

Xylan Derivatives: Benzyl Ethers, Synthesis, and Characterization

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ABSTRACT: The -2,3-bis(benzyl ether) of xylan, a natural polysaccharide, has been prepared by using a new benzylation method. This method was first tested on methyl- β -D-xylopyranoside, the monomer model of xylan. It implies the use of potassium hydroxyde, a crown ether as a catalyst, and benzyl bromide as a benzylation agent. Perbenzylated xylan is obtained with a good yield (80%) in a one-step reaction. It is soluble in most organic solvents. The ^{13}C - and ^1H -NMR spectra of this polymer were assigned and are typical of a regular linear polymer. Differential thermal analysis and thermogravimetry indicate the temperature range at which this polymer can be processed at high temperature. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 455–460, 1998

Key words: polysaccharides; xylan; benzylation; organic soluble xylan derivative

INTRODUCTION

Benzyl ethers are efficient substituting groups for polyols and are stable in acidic and basic conditions. They can be removed by hydrogenolysis (H_2/Pd) to regenerate the original polyol. Xylans are natural polysaccharides, essentially found in the walls of wood cells. One of the major compound is the poly- $\beta(1-4)\text{D}$ -xylopyranosyl polymer, branched with short chains or units of different sugars. These branched sugar units can be easily cleaved in an oxalic acid solution, leaving a linear poly- $\beta(1-4)\text{D}$ -xylopyranosyl chain.¹ Each constitutive unit then contains two hydroxyl reactive groups. Xylan is difficult to dissolve in organic polar solvents like all $\beta(1-4)$ linked polysaccharides as, for example, cellulose. The reaction of the hydroxyl functions yields either ethers, esters, or carbamate derivatives. This leads to organic soluble polymers, as it has been widely shown for cellulose derivatives. However, little attention

has been paid to xylan derivatives. Xylan diacetate was mentioned and found to be soluble in organic solvents only when its molecular weight was low,² while xylan dimethyl ether was found to be soluble in chloroform.³ We have shown that xylan aromatic carbamates present a good solubility in polar organic solvents such as dimethylsulfoxide, *N,N*-dimethylacetamide and *N,N*-dimethylformamide.⁴ The aim of this work is the preparation of bis(benzyl ether) of xylan by using a new benzylation method, as well as the characterization of this polymer by using spectroscopic and thermic analytical methods.

EXPERIMENTAL

Methyl 2,3,4-tri-*O*-benzyl- β -D-xylopyranoside (2)

1 g of methyl β -D-xylopyranoside (Sigma, St. Louis, MO, USA) (see Scheme 1) is dissolved in 20 mL of dry acetonitrile. 0.25 g of the catalyst 18-crown-6 ether (Janssen Chimica, Geel, Belgium) is added to the solution, then 3.5 g of potas-

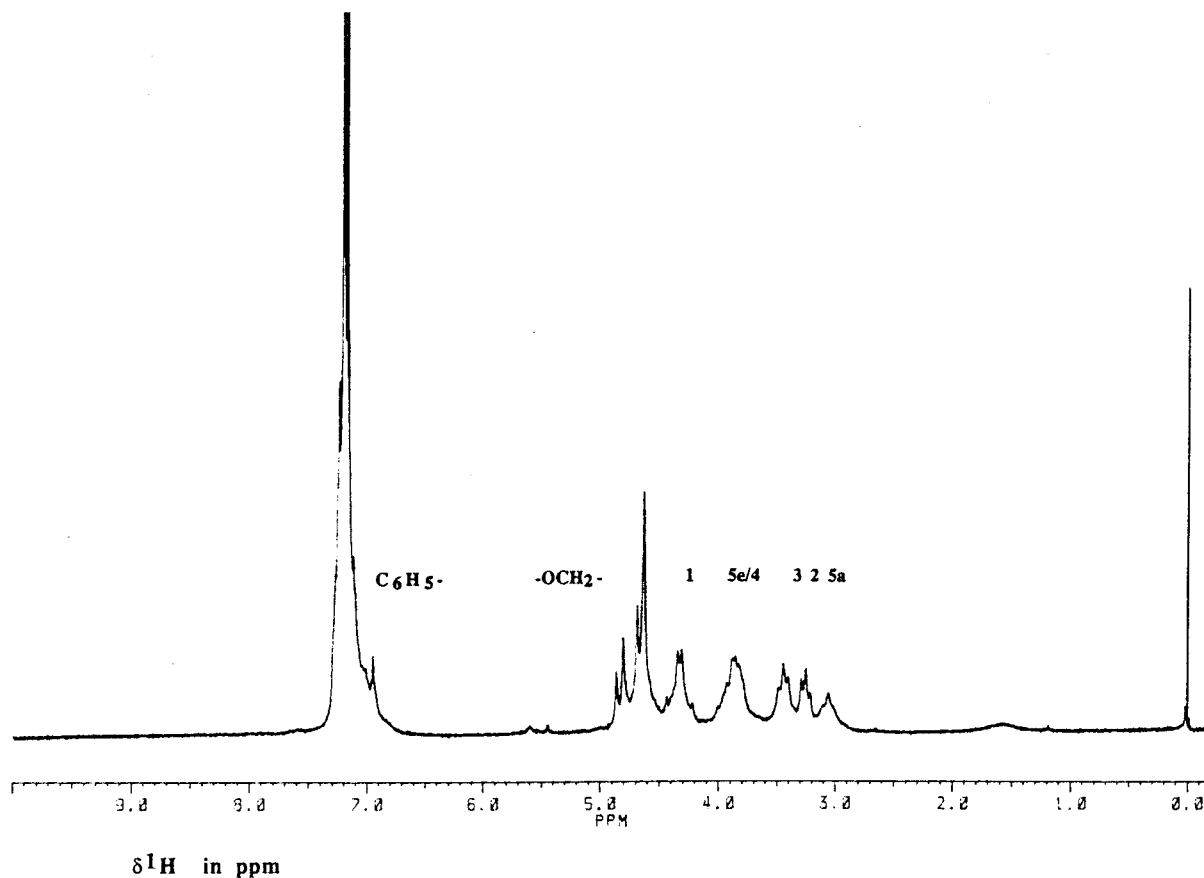


Figure 1 200 MHz ^1H -NMR spectrum of 2,3-di-*O*-benzyl- β -D-xylan in CDCl_3 solution.

(3) repeating unit (see formulas). The tri-*O*-benzyl ether of this monosaccharide is easily obtained and characterized (see the Experimental section).

The extrapolation of the benzylating reaction conditions used for the monomer leads to a partially substituted polymer not soluble in organic solvents, as can be expected for the completely substituted compound. When the aprotic solvent acetonitrile is replaced by dimethylsulfoxide, the complete substitution is obtained in a one-step reaction in the following experimental conditions: 3 mol of benzyl bromide per mole of hydroxyl; temperature, 70°C; reaction time, 24 h. The infrared (IR) spectrum of the substituted polymer (film prepared from a chloroform solution) reveals an important decrease of the OH vibration at 3400 cm^{-1} . However, as in the case of the monomer, there remains a small absorption that can originate either from unsubstituted hydroxyl groups or from adsorbed water. In order to be sure of the complete substitution of all the hydroxyl groups of the chain, polymer (4) has been submitted to a second benzylation reaction in the same experi-

mental conditions. After a two-step reaction, the new polymer presents exactly the same spectra as polymer (4), and particularly a small hydroxyl absorption band located at 3400 cm^{-1} in its IR spectrum. It can be concluded that this remaining hydroxyl vibration originates from adsorbed water molecules.

The ^1H -NMR spectrum of (4) in a CDCl_3 solution is shown in Figure 1. This spectrum has been assigned by using the two-dimensional $^1\text{H}/^1\text{H}$ homonuclear nuclear magnetic resonance (NMR), and one must notice the two methylenoxy signals corresponding to the benzyl substituents, respectively, at 4.68 and 4.48 ppm. The ^{13}C -NMR spectrum of (4) is shown in Figure 2 and characterizes two carbon signals, C-3 and C-2, strongly shifted to high chemical shift values ($\delta_{\text{C-3}} = 82$ and $\delta_{\text{C-2}} = 81.4$ ppm) due to the benzyl ether substitution. The assignment of the ^{13}C -NMR spectrum has been obtained via the $^1\text{H}/^{13}\text{C}$ two-dimensional heteronuclear NMR technique. These spectra are characteristic of a regularly and fully substituted ether derivative of xylan.

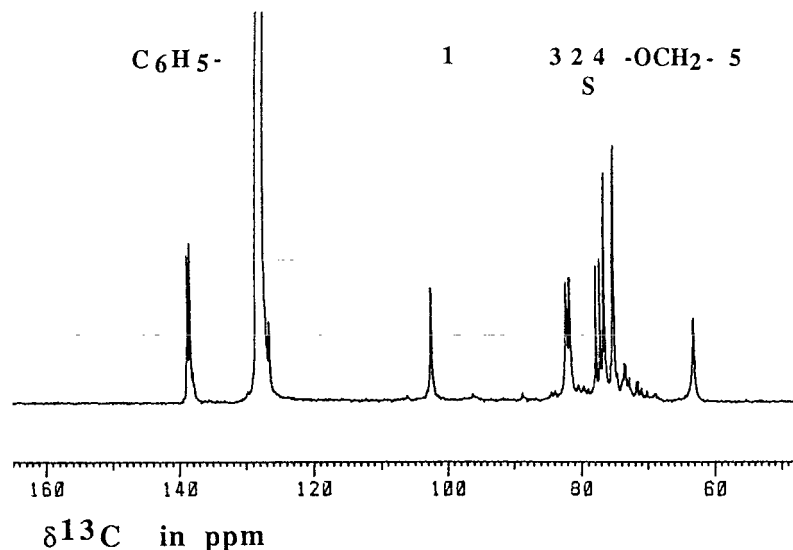


Figure 2 ^{13}C -NMR spectrum of 2,3-di-*O*-benzyl- β -D-xylan in CDCl_3 solution (50 MHz). S represents CDCl_3 signals.

Thermal Properties

The substitution of the xylan hydroxyl groups brings about an excellent solubility in classical organic solvents and, at the same time, a new thermal behavior. Figure 3 shows the DTA diagrams of the original xylan (3) [Fig. 3(A)] and

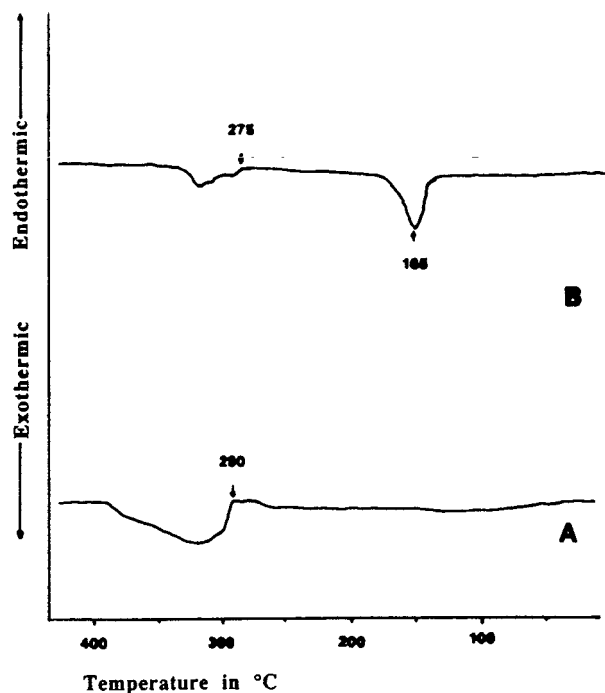


Figure 3 Differential thermal analysis (DTA) curves of (A) xylan and (B) 2,3-di-*O*-benzyl- β -D-xylan.

of the benzylated polymer (4) [Fig. 3(B)]. Xylan presents the same behavior as most linear polyhydroxylated polymers, showing only one exothermic transformation at high temperature (275°C), corresponding to its decomposition.

Polymer (4) shows the following two exothermic transformations: one at 165°C in the solid state; and a second one at 275°C, which corresponds to the degradation temperature. The observation on a melting apparatus indicates no visible transformation up to 205°C, temperature where the solid polymer starts softening up to 225°C. In this temperature range, the DTA curve shows no endothermic transformation, which is an indication of an amorphous polymer. When polymer (4) was submitted to a first heating run, up to 180°C, and then cooled at room temperature; the second heating indicates only one exothermic transformation at 275°C. The unexplained solid–solid transformation at 165°C is then irreversible. It can be mentioned that the intensity of this transformation is sometime less important than that shown in Figure 3(B); depending on the sample.

Figure 4 shows the thermogravimetry curve of polymer (4). There is a noticeable weight loss (15%) beginning at 230°C, in the softened state, followed by pyrolysis at 275°C, as indicated on the DTA curve. This thermal study indicates that di-*O*-benzyl xylan is an amorphous polymer that presents a softening temperature range between 205 and 225°C, and that its thermal decomposition begins at 230°C.

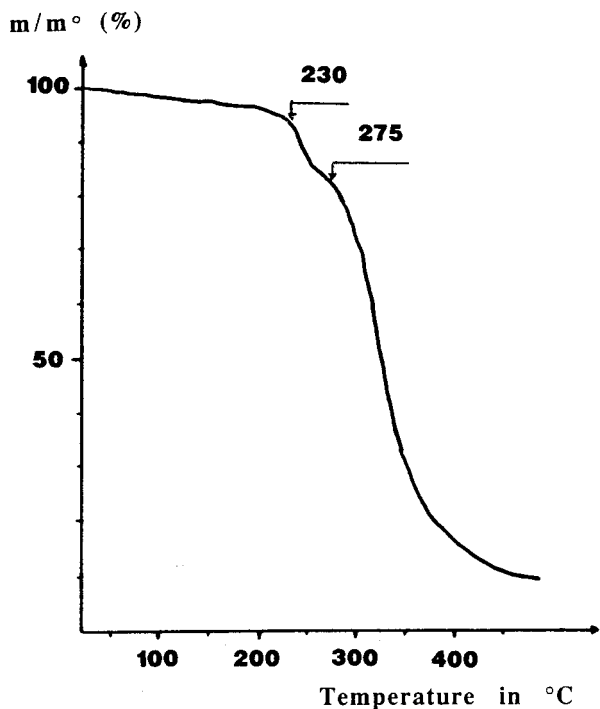


Figure 4 Thermogravimetric analysis of 2,3-di-O-benzyl- β -D-xylan.

Viscosity Measurements

Natural xylans are known to have a low molecular weight value. It is generally admitted that they have a degree of polymerization in the range of

several hundreds.⁹ The intrinsic viscosity of a solution of di-O-benzyl xylan in chloroform has been determined (Fig. 5). The extrapolated value at zero concentration $[\eta] = 0.27 \text{ dL g}^{-1}$ is low and indicates a low molecular weight value. In Figure 5(B) is shown the intrinsic viscosity of a polymer that has been obtained after a two-step reaction. As expected, the benzylation is achieved in basic reaction conditions and thus induces a noticeable degradation of the polymer chain since the intrinsic viscosity decreases from 0.27 to 0.24 dL g⁻¹.

CONCLUSION

It has been shown that the perbenzylated ether of xylan can be obtained in a good yield, in a one-step reaction, by a new method involving the use of a crown ether as a catalyst and benzyl bromide as benzylating agent. The perbenzyl xylan is shown to be a regular linear polymer thanks to NMR spectroscopy, which reveals a well-resolved ¹³C-NMR spectrum based on the five signals of the D-xylopyranosyl repeating unit.

The substitution of the two hydroxyl groups of the xylan chain induces, as expected, a great change in the physical properties of solubility and thermal behavior. It presents thermoplastic properties that allow its processing in a softened state between 205 and 225°C, without degradation of the polymer chain.

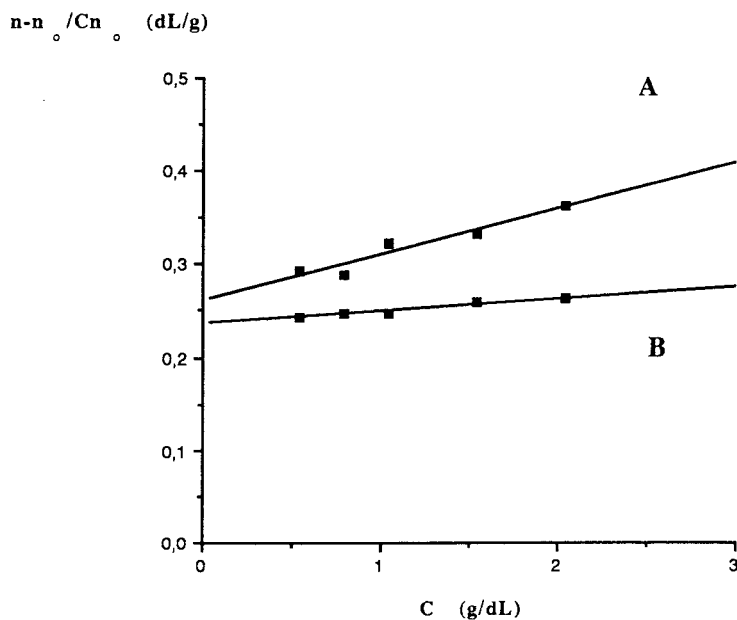


Figure 5 Intrinsic viscosity measurement of 2,3-di-O-benzyl- β -D-xylan at 25°C in a chloroform solution: (A) after one reaction step; (B) after two reaction steps.

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