

Two-dimensional NMR Spectroscopy Study of Ethyl Substitution on Cellulose

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Introduction

Biopolymers are a diverse range of macromolecules including a range of technologically useful engineering polymers. Materials such as the *cellulosics* have been utilised since antiquity. Cellulose (Figure 1) is synthesised by plants from CO₂ and sunlight, and as such represents an entirely renewable and green house neutral material. Owing to the intra-chain hydrogen bonding the cellulose chain is very stiff and insoluble in most solvents.

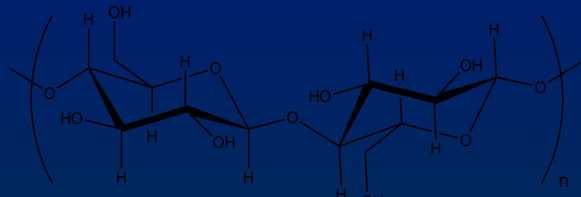


Figure 1: Cellulose is the important cell wall polymer of β-1,4-linked D-glucopyranose.

Ethyl cellulose (EC) is the ethyl ether of the polymer of β-1,4-linked D-glucopyranose of the important cell wall polymer cellulose (Figure 1). It is synthesized by the reaction from wood pulp swollen with sodium hydroxide solution with ethyl chloride. The effect of the substitution is to produce a polymer which is soluble in a wider range of solvents due to the disruption of intra-chain hydrogen bonding. The chemistry, or exact substitution of ethyl groups around the pyranose rings is not well defined and is usually expressed in terms of number of ethyl substitutions per pyranose ring. Rather than being defined by the chemistry EC is usually defined by the manufacturing process.

Aim

Here we seek to measure the degree of ethyl substitution (DOS) and site of substitution (SOS) around the glucose rings.

Experimental

All NMR experiments were performed on a Bruker DMX600 with a QNP probe. The following Bruker pulse programs were used; HMBC – hmbcgp1pndqf, HSQC – hsqcctgpsi, ¹³C – zgpg30 (with bi-level waltz16 decoupling for the suppression of coupling artefacts) and zgig30.

A solution of EC 700 μl (76.9 mg) was prepared in C₆D₆.

Trioxane was used as an internal standard for purposes of quantification. 20 μl of a stock solution of 125.7 mg (1.40 mmol) in 200 μl C₆D₆ was added to the EC solution.

Results

Solvent Survey by 1D NMR

Factors such as solubility, peak resolution and residual solvent peaks all play a role in the choice of solvent. The solubility of EC in this case is the limiting factor. Deuterated benzene provided the best combination of signal dispersion and EC solubility.

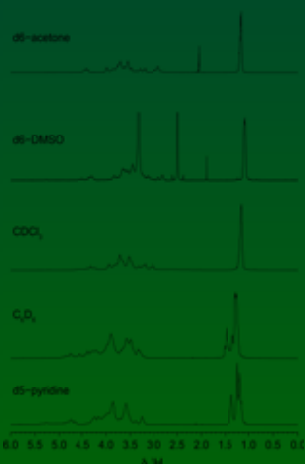


Figure 2: The ¹H spectra of ethyl cellulose (20 mg) in a variety of solvents. Acquired on a Bruker DMX600 at 298 K.

Assignment by 2D NMR (SOS)

Virtually complete assignment of EC was achieved from the HMBC spectrum.

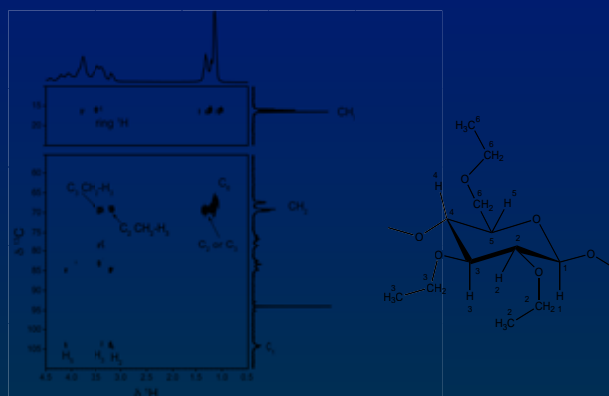


Figure 3: HMBC spectrum of ethyl cellulose (76 mg) in a C₆D₆. Acquired on a Bruker DMX600 at 314 K. The numbering of assigned peak is shown in the accompanying sugar.

Quantification of DOS by 2D NMR

A variety of methods to determine the DOS can be performed. HSQC provides the opportunity to determine the DOS with the use of an appropriate internal standard. A combination of HMBC and HSQC allowed for the quantification of SOS as well.

Integration of the HSQC cross peaks in Figure 4 show that the C₆ and C₂ sites are completely ethylated while the C₃ site is only 25% ethylated, a small amount of C₂ like ethylation was also observed. It is the C₃ site which is largely responsible for intrachain H-bonding.

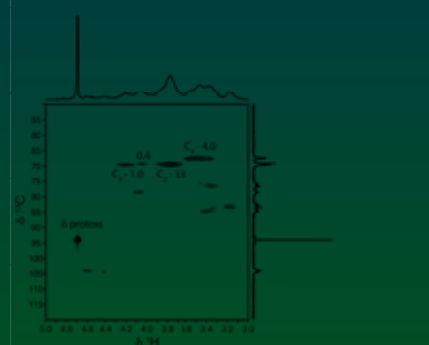


Figure 4: HSQC spectrum of ethyl cellulose (76 mg) in a C₆D₆. Acquired on a Bruker DMX600 at 314 K. A coupling constant of 155 Hz was used for selection.

Conclusion

¹D NMR is insufficient in resolution to give accurate assessment of ethylation (DOS/SOS) via integration.

²D HMBC NMR allows for assignment of both the ¹H and ¹³C spectra provide complete SOS information.

Integration of the 2D HSQC spectrum allows for the DOS to be determined.

References

- Roslund, M.U., et al., *Complete assignments of the (1)H and (13)C chemical shifts and J(H,H) coupling constants in NMR spectra of D-glucopyranose and all D-glucopyranosyl-D-glucopyranosides. Carbohydr Res.* 2008. **343(1)**: p. 101-12.
- Zhang, L. and G. Gellerstedt, *Quantitative 2D HSQC NMR determination of polymer structures by selecting suitable internal standard references. Magnetic resonance in chemistry : MRC.* 2007. **45(1)**: p. 37-45.