitution than the later ones and in this case the effect of the system will be acting in the same direction as the inherent properties of the polymer.

When using acetone-hexane, the conditions will be different. In this case the highly substituted chains, upon the addition of hexane, would be expected to remain longest in solution due to their hydrophobic character, whereas these chains that contain least nitrate and accordingly most hydroxyl groups should be precipitated first. Here, obviously the effect of the solvent-nonsolvent system will be directly opposite to that of the polymer, the first fractions averaging less nitrate groups than the later ones.

Besides these factors, others will also be operative, such as for example the "reverse-order precipitation" first studied by Morey and Tamblyn (70, 71) and the "tail-effect" recently discussed by Scott (72). The former involves precipitation of a low-molecular weight fraction before a higher one and is probably due to end-group effects. The second phenomenon, which is more often encountered, is a result of the thermodynamic conditions governing all fractionations based on solubility methods, resulting in formation of fractions of increasing instead of decreasing molecular weight during the initial stages of the fractional precipitation. This is due to the inclusion of larger quantities of low-molecular weight material within the first, very high molecular weight fractions than in the later ones, and is caused by the highly swollen state in which these fractions are obtained. Fractionation theories, the more important ones of which have been summarized by Cragg and Hammerschlag (1), by Morey and Tamblyn (70, 71) and by Scott (72), make it clear that complete separation of long and short-chain material cannot be achieved in only one step, but only gradually is approached as the number of fractionation stages is increased. The presence of shorter chains besides the remainder of the material in all fractions obtained on precipitation, but especially in the very first ones, is therefore not an effect of mechanical coprecipitation but a phenomenon inherent in the fractionation itself and therefore impossible to avoid.

It is evident from what has been discussed above that there are many factors tending to complicate the fractional precipitation of cellulose nitrates. Some of these are apparent from the results obtained here. In most cases, as is seen from Tables XII-XXV, the first fraction exhibited a lower degree of polymerization than the next following ones, a result of the above-mentioned "tail-effect". The low-molecular weight material included in this first fraction had a low nitrate substitution and the average nitrogen content of the entire material was therefore also lower than that of the following ones. With this exception, the nitrate substitution decreased with decreasing molecular weights in all cases where water was used as precipitant, which was in agreement with the results obtained previously by Timell (20). The last fraction invariably exhibited a very low nitrogen content, usually 9-10%. This material represented, as had been shown previously by Miller and Timell (15), the most accessible, short-chain portion of the cellulose microfibrils.

With hexane as precipitant the effects on the fractionation of the properties of the nitrate itself and the fractionating system were opposite as was mentioned previously. In this case the trend in nitrogen content of the fractions was therefore less clear. Disregarding the first fraction, there was, however, usually a gradual increase in nitrate substitution with decreasing molecular weight, a phenomenon that was caused by the lower solubility in the acetone-hexane system of the lower substituted chain molecules. At the end of the fractionation the influence of the nitrate distribution of the derivative became predominant, and within the later fractions there was a gradual decrease in nitrogen content with decreasing degree of polymerization. It was rather significant that the final fraction, although not quite as low in nitrogen content as the corresponding ones obtained with water, still was considerably less substituted than any of the others.

If, among the curves obtained with acetone-water, the two pertaining to the trinitrate are considered, it is evident that the chain-length distributions indicated in these two cases are practically identical, thus showing the excellent reproducibility of the fractionation method. In this respect the present investigation thus corroborates the results of Mitchell (34). The S-shaped integral curve follows the experimental points very closely, which is probably partly due to the fact that fractions of approximately the same size were isolated throughout these two experiments in accordance with the recommendations of Doty and Spurlin (73). The frequency weight distribution corresponding to the integral one shows a Gaussian (and accordingly symmetrical) chain-length distribution, extending from an approximate lower D.P. limit of 500 up to an upper one of 2,600.

The weight average degree of polymerization after fractionation was 1,650 and 1,670, respectively, indicating that no depolymerization occurred during the fractionation. The average nitrogen content, however, was only 13.96 and 14.02%. It is evident from the summary presented in Table XXVI that the average nitrogen content of the nitrates, which throughout was estimated on material recovered after viscosity determinations, was somewhat lower after than before fractionation. The weight average degrees of polymerization after fractionation were generally somewhat higher, on the other hand, than the original value of 1,700, especially in those cases where hexane was used as the precipitant. If the nitrate substitution of the material used for estimating the intrinsic viscosity were higher than that which was analyzed for nitrogen, a too high correction factor would be applied to the viscosity, thus resulting in too high D.P. values. It seems clear, therefore, that although a part of the denitration took place during the fractionation, another part undoubtedly occurred during, or after, the viscosity measurements.

TABLE XXVI

Summary of nitrogen contents and degrees of polymerization of cellulose nitrates No. 1-9.

Sample No.	Nitrogen, % Before Fractionation	Nitrogen, % After Fractionation	D.P. After Fractionation
Acetone-Water System			
1	13.52	13.29	1775
2	13.64	13.77	1755
3	13.70	13.63	1630
4	13.76	13.48	1765
5	13.82	13.26	1745
6	13.86	13.43	1750
7	13.94	13.69	1690
9	14.14	14.02	1670
Acetone-Hexane System			
1	13.52	13.37	1800
5	13.82	13.53	1890
6	13.86	13.73	1900
7	13.94	13.87	1865
8	14.14	14.05	1770

A comparison between the seven curves obtained for the partially substituted nitrates with that valid for the trinitrate reveals the rather surprising fact that all of them show the same chain-length distribution, both the position and the character of the integral curves being almost the same throughout. The experimental points are more scattered for the lower substituted specimens and especially for that containing 13.52% nitrogen but this was not entirely unexpected in view of the greater chemical non-uniformity of these samples. The main significance of the results seems to be that the influence of the average nitrate substitution on the results obtained on fractional precipitation of cellulose nitrates is considerably less than has hitherto been assumed, at least as long as a one-stage procedure such as that recommended by the American Chemical Society (34) is applied. From what was mentioned previously it is evident that the nitrogen content must have some effect on the fractionation of a polymer such as cellulose nitrate. The absence of any such influence therefore probably also indicates the rather crude nature of the fractionation procedure.

In some cases, namely those pertaining to samples No. 1, 3, 4, 5 and 6, there is a definite indication of a second inflection prior to the main one, corresponding to a second maximum in the frequency distribution. The fact that no indication of this second maximum was to be found in the curves obtained with the two highest-substituted specimens strongly suggested that the second maximum was an artifact, caused by the greater chemical non-uniformity of the lower-substituted products. Similar phenomena have been encountered elsewhere (64, 65) and show that caution should always be exerted when interpreting results from fractionations of non-uniform high polymers. Such a care has also been urged recently by Doty and Spurlin (73) but seems to have been completely neglected in most previous studies on the chain-length distribution of cellulose.

If the results obtained with acetone-hexane are considered, it is apparent that they were very similar to those noted with acetone-water. The integral curves for the partially-substituted specimens were similar to that obtained with the trinitrate and all of them gave the same distribution as the nine previous ones. As was referred to above, the two solvent-nonsolvent systems differed mainly in the way the nitrates were fractionated chemically. This influence was found to be negligible when water was used and the same results accordingly should be expected with either of the two solvent systems, as was indeed found to be the case. Generally, acetone-hexane appeared to give a less satisfactory separation than did acetone-water; nor did it allow isolation of as many fractions as the latter. These facts, together with the greater experimental difficulties involved, especially in recovering the fractions, would make the decision of Mitchell (34) to give preference to water as the precipitant in the suggested standard method, seem a very wise one.

Summarizing, it might be stated that, provided the average nitrogen content is not below 13.5%, the influence of the latter on the results obtained in applying a one-stage fractional precipitation to cellulose nitrates is negligible. Better and more easily interpreted data, however, are usually observed with high-substituted derivatives and such products should therefore be employed whenever possible.

SUMMARY AND CLAIMS TO ORIGINAL RESEARCH

1. Nitration of cotton linters with nitrogen pentoxide in either nitric acid or carbon tetrachloride did not produce a trinitrate and was accompanied by appreciable depolymerization.

2. Addition of nitrogen pentoxide or boron trifluoride to the standard nitrating mixture composed of nitric acid, phosphoric acid and phosphorus pentoxide did not increase the nitration level.

3. Nitration of purified cellulose with a mixture of nitric acid, acetic acid and acetic anhydride in a weight proportion of 43:32:25 produced a completely-substituted cellulose containing the theoretical maximum amount of nitrogen, 14.14%, with no degradation. An alcoholic extraction was found to be unnecessary in the stabilization stage.

4. The solubility properties of the nitrates prepared by the above procedure were not as favorable as those of nitrates made with the standard mixture, thus indicating the very heterogeneous nature of the esterification in the former case.

The above part of this study has been published in Svensk Papperstidning 58, 281 (1955).

5. As evidenced by the fractional precipitation in duplicate of the cellulose trinitrate, excellent reproducibility was obtained by use of the suggested standard method.

6. Using a system of acetone and water, eight samples of cellulose nitrates, the nitrogen contents of which ranged from 13.52 to 14.14%, were fractionated by the precipitation technique. The nitrate substitution of the fractions decreased with decreasing degree of polymerization. All integral weight distribution curves agreed not only among themselves but also with that found for the trinitrate. The average degree of substitution, and thus the chemical uniformity, accordingly had a negligible effect on the fractionation results.

7. Fractional precipitation of five of the nitrates in a system of acetone and hexane yielded data very similar to those obtained with acetone and water. The results were thus independent of the solvent-precipitant system used. Acetone-water was, however, the preferred solvent-nonsolvent system.

8. Evidence for a second inflection point was present in the integral distribution curves of the samples of lower nitration level. Since this phenomenon was not noticed with the more highly-substituted samples, this additional inflection was judged to be an artifact, caused by the chemical non-uniformity of the samples.

9. Summarizing, it was evident that any cellulose nitrate of approximately the same degree of polymerization as that used in the present study could be used for fractionation purposes if the nitrogen content was above 13.5%. Separation as well as reproducibility improved considerably, however, with increasing nitrate substitution and reached a maximum at the trinitrate level.

The material which is summarized in points 5 through 9 has been published in Svensk Papperstidning 59, 73 (1956).

REFERENCES

1. Cragg, L. H. and Hammerschlag, H., Chem. Rev. 39, 79 (1946).
2. Conrad, C. M., Ind. Eng. Chem. 45, 2511 (1953).
3. Sihtola, H., Paper and Timber (Finland) 30, No. 6, 90 (1948).
4. Wannow, H. A., Melliand Textilber. 30, 519 (1949); Das Papier 5, 75 (1951).
5. Broughton, G., Tappi 37, 61 (1954).
6. Schieber, W., Paper-Fabr. 37, 245 (1939).
7. Atchison, J. E., Paper Trade J. 116, No. 22, 23 (1943).
8. Mitchell, R. L., Ind. Eng. Chem. 38, 843 (1946).
9. Heuser, E., Shockley, W., and Kjellgren, R., Tappi 33, 101 (1950).
10. Jörgensen, L., "Studies on the Partial Hydrolysis of Cellulose", Emil Moestue Als., Oslo, 1950.
11. Heuser, E. and Jörgensen, L., Tappi 34, 443 (1951).
12. Timell, T. E. and Purves, C. B., Svensk Papperstidn. 54, 303 (1951).
13. Timell, T. E., Svensk Papperstidn. 56, 311 (1953).
14. Smith, T. H., Norsk Skogind. 8, 402 (1954).
15. Miller, B. and Timell, T. E., Textile Research J., in press.
16. Wannow, H. A. and Thormann, F., Kolloid-Z. 112, 94 (1949).

17. Roseveare, W. E. and Poore, L., Ind. Eng. Chem. 45, 2518 (1953).

18. Timell, T. E. and Jahn, E. C., Svensk Papperstidn. 54, 831 (1951).

19. Timell, T. E., Svensk Papperstidn. 58, 1 (1955).

20. Timell, T. E., Svensk Papperstidn. 58, 234 (1955).

21. Meffroy-Biget, A. M., Bull. soc. chim. France No. 4, 458 (1954).

22. Brown, R. K. and Purves, C. B., Pulp Paper Mag. Can. 48, No. 6, 100 (1947).

23. Scherer, P. C. and Masuelli, F. J., Rayon and Synthetic Textiles 30, No. 2, 47 (1949).

24. Scherer, P. C. and Rouse, B. P., Rayon Text. Monthly 29, No. 8, 55 (1948).

25. Rosenthal, A. J. and White, B. B., Ind. Eng. Chem. 44, 2693 (1952).

26. Sihtola, H. and Svedberg, The, Acta Chem. Scand. 2, 474 (1948).

27. Wannow, H. A., Kolloid-Z. 102, 29 (1943).

28. Lindsley, C. H. and Frank, M., Ind. Eng. Chem. 45, 2491 (1953).

29. Timell, T. E., Pulp Paper Mag. Can. No. 7, 10 (1955).

30. Schulz, G. V. and Kömmerling, I., Makromol. Chem. 9, 25 (1952).

31. Abadie, F. A., Norsk Skogind. 7, 68 (1953).

32. Harland, W. G., J. Textile Inst. 45, T692 (1954).

33. Riiber, O., Norsk Skogind. 9, 204 (1955).

34. Mitchell, R. L., Ind. Eng. Chem. 45, 2526 (1953).

35. Timell, T. E., Ind. Eng. Chem. 47, 2166 (1955).

36. Alexander, W. J. and Mitchell, R. L., Ind. Eng. Chem. 21, 1497 (1949).

37. Berl, E. and Rueff, G., Cellulosechem. 14, 115 (1933).

38. Berl, E., Ind. Eng. Chem., Anal. Ed., 13, 322 (1941).

39. Staudinger, H. and Mohr, R., Ber. 70, 2296 (1937).

40. Jullander, I., "Studies on Nitrocellulose", Arkiv. kem. Min. Geol. 21A, No. 8, Stockholm, 1945.

41. Harland, W. G., J. Textile Inst. 45, T678 (1954).

42. Gralèn, N., "Sedimentation and Diffusion Measurements on Cellulose and Cellulose Derivatives", Uppsala, 1944.

43. Golova, O. P. and Ivanov, V. I., "Über das Molekulargewicht der Zellulose", Akadamie Verlag, Berlin, 1953.

44. Cope, W. C. and Barab, J., J. Am. Chem. Soc. 39, 504 (1917).

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

46. Newman, S., Loeb, L., and Conrad, C. M., J. Polymer Sci. 10, 463 (1953).

47. Timell, T. E., Svensk Papperstidn. 57, 777 (1954).

48. Niederl, J. B. and Niederl, V., "Micromethods of Quantitative Organic Elementary Analysis", Sec. Ed., John Wiley and Sons, New York, 1942, pp. 199-202.

49. Fontaine, T. D., Ind. Eng. Chem., Anal. Ed., 14, 77 (1942).

50. Sookne, A. M. and Harris, M., J. Research Nat. Bur. Standards 26, 205 (1941).

51. Vollmert, B., Makromol. Chem. 6, 78 (1951).

52. Dalmon, R., Chédin, J., and Brissaud, L., Compt. rend. 201, 664 (1935).

53. Bouchonnet, A., Trombe, F., and Petitpas, G., Bull. soc. chim. France (5) 4, 500, 894 (1937).

54. Timell, T. E., Svensk Papperstidn. 57, 913 (1954).

55. Dalmon, R., Compt. rend. 201, 1123 (1935).

56. Chédin, J. and Fénéant, S., Compt. rend. 229, 115 (1949).

57. Chédin, J. and Tribot, A., Bull. assoc. ind. papetière 5, 435 (1951).

58. Chédin, J., Kolloid-Z. 125, 65 (1952).

59. Chédin, J. and Tribot, A., Mim. services chim. état (Paris) 36, 31 (1951).

60. Timell, T. E., Svensk Papperstidn. 57, 844, 913 (1954).

61. Hermans, P. H., "Physics and Chemistry of Cellulose Fibres", Elsevier Publishing Company, New York, 1949, pp. 91-95.

62. Schulz, G. V., Z. phys. Chem. B46, 137 (1940); B47, 155 (1940).

63. Brissaud, L. and Ronssin, S., Bull. assoc. tech. ind. papetière 4, 107 (1953).

64. Snyder, J. L. and Timell, T. E., Svensk Papperstidn. 58, 889 (1955).

65. Timell, T. E., Svensk Papperstidn., in press.

66. Spurlin, H. M., Trans. El. Chem. Soc. 73, 95 (1938).

67. Spurlin, H. M., J. Am. Chem. Soc. 61, 2222 (1939).

68. Spurlin, H. M., in Ott, E., Spurlin, H. M., and Grafflin, M., eds., "Cellulose and Cellulose Derivatives", Part II, Interscience Publishers, New York, 1954, pp. 673-712.

69. Cherubin, G., Bull. soc. chim. France 2, 1992 (1954).

70. Morey, D. R. and Tamblyn, J., J. Phys. Chem. 50, 12 (1946).

71. Morey, D. R. and Tamblyn, J., J. Phys. and Colloid Chem. 51, 721 (1947).

72. Scott, R. L., Ind. Eng. Chem. 45, 2532 (1953).

73. Doty, P. M. and Spurlin, H. M., in Ott, E., Spurlin, H. M., and Grafflin, M., eds., "Cellulose and Cellulose Derivatives", Part III, Interscience Publishers, New York, 1955, pp. 1134-1188.