Macromolecular Research
https://doi.org/10.1007/s13233-023-00179-w

Online ISSN 2092-7673
Print ISSN 1598-5032

ARTICLE

Synthesis and characterization of a new cellulose ether derivative: sodium levulinate cellulose

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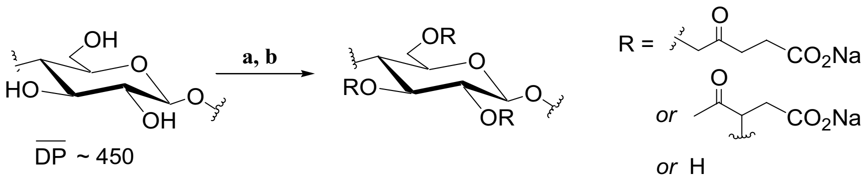
Received: 24 February 2023 / Revised: 9 June 2023 / Accepted: 12 June 2023

Abstract

Sodium levulinate cellulose (SLC) was prepared as a new longer carbon chain analog for carboxymethyl cellulose (CMC) in 66–94% yield using the Williamson ether synthesis reaction between sodium hydroxide treated cellulose and brominated levulinic acid in aqueous *iso*-propanol medium under thermal and microwave conditions. Levulinate cellulose ether produced was characterized by FT-IR, TG–DTA, X-ray and proton NMR. The thermal reactions carried out at 90 °C for 3 and 24 h gave SLC products with degrees of substitutions of 0.48 and 0.86, respectively, whereas the microwave synthesis product showed a degree of substitution of 0.32 as determined by ASTM D1439-03 method used for CMC.

Graphical abstract



a. 40% aq. NaOH, ^{i}PrOH, 23 °C, 15 min.
b. Sodium bromolevulinate (1.2 eqv.), 0 - 23 °C, 1 h; then oil bath, 90 °C, 3-24 h. or microwave 120 s.

Keywords Cellulose derivative · Levulinate ether · Williamson synthesis · 5-Bromolevulanic acid · 3-Bromolevulanic acid

1 Introduction

Cellulose is the most abundant renewable carbon-based material and chemical modification of this linear polysaccharide is a very attractive approach for producing sustainable macromolecular materials with interesting properties and numerous applications [1]. Among diverse cellulose-modified functional materials, esters and ethers are the most well-known derivatives; which are prepared by esterification or by nucleophilic reaction of hydroxyl groups with electrophiles such as alkyl halides or epoxides [2, 3]. The most common cellulose esters area: acetate, xanthate, phosphate, sulfate, and phthalate; whereas, carboxymethyl, hydroxy propyl methyl, ethyl, sulfoethyl and cyanoethyl cellulose are the widely studied cellulose ethers [4, 5]. These cellulose derivatives find use in an exceptionally wide range of large-scale applications including thickeners in the food industry [6], emulsifiers [7], food packaging [8], binders in Li-ion battery electrodes [9], lubricants and rheology modifiers in oil field [10–12], membranes [13, 14], biomedical and pharmaceutical applications [15, 16], sensors [17, 18], cosmetics and personal care formulations [19–21].

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Among all the commercially available cellulose derivatives, carboxymethyl cellulose (CMC) is the most widely used and methylcellulose (MC), can be ranked as the next derivative with the largest consumption [22, 23]. Toothpaste formulations and biodegradable packaging are expected to create stable revenue streams for CMC manufacturers in this decade and the global CMC market is projected to cross US$ 1.85 B by 2031 [24]. CMC is generally prepared by a reaction of aqueous sodium hydroxide-treated cellulose with the sodium salt of chloroacetic acid [25, 26]. Theoretically, all three hydroxyl groups of cellulose per anhydroglucose unit can be etherified if an excess of chloroacetic acid is used; however, complete substitution is rarely achieved. The degree of substitution (DS) in CMC depends on the application and most food-grade CMC have a degree of substitution values in the 0.7–0.8 range, but some products may have a degree of substitution as low as 0.4 as well [25, 27]. The common alkyl cellulose derivatives, methyl and ethyl cellulose are prepared by a reaction of methyl or ethyl chloride with aqueous sodium hydroxide-treated cellulose and these derivatives are mostly used as adhesives and thickeners [3, 28].

Levulinic acid (LA) or 4-oxopentanoic acid is an important new generation feedstock and this key renewable chemical can be produced from abundant lignocellulosic biomass also via a series of reactions involving hydrolysis of cellulose, dehydration to 5-hydroxymethylfurfural and rehydration [29–31]. Besides, levulinic acid was listed as one of the top 12 most promising value-added chemicals from lignocellulosic biomass by the Biomass Program of the US Department of Energy in 2004 [32]; furthermore, continues to rank highly in more recent surveys of major bio-refinery target products [33].

As far as we are aware there are only two reports on the preparation of a levulinic acid derivative of cellulose and both these are on the preparation of cellulose esters by reacting the carboxylic acid group of levulinic acid with -OH groups of cellulose as shown in Fig. 1. In the first example, Zheng and co-workers reported a homogeneous acylation of cellulose in *N*,*N*-dimethylacetamide—LiCl medium using differently activated levulinic acid derivatives, including in situ activation with *p*-toluenesulfonyl chloride, dicyclohexylcarbodiimide, trifluoroacetic anhydride or 1,1′-carbonyldiimidazole. Furthermore, they compared these activation methods and achieved a degree of substitution values as high as 2.42 in the esterification reaction [34]. In the more recent instance, Pei and co-workers prepared cellulose levulinate esters with DS values in the 0.15 to 2.04 range by the reaction between cellulose dissolved in 1,8-diazabicyclo[5.4.0]undec-7-ene/dimethyl sulfoxide/carbon dioxide solvent system and α-angelica lactone, without the addition of external catalysts or condensation reagents [35]. The highest DS values were obtained for reactions carried out at 120 °C, 0.5 h, and using 5: 1 molar ratio of α-angelica lactone to the hydroxyl groups in cellulose [35].

Our interest in processing cellulose and conversion to value-added products has led to the development of simple and scalable methods for the synthesis of novel cellulose derivatives and cellulose-containing hybrid materials [36–39]. In the present work, we have prepared a novel levulinic acid-based ether derivative of cellulose as a longer carbon chain analog as well as a higher molecular weight substitute to well-known carboxymethyl cellulose. This new cellulose-sodium levulinate ether derivative shown in Fig. 2 presents derivatization through a more stable ether link, rather than the relatively

Fig. 1 Levulinate ester synthesis reaction previously reported in literature by Zheng et al. [34] and Pei et al. [35]

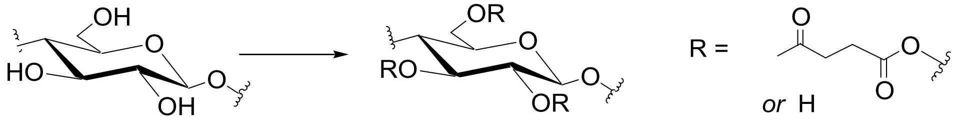
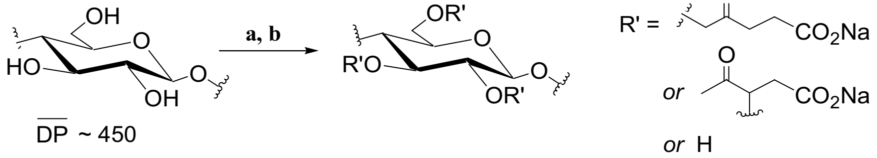


Fig. 2 Synthesis of sodium levulinate cellulose (SLC)



a. 40% aq. NaOH, $^{i-}$PrOH, 23 °C, 15 min.

b. Sodium bromolevulinate (1.2 eqv.), 0 - 23 °C, 1 h; then oil bath, 90 °C, 3-24 h. or microwave 90 °C, 3 h.

labile ester link reported in previous work shown in Fig. 1 [34, 35]. Furthermore, in comparison to carboxymethyl cellulose, this work presents a significant upgrade in a derivatized group from two carbons to five carbons. In addition, the levulinic acid-derived five-carbon chain is incorporating a keto functional group, opening the possibility of cross-linking sodium levulinate ether cellulose chains using suitable cross-linking agents such as polyamines.

In the present approach, LA is first brominated with bromine in the presence of urea, using a newly published procedure as shown in Fig. 3 [40]. Until recently, selective bromination of the 5-position of LA is a challenging area; however, in their latest work, Hoye et al. have shown that the addition of urea can significantly improve the 5-bromolevulinic acid yields in brominations carried out in methylene chloride at room temperature. We have followed this latest technique of producing a bromolevulinic acid mixture with 5-bromolevulinic acid as the major product and 3-bromolevulinic acid as the minor product. This brominated levulinic acid mixture was used in the preparation of sodium levulinate cellulose without separation of brominated levulinic acids.

2 Experimental

2.1 Materials and instrumentation

Sigmacell cellulose (DP ~ 450, from cotton linters, Cat. No. S6790), levulinic acid (98%), bromine (> 99.5%) and sodium hydroxide (> 97%) were purchased from Aldrich Chemical Co. Brominated levulinic acid with 5-bromolevulinic acid (5-BrLA) and 3-bromolevulinic acid (3-BrLA) in 56:35 ratio was prepared in 88% yield using a published method as shown in Fig. 2; procedure and ^{1}H NMR data are included in the supplementary material (SM1) [40]. Microwave reaction samples were heated using a Discover 2.0 model microwave synthesizer in a 100 mL Pyrex reaction vessel. Pyrolysis of sodium levulinate cellulose samples was carried out in a 1.4X15 cm Pyrex tube inserted into a Thermo Scientific Lindberg Blue M Mini-Mite tube furnace. FT-IR spectra were recorded on a Thermo Nicolet IR 200 spectrometer using KBr pellets. ^{1}H NMR was recorded on a Eclipse 1, JEOL ECS 400 MHz spectrometer in DMSO-*d6*: D_2O 4:1 as the solvent. SLC Sample was dissolved in DMSO-*d6*: D_2O 4: 1 solvent mixture at room temperature by manually holding the NMR sample tube for 2 min. on a VWR scientific mini vortex mixture at 3000 rpm. Attempts to dissolve staring cellulose in the same solvent by this method were not successful. Thermogravimetric-differential thermal analysis (TG–DTA) was carried out on a TA instruments TGA 2050 system. X-ray diffractograms of the samples were recorded using a Shimadzu, XRD-7000 diffractometer with Cu Kα radiation 1.54060 Å, voltage 40 kV, current 30 mA and scanning was conducted from 10° to 80°.

2.2 Synthesis of sodium levulinate cellulose ether by oil-bath heating

Sigmacell cellulose (0.500 g, 1.85 mmol glucose units) was suspended in 2.00 mL of *iso*-propanol and 2.00 mL of 40% (w/v) aqueous sodium hydroxide was added under magnetic stirring at room temperature (23 °C) over a period of 15 min. Then the suspension was cooled in an ice-water bath and brominated levulinic acid (0.390 g, 2.00 mmol) was added over a period of 15 min with magnetic stirring. The mixture was allowed to warm to room temperature for 1 h, and after that heated in an oil bath at 90 °C, for 3–24 h. Reaction mixture was cooled to room temperature, diluted with 5 mL of 70% aq. ethanol, decanted to remove the liquid and solid was repeatedly washed with 70% aqueous ethanol, dried in an oven at 50 °C for 24 h. to give sodium levulinate cellulose as a pale yellow powder. The percent yields and degree of substitutions of sodium levulinate cellulose products are shown in Table 1.

2.3 Synthesis of sodium levulinate cellulose ether by microwave heating

Sigmacell cellulose (0.500 g, 1.85 mmol glucose units) was suspended in 2.00 mL of *iso*-propanol and 2.00 mL of 40%

Table 1 Reaction conditions, yield, weight percentage of Na_2CO_3 residue and degree of substitution (DS) in the synthesis of sodium levulinate cellulose

Entry	Reaction conditions	Yield (%)	Weight percentage of Na_2CO_3 residue (%) at 650 °C	DS
1	Oil bath; 90 °C, 3 h	85	11.2	0.48
2	Oil bath; 90 °C, 24 h	94	16.8	0.86
3	Microwave; 90 °C, 3 h	66	8.2	0.32

0.500 g of Sigmacell cellulose and 0.390 g brominated levulinic acid were used in all experiments

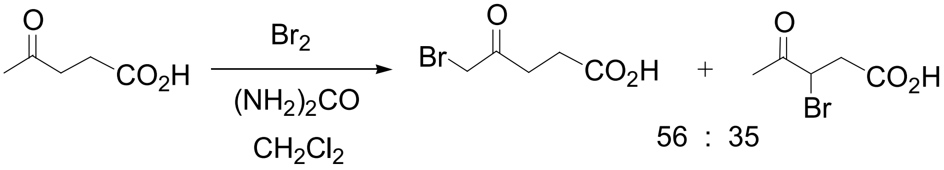


Fig. 3 Bromination of levulinic acid [40]

(w/v) aqueous sodium hydroxide was added under magnetic stirring at room temperature (23 °C) over a period of 15 min. Then the suspension was cooled in an ice-water bath and brominated levulinic acid (0.390 g, 2.00 mmol) was added over a period of 15 min. with magnetic stirring. The mixture was allowed to warm to room temperature for 1 h.; magnet was removed and heated using microwaves in a 100 mL Pyrex reaction vessel at 90 °C for 3 h. The reaction mixture was allowed to cool to room temperature and processed as in experiment 2.2. The percent yield and degree of substitution of the product are shown in Table 1.

2.4 General procedure for pyrolysis of sodium levulinate cellulose samples prepared by procedures 2.2 and 2.3

Sodium levulinate cellulose (0.200 g) was placed in a 1.4 × 15 cm quartz tube and pyrolyzed in the air using a tube furnace at 650 ± 1 °C for 30 min. The sample was allowed to cool to room temperature, weighed and analyzed using FT-IR, and representative FT-IR spectra from entry 2 in Table 1 and anhydrous sodium carbonate are included in the supplementary material (SM1). The w/w percentages of anhydrous Na_2CO_3 residue (%) formed after pyrolysis of SLC samples are shown in column four of Table 1.

2.5 Determination of degree of substitution (DS) of sodium levulinate cellulose (SLC) using ASTM D1439-03 titration method

The DS of sodium SLC products was determined by the American Standard Test Method (ASTM) D1439-03 available for sodium CMC. The SLC sample (0.200 g) was stirred with 3.5 mL of 95% aq. ethanol for 5 min. at room temperature and then 0.25 mL of 65% nitric acid was added and heated at 70 °C for 5 min to convert to the acid form. The acidic form of the product was washed by 80% aq. ethanol (3 × 3 mL) and 5 mL of methanol, dried at 105 °C for 3 h. The dried product was mixed with 10 mL of deionized water, 20.0 ml of 0.10 M aq. NaOH and boiled for 10 min. The resulting suspension was titrated with 0.10 M aq. HCl by using phenolphthalein as the indicator to determine the degree of substitution and these values are shown in column five of Table 1.

3 Results and discussion

3.1 Synthesis of sodium levulinate cellulose by oil-bath and microwave heating

Levulinic acid was brominated according to the literature procedure using bromine in methylene chloride in the presence of urea to give a mixture containing 5-bromolevulinic and 3-bromolevulinic acids in 56: 35 ratio as shown in Fig. 3 [40]. This brominating procedure (SM1) was specifically selected for the synthesis of brominated levulinic acid as Xu and co-workers have shown that the addition of urea can significantly improve the proportion of 5-bromolevulinic acid [40]. The brominated levulinic acid mixture was next used in cellulose derivatization reactions without separating the isomers as both brominated levulinic acid isomers can be expected to react in the ether formation via nucleophilic substitution reactions as shown in Fig. 2. Cellulose derivatization via Williamson ether synthesis was tested under oil-bath heating and microwave heating conditions as described in procedures 2.2 and 2.3. The sodium levulinate cellulose ether products formed were purified by repeated washing with 70% aqueous ethanol to remove salts and excess bromolevulinic acid. Oil bath heating experiments gave higher SLC yields and products with higher DS values than the microwave hearting experiment. The reaction conditions, yields, weight percentages of Na_2CO_3 residue at 650 °C, and degree of substitution determined using ASTM D1439-03 method in the synthesis of sodium levulinate cellulose (SLC) by oil-bath and microwave heating are shown in Table 1. First, the average number of sodium levulinate ether units per glucose unit of cellulose or degree of substitution was determined by adopting ASTM D1439-03 standard method available for carboxymethyl cellulose. In this method SLC was first converted to its acid form by treatment with nitric acid, excess acid was removed and dried. Second, a weighed amount of dry solid was treated with an excess of sodium hydroxide to convert back to the sodium form of cellulose levulinate. Thirdly the excess sodium hydroxide was back titrated with standard 0.10 M aq. HCl to determine the degree of substitution shown in column five of Table 1. The percentage yields for SLC samples prepared under different conditions shown in column three of Table 1 were calculated using the formula:

$$\text{SLC Yield}(\%) = \frac{\begin{array}{c}\text{Moles of SLC calcualted using molecular weights of glucose levulinate}\\ \text{units as determined by ASTM D1439}-03\text{ DS values}\end{array}}{\text{Moles of glucose units in cellulose used for the reaction}} \times 100\%$$

The weight percentage of Na_2CO_3 residue at 650 °C shown in column 4 of Table 1 were determined using TGA as in representative TGA profile for sodium levulinate cellulose from entry 2 in Table 1. shown in Fig. 5.

The initial derivatization experiment was carried out using oil bath heating at 90 °C for 3 h. resulted in a product with a low DS of 0.48, but in a reasonably good 85% yield. As cellulose is only sparingly soluble in *iso*-propanol—aqueous sodium hydroxide medium used, the reaction appeared to be very slow. Therefore, in an attempt to improve the DS, the reaction was carried out for 24 h. at 90 °C, which produced the highest SLC yield of 94% and DS value of 0.86 as shown in entry 2 of Table 1. Microwave heating was also tested as an alternative to oil-bath; however a 90 °C for 3 h. reaction resulted in a lower DS of 0.32 and a yield of 66% as shown in entry 3 of Table 1.

The representative FT-IR, TGA, X-ray and proton NMR of samples are shown in Figs. 4, 5, 6 and 7, respectively. In addition, the highest yielding experiment: 90 °C, 24 h. (entry 2 in Table 1) was repeated in × 10 scale using 5.000 g of Sigmacell cellulose to check the scalability of the method. This experiment yielded practically the same 94% yield and the product is identical to the small-scale experiment product, showing that the experiment can be scaled up without compromising the yield.

3.2 Characterization of sodium levulinate cellulose

3.2.1 FT-IR

New sodium levulinate cellulose samples produced under oil-bath heating and microwave heating conditions were characterized by FT-IR, TGA, X-ray and proton NMR spectroscopy. The representative FT-IR spectrum of sodium levulinate cellulose sample prepared under oil bath heating, 90 °C, 24 h (entry 2, Table 1) is shown in Fig. 4a. In addition, FT-IR spectrum of starting material, Sigmacell cellulose (DP ~ 450), is shown in Fig. 4b for comparison. FT-IR spectra of both cellulose and SLC show the characteristic absorptions at 3300–3400 and around 2900 cm^{-1} representing –OH and C–H stretching. The carbonyl stretching absorption peak is expected to be one of the strongest peaks in a pure carbonyl compound. However, the sodium

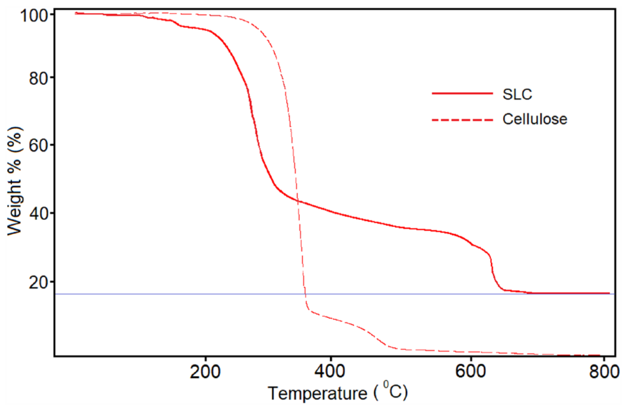


Fig. 5 Thermogravimetric analysis (TGA) of cellulose and sodium levulinate cellulose from entry 2 in Table 1

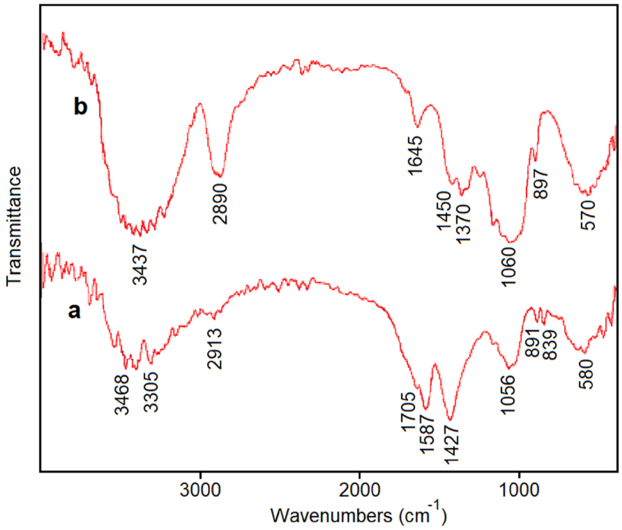


Fig. 4 FT-IR spectra, **a** sodium levulinate cellulose from entry 2 in Table 1, **b** cellulose

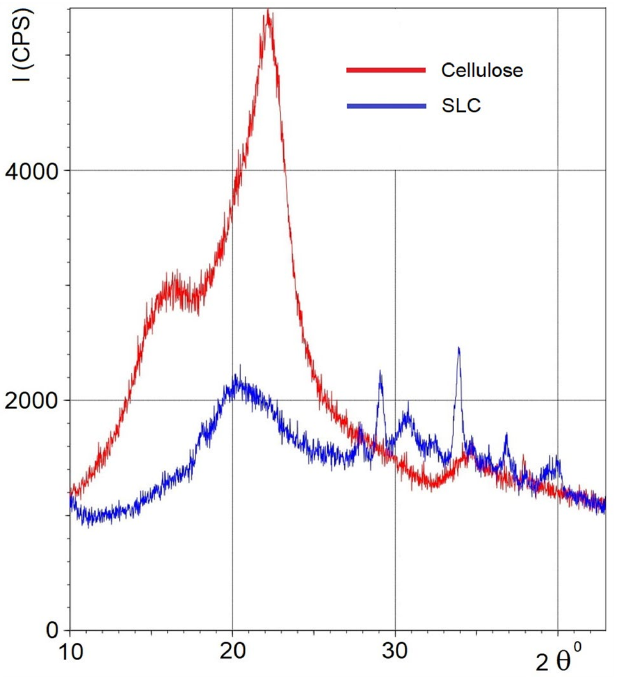


Fig. 6 X-ray diffractograms of cellulose and sodium levulinate cellulose from entry 2 in Table 1

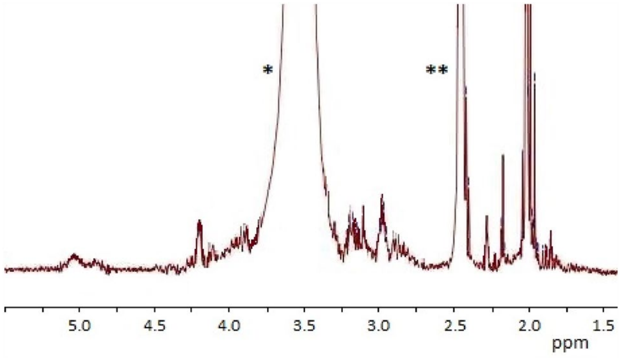


Fig. 7. ^{1}H NMR of sodium levulinate cellulose from entry 2 in Table 1. Solvent: DMSO-*d6*: D_2O 4:1, * HDO, ** DMSO

levulinate cellulose from entry 2 in Table 1, with the highest DS value of 0.82 has 0.82/3.0 or only 27% of possible –OH groups substituted with levulinate groups. Therefore, the IR spectrum of the product shows only a relatively weak ketone carbonyl absorption at 1705 cm^{-1} and a strong carboxylate absorption at 1587 cm^{-1} in Fig. 4a. Nevertheless, these two absorptions are clear evidence for partial derivatization of –OH groups of cellulose as the IR spectrum of starting cellulose in Fig. 4b has no similar absorptions. Furthermore, the peak at 1587 cm^{-1} in Fig. 4a of SLC due to carboxylate C=O stretching is comparable to the sodium carboxylate C=O peak reported for CMC at 1585 cm^{-1} [41]. The peaks at 1427 and 1056 cm^{-1} in the spectrum of SLC are attributed to the C–O and C–O–C stretching vibration of the pyranose ring [41, 42]. In addition, Chung et al. have assigned a strong absorption at 1056 cm^{-1} to the C–O–C asymmetric in-plane ring stretch during their work on cotton cellulose; this report also further supports our assignment [43].

3.2.2 TGA and analysis of residue after pyrolysis at 650 °C in air

TGA Experiments on SLC were carried out in the air to stimulate and study the thermal stability of new SLC under natural conditions. The representative TGA of sodium levulinate cellulose from entry 2 in Table 1 and TGA of staring material cellulose (DP ~ 450) are shown in Fig. 5. Pure cellulose decomposes in two steps centered at 350 and 462 °C, with weight losses of 89 and 11% leaving no residue. Whereas, SLC decomposes in two major steps at 256 and 617 °C with weight losses of 58 and 25% respectively. Yáñez-S et al. have studied the synthesis of CMC from bleached organosolv fibers of *Eucalyptus nitens* and compared TGAs of the CMC with that of original cellulose fibers [44]. During this work, they observed the decomposition of CMC at a lower temperature than the original cellulose fibers and attributed it to decarboxylation processes of carboxylated glucose units and/or carboxymethyl group decomposition [44]. Similarly, the new SLC prepared also showed a lower decomposition temperature than Sigmacell cellulose used; most likely due to decarboxylation processes of sodium levulinate side chains on glucose units.

In addition, unlike cellulose, SLC leaves a white residue of 17% by weight and as an attempt to identify the residue remain after 650 °C, we have experimented with pyrolysis of a 0.200 g sample as described in procedure 2.4. FT-IR spectra of the pyrolysis residue of entry 2 in Table 1 SLC sample and anhydrous sodium carbonate are included in the supplementary material (SM2). The IR spectrum of the SLC 650 °C pyrolysis residue showed two strong peaks at 1449.62 and 871.07 cm^{-1}; whereas, anhydrous Na_2CO_3 showed the same two peaks at 1448.20 and 876.86 cm^{-1} confirming the residue as Na_2CO_3. The anhydrous Na_2CO_3 residues formed were weighed and the weight percentages of residues formed under different SLC preparation conditions are listed under column four in Table 1.

3.2.3 X-ray

The representative powder X-ray diffractograms of sodium levulinate cellulose from entry 2 in Table 1 and staring cellulose are shown in Fig. 6. The DP ~ 450 cotton cellulose shows peaks at $2\theta = 16$, 22 and 34° characteristic of 101, 002 and 040 reflections of cellulose Iβ [45]. In comparison, the SLC sample showed a shift in cellulose 002 peak to 20°, and three additional peaks were observed at $2\theta = 29°$, 31° and 33°. Complete X-ray data of this SLC sample is included in the supplementary material (SM3). The Segal crystallinity index (CI) % of starting cotton cellulose (DP ~ 450) used and SLC sample (entry 2, Table 1) were calculated using the following formula [46]:

$$\mathrm{CI} = \frac{I_{t-I_a}}{I_t} \times 100\%$$

where I_t is the total intensity of the cellulose Iβ peak at $2\theta = 22°$ and I_a is the amorphous intensity of cellulose Iβ at $2\theta = 16°$. The calculated Segal crystallinity values of cellulose (DP ~ 450) used and the SLC sample were 46 and 45%, respectively; indicating that there is no significant change in crystallinity due to sodium levulinate derivatization of cellulose. Wei et al. have observed a small decrease in the crystallinity of cellulose after the preparation of carboxymethyl derivatives due to the partial destruction of the crystallinity of cellulose [47]. However, it is difficult to compare the crystal packing of CMC with SLC due to wide difference in length between cellulose and charged sodium carboxylate group in the two derivatives.

3.2.4 ^{1}H NMR

^{1}H NMR of sodium levulinate cellulose is shown in Fig. 7 and full-scale spectrum is included in the supplementary material (SM4). The –CH_2–CO groups and –CH_3 groups of levulinate pendant groups attached to cellulose are observed between 1.8 and 2.6 ppm. The –CH, –CH_2 protons of the polysaccharide are observed in the range of 2.75–4.25 ppm and the center of this region is masked by a broad HDO peak from the solvent. The broad peak at 4.8–5.2 ppm is due to the anomeric hydrogens of SLC polysaccharide [48].

4 Conclusion

In summary, we have shown that sodium levulinate cellulose with different degrees of substitutions can be prepared in heterogeneous phase Williamson ether syntheses reaction between sodium hydroxide treated cellulose and a mixture of 5-bromolevulinic and 3-bromolevulinic acid in 56: 35 ratio under oil-bath or microwave heating. Cellulose derivatization using oil-bath heating gave better yields than reactions under microwave conditions. The sodium levulinate cellulose product with the highest yield of 94% and a reasonable degree of substitution of 0.86 was obtained under oil bath heating at 90 °C for 24 h. Pyrolysis of sodium levulinate cellulose at 650 °C in the air leaves a white residue and was identified as anhydrous sodium carbonate. The Segal crystallinity index measured using X-ray crystallography does not show a significant change due to derivatization with sodium levulinate. In conclusion, we have developed a simple method for the preparation of a new higher-carbon analog and a renewable carbon-based potential substitute for carboxymethyl cellulose with numerous applications. This new cellulose derivative has an advantage over carboxymethyl cellulose due to the possibility of cross-linking between cellulose chains via the ketone carbonyl group in the levulinate appendix, which is not available in carboxymethyl cellulose.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s13233-023-00179-w.

Acknowledgements We thank United States National Science Foundation grants CBET-1704144, HRD-1036593, Welch Foundation grant L0002-20181021 and United States Department of Energy-National Nuclear Security Administration (DOE-NNSA) grant DE-NA0003947 for financial support.

Author contributions Data collection and analysis were performed by LJL, DW and CDGR. The first draft of the manuscript was written by ASA and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Declarations

Conflict of interest The authors have no relevant financial or non-financial interests to disclose.

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