Industrial Crops and Products 101 (2017) 75–83

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Oxyalkylation of lignin with propylene carbonate: Influence of reaction parameters on the ensuing bio-based polyols

Isabell Kühnel[a], Bodo Saake[a], Ralph Lehnen[b,*]

[a] *Department of Wood Science and Chemical Wood Technology, University of Hamburg, Leuschnerstraße 91b, 21031 Hamburg, Germany*
[b] *Thünen Institute of Wood Research, Leuschnerstraße 91b, 21031 Hamburg, Germany*

ARTICLE INFO

Article history:
Received 21 June 2016
Received in revised form 18 January 2017
Accepted 2 March 2017

Keywords:
Organosolv lignin
Cyclic organic carbonate
Propylene carbonate
Bio-based polyols
^{1}H NMR
^{31}P NMR

ABSTRACT

Beech wood organosolv lignin was modified with propylene carbonate (PC) in an efficient, facile and solvent-free procedure without using highly toxic and explosive propylene oxide (PO). Comparative studies of the oxyalkylation procedure were performed varying crucial reaction conditions. The results of FTIR, ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectroscopic analyses revealed that the OH group activation of lignins differed significantly depending on catalyst, catalyst to lignin ratio, reaction time, temperature and PC amount. Under optimized reaction conditions using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as catalyst, a degree of substitution (DS) of 0.92 and chain lengths of up to 4.6 propyl units were achieved, yielding 0.3% of carbonate linkages in the grafted chain. This oxyalkylation procedure using safe and non-toxic PC represents a promising alternative to PO for the preparation of lignin polyols concerning the substitution of conventional petroleum-based polyols.

1. Introduction

In the field of polymeric materials, oxyalkylation with propylene oxide (PO) is a widely established method for the production of polyols as precursors for the polyurethane production. This oxypropylation represents a chain extension reaction forming grafts of poly(propylene oxide), whose introduction to biomass residues are of great interest (Aniceto et al., 2012; Gandini and Belgacem, 2008). This reaction is frequently in focus for a variety of renewable resources such as several lignins (Cateto et al., 2009; Cui et al., 2013; Nadji et al., 2005), sugar beet pulp (Pavier and Gandini, 2000a,b), cork (Evtiouguina et al., 2002), olive stones (Matos et al., 2010), date seeds (Briones et al., 2011), rapeseed cake residue (Serrano et al., 2010), cellulose fibers (de Menezes et al., 2009; Gandini et al., 2005), starch granules (de Menezes et al., 2007), chitin and chitosan (Fernandes et al., 2008) and tannin (Garcia et al., 2013; Arbenz and Avérous, 2015).

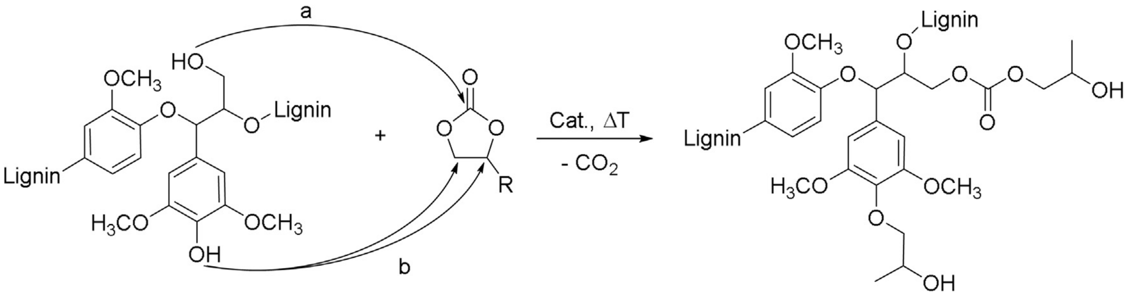
The pioneering work on oxypropylation of biomass based feedstocks was carried out with lignins (Wu and Glasser, 1984). Being one of the most abundant biopolymers and its growing availability, lignin is still a promising bio-phenolic macromolecule for the development of value-added chemicals and bio-based polymers. To overcome the obstacles in terms of limited reactivity, accessibility and solubility of lignin, the oxyalkylation with PO has been proven (Cateto et al., 2009; Cui et al., 2013; Nadji et al., 2005; Wu and Glasser, 1984), thus contributing to substitution of conventional polyols in polyurethane synthesis (Saraf et al., 1985; Rials and Glasser, 1986). However, a major drawback of this reaction procedure is the high level in safety precautions due to the high vapor pressure and explosive vapors, flammability, toxicity, and carcinogenicity of PO. The use of this toxic oxyalkylating agent is no longer a motivating target due to environmental and hazardous problems. Therefore, much more safe, non-toxic and eco-friendly oxyalkylating agents, e.g. cyclic organic carbonates are favored. Low toxicity, high boiling and flash points, low vapor pressure, biodegradability and high solubility (Clements, 2003; Liebert, 1987; Schäffner et al., 2009) making cyclic organic carbonates both attractive solvents in synthesis and catalysis (Schäffner et al., 2010), and versatile building blocks in synthetic chemistry due to their variable side chains (Parrish et al., 2000; Sonnati et al., 2013). A well-known and commercially available representative (Huntsman Corporation, 2001, 2010) of this compound class is propylene carbonate (PC). Because of its high boiling point (242 °C), high flash point (135 °C) and low volatility (0.04 hPa at 20 °C) (Table 1) compared to PO, PC is a low volatile solvent and chemical building block making it easy to handle.

The increasing sustainable awareness powers the development of new sustainable production routes. Several research groups have

---

* Corresponding author.
E-mail address: ralph.lehnen@thuenen.de (R. Lehnen).

http://dx.doi.org/10.1016/j.indcrop.2017.03.002



Scheme 1. Oxyalkylation of lignin via alcohol attack at carbonyl carbon (a) and alkylene carbon (b) of propylene carbonate.

Table 1
Properties of propylene oxide (PO) and propylene carbonate (PC).

Property	PO	PC
Melting point [°C]	−112	−49
Boiling point [°C]	34	242
Flash point [°C]	−37	135
Vapour pressure [hPa at 20 °C]	588	0.04
Density [g cm^{-3}]	0.83	1.20

been investigated the direct synthesis of cyclic organic carbonates with CO_2 or CO as building block (Sakakura and Kohno, 2009; Sonnati et al., 2013).

In the patented literature, the first report on oxyalkylation using cyclic organic carbonates could be traced back to 1948 (Carlson, 1948), while the first studies on oxyalkylation using cyclic carbonates and lignin was published by Monson and Dickson (1953). More detailed reports were recently published, where beech wood organosolv lignin was oxyalkylated with PC generating a uniform lignin polyol with exclusively aliphatic hydroxyl groups (Kühnel et al., 2015). This promising method of oxyalkylation was also adapted for the modification of tannins (Duval and Avérous, 2016). In addition, the oxyalkylation of xylan with propylene carbonate in ionic liquids was reported (Zhang et al., 2015). A more efficient oxyalkylation of xylan was recently presented by Akil et al. (2016) using PC in DMSO, in which hydroxyalkyl xylans with a degree of substitution of up to 1.5 could be observed.

PC and in general all cyclic organic carbonates can react with aromatic and aliphatic alcohols according to two reaction pathways due to their electrophilic sites: one carbonyl carbon and two alkylene carbons. Aliphatic alcohols tend to attack the carbonyl carbon atom leading to carbonate linkages (Scheme 1a), while aromatic alcohols can attack the alkylene carbon atoms and ether linkages with subsequent loss of CO_2 (Scheme 1b). This oxyalkylation allows the production of polyether polyols with primary and secondary hydroxyl groups.

As cyclic organic carbonates are excellent solvents (Chernyak, 2006) and reagents for the preparation of lignin polyols with high amounts of flexible and accessible OH, this synthesis strategy provide lignin polyols for PU applications in a non-toxic, solvent-free and environmentally friendly way (Kühnel et al., 2015). The lignin polyols previously synthesized, had 80% substituted OH groups and a grafted chain length of 1.2 propyl units. To gain more insights into the oxypropylation of lignin by propylene carbonate the variation of reaction parameters could provide important information in terms of control and optimization of this oxyalkylation procedure. Within this study, the oxyalkylation of beech wood organosolv lignin with propylene carbonate was investigated regarding the influence of catalyst, catalyst to biomass ratio, reaction time, temperature and propylene carbonate amount.

2. Materials and methods

2.1. Materials

Organosolv lignin was produced at the Thünen Institute of Wood Research (Hamburg, Germany) by means of ethanol/water (1:1, w/w) pulping of beech wood (OL) and a liquor to biomass ratio of 4:1 (w/w). Organosolv lignin was precipitated in the 2-fold amount of water, filtered and dried in a vacuum oven at 30 °C over P_2O_5 (Puls et al., 2009).

All chemicals were purchased from commercial suppliers and used as received: 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, Aldrich, 98%), potassium carbonate (Merck, 99%). The cyclic organic carbonate Jeffsol® propylene carbonate was kindly supplied by Huntsman Corporation (Belgium).

For NMR analysis the following chemicals were obtained and used as received without further purification: deuterated dimethylsulfoxide (DMSO-d_6, Deutero GmbH, 99.8%), deuterated chloroform ($CDCl_3$, Deutero GmbH, 99.8%), pyridine (VWR, 99.8%), 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP, Aldrich, 95%), chromium(III)acetyl-acetonate (Aldrich, 97%), cholesterol (Aldrich, 99%), hexamethyldisiloxane (HMDSO, Aldrich, ≥99.5%), 1,3,5-trioxane (Aldrich, ≥99%).

2.2. Oxyalkylation of lignin

Lignin (1.0 g, 5.17 mmol OH g^{-1}), 10 – 50 eq of propylene carbonate and 0.075 – 0.5 eq of DBU (or 0.1 eq of K_2CO_3) were allowed to react in the temperature range of 100 – 170 °C for 0.5 – 24 h while stirring in N_2 atmosphere. After completion of the reaction, the crude product was precipitated in the 10-fold amount of deionized acidified water. The precipitated product was membrane filtered (polyethersulfone, pore size: 0.22 µm) and washed with 5 × 50 mL water. The isolated product was dried in a vacuum oven at 30 °C over P_2O_5.

2.3. Characterization

Methoxy group content was determined according to Vieböck and Schwappach (1930). The mean of three measurements was calculated after calibration with vanillic acid.

C, H, N and S elemental analysis of the dry lignin samples was determined in duplicate using the elemental analyzer vario EL cube (Elementar, Germany).

FTIR spectra of the lignin samples were obtained with a Bruker Vector 33 instrument. Spectra were collected from 3750 to 530 cm^{-1} with 60 cumulative scans and a resolution of 4 cm^{-1}.

^1H NMR spectroscopy of lignin samples (30 mg) was performed by dissolving the sample in 0.60 mL DMSO-d_6. The spectra were measured with a Bruker Avance III HD 400 MHz spectrometer and the following acquisition parameters were used: 40 °C, 6006 Hz spectral window, 64 scans, a 4.0 s acquisition time and 20 s delay