Isabell Kühnel, Jacob Podschn, Bodo Saake and Ralph Lehnen*

Synthesis of lignin polyols via oxyalkylation with propylene carbonate

Abstract: An efficient, nontoxic, and solvent-free oxyalkylation of European beech wood organosolv lignin (OL) has been developed. Two approaches were studied: a direct reaction of lignin with propylene carbonate (PC) and a two-step reaction of lignin with maleic anhydride (MA) followed by oxyalkylation with PC. The structural analysis of lignin polyols was performed by $^1$H NMR, $^{13}$C NMR, $^{31}$P NMR, and FTIR spectroscopy. It was demonstrated that PC was able to almost completely oxypropylate aliphatic and phenolic OH groups. Moreover, the carboxylic acid groups of maleated OL were fully oxypropylated by PC. This modification strongly facilitates the generation of a uniform lignin polyol applicable as a biobased component in polyurethanes and polyesters based on cyclic organic carbonates.

Keywords: FTIR, lignin polyol, NMR spectroscopy, organosolv lignin, oxyalkylation, propylene carbonate

DOI 10.1515/hf-2014-0068
Received March 7, 2014; accepted October 27, 2014; previously published online December 10, 2014

Introduction

The demand for renewable energy sources and raw materials of plant origin is increasing in view of the limited reservoir of fossil resources, climate change, and the ever-growing demand for energy and fuels. In analogy to the workup procedure of petrochemicals, one speaks about the modern valorization of biomass residues as biorefinery, which should contribute to the comprehensive and sustainable production of biofuels, basic and fine chemicals, or biomaterials. In this context, the lignocellulose feedstock biorefinery has a promising future due to its sustainability and good availability of biomass. The ecofriendly organosolv processes offer the possibility for a better utilization of the components of lignocellulosic materials such as cellulose, hemicelluloses, waxes, proteins, and terpenes, which could partly substitute traditional petrochemicals (Kamm and Kamm 2004).

Lignin as a byproduct of pulping is frequently in focus for the development of value-added chemicals (Bozell et al. 2007) and biobased polymers (Doherty et al. 2011), such as for polyurethanes (PUs) (Glasser and Hsu 1977; Thring et al. 1997; Borges da Silva et al. 2009). The research objective is to integrate lignin into existing polymer formulations to improve their mechanical and thermal properties and to substitute petrochemical educts. Due to the large number of aliphatic and phenolic hydroxy groups (OH$_{\text{aliph}}$ and OH$_{\text{phen}}$, respectively), lignin is suitable as a polyol in PU synthesis. The direct incorporation of lignin often leads to low-value products (Wu and Glasser 1984). To overcome these limitations, chain-extended hydroxyalkyl lignins were evaluated as precursors in PU applications.

Usually, the chemical modification of lignin is achieved by oxyalkylation with different alkylene oxides, especially propylene oxide (PO) (Wu and Glasser 1984; Nadji et al. 2005; Cateto et al. 2009). In this case, the OH groups in lignin, especially OH$_{\text{phen}}$, were extended by hydroxypropyl units and were then less affected by steric and/or electronic constraints. Moreover, the relative reactivity of OH$_{\text{aliph}}$ groups with isocyanates is significantly higher compared to OH$_{\text{phen}}$ (Janik et al. 2014). This modification route leading to lignin-based polyether polyols contributes to uniformity, reactivity, and solubility of lignins and is helpful for the substitution of conventional polyols in PU synthesis (Saraf et al. 1985; Rials and Glasser 1986).

The handling of PO involves considerable risks due to its high vapor pressure, flammability, toxicity, and carcinogenicity. With this regard, five-membered cyclic organic carbonates (Figure 1a) represent an attractive and promising alternative to PO. This compound class is characterized by low toxicity, high boiling and flash points, low vapor pressure, biodegradability, and high solvency (Liebert 1987; Clements 2003; Schäffner et al. 2009). Due to these
“green” properties, cyclic organic carbonates represent attractive solvents in synthesis and catalysis (Schäffner et al. 2010). Moreover, they have a great potential as building blocks in synthetic chemistry with their variable side chains. Novel synthetic routes facilitate the sustainable production of cyclic organic carbonates (Sakakura and Kohno 2009; Schäffner et al. 2010). A promising and well-known representative of this compound class is propylene carbonate (PC). Owing to its large liquid temperature range, low price, and high polarity, PC can be used as a solvent in natural gas processing and catalysis, as an electrolyte in lithium batteries, and as a synthetic building block (Parrish et al. 2000).

In this study, PC should be investigated as an alternative reactant for the oxypropylation of European beech wood (*Fagus sylvatica* L.) organosolv lignin (OL). A synthesis route should be developed including the reaction of lignin with PC and a two-step reaction of OL with maleic anhydride (MA) followed by oxyalkylation with PC. The objective of this two-step modification route is the introduction of a maleic acid spacer to improve the solubility and accessibility of the lignin. The maleated products will be subsequently subjected to oxyalkylation with PC, which leads to a chain-extended polyether with terminated hydroxy groups. The expectation is, that in both oxyalkylation routes, PC will function as an

---

**Figure 1** Chemical formulas and reactions: (a) five-membered cyclic organic carbonates, (b) direct oxyalkylation of OL with PC to obtain hOL, (c) first step of oxyalkylation: esterification with MA resulting in mOL, and (d) second step of oxyalkylation: reaction of mOL with PC leading to hmOL.
excellent solvent and reagent for the preparation of lignin polyols with high amounts of flexible and accessible OH, which could substitute the conventional petroleum-based polyols in PU applications.

Materials and methods

Organosolv pulping: OL was produced at the Thünen Institute of Wood Research (Hamburg, Germany) by means of ethanol/water pulping of beech wood (F. sylvatica L.) chips (Puls et al. 2009). Pulping conditions: t=1.5 h, liquor-to-wood ratio=4:1, T=170°C, c[H2SO4]=0.5% based on dry wood, and ethanol/water=1:1. All reagents were obtained from commercial suppliers and used without further purification.

Direct oxyalkylation of lignin: OL (1.0 g; 6.52 mmol OH g⁻¹) was dissolved in 5.2 ml of PC (61.1 mmol), and 91.9 mg of K2CO3 (0.66 mmol) were added. The mixture was allowed to react at 170°C for 3 h under stirring in N2 atmosphere. After the completion of the reaction, the mixture was cooled to room temperature and added to 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 P2O5.

Two-step oxyalkylation of lignin: According to Thielemans and Wool (2005), OL (1.0 g; 6.52 mmol OH g⁻¹) was first esterified with MA (10.0 g; 102.0 mmol) in 20 ml of 1,4-dioxane. A total of 1 ml of the catalyst solution [0.5 g of 1-methylimidazole in 10 ml (0.57 mmol) of 1,4-dioxane] was added. The reaction mixture was stirred at 50°C under N2 atmosphere overnight. The mixture was cooled to room temperature and added to the 10-fold amount of deionized acidified water. The precipitated maleated OL (mOL) was membrane filtered followed by washing with water until the pH of the filtrate was neutral. The isolated product was dried in a vacuum oven at 30°C over P2O5. The mOL was then oxypropylated as described above for OL.

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

FTIR spectroscopy: The Fourier transform infrared (FTIR) spectra of the modified lignin samples were obtained with a Bruker Vector 33 instrument. The spectra were collected from 3750 to 530 cm⁻¹ with 60 cumulative scans and a resolution of 2 cm⁻¹.

NMR spectroscopy: Nuclear magnetic resonance (NMR) spectroscopy (¹H, ¹³C, and ³¹P) was performed on a Varian Mercury 400 MHz spectrometer. The ¹H NMR spectroscopy of lignin samples (30 mg) was performed by dissolving the sample in 0.80 ml dimethylsulfoxide (DMSO-d₆). Acquisition parameters: 40°C, 6006 Hz spectral window, 128 scans, a 2.0 s acquisition time, and 10 s delay between pulses. Quantitative ¹H NMR analysis was performed on lignin samples containing a defined amount of N,N-dimethylformamide (DMF) as an internal standard (amide proton at 7.95 ppm as reference).

¹³C NMR spectroscopy was performed following a procedure described by Capanema et al. (2004). In brief, 160 mg of lignin sample were dissolved in 0.80 ml of DMSO-d₆, followed by the addition of 2.8 mg of chromium(III)acetylacetonate as a relaxation agent. Acquisition parameters: inverse gated decoupling, 40°C, 25 000 Hz spectral window, 20 000 scans, 1.4 s acquisition time, and a 2.0 s delay between pulses.

³¹P NMR spectroscopy was performed according to Granata and Argyropoulos (1995). Acquisition parameters: 25°C, 11 990 Hz spectral window, 256 scans, and a 20 s delay between pulses. The calculation of OH groups was based on the integration of the following spectral regions: OH₀ₕₖₚ (149.6–145.6 ppm), 9-substituted units (144.2–141.2 ppm), guaiacyl-OH (141.0–138.7 ppm), p-hydroxyphenyl-OH (138.7–137.2 ppm), and carboxylic acids (135.9–133.8 ppm). Cholesterol served as an internal standard.

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

Size exclusion chromatography (SEC): DMSO with 0.1% LiBr was used as an eluent with a polymer standard service (PSS) column set of two Polargel-M® (25×300 mm) columns and a guard column (75×50 mm). The flow rate was 0.5 ml min⁻¹ at 60°C. Glucose and polyethylene glycol standards (180–82 250 g mol⁻¹; Polymer Laboratories) were used for calibration using an RI detector (RI 71, Shodex). The samples were dissolved (c=1 mg ml⁻¹) and shaken in the eluent for 24 h at room temperature. Sample detection was performed using an UV detector (UV 2077, Jasco) at 280 nm, and phenol red was used to match detectors. Data were recorded and evaluated using WinGPC Unichrom V8.10 (PSS).

Results and discussion

For the production of a lignin-based polyether polyol, an OL was selected because of its high purity and hydroxy content and low molecular weight (MW) (Table 1). OL was chemically modified via oxyalkylation with PC and a two-step reaction with MA followed by oxyalkylation. Due to the high solubility of lignin in PC, the reaction can be performed without other organic solvents. The excess of PC can be regained by vacuum distillation.

Direct oxyalkylation of lignin

In a one-step modification route, OL was reacted with PC. During the reaction of PC with OH groups, ring opening and loss of CO₂ occurred and two different reaction products were obtained because of the different nucleophilicity and steric hindrance of OH₀ₕₖₚ and OH₀ₚₚₚₚ groups (Figure 1b). The formation of carbonate structures by the attack of the OH₀ₕₖₚ groups on carbonyl carbon atom of PC can be neglected, because alkaline catalysts such as K₂CO₃

Unauthenticated
and high temperatures (>170°C) favored etherification (Rokicki and Kowalczyk 2000; Tomczyk et al. 2012).

The FTIR spectra of beech wood OL and hydroxypropylated OL (hOL) are presented in Figure 2a. Besides the typical lignin bands, characteristic vibrations can be observed due to hydroxypropylation. New C-H stretch bands for methyl and methylene groups (2800–3000 cm⁻¹) appeared. Furthermore, a slightly decreased band intensity of primary alcohols (1030 cm⁻¹) and an increased band intensity of secondary alcohols, alkyl aryl ethers (1100 cm⁻¹), and alkyl ethers (852 cm⁻¹) were visible. Accordingly, the reaction of OH groups with PC was successful.

The 31P NMR spectra of the starting OL and its reaction product hOL (Figure 2b) showed that both condensed and uncondensed syringyl, guaiacyl, and p-hydroxyphenyl units were completely hydroxypropylated. Additionally, two distinct broad signals appeared in the aliphatic region. The signal recorded between 146.5 and 149.5 ppm appeared in the same region as primary and secondary OHaliph groups of the initial lignin. The other signal (145.5–146.5 ppm) can be assigned to the new OHaliph groups formed by ring-opening attachment of PC. As observed by 31P NMR spectra, the OHphen groups disappeared and simultaneously new OHaliph groups arose. The quantitative evaluation of OH group contents for the initial OL and hOL based on 31P NMR is presented in Table 2. Under the reaction conditions, all OHphen groups and almost all OHaliph groups were oxypropylated. As a result of the direct oxyalkylation with PC, lignin polyls with exclusively aliphatic OH groups were generated. This OH profile was similar to that of lignin polyls synthesized by oxyalkylation with PO (Ahvazi et al. 2011; Sadeghifar et al. 2012).

The 1H NMR spectrum of the hOL (Figure 2c) exhibited three distinct regions, which can be assigned to aromatic

![Image of Figure 2](https://example.com/figure2.png)

**Figure 2** Spectroscopic analyses of OL and hOL: (a) FTIR spectra, baseline-corrected and normalized to \(\nu(C=C)\) aromatic units at 1500 cm⁻¹, (b) 31P NMR spectra, (c) 1H NMR spectra, and (d) 13C NMR spectra.

### Table 1 Characterization of beech wood OL.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>OL</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (%)</td>
<td>62.0</td>
</tr>
<tr>
<td>H (%)</td>
<td>6.2</td>
</tr>
<tr>
<td>N (%)</td>
<td>0.3</td>
</tr>
<tr>
<td>S (%)</td>
<td>0.0</td>
</tr>
<tr>
<td>O (%)(^a)</td>
<td>31.5</td>
</tr>
<tr>
<td>OHphen (mmol g⁻¹)</td>
<td>2.13</td>
</tr>
<tr>
<td>OHaliph (mmol g⁻¹)</td>
<td>4.37</td>
</tr>
<tr>
<td>OMe (%)</td>
<td>21.2</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>(M_f) (g mol⁻¹)</td>
<td>4100</td>
</tr>
<tr>
<td>(M_w) (g mol⁻¹)</td>
<td>1278</td>
</tr>
<tr>
<td>(C_9) (g mol⁻¹) (theoretical)</td>
<td>200</td>
</tr>
</tbody>
</table>

\(^a\)By difference to 100.

\[C_{900} H_{690} O_{131} (OH_{phen})_{43} (OH_{aliph})_{84} OMe_{137}.\]
OH group signal cannot be assigned exactly, the 31P NMR lapped with the signal of methoxy groups. Although the groups were formed. Taking into account that 3.64 mmol g⁻¹ accordance with 31P NMR results. Furthermore, the signal OHaliph groups (based on 31P NMR data; Table 2) were the OH group. The 1H NMR data allowed the calculation of hydroxypropyl unit can be attached per lignin-derived multioxypropylation was possible, thus more than one alkyl OH groups. Due to the formation of new OH groups, and FTIR analyses indicated the formation of hydroxyamide proton of DMF at 7.95 ppm), 4.67 mmol g⁻¹ methyl groups (13–22 ppm) as well as methyl- and methine carbons (63–80 ppm) arose, which were indications for the formation of ether bonds due to PC attachment.

According to the literature, the oxyalkylation reaction with PO is always accompanied by the occurrence of homopolymerization (Wu and Glasser 1984). In the case of PC, such ring-opening polymerizations required special catalysts, high reaction temperatures (>170°C), and several days of reaction time for the formation of copolymers of poly(propylene ether carbonate) (Soga et al. 1977). Because of the moderate reaction conditions in the present study (170°C, 3 h, atmospheric pressure), a copolymer formation should not be expected. Indeed, the absence of signals for nonetherified functional groups in the aromatic region (148, 137, 135, and 104 ppm). Additionally, in the aliphatic region, new signals of methyl groups (13–22 ppm) as well as methylene and methine carbons (63–80 ppm) arose, which were indications for the formation of ether bonds due to PC attachment.

According to the quantitative 31P and 1H NMR analyses and assuming that a C₉ unit of the initial lignin has an MW of about 200 g mol⁻¹ (Table 1), for hOL, the C₉ unit has a theoretical MW of 300 g mol⁻¹. Based on this, a decrease of OH groups to 4.3 mmol g⁻¹ could be calculated. The OH group content determined by 31P NMR spectroscopy (3.64 mmol g⁻¹) was slightly lower than the theoretical value, which will be further discussed below along with the MW determination.

The 13C NMR spectrum of oxypropylated lignin (Figure 2d) exhibited two distinct regions, which can be assigned to aromatic (96–160 ppm) and aliphatic (12–92 ppm) carbon atoms. The comparison showed intensity reductions of the signals referring to nonetherified functional groups in the aromatic region (148, 137, 135, and 104 ppm). Additionally, in the aliphatic region, new signals of methyl groups (13–22 ppm) as well as methylene and methine carbons (63–80 ppm) arose, which were indications for the formation of ether bonds due to PC attachment.

Two-step oxyalkylation of lignin

A two-step modification of OL was carried out via the following steps (Figure 1c and d): (I) reaction with MA and (II) reaction of the maleated lignin with PC. The FTIR spectra of OL treated with MA (mOL) followed by oxyalkylation with PC (hmOL) are presented in Figure 3a. Both spectra of modified lignins showed new bands of stretching vibrations of methyl and methylene groups (2800–3000 cm⁻¹), carbonyl units (1730 cm⁻¹), methine groups of maleic acid (1616 cm⁻¹), as well as ester units (1160 and 830 cm⁻¹). More specific for the mOL was the broad band at 2440 to 2670 cm⁻¹, which indicated the formation of free carboxylic acid groups, whereas the bands of secondary OH (1100 cm⁻¹) and primary OH (1030 cm⁻¹) groups proved the successful hydroxypropylation to hmOL.

### Table 2 31P NMR characterization and MW determination by SEC of beech OL and its derivatives (see Figure 1).

<table>
<thead>
<tr>
<th>Functional group</th>
<th>OL</th>
<th>hOL</th>
<th>mOL</th>
<th>hmOL</th>
</tr>
</thead>
<tbody>
<tr>
<td>COOH</td>
<td>0.05</td>
<td>0.00</td>
<td>2.99</td>
<td>0.00</td>
</tr>
<tr>
<td>OH₉phen</td>
<td>2.13</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>G unit</td>
<td>0.69</td>
<td>0.00</td>
<td>0.43</td>
<td>0.00</td>
</tr>
<tr>
<td>H unit</td>
<td>0.04</td>
<td>0.00</td>
<td>0.02</td>
<td>0.00</td>
</tr>
<tr>
<td>5-substituted units</td>
<td>1.02</td>
<td>0.00</td>
<td>0.85</td>
<td>0.00</td>
</tr>
<tr>
<td>Σ OH₉phen</td>
<td>2.13</td>
<td>0.00</td>
<td>1.31</td>
<td>0.00</td>
</tr>
<tr>
<td>OH₉aliph</td>
<td>4.37</td>
<td>3.64</td>
<td>1.15</td>
<td>3.67</td>
</tr>
<tr>
<td>Σ OH</td>
<td>6.52</td>
<td>3.64</td>
<td>5.45</td>
<td>3.67</td>
</tr>
<tr>
<td>Mₛ (g mol⁻¹)</td>
<td>4100</td>
<td>9900</td>
<td>7400</td>
<td>8600</td>
</tr>
<tr>
<td>Mₛ' (g mol⁻¹)</td>
<td>1000</td>
<td>2100</td>
<td>2100</td>
<td>3400</td>
</tr>
<tr>
<td>Mₛ'/Mₛ</td>
<td>4.1</td>
<td>4.7</td>
<td>3.5</td>
<td>25.3</td>
</tr>
</tbody>
</table>
The comparison of the 31P NMR spectra of OL and mOL revealed that the majority of the OH groups were esterified with MA, in which carboxylic acids were formed (Figure 3b; Table 2). Whereas the OH aliph groups can be converted to about 75% (1.2 mmol g⁻¹) with MA, the OH phen can be esterified to about 40% (1.3 mmol g⁻¹). Interestingly, the OH aliph groups reacted preferably with MA, whereas the OH phen groups had a lower reactivity to MA (Table 2). This observation can be explained by the predominating steric hindrance (S ring > G ring), although the nucleophilicity of the OH phen groups was slightly increased by the mesomeric effect of aromatic methoxy groups (S ring > G ring).

The 31P NMR spectral analyses of mOL and hmOL revealed that the majority of the OH groups were esterified with MA, in which carboxylic acids were formed (Figure 3b; Table 2). Whereas the OH aliph groups can be converted to about 75% (1.2 mmol g⁻¹) with MA, the OH phen can be esterified to about 40% (1.3 mmol g⁻¹). Interestingly, the OH aliph groups reacted preferably with MA, whereas the OH phen groups had a lower reactivity to MA (Table 2). This observation can be explained by the predominating steric hindrance (S ring > G ring), although the nucleophilicity of the OH phen groups was slightly increased by the mesomeric effect of aromatic methoxy groups (S ring > G ring).

The 31P NMR spectral analyses of mOL and hmOL showed that, in addition to the genuine lignin OH groups, all terminal carboxyl groups of the MA reacted with PC. In contrast to the oxyalkylation with PO, the carboxylic acids of the maleated lignin were not completely hydroxypropylated (Ahvazi et al. 2011). In analogy to the spectrum of hOL, two distinct broad signals were seen in the aliphatic region, which can be assigned to the remaining OH groups in OL (146.5–149.5 ppm) and the hydroxypropyl OH groups (145.5–146.5 ppm). With this two-step modification, a lignin polyol with an extended carbon skeleton can be synthesized, which contained exclusively aliphatic OH groups (Table 2).

The results indicated that both direct and two-step oxyalkylation by PC can be done at less severe reaction conditions (170°C, ambient pressure, 3 h) compared to the modification procedure based on PO (up to 30% KOH, pressure of 3 MPa, temperatures up to 280°C).

**MW determination**

The calculated weight average ($M_w$) and number average ($M_n$) MW and the polydispersity $D (M_w/M_n)$ are presented in Table 2. The results of MW distributions (MWD) of the modified lignin samples showed a shift to higher MW (Figure 4). For mOL, the $M_w$ of 7400 g mol⁻¹ and polydispersity of 3.7 were determined. This result showed in combination with spectroscopic data that esterification with MA generated a chain-extended polymer of more uniform structure. In contrast, hOL had a higher $M_w = 9900$ g mol⁻¹ and polydispersity of 4.7. Based on the quantitative ¹H and ³¹P NMR analyses of hOL, a theoretical MW of the C₉ unit could be calculated to be about 300 g mol⁻¹, which corresponded to a theoretical MW of 6150 g mol⁻¹. The further increase to 9900 g mol⁻¹ (hOL) and the decrease of OH group content could be the result of condensation reactions within the highly functional and branched polymeric structure of lignin. According to several authors, the following reactions may occur even at low temperatures: cleavage of low MW compounds (Kawamoto and Saka 2007; Kawamoto et al. 2007; Ohashi et al. 2011), activation of radicals (Sazanov and Gribanov
2010), and homolytic bond scission (Nakamura et al. 2007). These thermally induced processes could contribute to radical coupling within the lignin structure (Sadeghifar et al. 2012; Cui et al. 2013). An increase of MW can also be observed for hmOL. The $M_w$ of hmOL produced by oxypropylation of mOL reached up to 86 000 g mol$^{-1}$, which was an 11-fold increase compared to the MW of the starting material mOL. The synthesized hmOL had a broad MWD with significant increase in polydispersity ($D=25.3$) and modality.

In addition to radical coupling reactions, the alkylation/esterification of carboxylic acids with cyclic carbonates could occur. The OH group of oxypropylated mOL could react with the carboxylic acid of maleated lignin resulting in a coupling of two lignin molecules. These reactions could contribute to the high MW.

Conclusions

Lignin polyols were successfully synthesized with PC as an oxyalkylating reagent for technical (OL) and maleated beech wood OL (mOL). Spectroscopic analyses (FTIR, $^1$H, and $^{31}$P) revealed that the direct oxypropylation of OL led to a complete oxypropylation of both condensed and uncondensed phenolic units and almost all aliphatic hydroxy groups. With the two-step oxyalkylation of OL, the phenolic OH groups and the carboxylic acid groups were completely oxypropylated. These two approaches generated lignin polyols with an extended carbon skeleton, which contained exclusively aliphatic hydroxy groups. The MW of oxypropylated lignins increased due to the addition of hydroxyalkyl chains and coupling reactions. Also in the case of maleated lignin, a significant increase of MW was detected. Multi oxyalkylation was a minor reaction if PC was applied compared to oxyalkylation by PO. Due to its easy handling, low toxicity, volatility, and flammability, PC provides a convenient alternative to PO. This oxyalkylation procedure by means of PC has a high potential for the preparation of lignin polyols in a large scale and will be further investigated with special emphasis on the derivatives of cyclic organic carbonates.

Acknowledgments: This research was funded by the Federal Ministry of Food and Agriculture (BMEL) and supported by Fachagentur Nachwachsende Rohstoffe eV. (FNR project: Lignocellulose-Bioraffinerie II, FKZ: 22019009). The authors gratefully acknowledge Andreas Schreiber, Bernhard Ziegler, Sascha Lebioda, Christiane Riegert, Martina Heitmann, and Alexander Stücker.

References


Ohashi, Y., Uno, Y., Amirta, R., Watanabe, T., Honda, Y., Watanabe, T. (2011) Alkoxyl- and carbon-centered radicals as primary


