



Safe and non-toxic hydroxyalkylation of xylan using propylene carbonate

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ABSTRACT

Xylan is an abundant polysaccharide consisting of xylose units and has gained a significant increase in research interest in the last decades. Hydroxyalkylation of xylan is a way of modifying xylans to achieve xylan ethers with better water solubility as well as to form materials which can be used for gels, films or packaging applications. In this work, hydroxyalkylation is performed with non-toxic propylene carbonate in dimethyl sulfoxide (DMSO) with alkaline 1,8-Diazabicyclo [5.4.0]undec-7-ene (DBU) as catalyst. In this way highly toxic and explosive, but currently widely used propylene oxide can be avoided. A decarboxylation step is taking place during the reaction, making the product identical to the one, which can be obtained by using epoxides. The obtained products show degrees of substitution between 0.1 and 1.5 with low tendencies for homopolymerization along the side chain. Therefore the procedure allows the tailored production of xylan ethers via hydroxyalkylation. The products are characterized by one- and two-dimensional NMR- as well as FTIR-spectroscopy, mass spectrometry, SEC and regarding their water solubility.

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1. Introduction

Xylan is a bio-polymer consisting of xylose monomer units which are β -(1 → 4)-linked. It is one of the most abundant substances in hard wood and annual plants and thus is a potential source for high performance materials from renewable resources. The biodegradability of xylan is a further advantage compared to conventional, petroleum-based materials [1–3].

Therefore, a growing interest in utilization and derivatization of xylan has emerged in the last decades. Several different methods to modify the bio-polymer have been reported. Early successful modifications were performed around the years 1950–1960, when *Glaudemans* and *Timell* successfully methylated [4] as well as acetylated [5] xylan from white birch wood. Several other derivatizations were performed at that time, including higher esters [6] and carboxymethylation [7]. After 1990, the interest in further research on properties and applications of modified xylan increased for a complete usage of annual plants. Recent publications reported a variety of possible routes to achieve highly modified xylans, making it an alternative to cellulose and starch. Currently there are two possible applications: Pharmaceutical as well as thermoplastics and gels [8]. For pharmaceutical purposes, xylans are modified by long aliphatic esters and sulfate groups, leading to substances that can be used in the prevention and treatment of articular diseases [9]. Furthermore, recent studies showed anticoagulant

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effects for a variety of sulfated polysaccharides [10,11]. Additionally, antiviral and cancerostatic effects were monitored for the sulfate derivatives [12–14].

For creating thermoplastic polymers from xylan, hydroxyalkylation is the most common approach, leading to an etherification of the original hydroxyl group in combination with a chain extension of the side group and the formation of a new hydroxyl group. Hydroxyalkylation of polysaccharides have been conducted on cellulose [15] and starch [16], leading to widely commercial available products. Examinations on hydroxyethylated [17] and hydroxypropylated [18] cellulose showed a significant increase in water solubility. For technical xylans hydroxyalkylation therefore is an interesting method to overcome the difficulties of dissolving. These are caused by the high number of hydrogen bonds between the single polymer chains [19]. Hydroxypropylation of xylan was first reported by Glasser et al. [20] and further researched by Jain et al. [21], using xylan from barley husks and propylene oxide in an alkaline medium, achieving DS-values from 0.2 to 2. Recent studies on hydroxypropylation have been performed by Laine et al. [22] as well as Mikkonen et al. [19], utilizing xylan from birch wood. Those reports showed the potential of modified xylans as packaging materials due to significant reduction of water and oxygen permeability.

Epoxides are generally considered to be toxic, cause cancer and also to be highly explosive, making it difficult and hazardous to work with. It has to be noted that hydroxyalkylated starch and cellulose, obtained with epoxides in a cheap synthesis, are used in many applications. However, there might be a demand for less toxic alternatives, especially for applications in companies with versatile product profiles or small production facilities. Five-membered cyclic organic carbonates seem to be a suitable substance class in this matter. They are closely related to epoxides since they can be synthesized by the addition of carbon dioxide to the former mentioned. This was first reported by Nomura et al. [23].

For the presented study propylene carbonate (PC) was chosen for derivatization, since PC bears a low toxicity [24] and is generally considered as a green chemical which can be produced from renewable resources [25,26]. Additionally, PC is well suited for synthesis due to its liquid state at room temperature, its high boiling point ($b_p = 242\text{ }^\circ\text{C}$) and low vapor pressure, making it a safe chemical that is easy to handle. The advantages of PC as a solvent, for example, for paint stripping and degreasing, are already widely known [27,28]. Due to its low toxicity it is also used as a carrier solvent for topically applied cosmetics and medications [25,29]. The first report on hydroxyalkylation of starch and glucose with cyclic organic carbonates was published by Pope in 1984 [30]. Using ethylene carbonate, a DS 0.31 was achieved after three hours at $140\text{ }^\circ\text{C}$ with tetra-*n*-ethyl ammonium bromide as catalyst [30]. Recently, Kühnel et al. published the hydroxyalkylation of lignin [31]. Both, aliphatic and phenolic hydroxyl groups in lignin could be derivatized completely by dissolving lignin in PC, using potassium carbonate as catalyst at $170\text{ }^\circ\text{C}$. High temperatures are of major importance as hydroxyalkylation with cyclic organic carbonates involves decarboxylation. Recently, Zhang et al. published the graft polymerization of xylan with propylene carbonate [32], using ionic liquids as solvent. However, the group was only able to obtain xylans with a DS in the range of 0.2–0.5.

In the present study the hydroxyalkylation of xylan is reported using propylene carbonate in DMSO with 1,8-Diazabicyclo [5.4.0]undec-7-ene (DBU) as catalyst. Two different xylans are compared with special focus on the effect of reaction time, temperature, and amount of xylan in the solution. Samples are analyzed mainly by one and two-dimensional NMR-spectroscopy regarding the degree of substitution (DS) and molar substitution (MS), and are further characterized by FTIR-spectroscopy, mass spectrometry, SEC as well as their water solubility.

2. Experimental section

2.1. Materials

Arabinose-enriched xylan (OX) was isolated from oat spelts by potassium hydroxide extraction as published previously [33]. Analysis yielded a molecular weight of $M_w = 23,500\text{ g/mol}$, a polydispersity index (PDI) of 2.2 as well as an arabinose content of approximately 9 mol% and a 4-O-methylglucuronic acid (4-MGA) content of 4 mol%. Beech wood xylan (BX) was isolated analogously to OX from holocellulose, which was obtained by sodium chlorite delignification of beech wood according to [34]. Analysis yielded a molecular weight of $M_w = 19,100\text{ g/mol}$ and a PDI of 1.5 with a 4-MGA content of 10 mol%.

For derivatization, DMSO (for synthesis, >99%) was purchased from Merck (Darmstadt, Germany), propylene carbonate ($\geq 99.7\%$) from Roth (Karlsruhe, Germany), 1,8-Diazabicyclo [5.4.0]undec-7-ene (DBU, 99%) and tetra-*n*-butylammonium bromide (98+%) were obtained from Alfa Aesar (Karlsruhe, Germany), diethyl ether (>99%) from VWR (Darmstadt, Germany), acetone (99.5%) from BCD Chemie (Hamburg, Germany) and deuterated DMSO (99.8%) from Deutero (Kastellaun, Germany). Propylene carbonate was stored over molecular sieve (0.3 \AA), other chemicals were used without further purification.

2.2. Derivatization of oat spelt xylan

To achieve a satisfying solution state, 1.05 g xylan (5.02 mmol anhydro xylose) were suspended in 10.5 g DMSO (10% w/w) and stirred for 16 h at $50\text{ }^\circ\text{C}$. After the solution was heated to $100\text{ }^\circ\text{C}$, 10.5 g (102 mmol) propylene carbonate and 55 μL (0.35 μmol) DBU were added. Subsequently, the solution was heated to $140\text{ }^\circ\text{C}$ or $160\text{ }^\circ\text{C}$, respectively. Reaction time was measured when the destined temperature was reached, with reaction times of 0, 40, 80, 160 and 240 min being examined.

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