

The Dissolution of Cellulose in Anhydrous Chloral/ Aprotic Solvents

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Synopsis

Two new approaches toward the chemical modification and rapid dissolution of cellulose pulp in aprotic solvents containing chloral are presented. In the first method, cellulose pulp is water activated and then solvent exchanged prior to the addition of chloral. In the second method, cellulose pulp is heated in refluxing solvent and then cooled to ambient temperature before the addition of chloral. The methods do not entail the use of catalysts but require the preactivation of the pulp prior to treatment with chloral. Clear solutions obtained by the water activation-solvent exchange method were cast into films, and after washing with water the product was soluble in a variety of organic solvents including acetone. IR and NMR (^1H and ^{13}C) analyses as well as chemical analyses led to the conclusion that a cellulose chloral hemiacetal with a DS of 2.2 is initially formed which then slowly decomposes upon standing at 23°C to a relatively stable hemiacetal of DS 0.4. Complete regeneration to cellulose results upon standing for an extended period or treatment with 1 N acetic acid at 80°C , 1 N HCl at 50°C , 0.5% NH_4OH or 0.1 N NaOH at 23°C . When solutions, obtained by the hot solvent activation method, were coagulated in water at ambient temperature, regenerated cellulose was obtained. In both methods, little or no degradation of the regenerated cellulose resulted.

INTRODUCTION

Considerable interest in the commercial utilization of cellulose has recently been emphasized as a result of petroleum shortages and high prices. Although cellulose is the most abundant replaceable organic raw material in the world, the transformation of cellulose to many end-use applications has been limited, mainly because of its unique physical properties and complex morphology. Cellulose itself does not melt, and, because of the presence of strong hydrogen bonding in both its crystalline and amorphous regions, cellulose dissolves in few solvents, most of which are multicomponent inorganic or organic solvents. Therefore, the search for a convenient solvent system for cellulose is the key to many potential end-use applications where dissolution followed by coagulation (spinning, molding, etc.) would lead to many useful products.

The dissolution of cellulose pulp in polar aprotic solvents containing anhydrous chloral is not new.¹⁻⁷ In 1971, it was reported in a patent by Nakao and Yamazaki² that cellulose and its graft copolymers dissolved in a number of polar aprotic solvents in the presence of 5-10 mol anhydrous chloral/anhydroglucose residue, depending on the solvent used. A number of polymers were also soluble in the cellulose solution, and spinning and film casting of polymer-cellulose solutions were successfully carried out. A major drawback to this method of dissolution, however, was that complete cellulose dissolution was slow, requiring several weeks.

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Other investigators have reported on the use of catalysts to enhance the dissolution of cellulose in anhydrous chloral/aprotic solvents. Thus, Okajima and co-workers^{3,4} employed several organic amines, such as pyridine, tripropylamine, and triethylamine, as catalysts. With these catalysts, dissolution of cellulose was rapid, especially with Et₃N, to give highly colored solutions. Clermont and Manery⁵ also utilized pyridine for enhancing the rate of cellulose dissolution in a chloral/DMF mixture. In their work, a cellulose/chloral/pyridine/DMF solution was prepared in about 18 h and then acetylated with acetic anhydride under various conditions to give reaction products containing both acetyl groups and chlorine in yields up to 35% acetyl and 38% chlorine at 70°C.

Tepteleva⁶ investigated the reaction of free hydroxyl groups in cellulose acetate with chloral in various solvents and reported that DMF was a poor reaction medium. However, in a previous report,⁷ chlorinated cellulose acetate products were obtained containing up to 17% chlorine by undergoing the reaction in methylene chloride, acetic acid, or benzene media.

It is apparent that the chloral/aprotic solvent system for cellulose has not, thus far, been attractive as a possible commercial system for the production of fibers, films, or other shaped cellulosic products, mainly because of the requirement for the presence of catalysts or of the length of time for cellulose dissolution. Both of these factors would necessarily render this system quite costly.

In the present work, modified methods of cellulose solution preparation in anhydrous chloral/aprotic solvent mixtures are presented, which do not require the use of catalysts and which effect the dissolution of cellulose in several hours. Furthermore, the nature and properties of the cellulose derivative formed in the dissolution process are characterized by infrared spectroscopy and both proton and ¹³C Fourier transform (FT) NMR spectroscopy as well as scanning electron microscopy.

EXPERIMENTAL

Materials

A prehydrolyzed kraft bleached pulp (ITT Rayonier Cordenier-J-LV grade) with a DP of 500 was Abbé cut into a finely powdered form and used in most of the study. Avicel PH-105 microcrystalline cellulose from FMC was also used in some solution preparations.

The aprotic solvents, dimethyl formamide (DMF), dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), and *N*-methyl-2-pyrrolidone (NMP) were used as supplied from Aldrich. Anhydrous chloral was reagent grade. All the halogeno carbonyl and halogeno cyano compounds were purchased from Aldrich.

Chlorine Analysis

Chlorine analyses were conducted by the Schöniger method⁸ using a Thomas-Ogg "Infrared Igniter" apparatus manufactured by Arthur H. Thomas Co., Philadelphia, PA, or by microcombustion at Childers Laboratories, Milford, NJ.

Spectroscopic Analyses

Infrared spectra were run on a Perkin-Elmer Grating Infrared Spectrophotometer, Model 521 at ambient temperature.

NMR analyses were conducted as follows:

A 3.7/23.3/73.0 Cordenier-J-LV/ CCl_3CHO /DMF solution was coagulated in water in a Waring blender, and the product suction filtered, washed with water, squeezed, and redissolved in acetone. A film was cast from the solution and the acetone evaporated with a stream of nitrogen. The dried film (ca. 0.21 g) was redissolved in 3 mL acetone- d_6 in a 10-mm NMR sample tube, and the proton NMR spectrum was run on a JEOL FX-90Q (90 MHz) pulsed FT-NMR spectrometer, operated at a frequency of 89.56 MHz and interfaced to a Texas Instruments data acquisition and processing computer system. The spectral width was 1,000 Hz with 8K real data points in the transformed spectra. The observed spectrum (Fig. 5) was obtained after eight accumulations after an excitation pulse corresponding to a "flip angle" of 25° . Chemical shifts were determined relative to tetramethylsilane (TMS).

The ^{13}C NMR spectra of a 3.7/23.3/73.1 Cordenier-J-LV/chloral/DMF solution as well as that of the coagulated film of the cellulose-chloral derivative as described above are displayed in Figures 6 and 7, respectively. The NMR spectra were recorded on the same spectrometer, operated at 22.5 MHz and spectral width of 5,000 Hz. The observed spectra were obtained after 62,000 and 9,065 accumulations, respectively, each after an excitation pulse corresponding to a "flip angle" of 45° . Chemical shifts were determined relative to the ^{13}C chemical shift of TMS carbon (0 ppm).

Scanning Electron Microscopy (SEM)

SEM photographs were taken on an AMR scanning electron microscope model 1000A. Samples were coated; with 100 Å of gold/palladium.

Preparation of Cellulose/Chloral/Aprotic Solvent Solutions

(A) The following procedure is representative of the dissolution of cellulose pulp in chloral/aprotic solvent system by the water activation-solvent exchange method. The same procedure was also followed in the investigation of halogeno carbonyl and halogeno cyano compounds in DMAc solution for dissolving cellulose pulp.

Abbé-cut Cordenier-J-LV pulp (0.5 g, 3.09 mmol) was slurried in 20 g water for 5 min, suction filtered, rinsed with 20 mL DMAc, squeezed with a rubber diaphragm for 5 min, and then transferred to a beaker containing 20 mL DMAc. After soaking for 30 min in the DMAc, the pulp was filtered through a sintered glass funnel, squeezed as before for 10 min, and weighed. The activated and solvent exchanged pulp was then stirred into a solution of 8 g (54.2 mmol) anhydrous chloral in a total of 20 g DMAc. The mixture was stirred for 18 h at 23°C to give a clear and viscous cellulose/chloral/DMAc solution of composition 1.8/28.1/70.2 by weight. The solution could be cast into films or coagulated into flakes in a Waring blender using water as coagulant. The films were partly transparent and were analyzed by infrared spectroscopy after thorough washing in a water bath to remove residual chloral and DMAc. The IR spectrum shown in Figure 1 displays a strong absorption peak at 810 cm^{-1} indicative of a group containing a carbon atom bonded to more than one chlorine atom.⁹

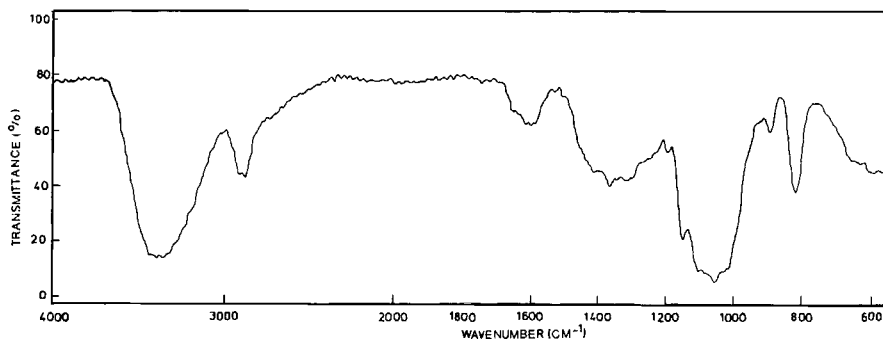


Fig. 1. IR spectrum of cellulose chloral hemiacetal film.

(B) The following procedure is typical of the dissolution of cellulose pulp in chloral/aprotic solvent system by the hot solvent activation technique.

Abbé-cut Cordenier-J-LV pulp (1.0 g, 6.17 mmol) was heated in 39.9 g refluxing DMF for 30 min. The slurry was cooled to ambient temperature, then treated with anhydrous chloral (9.1 g, 61.7 mmol, 10M excess on cellulose), and stirred at 23°C. Dissolution of the pulp took place in 30 h to form a clear solution of composition 2.0/18.2/79.8 by weight. Regeneration of the solution in water results in the complete regeneration of cellulose.

Determination of Degree of Substitution (DS)

A freshly coagulated film (0.39 g) obtained from a 3.4/27.2/69.4 Cordenier-J-LV/chloral/DMF solution, prepared by the water activation-solvent exchange method, was soaked in 0.1 N NaOH solution for 10 min. Effervescence was noted. The film was washed with dilute H₂SO₄ solution for 1 min, then with water, and finally air-dried to give an opaque film weighing 0.13 g. IR (KBr pellet) analysis of the film indicated the absence of the 810 cm⁻¹ absorption peak (Fig. 8). The DS was calculated by the following expression:

$$DS = \frac{(\text{wt cellulose derivative}) - (\text{wt regenerated cellulose})}{\frac{\text{wt regenerated cellulose}}{162} \times \text{mol wt chloral}}$$

RESULTS AND DISCUSSION

The process of cellulose dissolution in organic or inorganic solvent systems to form either underivatized or derivatized cellulose solutions involves two separate and distinct stages. The first is an activation stage wherein the cellulose pores are opened up and rendered accessible to the solvent system. In the second stage, the actual process of dissolution and/or derivatization takes place.¹⁰

With this concept in mind, new approaches toward the chemical modification and dissolution of cellulose pulp in anhydrous chloral/aprotic solvent systems were developed. Thus, when cellulose pulp was previously activated in water, solvent-exchanged in a polar aprotic solvent such as DMF, DMAc, NMP, or DMSO, and then added to a solution of anhydrous chloral in one of the above-mentioned solvents, dissolution was achieved at room temperature in a few hours, depending on the concentrations of cellulose and chloral in the mixture. Cel-

lulose/chloral/DMF solutions of up to 6.4% cellulose of DP 500 were prepared by this method. Optimization of cellulose concentration in this solvent system was not investigated. It was found, however, that a critical chloral/cellulose molar ratio of 4 was necessary to effect the dissolution of the pulp in the chloral/DMF system, although molar ratios above 4 were found to give better results. Table I lists the various systems studied, the conditions of the experiment, and the results obtained.

An alternative method for the activation of cellulose pulp involves treatment of the cellulose in refluxing aprotic solvent for 30 min, followed by cooling to ambient temperature. Upon addition of anhydrous chloral to the activated pulp slurry, dissolution occurs over a period of 30 h.

Both the water activation-solvent exchange and the hot solvent activation methods for cellulose dissolution in chloral/aprotic solvent offer significant advantages. In the first place they are rapid and secondly do not require the presence of a catalyst which would add to the complexity and overall cost of recovery and recycle of the components of the solvent system.

The cellulose/chloral/aprotic solvent system could be coagulated in the form of films or fibers in aqueous media, such as water, aqueous acetic, hydrochloric, and sulfuric acids, saturated sodium bisulfite, and ammonium hydroxide solution, and also in hexane. Solvents such as methanol, cyclohexanol, dichloromethane, and chloroform were unsuccessful in coagulating the cellulose.

The infrared spectra of the films obtained from the cellulose/chloral/aprotic solvent systems which were prepared by the water activation-solvent exchange method and coagulated in water displayed a strong absorption peak at 810 cm^{-1} , which was attributed to a group containing a carbon atom linked to more than one chlorine atom⁹ (Fig. 1). The coagulated product was soluble in methanol, isopropanol, acetone, and tetrahydrofuran, but insoluble in chloroform and dichloromethane. For example, when the product was taken into acetone, a colorless and viscous solution was obtained which could be cast into a film after

TABLE I
Summary of Experimental Conditions for Dissolving Activated Cellulose Pulp^a in Chloral/
Aprotic Solvents

Solvent	Composition of cellulose/chloral/solvent	[Chloral]/ [cellulose]	Method ^b	Result
DMF	3.7/23.3/73.0	7.0	A	Dissolution in 30 h
DMF	3.4/27.2/69.4	4.4	A	Dissolution in 48 h
DMF	4.0/14.8/81.2	4.0	A	Dissolution in 48 h
DMF	4.2/11.5/84.3	3.0	A	No dissolution
DMF	4.4/7.8/87.6	2.0	A	No dissolution
DMF	6.4/29.3/64.2	5.0	A	Dissolution in 48 h
DMF	5.3/23.8/65.9	6.0	A	Dissolution in 24 h
DMSO	3.3/26.3/70.4	4.4	A	Dissolution in 48 h
DMAc	1.8/28.1/70.2	17.6	A	Dissolution in 48 h
Acetone	2.7/42.4/54.9	17.0	A	No dissolution
MeNO ₃	2.0/16.3/81.6	8.8	A	No dissolution
DMF	2.0/18.2/79.8	10.0	B	Dissolution in 30 h
DMF	2.2/9.1/88.7	4.5	B	Dissolution in 1 week

^a Abbé-cut prehydrolyzed kraft bleached pulp (Cordenier-J-LV), DP 500.

^b Method A: water activated, solvent exchanged pulp; method B: hot solvent activation.

evaporation of the acetone with a stream of air. Upon standing for a few minutes at ambient temperature, the films became insoluble in acetone and their IR spectra displayed a weaker 810 cm^{-1} absorption peak, indicating that significant decomposition had taken place (Fig. 2).

It is clear that a cellulose-chloral derivative with a high degree of substitution (DS) is initially formed which subsequently and spontaneously decomposes to a lower DS derivative upon standing. An established criterion for dissolution of cellulose derivatives in organic solvents is that the DS is usually 2 or more. Thus in the present system a DS of about 2 would be expected.

Analysis for chlorine content by the Schöniger method⁸ of a film obtained from the coagulation in water of a 3.4/27.2/69.4 Cordenier-J-LV/chloral/DMF solution gave a value of $41.5 \pm 1.8\%$ of chlorine. The DS of the initially formed cellulose derivative was determined by alkaline hydrolysis in 0.1 N NaOH solution and calculated to be about 2.2. Assuming that the cellulose derivative is the chloral hemiacetal with a DS of 2.2, the theoretical chlorine content would have been 48.2%. The discrepancy between theoretical and experimental values could be attributed to the rapid rate of decomposition of the initially formed derivative during the film casting procedure. The lower DS derivative obtained upon standing is stable for at least 1 week and consists of 17.85% chlorine, which corresponds to a DS of 0.36. An SEM micrograph of the latter film shows rod shaped particles on a smooth background (Fig. 3). The surface structure of an Abbé-cut Cordenier-J-LV pulp fiber is also displayed in an SEM micrograph (Fig. 4).

The hemiacetal structure was also studied by ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectrum of the cellulose derivative in acetone- d_6 solution (8% by weight) is shown in Figure 5.

The main features of the spectrum are supportive of a cellulose hemiacetal structure. Thus the signal centered at 3.16 ppm is assigned to the seven methine and methylene protons as well as the hydroxyl groups of the cellulose chloral hemiacetal. The signals centered at 5.18 and 5.28 ppm are attributed to the protons of the hydrate, dimer, and polymer of chloral. Two cellulose hemiacetal protons appear as doublets centered at 6.58 ppm ($J = 7\text{ Hz}$), while the third hemiacetal proton occurs at 7.70 ppm. The integrated intensity of the latter signal is calculated to be approximately 16% of the signals at 6.58 ppm which corresponds to a DS of 0.32, which adds up to a total of 2.32 substituted sites per anhydroglucose moiety.

The structure of the cellulose derivative was further investigated by consid-

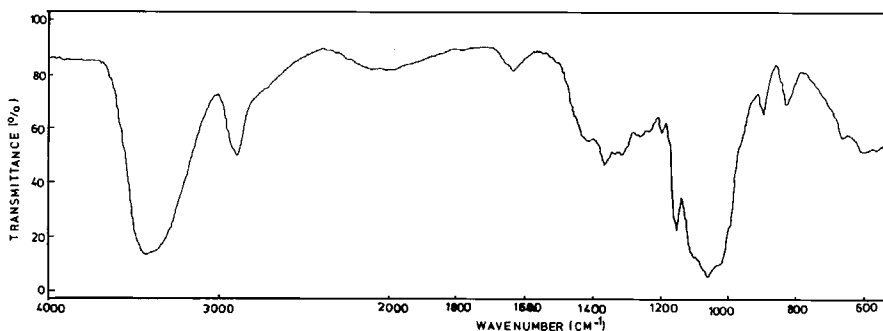


Fig. 2. IR spectrum of partially hydrolyzed cellulose chloral hemiacetal film.



Fig. 3. Scanning electron micrograph of the partially hydrolyzed cellulose chloral hemiacetal film. The featured platelets probably represent unevenly hydrolyzed domains.

ering the ^{13}C NMR spectra of a 3.7/23.3/73.0 Cordenier-J-LV/chloral/DMF solution, prepared by the water activation-solvent exchange method, and that of a cellulose chloral hemiacetal film dissolved in acetone- d_6 , as shown in Figures 6 and 7, respectively. The chemical shifts of the ^{13}C absorptions of the cellulose/chloral/DMF solution are presented in Table II. Peak assignments were designated by comparison with the ^{13}C shifts of underivatized cellulose in *N*-methylmorpholine-*N*-oxide/DMSO solution, hydroxymethyl cellulose prepared by the dissolution of cellulose in paraformaldehyde/DMSO,¹¹ and the use of standard tables of ^{13}C chemical shifts.¹² The important features of the spectrum in Figure 6 are the signals at 96.326 and 98.005 ppm due to the trichloromethyl carbons, and the signals at 101.526 and 100.335 ppm due to the pseudoanomeric carbons of the hemiacetal derivative.

The ^{13}C NMR spectrum of the cellulose chloral derivative in acetone- d_6 solution, in contrast to that of cellulose/chloral/DMF solution is simple (Fig. 7). The peaks due to excess chloral and DMF solvent are virtually absent which excludes the possibility of the presence of free chloral on the cellulose causing solubilization. On the other hand, the spectrum does not distinctly show the characteristic peaks of the anhydroglucose unit, but displays quite clearly the carbon atoms of the trichloromethyl group in the cellulose hemiacetal at 96.492 ppm.

These spectra support the proposed structure of a hemiacetal derivative with one chloral unit attached to each of C-6, C-2, and C-3 to varying degrees of substitution. These results are similar to those obtained by Gagnaire, Mancier, and

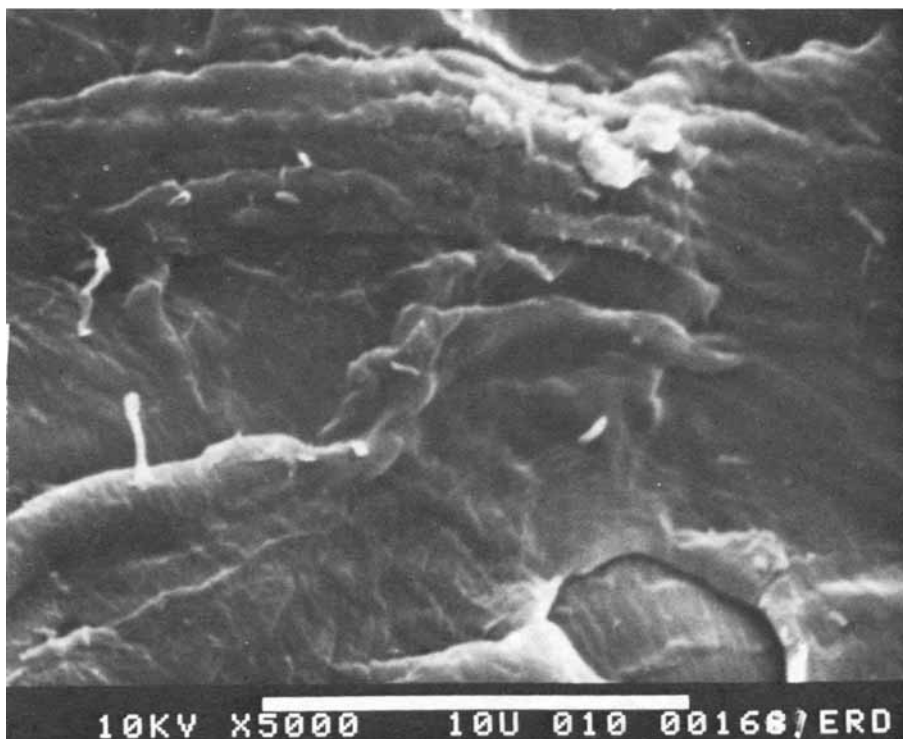


Fig. 4. Scanning electron micrograph of prehydrolyzed kraft pulp (Abbé-cut Cordenier-J-LV grade).

Vincendon in their study of the ^{13}C spectrum of a cellulose/ $(\text{CH}_2\text{O})_x$ /DMSO solution,¹¹ in which they concluded that the methylol derivative was a statistical derivative mainly substituted on C-6 with some substitution occurring at C-2 and C-3. They also pointed out that substitution occurred at C-6 by polyoxy-methylene units. Similar conclusions were reached by Baker, Schroeder, and Johnson in their investigation of the ^1H NMR spectrum of hydroxymethyl cellulose triacetate, prepared from the acetylation of cellulose/ $(\text{CH}_2\text{O})_x$ /DMSO solutions.¹³ In the present chloral system, however, there is no evidence for a similar polyoxytrichloromethylene unit on the cellulose chain.

It was observed that when the cellulose/chloral/aprotic solvent solutions, prepared by the water activation-solvent exchange method, were coagulated in 1 N acetic acid solution at 80°C , 1 N HCl solution at 50°C , or 0.5% NH_4OH solution at 23°C , and the product analyzed by IR, the peak at 810 cm^{-1} was absent, indicating that complete regeneration had taken place (Fig. 8). In contrast, when a cellulose/chloral/aprotic solvent solution, prepared by the hot solvent activation method is coagulated in water, cellulose is regenerated. The difference in the nature of the coagulated cellulose is probably due to the increased accessibility of the cellulose upon activation via the water activation-solvent exchange method as opposed to the hot solvent activation method. These observations have significant consequences with respect to recovery and recycle of the components of the system, particularly chloral. The feasibility of recovery and recycle of chloral is a critical factor for any possible commercial application of this system. Guinot has patented a process for the extraction and dehydration of chloral from its aqueous solutions in which a series of liquid-vapor extractions is conducted.¹⁴

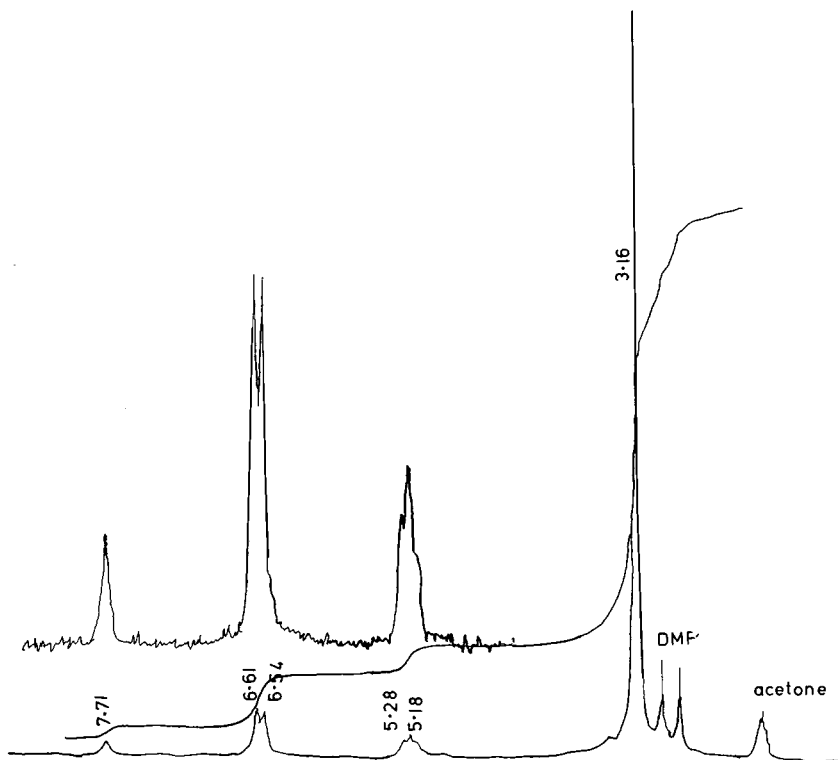


Fig. 5. ¹H NMR spectrum of cellulose chloral hemiacetal in acetone-d₆ solution.

Although chloral is used in a wide range of applications,¹⁵ there are some factors associated with its use that could present some drawbacks. In the first place, a corrosion problem exists with the chloral/aprotic solvent system which would require increased capital investment to install corrosion resistant equipment. Secondly, the inclusion of chloral as a Schedule IV "Controlled and Dangerous Substance" by the Drug Enforcement Administration could have an adverse effect on the potential commercial use of this system, despite the relatively low cost of chloral.

The reaction of cellulose with chloral to form the corresponding hemiacetal can be rationalized by the presence of the strong electron-withdrawing trichloromethyl group alpha to the aldehyde carbonyl group of chloral. Thus the strong inductive effect of the CCl₃ group would render the carbonyl carbon positive and therefore susceptible to attack by the cellulose hydroxyl oxygen atoms.

Extending this line of reasoning to other related systems, a series of halogeno carbonyl and halogeno cyano compounds was investigated in aprotic solvents for dissolving cellulose pulp. Thus, hexachloroacetone, α,α -dichloroacetophenone, 2,6-dichlorobenzaldehyde, *N,N*-dichlorourethan, chloroacetonitrile, trichloroacetonitrile, 2,6-dichlorobenzonitrile, and trifluoroacetamide dissolved in an aprotic solvent were investigated for dissolving water activated-solvent exchanged cellulose pulp (Table III). Of all the systems investigated, only chloral in DMF, DMAc, NMP, or DMSO solution was successful in dissolving cellulose. However, *N,N*-dichlorourethan, Cl₂NCO₂C₂H₅, gave a cellulose derivative containing 0.36% N and 0.22% Cl and displayed a weak IR absorption peak at 1710 cm⁻¹.

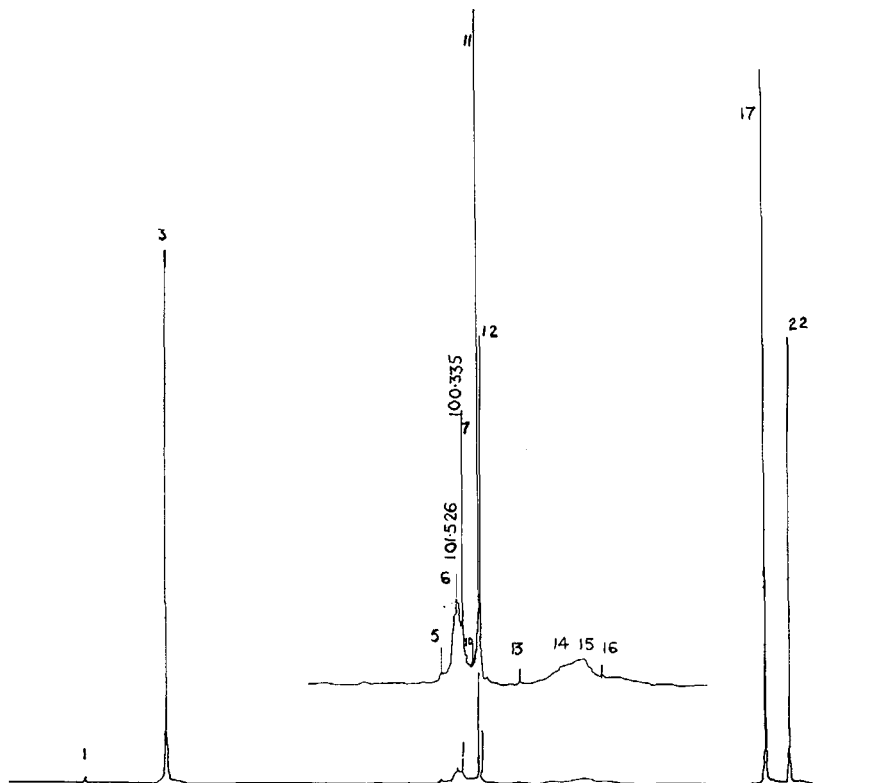


Fig. 6. ^{13}C NMR spectrum of a 3.7/23.3/73.0 cellulose/chloral/DMF solution.

CONCLUSIONS

New and improved methods are presented describing the chemical modification and dissolution of cellulose pulp in anhydrous chloral/aprotic solvent mixtures. Chemical and spectroscopic (IR and ^1H and ^{13}C NMR spectroscopy) investigations indicate that the water activated-solvent exchanged cellulose reacted with chloral to give the corresponding hemiacetal, initially with a DS

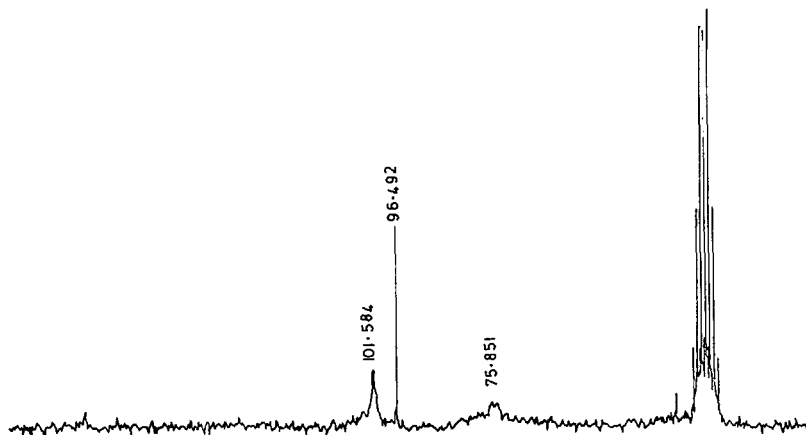
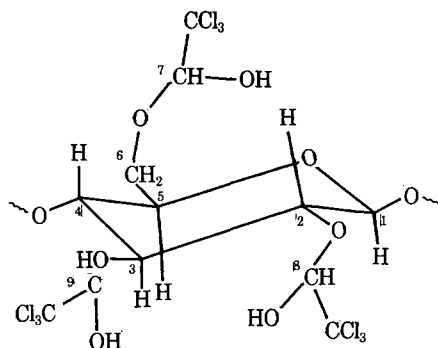


Fig. 7. ^{13}C NMR spectrum of cellulose chloral hemiacetal in acetone- d_6 solution.

TABLE II
 ^{13}C NMR Chemical Shifts of Cellulose/Chloral/DMF Solution



Peak no.	Chemical shift (ppm)	Assignment
1	179.863	Excess CCl_3CHO in solution
3	162.906	$(\text{CH}_3)_2\text{NCHO}$ solvent
5	104.777	C-1 of substituted anhydroglucose unit
6	101.526	C-1 of unsubstituted anhydroglucose unit superimposed on C-9 hemiacetal pseudoanomeric carbon
7	100.335	C-7,8 hemiacetal carbons (pseudoanomeric)
10	98.005	CCl_3 carbon of cellulose derivative
11	96.922	Excess CCl_3CHO in solution
12	96.326	CCl_3 carbons of cellulose derivative
13	88.091	Polychloral
14	79.586	C-4 of anyhydroglucose unit
15, 16	70.809–75.089	C-2,3,5 of substituted and unsubstituted anhydroglucose unit
	ca. 60–65	C-6 of substituted and unsubstituted anhydroglucose unit
17	36.246	$(\text{CH}_3)_2\text{NCHO}$ solvent
22	31.100	$(\text{CH}_3)_2\text{NCHO}$ solvent

of ca. 2.2, which then slowly decomposed upon standing at ambient temperature to a hemiacetal of DS ca. 0.4. Complete regeneration to cellulose resulted upon standing for several days or treatment with 1 N acetic acid at 80°C or 0.5% NH_4OH solution. When a solution of cellulose/chloral/aprotic solvent, prepared by the hot solvent activation method, is coagulated in water, cellulose is regenerated. The difference in the nature of the coagulated cellulose is attributed

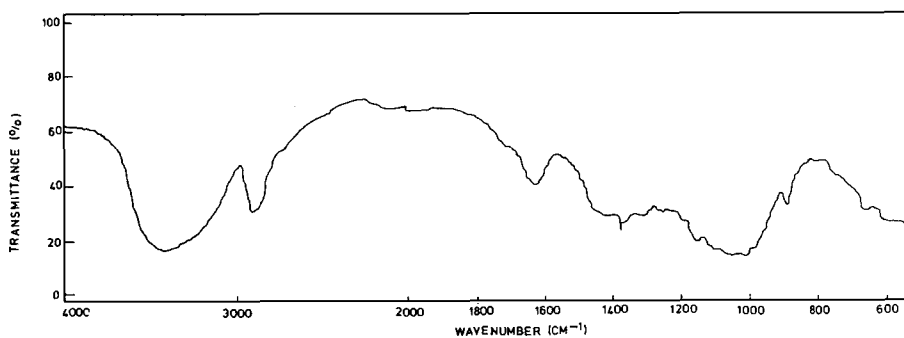
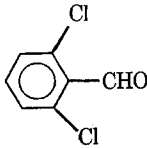
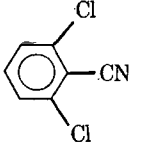


Fig. 8. IR spectrum of completely hydrolyzed cellulose chloral hemiacetal (KBr pellet).

TABLE III
Summary of Various Halogeno Carbonyl and Cyano Compounds/Aprotic Solvents for Dissolving Activated Cordenier-J-LV Pulp

Halogeno comp	Solvent	Composition	$\frac{\text{mol halogeno cpd.}}{\text{mol cellulose}}$	Observations
$(\text{CCl}_3)_2\text{CO}$	DMF	3.2/30.2/66.6	5.9	No dissolution
$\text{Cl}_2\text{HCCOC}_6\text{H}_5$	DMAc	2.0/16.2/81.7	7.0	No dissolution
$\text{Cl}_2\text{NCOOC}_2\text{H}_5$	DMAc	2.1/13.9/84.0	7.0	No dissolution
	DMAc	2.1/15.2/82.7	7.0	No dissolution
	DMAc	2.0/15.0/83.0	7.0	No dissolution
Cl_3CCN	DMAc	2.1/13.2/84.7	7.0	No dissolution
ClCH_2CN	DMAc	3.3/29.6/66.1	20.1	No dissolution
CF_3CONH_2	DMAc	3.4/27.2/69.4	11.8	No dissolution
CF_3CONH_2	DMSO	3.4/27.6/69.0	11.8	No dissolution

to differences in the accessibility of the cellulose as a result of the two methods of activation.

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