Preparation of Cellulose Triacetate and Cellulose Tricarbanilate by Nondegradative Methods

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Synopsis

A method for obtaining triacetate having a D.S. of 3.0 has been obtained by acetylating the cellulose with acetic anhydride-pyridine reagent containing a catalytic amount of acetyl chloride. The process is rapid and nondegradative. Cellulose tricarbanilate can be prepared without recourse to pyridine solutions by using dimethylformamide (DMF) as solvent and triethylenediamine (1,4-diazobicyclo[2.2.2]octane) as catalyst. The DMF solution of the cellulose tricarbanilate can be cast directly into films or the polymer easily recovered owing to the solubility of the reaction solvent and impurities in water.

INTRODUCTION

The usual method for cellulose acetate preparation is to subject cellulose to the action of acetic anhydride and sulfuric acid using glacial acetic acid as solvent. The resulting cellulose acetate sulfate triester is then desulfated to give a cellulose acetate of high D.S. (about 2.8). For higher-D.S. material, the partially deacetylated cellulose is again acetylated using perchloric acid as catalyst.[1] Although the reacetylation can be done with a minimum of degradation (depolymerization), the initial preparation of the cellulose acetate by the sulfuric acid method does cause degradation of the cellulose. Other methods of acetylating cellulose or its derivatives without reduction in the D.S. were found desirable; hence, other methods for acetylation were studied.

In a previous communication, the authors reported that dimethylformamide (DMF) containing a catalytic amount of triethylenediamine (1,4-diazobicyclo[2.2.2]octane) provided a method for rapidly converting cellulose derivatives to carbanilates.[2] This technique has been extended to the preparation of cellulose tricarbanilates in excellent yields using cellulose from three sources.

EXPERIMENTAL

All experiments were replicated at least three times in order to verify yields and procedures. Elemental analyses were performed by Schwartzkopf Microanalytical Laboratory. All chemicals and reagents were ACS reagent grade unless otherwise indicated.

Cellulose Source.   Gel cellophane prepared as previously described[2] was used for the low molecular weight material.   Cellulose from bleached wood pulp purified by the method of Rapson[3] was used for the intermediate-D.P. cellulose, and 80 × 80 bleached cotton print cloth was employed as the high-D.P. cellulose.   All cellulose materials were ground in a Wiley mill to 60 mesh dried at 78°C and 0.02 mm Hg prior to use.

Preparation of Films.   The polymer (1.5–2 g) is dissolved in the appropriate solvent and cast onto clean mercury as previously described.[2]

Degree of Polymerization (D.P.).*   The D.P.'s of the cellulose acetate samples were determined by hydrolysis of acetate group in DMSO–acetone (1:2).[8]   The intrinsic viscosities were measured in $1.0M$ cupriethylene-diamine, and the number-average degree of polymerization was estimated from D.S. $= ([\eta] \times 75.26)^{1.105}$, where $[\eta] = 13.3 \times 10^{-5} (M_n)^{0.905}$.   The cellulose monomer molecular weight (M_n) was taken as 162.

Acetyl Value.*   The sample was dissolved in 90/10 V/V methylene chloride–methyl alcohol and cast onto glass.   The resulting film was dried and scanned at 120°C using a P.E. 21 IR spectrophotometer with a NaCl prism.   The elevated temperature scan served to minimize interference from water/or residual acetic acid.

Residual Free Acid.*   The free acetic acid in the sample was determined by titration.

Cellulose Triacetate.   Thirty grams of finely ground (60 mesh) cellophane (or 12 g alpha-cellulose from wood pulp) previously dried at 110°C for 24 hr was added to a 1000-ml three-neck flask fitted with condenser and drying tube (Dririte) and mechanical stirrer.   DMF, 400 ml, 50 ml anhydrous pyridine, 50 ml acetic anhydride, and 2 ml acetyl chloride were added.   The solution was heated to 80°C.   An additional 50 ml acetic anhydride was added, and the solution was heated for 20 hr at 95°C.   The deep yellow-brown mixture was poured in a fine stream into a mixture of 95% ethanol and ice (1:1) with agitation.   Extra ice may be added to maintain the temperature below 30°C.   The nicely white fibrous material was suction filtered and air dried.   Purification can be effected by dissolving in the minimum volume of chloroform or methylene dichloride and precipitation into 95% ethanol in a Waring blender or by Soxhlet extraction for 24 hr with 95% ethanol.

Cellulose Tricarbanilate.   Finely ground (60 mesh) cellophane, 12 g (or 5 g alpha-cellulose from wood pulp or 2 g cotton cellulose), is added to a 1000-ml three-neck flask fitted with condenser and drying tube (Dririte) and mechanical stirrer previously dried at 110°C for 24 hr.   DMF, 500 ml, is added along with 300 mg triethylenediamine (practical grade).   The mixture is heated to 95–100°C, and 37 ml phenyl isocyanate is slowly added over 30 min (with a dropping funnel).   The solution is homogeneous within 30–60 minutes.   After 8 hr, the tan-brown solution is poured into 2000 ml boiling water to decompose the phenyl isocyanate and precipitate the

product. The fibrous product is suction filtered (Buchner funnel), slurried with 300 ml warm (30°C) 95% ethanol for 1 hr, and refiltered. Further purification can be accomplished by Soxhlet extracting the fibrous material with 95% ethanol. If films are desired from the higher-D.P. celluloses, the hot solution is diluted with DMF to a workable viscosity and/or concentration, and after cooling it it cast directly onto mercury. The films obtained upon evaporation of the solvent must be Soxhlet extracted with 95% ethanol to remove impurities. This procedure is suggested since the high-D.P. tricarbanilates (i.e., from wood pulp and cotton cellulose) redissolve with difficult y once they are precipitated and air dried.

DISCUSSION

Cellulose Triacetate

If only pyridine and acetic anhydride are employed to acetylate the cellulose, essentially no reaction takes place. Upon addition of a small amount (2 ml) of acetyl chloride, acetylation rapidly occurs and the cellulose dissolves. Apparently the reaction rate of cellulose hydroxyls with acetyl chloride is many times that of acetic anhydride. After reaction of acetyl chloride with cellulose, the hydrochloric acid which is formed may regenerate more acetyl chloride through a transesterification reaction; hence the acetylation reaction can continue. Such a mechanism has been proposed by Haskins and Schulze to explain the catalytic effect of pyridine hydrochloride in reactions of anhydrides.[5] After the cellulose has obtained a sufficient degree of substitution to dissolve in the reaction medium, it is quite likely that esterification of the cellulose hydroxyls by pyridine-catalyzed acetic anhydride occurs in addition to esterification by acetyl chloride. Since very little free HCl is present during the course of the reaction, no degradation (depolymerization) of the cellulose takes place. This was confirmed by intrinsic viscosity measurements which showed no change in the cellophane samples within the precision of the measurement (Table I). The results for wood pulp show a decrease in degree of polymerization; however, gels were noted in both the solutions and films for the acetylated wood pulp and may be due to incomplete solubilization of the higher molecular weight cellulose acetates. Since both cellophane and

TABLE I
Properties of Cellulose Acetate from Cellophane and Wood Pulp

Sample	Degree of Polymerization	Combined acetic acid	Free HAc, %
Wood pulp	618		
CTA from wood pulp	470	61.6	0.057
Cellophane	193 ± 10		
CTA from cellophane	211 ± 11	61.8	0.049

wood pulp were treated similarly, it would be expected that a change in D.P. to a third that of the original sample would have been readily measured in the cellophane. The smaller D.P. of cellophane ensured easy dissolution in the solvents employed. The average degree of polymerization of commercial cellulose acetate is about 200–300, which is much less than that of the purified wood pulp employed in this study.

Cellulose triacetate from both wood pulp and cellophane was found by infrared techniques to be highly acetylated having combined acetic acid values of nearly 99%. By elemental analysis, the samples had the requisite percentages for a cellulose triacetate of D.S. = 3. The slightly lower combined acetic acid values for the triacetate from wood pulp are quite likely due to the fact that the carbonyl and carboxyl groups which are formed during the purification procedures used for wood pulp do not form esters with acetic acid.

Both samples were found to have very little free acetic acid.

Cellulose Tricarbanilates

Phenyl isocyanate has been shown to react completely with all the free hydroxyls of cellulose[6] and to be quite resistant to hydrolysis in both alkali and acidic media.[7] The usual procedure calls for the use of pyridine as the reaction medium; however, this complicates the resulting purification and prohibits the direct solution casting of films from the reaction mass. Past work from this laboratory has shown that carbanilation of cellulose derivatives could be accomplished using DMF with triethylenediamine catalyst.[2] This mixture was found to also be an effective reaction medium for the direct carbanilation of cellulose. Further, films could be cast directly from the reaction mixture for the high molecular weight celluloses. We found that once the high-D.P. celluloses were carbanilated and recovered by precipitation from the reaction mixture, they resisted attempts to redissolve them, often giving gels. As the D.P. of the cellulose source increases, it is necessary to reduce the amount of cellulose which can be reacted due to viscosity problems.

Recovery of the cellulose carbanilate is obtained by pouring the reaction mixture into boiling water which destroys the excess phenyl isocyanate by converting it to aniline and carbon dioxide which, along with the catalyst, are water soluble.

When the hot water-washed tricarbanilate prepared from cellophane is solvent cast into films, a highly crystalline brittle film is obtained which has unusual crystallization patterns (Fig. 1). If the tricarbanilate is extracted in a Soxhlet with ethanol prior to film formation, the highly crystalline film is not obtained. Instead, the usual clear film was produced. Recovery of the extract from the ethanol showed it to have very nearly the same melting point as the extracted carbanilate (279° versus 281°C). Evidently, the cellophane contains some low-D.P. material which can act as points around which crystallization can occur. For example, when 100 mg cellobiose octaphenylcarbamate (mp 272–284°C) was dissolved with 1.5 g ethanol-
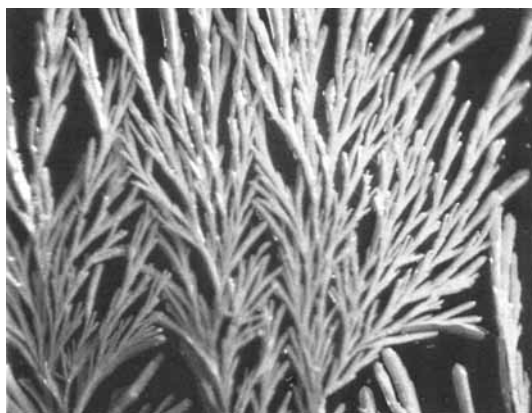
(a)

(b)

Fig. 1. Crystallization patterns obtained during film casting with non-Soxhlet-extracted cellulose tricarbanilate prepared from cellophane: (a) 100×; (b) 40×.

extracted cellulose tricarbanilate and cast onto mercury, a slightly opaque film was obtained.

The three benzene rings provided by the phenylurethane group enable an accurate determination of the degree of substitution to be estimated from the elemental analysis. Except for the tricarbanilate from wood pulp, the analysis was essentially the same as theory (Table II). Again, the effect of carboxyl and carbonyl groups in reducing the possible degree of substitution may be responsible for the lower analysis. The slightly lower carbon analysis for the cotton samples may be due to effects of bleaching which can form

TABLE II
Elemental Analysis for Cellulose Acetate and Tricarbanilates
Prepared from Various Cellulose Sources

Sample	Elemental analysis, %		
	C	H	N
Cellulose triacetate			
$C_{12}H_{16}O_8$			
Theory	50.0	5.6	
Cellophane	49.8	5.6	
Wood pulp	49.8	5.5	
Cellulose tricarbanilate			
$C_{27}H_{25}O_8N_3$			
Theory	62.4	4.9	8.1
Cellophane	62.4	5.0	8.1
Wood pulp	61.2	5.1	
Cotton	62.1	4.8	7.8

oxycellulose and/or result in carboxylation of some of the hydroxyl groups. Cellulose tricarbanilates made from cellophane can be solution cast into films from acetone. For higher-D.P. cellulose carbanilates, DMF was found to provide better results.

SUMMARY

Cellulose triacetate and cellulose tricarbanilates in which all available hydroxyl groups are substituted have been prepared by new methods. Since the reactions are nondegrading, they may be employed as blocking or covering groups or for converting the cellulose into easily soluble derivatives. In the case of the carbanilates, it is possible to solution cast films directly from the reaction medium. Low molecular weight fractions may cause the film to be highly crystalline unless these material are removed prior to film casting.

References

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