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Iodine catalyzed esterification of cellulose using reduced levels of solvent ☆

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Abstract

We have developed a novel process for esterification of cellulose with acetic anhydride in the presence of a catalytic amount of iodine to produce cellulose triacetate. At room temperature, 12 h was required for complete esterification which was reduced to 10 min when the reaction was conducted at 100 °C. The production of cellulose triacetate and the degree of substitution was confirmed by NMR analysis and by titration. Both reaction temperature and the amount of iodine influenced the amount of cellulose converted to CTA as well as the molecular weight of the product. Careful characterization of the cellulose triacetate produced in the iodine catalyzed esterification revealed the presence of small amounts of acetylated carbohydrate oligomers which acted as a plasticizer for the cellulose triacetate.

Keywords: Cellulose; Cellulose triacetate; Cellulose tripropionate; Acetic anhydride; Iodine

1. Introduction

Few polymers can boast such a long pedigree as cellulose acetate (CA). In 1865, Schutzenberger reacted cellulose in sealed tubes at 180 °C with acetic anhydride and is generally attributed with the discovery of cellulose acetate. But it was not until 1904, when Miles found that partially saponified triacetate was soluble in acetone, that the commercial feasibility was recognized. In 1919, Brothers Henri and Camille Dreyfus introduced the first cellulose based yarn to the market, called Celanese (Treiber, 1985). Commercial production of cellulose esters has continued until this day.

Cellulose acetate is typically prepared using wood pulp which is a renewable resource. At degrees of substitution (DS) less that about 2.5 and under appropriate conditions cellulose acetate is biodegradable (Buchanan, Gardner, & Komarak, 1993; Gardner et al., 1994; Komarek, Buchanan, Gardner, & Gedon, 1993). Many types of cellulose esters are now produced commercially which are utilized in a vast array of applications (Edgar et al., 2001).

The prospects for future cellulose ester applications are bright. For example, cellulose triacetate (CTA) has long been widely used as film base in the photographic industry. Although traditional photography is shrinking as society moves to the digital age, CTA continues to grow as it is now the polymer of choice as protective films in liquid crystalline displays which are widely used in digital devices (Edgar et al., 2001). Given this background; new processes which allow improved conversion of cellulose to cellulose derivatives such as CTA are of high importance.

In a previous account, Biswas et al. reported that cellulose could be converted to CTA using a catalytic amount of

☆ Names are necessary to report factually on available data: however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name USDA implies no approval of the product to the exclusion of others that may also be suitable.

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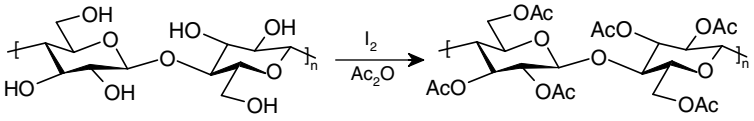

Fig. 1. Conversion of cellulose to cellulose triacetate, *n* is typically 400–1000.

I_2 in the presence of acetic anhydride (Fig. 1) (Biswas, Shogren, & Willett, 2005). Our objective in this work was to explore the effect of temperature and catalyst loading on reaction kinetics and the physical properties of the CTA produced under these conditions. We hoped to develop a process that required less or no solvent to produce CTA.

2. Experimental

2.1. Chemicals

Cellulose samples (7% moisture) were obtained from Sigma. Carbohydrate analysis of the cellulose revealed that it contained 1.44 wt% xylose and 1.41 wt% mannose. The DP of the cellulose estimated from the cuene intrinsic viscosity was 456 (Evans & Wallis, 1989). Acetic anhydride, chloroform, dimethylacetamide (DMAc), ethyl alcohol, lithium chloride (LiCl) and iodine were obtained from Aldrich. All chemicals were used without further purification.

2.2. General methods

Pierce Reacti-Vial™ glass vials, 10 ml, equipped with magnetic stirrers were used as reactors and a Pierce Reacti-Therm™ heating block was used as the conventional heat source. Samples for IR spectra were prepared from one milligram of powder and acquired on a Nicolet Avator 370 midrange Fourier Transform Infrared spectrometer using a SenIR Duroscope diamond ATR. NMR spectra were collected using a JEOL Model Eclipse+ 600 NMR spectrometer. The sample (10 mg) was dissolved in 0.5 mL of DMSO-d_6 containing TFA-d and added to a 5-mm OD NMR tube. The spectra were collected at 80 °C. Chemical shifts for the proton NMR spectra were referenced to TMS at 0.0 ppm. Molecular weights were determined using an Agilent gel permeation chromatograph equipped with an RI detector and a Polymer Laboratories 10 μm PL gel column. The operating temperature was 40 °C and the mobile phase was *N*-methyl pyrrolidone containing 1 wt% glacial acetic acid at a flow rate of 0.8 mL min^{-1}. The column calibrants were monodisperse polystyrene standards. Appropriate calibration parameters were used to convert the molecular weights to absolute molecular weights. Modulated differential scanning calorimetry (DSC) curves were obtained using a Q1000 TA spectrometer. First scan DSC heating curves were obtained by heating from 0 to 325 °C at 5° min^{-1} with a modulation of 2° every 60 s. Prior to collecting the spectra, the instrument was calibrated versus indium–tin–water.

2.3. Preparation of CTA at room temperature

A glass vial equipped with a magnetic stirrer, 0.57 g of cellulose (3.5 mmol of anhydroglucose units or AGU), 3.8 g (37.2 mmol) of acetic anhydride and 80 mg (0.63 mmol) of iodine was covered and stirred at room temperature. After the desired time the reaction mixture was then treated with a saturated solution of sodium thiosulfate (2 mL) with stirring. The mixture color changed from dark brown to colorless, indicating the transformation of iodine to iodide. The mixture was poured into 50 mL of ethanol and stirred for 15–30 min. The solid, which consisted of CTA and unreacted or cellulose acetate was filtered and washed with water and then dried in a vacuum oven at 60 °C. The sample was then dissolved in chloroform to give hazy solutions containing fiber or gels. In order to isolate CTA, the hazy solutions were filtered and poured into ethyl alcohol. As the reaction time increased, haziness of the unfiltered product chloroform solution decreased indicating higher amount of CTA in the solid. Thus, the product obtained after 12 h gave a clear chloroform solution and we concluded cellulose was fully converted to CTA.

2.4. Preparation of CTA at 100 °C

A glass vial equipped with magnetic stirrer, 0.57 g of cellulose (3.5 mmol of anhydroglucose units or AGU), 1.9 g (18.6 mmol) of acetic anhydride and 40 mg (0.16 mmol) of iodine was heated at 100 °C for 10 min. The reaction mixture was then cooled to room temperature and treated with a saturated solution of sodium thiosulfate (2 mL) with stirring. The mixture color changed from dark brown to colorless, indicating the transformation of iodine to iodide. The mixture was poured into 50 mL of ethanol and stirred for 15–30 min. [See RT prep above] The product was filtered and washed with water and then dried in a vacuum oven at 60 °C. The degree of substitution (DS) of the cellulose acetate was 3.0. The cellulose acetate (1.53 g) was obtained in 94.8% yield before extraction with $CHCl_3$.

2.5. Determination of DS

The DS values of the cellulose acetates were determined using NMR spectroscopy. The DS was further confirmed by titration with aqueous sodium hydroxide solution (ASTM, 2004).

3. Results and discussion

In order to get an estimate of the kinetics of the reaction, seven reactions of cellulose with acetic anhydride and

Table 1
Characterization of CTA produced by iodine catalyzed acetylation of cellulose at room temperature

Reaction time	I_2 (mole%)	Yield (%)[a]	DS ^{1}HNMR	M_n	M_w	M_z	T_g (°C)	ppm Iodine[b]
(1)	(1)	(1)	2.90	43,850	131,892	269,337	191	(1)
1 h	9	2.2	–	28,867	92,681	188,933	175	9
3 h	9	8.0	3.04	40,577	111,534	219,371	176	9
5 h	9	16.5	3.06	35,252	109,688	235,772	179	5
7 h	9	30.0	3.07	33,697	107,524	226,435	177	42
12 h	9	90.0	3.04	60,013	131,744	222,136	175	52
20 h	9	90.0	3.04	54,751	130,737	236,340	179	64
24 h	9	93.0	3.04	57,330	139,488	256,658	180	45

1. CTA produced by traditional methods using H_2SO_4 as the catalyst.
[a] Yield after extraction with chloroform.
[b] Based on recovered CTA after extraction of reaction product with chloroform followed by precipitation in EtOH. ND = none detected.

iodine at room temperature were carried out for different periods of time. After one hour we quenched the first reaction with ethanol and isolated the solid product that was a mixture of unreacted cellulose, CA, and CTA. Similarly, other reactions were stopped after 3, 5, 7, 12, 20, and 24 h. As CTA is soluble in chloroform we dissolved the product in chloroform and filtered to remove the CTA. The chloroform solution was precipitated with ethanol to isolate the CTA. Table 1 shows that after 1 h, a 2.2% yield of CTA was obtained. The yield of CTA increased with reaction time until the yield of CTA leveled off near 90% after 12 h. After a reaction time of 12 h, all of sample was soluble in chloroform indicating that the conversion of cellulose to CTA was complete.

All of the CTA produced by the iodine catalyzed process were extensively characterized by ^{1}H NMR, GPC, and by modulated DSC (Table 1). For comparative purposes, CTA produced by traditional methods using H_2SO_4 as the catalyst was also characterized and this data is also included in Table 1. In the case of CTA produced by H_2SO_4 catalysis, M_w was 132 K and the T_g was 191 °C. In the case of the CTA produced by the iodine catalyzed process, the M_w for the 1 h sample was 92 K. Parallel with the increasing yield of product, M_w increased with increasing reaction time until a plateau in M_w near 130–140 K was achieved. As would be expected with increasing M_w, the T_g also increased. The level of iodine remaining in the sample was small, ranging from about 5 to 65 ppm. As can be seen from Table 1, all of the products isolated from the chloroform solution were fully acetylated. Detailed examination of the ^{1}HNMR spectra of the CTA produced revealed that they all contained small levels of what appear to be peracetylated carbohydrate oligomers (*vide infra*).

The extent of acetylation of cellulose for these reactions was evaluated using infrared (IR) spectroscopy. The IR spectra of each of the products prior to chloroform extraction, which contain unreacted cellulose and cellulose ester, gave the relative amount of total acetyl content. The higher acetyl content with increasing reaction time is shown in the IR spectra detailed in Figs. 2 and 3 (for clarity, only 4 samples are shown). With increasing substitution there is observed: a reduced intensity of the region associated with the stretching of the hydroxyls (3600–3000 cm^{-1}), an

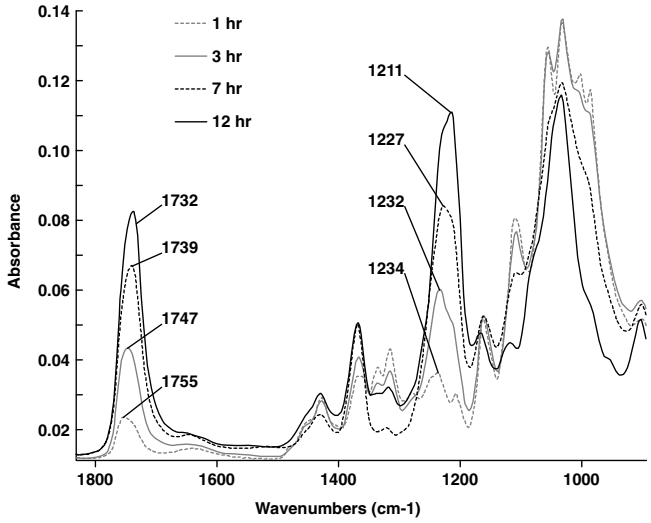

Fig. 2. IR spectra (900–1850 cm^{-1}) showing higher acetyl content with increasing reaction time.

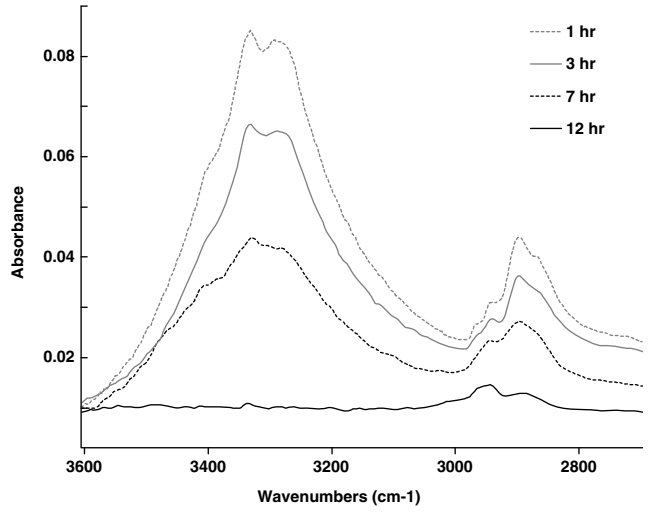

Fig. 3. IR spectra (2700–3600 cm^{-1}) showing lower hydroxyl content with increasing reaction time.

increased intensity in the regions associated with C=O stretching (1800–1650 cm^{-1}), and an increased intensity in the regions associated with the methyl of the acetyl group (1300–1200 cm^{-1}). The increased intensity at ~1380 cm^{-1}

can be attributed to a bending mode of the methyl hydrogens of the acetyl residue.

The region around 1000 cm^{-1} is more complex. Analysis indicates the peak of the unreacted cellulose is associated with the free ring hydroxyls and the methines of the pyranose ring. As acylation occurs, there is a decrease in this absorbance. However, there is an increase in intensity in the region from the methyl group of the acetylated product. This may explain the shouldering in the triacetylated product.

Detailed in Fig. 4 are the absorbances for the carbonyl and hydroxyl peaks. Attempts were made to fit these results to pseudo first order kinetics using the cellulose hydroxyl (assuming excess acetic anhydride) and second order kinetics. These calculations did not yield plots with reasonable linear fits. This suggests that the reaction is not a simple first or second order reaction. The reaction is complicated by several factors. At the beginning of the reaction, the reaction is heterogeneous, and initially the surface will preferentially acetylate. With time more acetylation will take place and at some DS, the acetylated cellulose will become soluble in the reaction medium and the remaining unreacted hydroxyls will acetylate. This is consistent with the observed relationship between yields and DS, where at short reaction times, where the yield is low, the DS is high. Beyond the heterogeneous nature, it is known that the primary and secondary hydroxyls of cellulose have different reaction rates (Cramer, Hockett, & Purves, 1939; Gardner & Purves, 1942; Heuser, Heath, & Shockley, 1950; Mahoney & Purves, 1942). In addition, the solubility of the cellulose will change as the hydroxyls are acetylated, which will change the actual concentration of hydroxyls available for reaction with time. These two factors will make the kinetics complicated.

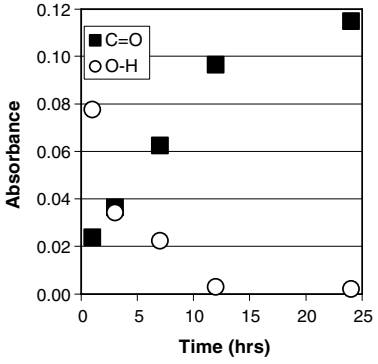

Fig. 4. Absolute absorbance of carbonyl (1747 cm^{-1}) and hydroxyl (3332 cm^{-1}) peaks with time.

As illustrated in Table 2, when the reaction was carried out at 100 °C for 10 min, a different outcome relative to the room temperature reactions was obtained. With 1 mole% I_2, ca. 18% of the cellulose was converted to CTA. As the mole% of catalyst was increased, the yield of CTA increased reaching 94% at 4.3 mole% I_2. Relative to the CTA produced by H_2SO_4 catalysis and the CTA produced by I_2 catalysis at RT, all of the CTA produced by the iodine catalyzed process at 100 °C had lower molecular weights (M_w = 28–60 K). Lower catalyst levels gave CTA with higher molecular weights. Detailed examination of the ^{1}HNMR spectra of the CTA produced by the iodine catalyzed process revealed that these samples all contained variable levels of peracetylated carbohydrate oligomers (Fig. 5). The levels of these oligomers in the CTA were higher in the CTA produced at 100 °C relative to the CTA produced at RT. Observation of peracetylated carbohydrate oligomers is consistent with reduced molecular weights. Furthermore, these peracetylated carbohydrate oligomers can influence the physical properties of the CTA (*vide infra*).

Thermal analysis of CTA presents many difficulties due to the fact that the melting temperature of CTA is above the temperature of onset of thermal degradation (Buchanan, Hyatt, Kelley, & Little, 1990; Kamide & Saito, 1985). Removal of thermal and mechanical history in classical DSC experiments requires that the sample be heated to near or above the melting temperature. In the case of CTA, since this temperature is above or near the decomposition temperature, T_m, H_f, and T_g can only be estimated using classical DSC protocol. Prior studies have estimated the T_m of CTA to be 300–306 °C and the T_g to be between 175 to 190 °C. For this reason, we prefer modulated DSC in the analysis of CTA as this technique separates the heat flow into reversing and non-reversing components and allows one to more easily observe behavior such as loss of volatile components, crystallization and melting endotherms.

Fig. 6 shows a typical modulated DSC for CTA prepared by iodine catalysis; analyses of this and other samples are summarized in Tables 1 and 2. For CTA produced by traditional methods using H_2SO_4 as the catalyst, we obtained a T_g of 191 °C. In the case of the CTA prepared by

Table 2
Characterization of CTA produced by iodine catalyzed acetylation of cellulose at 100 °C for 10 min

I_2 (mole%)	Yield (%)[a]	DS ^{1}HNMR	M_n	M_w	M_z	T_g (°C)	ppm Iodine[b]
(1)	(1)	2.90	43,850	131,892	269,337	191	(1)
1.0	17.8	3.07	12,366	39,426	86,919	170	ND
2.0	41.6	3.06	11,918	33,030	66,016	155	ND
3.4	70.2	3.09	12,537	33,398	68,750	147	ND
4.3	94.3	3.09	11,228	27,723	52,802	146	ND

1. CTA produced by traditional methods using H_2SO_4 as the catalyst.
[a] Yield after extraction with chloroform.
[b] Based on recovered CTA after extraction of reaction product with chloroform followed by precipitation in EtOH. ND = none detected.

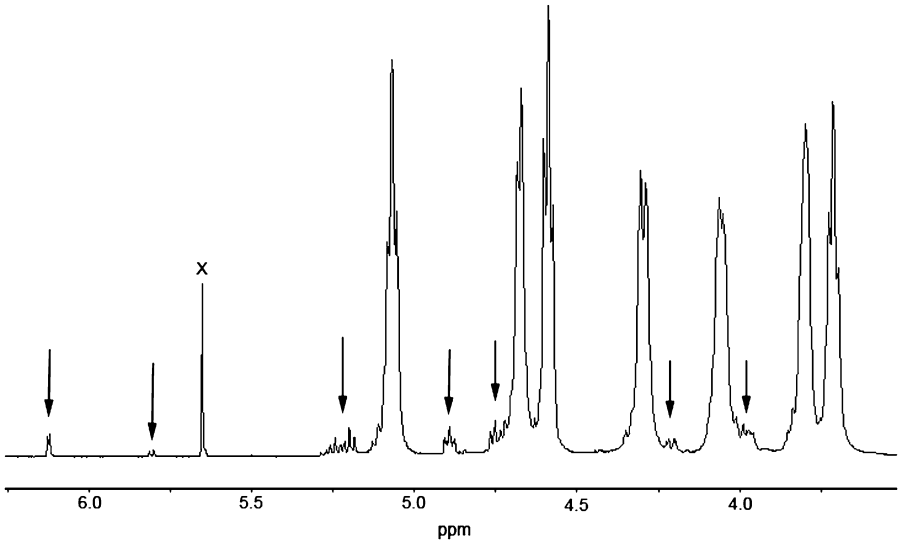

Fig. 5. Proton NMR spectrum (DMSO-d_6, 80 °C) of CTA produced by an iodine catalyzed reaction of cellulose with acetic anhydride. X denotes chloroform; arrows denote carbohydrate oligomers.

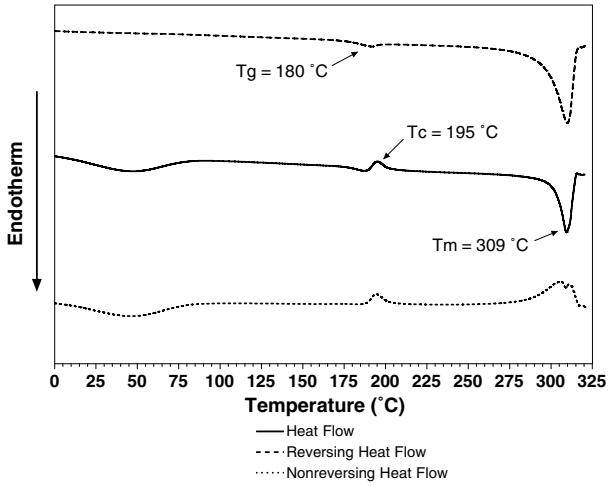

Fig. 6. Modulated DSC for CTA produced by a I_2 catalyzed reaction of cellulose with acetic anhydride.

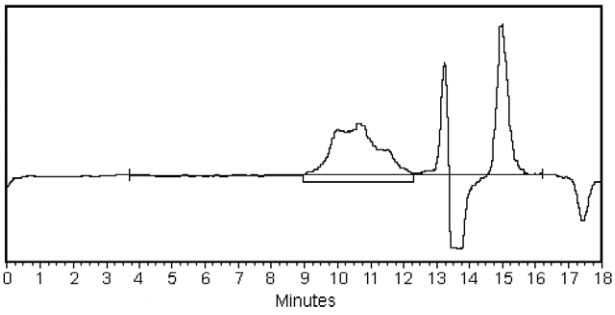

Fig. 7. GPC spectrum of cellulose tripropionate produced by I_2 catalyzed reaction of propionic anhydride with cellulose.

iodine catalysis, the glass transition temperatures ranged from 147 to 180 °C. The depression of the T_g for this series of cellulose triacetates is likely due to two factors. Relative to CTA produced using H_2SO_4 as the catalyst and the CTA produced by I_2 catalysis at RT, the M_w of the CTA samples prepared by iodine catalysis at 100 °C were lower which is known to lead to a depression of the T_g (Buchanan et al., 1990). Additionally, the low molecular weight oligomers present in the polymer (*vide supra*) can act as plasticizers which will result in depression of the T_g (Buchanan, Buchanan, Edgar, & Lambert, 2005).

In order to determine the versatility of the iodine catalyzed process in producing cellulose triesters, other aliphatic anhydrides were also evaluated. When propionic anhydride was allowed to react with cellulose at 100 °C cellulose tripropionate (DS = 3.08) was obtained in 45% yield. GPC indicated that the product had a lower molecular weight (M_w = 20 K) relative to the cellulose triacetates. Additionally, multiple peaks were observed in the GPC trace suggesting distinct molecular weight distributions (Fig. 7). Butyric and other longer chain anhydrides gave no reaction products. This is presumed to be due to lower solubility of cellulose and the corresponding cellulose esters in the longer chain, less polar anhydrides.

4. Conclusions

We have found that reaction of cellulose with acetic anhydride in the presence of a catalytic amount of iodine can result in the formation of CTA in good yield. At a reaction temperature of 100 °C using 4.3 mole% I_2, only 10 min was required to obtain a 94% yield of CTA. At ambient temperature, a higher catalyst loading (9 mole%) and longer reaction times (12 h) were required in order to achieve comparable yields of CTA. The amount of iodine catalyst also influenced the amount of cellulose converted to CTA as well as the molecular weight of the product. As with more traditional routes, the kinetics of this reaction are complicated by different hydroxyl reactivity and changes in solubility with substitution. This new methodology provides a simple, efficient, and reduced solvent

method of preparing CTA. However, it should be noted that reaction of propionic anhydride with cellulose was more difficult and that longer chain anhydrides did not provide the desired reaction.

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