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Short communication

Microwave-assisted synthesis of alkyl cellulose in aqueous medium☆

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ABSTRACT

Alkyl celluloses are commercial products that are made typically in an alcohol medium over the course of several hours. In this work an alternative, simplified synthesis of alkyl cellulose is reported, using microwave irradiation and aqueous alkaline medium. No alcohol is needed during the reaction. Reaction time is less than 30 min. Conversion varies from 54 to 87%. The degree of substitution varied from 0.2 to 1.0. The production of methyl cellulose and ethyl cellulose was confirmed by ^{13}C NMR and FTIR analysis.

1. Introduction

Microwave irradiation has been used for a variety of chemical reactions and processes (Bogdal, 2006; Hayes, 2004; Lidström, Tierney, Wathey, & Westman, 2001). In our laboratories, we have used microwave to make rapid modification of zein with octenyl succinic anhydride (Biswas, Sessa, Lawton, Gordon, & Willett, 2005), and prepare water-soluble and water-swellable starch acetates (Shogren & Biswas, 2006). Microwave irradiation has also been employed to facilitate extraction of phenolics in beans (Sutivisedsak et al., 2009) and buckwheat (Inglett, Rose, Chen, & Biswas, 2009). Microwave has been used to pre-treat wheat straw before saccharification and fermentation to ethanol (Saha, Biswas, & Cotta, 2008). Recently a promising and fast microwave-assisted synthesis of propargyl cellulose has been reported (Faugeras, Eichinger, Brouillette, Montplaisir, & Zerrouki, 2012). It seems attractive to use microwave irradiation to prepare alkyl ethers of cellulose.

Among the alkyl ethers of cellulose, methyl cellulose (MC) and ethyl cellulose (EC) are commercially the most important. MC is being used as thickener in personal care, coatings, and construction applications, as emulsifier in foods, as binder in medications, as sizing agent in paper and textiles, and as additive in pharmaceutical and agricultural uses (Grover, 1993). Currently methyl cellulose is made in two steps (Ciucanu & Kerek, 1984; Mansour, Nagaty, & El-Zawawy, 1994). The first step is a mercerization process involving the treatment of cellulose with NaOH and the formation of alkali cellulose. In the second step, alkali cellulose is added to isopropanol with NaOH, and a methylating agent like dimethyl sulfate or methyl iodide is added. A recent, alternative, synthesis uses urea and NaOH to dissolve cellulose, which is then methylated with dimethyl sulfate (Ke, Zhou, & Zhang, 2006).

Ethyl cellulose is widely used as an ingredient in formulations of coatings, adhesives and inks. It is also used as a food additive, emulsifier, drug tablet coating, microencapsulant, and food-contact packaging (Desmarais & Wint, 1993; Xu, Brickhouse, & Wang, 2003). Commercially it is made using cellulose and ethyl chloride at high pressure (Desmarais & Wint, 1993). It is shown in this work that microwave-assisted synthesis is an alternative and more facile reaction.

2. Experimental

2.1. Materials and equipment

Cellulose, NaOH, dimethyl sulfate, methyl iodide, ethyl iodide, and acetic acid were obtained from Sigma–Aldrich, St Louis, Mo, and used without further purification. Microwave irradiation was carried out on a sophisticated microwave reactor (Ethos 1600,

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Table 1
Summary of alkyl cellulose made with microwave-assisted synthesis at microwave (mw) temperature set at 75 °C.

No.	Starting material (wt)	Reagent (wt)	mw time (min)	Yield (%)	DS (from NMR)	Comments
1	Cellulose (1 g)	Dimethyl sulfate (2.5 g)	20	89	0.4	Average of duplicate runs
2	Cellulose (1 g)	Methyl iodide (2.75 g)	15	86	0.3	
3	Cellulose (1 g)	Dimethyl sulfate (1.3 g)	5 × 3	75	0.6	Split mw time
4	Cellulose (1 g)	Methyl iodide (1.3 g)	5 × 3	87	0.4	Split mw time
1D	Sample 1 (1 g)	Dimethyl sulfate (2.5 g)	20	90	0.8	Second methylation on sample 1
5	Cellulose (1 g)	Dimethyl sulfate (3.75 g)	15	83	0.7	Increase DMS dose; first methylation
5D	Sample 5 (0.7 g)	Dimethyl sulfate (2.63 g)	15	54	1.0	Second methylation; increase DMS dose
6	Cellulose (1 g)	Methyl iodide (4.13 g)	15	82	0.6	Increase MI dose; first methylation
6D	Sample 6 (0.7 g)	Methyl iodide (2.87 g)	15	74	1.0	Second methylation; increase MI dose
7	Cellulose (1 g)	Ethyl iodide (3.16 g)	15	96	0.2	First ethylation
7D	Sample 7 (1 g)	Ethyl iodide (3.16 g)	15	73	0.4	Second ethylation

Milestone Inc., Monroe, CT). This microwave reactor allowed highly accurate control of pressure, power and temperature. A typical setup involved a Teflon® stir bar in the reactor vessel, with moderate stirring employed during a reaction.

2.2. Synthesis of alkyl cellulose

In a typical procedure, 1.0 g cellulose (Sigma–Aldrich), 26.9 mL water, and 2.5 g NaOH were mixed together at room temperature for 1 h and then placed in a refrigerator at −20 °C overnight. The frozen mixture was thawed at room temperature. A spatula was used to break up the resulting gel. 20.6 ml water and 2.5 g dimethyl sulfate (or 2.75 g methyl iodide) were added, and the mixture was subjected to microwave irradiation at 75 °C for 15–20 min. The reaction mixture was cooled to 40 °C before the microwave reactor was opened. For work-up, 50 mL of 10% acetic acid was added to neutralize the pH of the mixture. 20 mL water was added with stirring. The solution was heated to 60 °C, and the precipitated methyl cellulose was filtered from the hot solution. The methyl cellulose was washed two more times with hot water and filtered hot. The product was dried in an 80 °C vacuum oven overnight. Weight recovered was 0.8613 g

The synthesis of ethyl cellulose was similar except that ethyl iodide (3.16 g) was used. The reaction proceeded in the same way except that cold water might be used for the work-up. To increase the DS, alkylation was sometimes done twice on the same samples.

2.3. NMR and FTIR analysis

Methyl and ethyl cellulose samples were dissolved in d_6-dimethylsulfoxide (DMSO) and placed in NMR tubes. NMR spectra were obtained by using DRX 400 spectrometer from Bruker Corporation (Karlsruhe, Germany) at a probe temperature of 60–70 °C. Standard instrument conditions were used for ^{1}H and ^{13}C spectra; chemical shifts were referenced to tetramethylsilane at 0 ppm. The FTIR spectra were collected using a single bounce Durascope from Sens IR on a Thermo Nicolet Avatar 370 Fourier Transform Infrared spectrometer to obtain mid-range ATR spectra. Data processing was conducted with the Omnic software package.

3. Results and discussion

As in conventional synthesis of methyl cellulose, the current reaction also consisted of two steps. In the first step, mercerization was done at −20 °C to produce an alkali cellulose gel. In the second step, an alkylating agent was added with water to the alkali cellulose and subjected to microwave heating. For a simple microwave reaction (15–20 min), the results for two runs (samples 1 and 2, with dimethyl sulfate and methyl iodide, respectively) are shown in Table 1, where yields of about 87% and degree of substitution (DS) of 0.3–0.4 were obtained.

In order to optimize the reaction, an effort was made to split the microwave reaction time to three internals of 5 min each. Between the internals, the reaction mixture was stirred vigorously. The results for these two samples (3 and 4) were similar to those

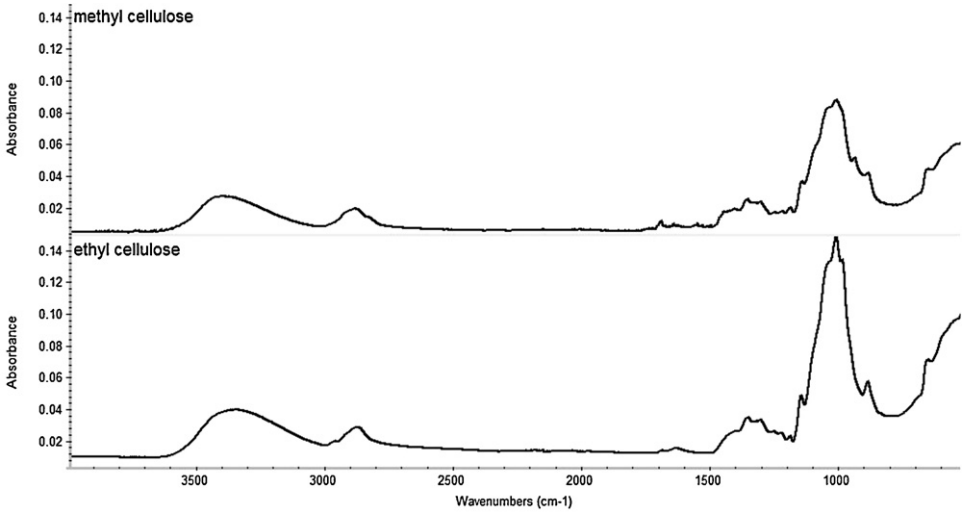

Fig. 1. FTIR spectra of methyl cellulose (sample 6D) and ethyl cellulose (sample 7D).

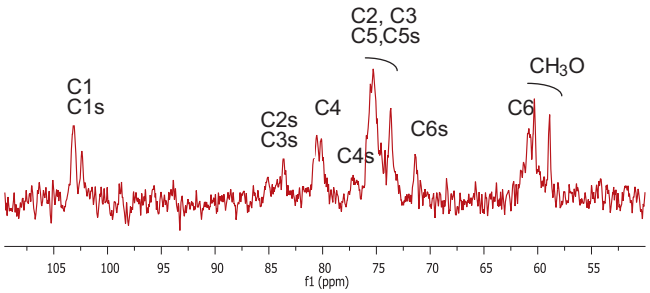

Fig. 2. ^{13}C NMR spectrum of methyl cellulose (sample 6D) in d_6-DMSO. In the spectral assignments, the number after C refers to the carbon position on the anhydroglucose ring; s refers to shift position after methyl substitution.

of samples 1 and 2 (Table 1), indicating that increased agitation was not beneficial. In another effort, sample 1 was methylated a second time (sample 1D); this produced a higher DS (0.8). The double methylation experiments were repeated with higher levels of dimethyl sulfate (samples 5 and 5D). The DS increased from 0.7 to 1.0 with double methylation. A similar double methylation was done using higher levels of methyl iodide (samples 6 and 6D). Again, the DS increased from 0.6 to 1.0 with double methylation. Thus, higher levels of alkylating reagents led to higher DS values.

The synthesis of ethyl cellulose was achieved in a similar manner, using ethyl iodide. In the first ethylation step, a low DS of 0.2 was obtained. After second ethylation, the DS was increased to 0.4. The lower DS obtained with EC may be related to the lower solubility of ethyl iodide in water.

The FTIR spectra of methyl cellulose and ethyl cellulose are shown in Fig. 1. The spectrum for methyl cellulose agrees with those reported in the literature (Levdik, Nikitin, Petrapavlovskii, & Vasileva, 1965; Rimdusit, Jingjid, Damrongsakkul, Tiptipakorn, & Takeichi, 2008). Thus, O—H stretching is found at ~3300 cm^{-1}, C—H stretching at ~2900 cm^{-1}, vibration of OCH_3 group at 950 and 1460 cm^{-1}, carbonyl stretching from glucose of the cellulose at 1643 cm^{-1}, C—O stretching from asymmetric oxygen bridge at 1163 cm^{-1}, and ring stretching at 896 cm^{-1}. The spectrum of ethyl cellulose also agrees with those reported in the literature (Arias, Lopez-Viota, Ruiz, Lopez-Viota, & Delgado, 2007; Feng et al., 2011), particularly with broad CH deformation vibrations at ~1400 cm^{-1}.

A typical ^{13}C NMR spectrum of methyl cellulose is shown in Fig. 2, with spectral assignments taken from the literature (Ke et al., 2006; Sekiguchi, Sawatari, & Kondo, 2002; Takahashi, Fujimoto, Barua, Miyamoto, & Inagaki, 1986). The DS for methyl cellulose can be determined by taking the sum of the intensities for peaks at ca. 50 ppm (methoxy and unsubstituted C6) and 70.0 (substituted C6), subtract the intensities of C1 and C1s peaks (at ca. 102 ppm) and divide by the intensities of the C1/C1s peaks. For ethyl cellulose the ^{13}C NMR spectrum is shown in Fig. 3, with approximate

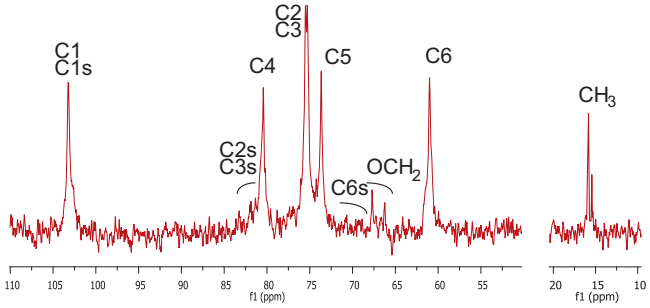

Fig. 3. ^{13}C NMR spectrum of ethyl cellulose (sample 7D) in d_6-DMSO. The number after C refers to the carbon position on the anhydroglucose ring; s refers to shift position after ethyl substitution.

assignments made through additive shift rules (Cheng & Bennett, 1991) and comparison with the literature assignments (Kimura, Asuma, & Gray, 1993; Xu et al., 2003). The DS can be obtained by taking the intensities of the methyl peaks at ca. 15 ppm and dividing by the intensities of the C1 and C1s peaks at ca. 102 ppm.

It is of interest that the use of microwave facilitates the alkylation of cellulose. It has been noted that microwave permits rapid transfer of thermal energy in the reaction mixture, and may increase the pre-exponential factor or decrease the activation energy in the Arrhenius equation (Lidström et al., 2001). For the alkylation of cellulose, microwave irradiation may also increase the mobility of the alkylating agent, decrease the viscosity and enhance the accessibility of alkali cellulose, thereby promoting a faster reaction.

4. Conclusion

Cellulose can be converted to methyl and ethyl cellulose in a fast and convenient method through a microwave-assisted reaction and the use of a microwave reactor. This new method of synthesis has the advantage of decreased reaction time, decreased usage of energy, and the use of water as the reaction medium (instead of alcohol). This method should be adaptable to the synthesis of other cellulose ethers.

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