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Synthesis of cellulose triacetate from cotton cellulose by using NIS as a catalyst under mild reaction conditions

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ABSTRACT

This research discusses the acetylation of cotton cellulose with acetic anhydride without solvents. The acetylation was done in the presence of different amounts of *N*-Iodosuccinimide (NIS) as a catalyst; this took place under mild reaction conditions. The extent of acetylation was measured by the weight percent gain (WPG) that varied from 24.71 to 71.83%. Cotton cellulose acetates, with the degree of substitution (DS) that ranged from 0.89 to 2.84, were prepared in one step. The cellulose triacetate, with a degree of substitution (DS) 2.84, was obtained. The WPG and DS were easily controlled by changing the reaction duration (1–5 h), and the concentration of the catalyst (0.05 g, 0.075 g and 0.10 g for 1 g of cellulose) in 25 ml of acetic anhydride. NIS was recognized as a novel and more successful catalyst for the acetylation of hydroxyl groups in cotton cellulose. Formation of the acetates and the calculation of the degree of substitution were performed by FT-IR, Raman, and ^{1}H NMR.

1. Introduction

Natural organic products, such as cotton, presently attract great attention for the development as they are the main source of cellulose in the production of cellulose acetates. Cotton mainly contains cellulose of high molecular weight ranging from 2.5×10^5 to 1×10^6 or more. Apart from cellulose, the major components of cotton, that make up more than 95% are other constituents that include lignin and hemicelluloses such as xylose or mannose (El Nemr, 2012).

Chemical modification of cellulose is one method of the production of value-added products. Acetylation has been the most widely used and most successful chemical modification. It replaces a hydrogen of hydroxyl group with an acetyl group. Cellulose acetate (CA) is one of the most industrial products with widely commercial applications (Bikales & Segal, 1971; Edgar et al., 2001; Heinze, Liebert, & Koschella, 2006; Waheed et al., 2014). Cellulose acetate is used commercially in cigarette filters, textile fibers, photographic films, oil paint, surface coatings (as additives), inks, and plastics (Gedon & Fengl, 2004; Rustemeyer, 2004). It is also a highly efficient adsorbent due to its porosity (Dai, Liu, Jia, & Ru, 2005). It has been found that cellulose diacetate (CDA), that has a degree of substitution (DS) ranging from 2.2 to 2.7 (Heinze & Liebert, 2001), readily undergoes decomposition by microorganisms (Buchanan, Gardner, & Komarek, 1993; Komarek, Gardner, Buchanan, & Gedon, 1993). This has attracted the attention of biodegradable plastic manufacturers. Cellulose triacetate (CTA), that has an average DS above 2.8 (Heinze & Liebert, 2001), is one of the most important cellulose esters due to its low toxicity and low flammability. It, therefore, has an important role in industrial applications (Goda, Sreekala, Gomes, Kaji, & Ohgi, 2006; He et al., 2015; Jandura, Riedl, & Kokta, 2000; Kiso, Kitao, & Nishimura, 1999; Sun, Sun, & Wen, 2001). CTA could be used in the removal of organic pollutants from water (Dai et al., 2005; Vinturella, Burgess, Coull, Thompson, & Shine, 2004). CTA is also used as protective films in liquid crystalline displays which are widely used in digital devices (Edgar et al., 2001).

Cellulose acetates have been prepared by Schatzenberger in 1965 after the reaction of cellulose with acetic anhydride in sealed tubes at 180 °C (Biswas, Shogren, & Willett, 2005). The commercial production of cellulose acetate has been recognized in 1919 and has continued until now. Cellulose acetate is typically made from wood pulp, which is a renewable resource, that then reacts with acetic anhydride and acetic acid in sulfuric acid (Bikales & Segal, 1971; Gedon & Fengl, 1993; Larock, 1989). Recently several methods have been developed for producing cellulose acetates, Biswas reported that Iodine can be used as a catalyst in acetic anhydride for the esterification of cellulose (Biswas et al., 2007, 2009; Biswas et al., 2005). The most commonly used acetylating reagents are acetic anhydride and acetyl chloride (Heinze & Liebert, 2004). Sulfuric acid or perchloric acid could be used as catalysts with an excess

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Table 1
NIS-catalyzed acetylation reaction of cotton cellulose: reaction conditions, weight gain, percentage yield of cellulose acetate and degree of substitution obtained using FTIR and Raman spectrum.

Sample no.	Wt. of cotton cellulose (g)	Ac_2O (ml)	Wt of NIS as catalyst	Reaction time (h)	Yield of CA (g)	WPG (%)	CA yield (%)	WG_{FTIR} (g)	WG_{Raman} (g)	DS_{FTIR}	DS_{Raman}
C-1	1	25	0.05	1	1.331	33.12	46.68	0.327	0.377	1.40	1.61
C-2	1	25	0.05	2	1.210	21.00	42.05	0.294	0.241	1.26	1.03
C-3	1	25	0.05	3	1.502	50.21	83.50	0.585	0.525	2.51	2.25
C-4	1	25	0.05	4	1.442	44.24	65.33	0.457	0.329	1.96	1.41
C-5	1	25	0.05	5	1.373	37.25	44.30	0.310	0.386	1.33	1.65
C-6	1	25	0.075	1	1.299	29.94	38.48	0.269	0.332	1.15	1.42
C-7	1	25	0.075	2	1.564	56.40	86.81	0.606	0.583	2.60	2.49
C-8	1	25	0.075	3	1.571	57.09	77.72	0.544	0.562	2.33	2.41
C-9	1	25	0.075	4	1.494	49.44	68.96	0.483	0.481	2.07	2.06
C-10	1	25	0.075	5	1.407	40.70	56.40	0.395	0.415	1.69	1.77
C-11	1	25	0.10	1	1.247	24.71	29.58	0.207	0.200	0.89	0.85
C-12	1	25	0.10	2	1.718	71.83	94.32	0.660	0.700	2.84	3.00
C-13	1	25	0.10	3	1.654	65.41	88.85	0.623	0.659	2.67	2.82
C-14	1	25	0.10	4	1.551	55.08	77.33	0.541	0.560	2.32	2.40
C-15	1	25	0.10	5	1.433	43.33	63.04	0.441	0.490	1.89	2.10
C-16	10	250	0.10	2	16.976	69.76	92.15	6.941	6.933	2.77	2.75

Wt: weight; CA: cellulose acetate; WPG: weight percentage gain; CA yield: reaction yield percentage of CA; WG_{FTIR}: weight gain calculated using FTIR spectrum; WG_{Raman}: weight gain calculated using FT-Raman spectrum; DS_{FTIR}: degree of substitution calculated using FTIR spectrum; DS_{Raman}: degree of substitution calculated using FT-Raman spectrum.

of acetic anhydride to produce cellulose acetates (Hummel, 2004). Other reported methods for esterification include base-catalyzed transesterification, and ring-opening reactions (Connors & Albert, 1973; Das, Ali, & Hazarika, 2014; Fan et al., 2013; Heinze et al., 2006; Fan et al., 2014). Pyridine and 4-dimethyl-amino pyridine (DMAP) (Hofle, Steglich, & Vorbruggen, 1978) have been used as acylation catalysts in chemical synthesis.

In the present work a new method for producing cellulose acetate (CA) from cotton cellulose was investigated. *N*-Iodosuccinimide was used as a novel and highly effective catalyst in the presence of acetic anhydride under a solvent free system. There have been no reports of its use as a catalyst for the acetylation of cotton cellulose using acetic anhydride. The effects of the reaction's duration and concentration of the catalyst were investigated too. The structure and properties of acetylated cotton cellulose were characterized by the weight percent gain (WPG). In addition FT-IR, Raman, and ^{1}H NMR were used to investigate the reaction product that was obtained.

2. Experimental

2.1. Chemicals and instruments

Cellulose samples were obtained from Fluka analytical (Sigma–Aldrich product). The degree of polymerization of the cellulose DP = 456 (Evans & Wallis, 1989). Acetic anhydride, ethyl alcohol, and *N*-Iodosuccinaimide (NIS) were supplied by Fluka analytical, and were used without further purification. ^{1}H NMR was obtained using JEOL Nuclear Magnetic Resonance Spectrometers 400 MHz. FTIR and Raman data were obtained using Bruker VERTEX 70 FT-IR spectrometer coupled to a RAMII FT-Raman module with Germanium detector that provided a spectral range of 3600–50 cm^{-1}.

2.2. Acetylation of cotton cellulose

A quantity (1.0 g) of commercial cotton cellulose was placed in a 250 ml round bottom flask that contained 25 ml acetic anhydride, and different weights of *N*-Iodosuccinaimide (NIS) catalyst (0.05, 0.075 and 0.10 g). The flask was then placed in a mantle at the reflux temperature using atmospheric pressure with a fitted reflux condenser. After the reaction took its time (1–5 h), the flask was removed. About 10 ml of ethanol was added, followed by the addition of 100 ml of distilled water to decompose the un-reacted acetic anhydride. The reaction mixture was filtered and washed by distilled water followed by ethanol. The products were then dried under vacuum in an oven at 45 °C for 48 h prior to re-weighing. To reduce errors and confirm results, each experiment was repeated in triplicate under the same conditions. Weight percent gain (WPG) of the cotton cellulose due to acetylation was determined according to:

$$WPG\% = \frac{\text{weight gain}}{\text{original weight}} \times 100$$

2.3. Test of mass production

A quantity (10 g) of commercial cotton cellulose was placed in a 500 ml round bottom flask that contained 250 ml acetic anhydride and 1 g of *N*-Iodosuccinaimide (NIS). The flask was then placed in a mantle at the reflux temperature using atmospheric pressure with a fitted reflux condenser. After 2 h of the reaction, the flask was removed. Then the above work method was repeated.

2.4. Determination of DS

The DS values of the cellulose acetates were determined using FT-IR spectra. The DS was further confirmed by Raman spectra and ^{1}H NMR.

3. Results and discussion

3.1. Influence of catalysts and reaction duration on the degree of acetylation

This present work shows how cotton cellulose was acetylated in acetic anhydride that contained different concentrations of NIS under the same reaction conditions, at different reaction times. As the data in Table 1 show, it is apparent that the usage of 0.05 g of NIS as a catalyst in 25 ml acetic anhydride for 1, 2, 3, 4, and 5 h in samples 1–3, resulted in an increment in the WPG from 33.12 to 50.50%. In samples 4 and 5, the WPG decreased from 44.24 to 37.25%. In samples 6–10, acetylation of the cotton cellulose was carried out in 0.075 g of NIS that acted as a catalyst under the conditions mentioned above. The WPG increased with an increment in the reaction time 1–3 h from 29.94 to 56.40 and 57.09%. The