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Palladium-Catalyzed Functionalization of Kraft Lignin: Ether Linkages through the Telomerisation Reaction

C. Dumont,^{a,b} R. M. Gauvin,^a F. Belva,^b and M. Sauthier^{a,*}

Abstract: Kraft lignin was efficiently functionalized with octadienyl ether linkages thanks to the palladium-catalyzed telomerisation of 1,3-butadiene. The comparison with molecular model substrates allowed to assess the grafting of phenols and alcohols and an optimization study lead to up to 69 % conversion of the total number of hydroxyl groups present in lignin. This catalytic study evidenced the partial oxidation of triphenylphosphine into triphenylphosphine oxide and triphenylphosphine sulfide by contaminants present in the industrial grade Kraft lignin. The telomerised lignin is a malleable material and preliminary study of thermal properties showed a decrease of the T_g values in comparison to the starting material.

Introduction

Lignin is one of the most abundant biopolymers available on Earth, after cellulose and chitin.^[1] Its structure is mainly composed by polyphenolic fragments linked with short, hydroxylated aliphatic chains. This complex network is obtained *in vivo* from the radical polymerisation of *p*-coumaryl alcohol (H), sinapyl alcohol (S) and coniferyl alcohol (G). Although only three monomers are involved, the structure of lignin is complex as there is a large diversity of possible linkages between these monomeric units, and as H/S/G proportions are highly dependent on the nature of the vegetal from which lignin was extracted.^[2] Moreover, the method of lignin separation from other components of the raw materials (cellulose, hemicellulose) further enlarges the number of lignins available, as each process implies a chemical modification of the biopolymer. Lignins are mainly obtained from the Kraft, sulfite and organosolv pulping techniques on scales that are considerable in the case of Kraft lignin^[3]. This biomaterial is currently used as an energy source from direct combustion and its chemical valorization is very attractive in a context of a global search for sustainable chemicals and products. Indeed, the aromatic / phenolic structures present within the lignin framework open interesting opportunities for the production of agro-based aromatics that are nowadays essentially obtained from oil refining. This approach implies an important chemical modification of the lignin which has to be depolymerized, and major challenges are still facing the chemists in terms of conversion and selectivity. The direct

use of lignin as component of plastics or hybrid materials is therefore an important alternative approach.^[4] In this context, chemical functionalization of lignin is required to access materials that can be processed, mixed with other polymeric materials^{[5],[6]} or used as macromonomers.^[7] The phenolic aromatic structure can be chemically modified according to classical organic reactions that are used in the chemistry of phenols.^[8] The phenolic and aliphatic hydroxyl groups are most particularly suitable to create new bonds and graft new functionalities. This has been achieved so far using mainly conventional synthetic methods. For instance, lignin esters are accessible from the reaction with acid anhydrides or acyl halides in the presence of bases.^[9] Lignin ethers can be obtained from a Williamson reaction with alkyl halides or epichlorohydrine.^{[10],[11]} More specifically, allyl ethers that introduce C-C unsaturations within the biopolymer are interesting for further chemical transformations, and have thus attracted more recent interest.^{[12],[13],[14]} More recently, the use of catalytic and clean reactions to allylate the hydroxyl groups in lignins has emerged as an important issue. Thus, the palladium-catalysed allylation of organosolv lignin has been recently performed with allylcarbonate,^[15] and it is likely that other allylic groups should be readily accessible from metal catalysed transformations. In this context, we show in the present contribution that the 1,3-butadiene telomerisation reaction^[16] is an efficient method to functionalize phenolic/aliphatic hydroxyl groups of an industrial grade Kraft lignin with allylic octadienyl chains (Scheme 1). This reaction of industrial relevance for the production of 1-octene from 1,3-butadiene has been essentially described so far with small aliphatic alcohols and polyols,^[17] carboxylic acids^[18] and substituted phenols.^{[19],[20]} In comparison to other allylation reactions used with lignins, the telomerisation reaction allows grafting longer bis-unsaturated aliphatic tails (2,7-octadienyls chains) according to a highly atom-economical reaction.

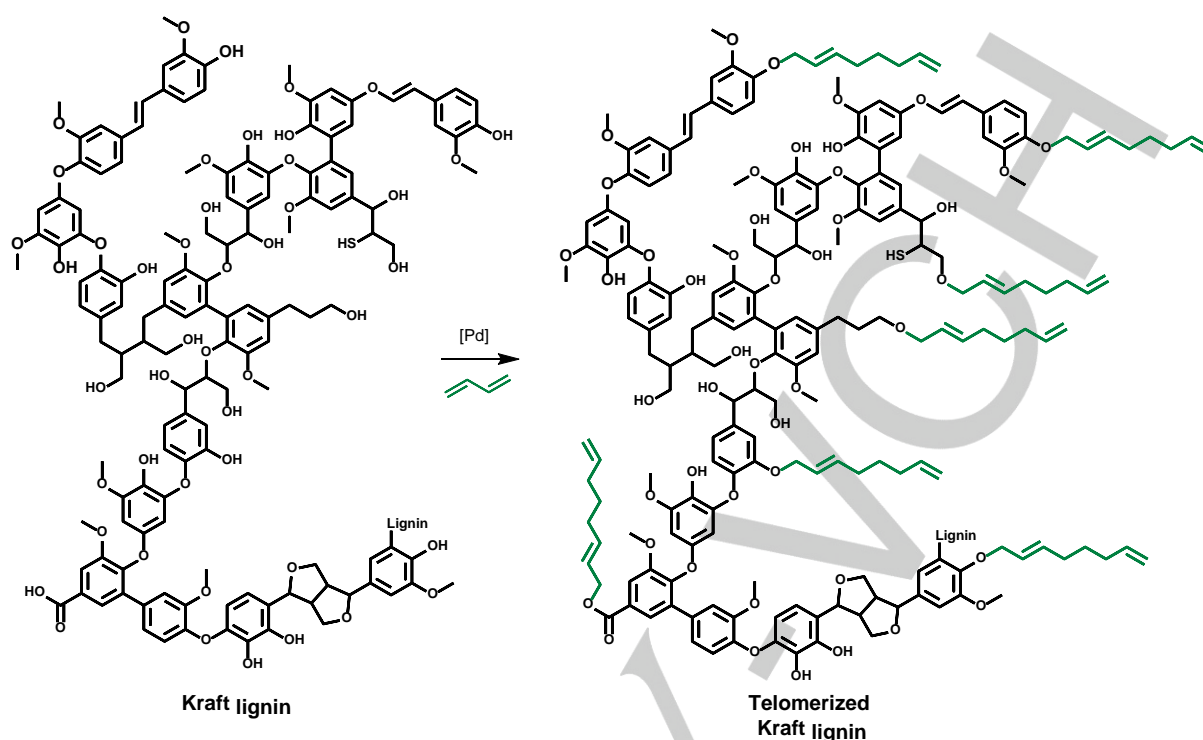
Results and Discussion

The telomerisation reaction has been applied to the transformation of Kraft lignin that shows a suitable solubility in an organic solvent such as THF (Scheme 1). Lignin has been initially reacted with 5 equivalents of 1,3-butadiene with respect to the total number of aliphatic and phenolic hydroxyl groups. The catalyst was generated *in situ* from the combination of Pd(OAc)₂ (1.1 mol %) and 6 equivalents of triphenylphosphine. After stirring the reaction mixture for 21 h at 80 °C, the product was precipitated with pentane and dried under vacuum.

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Scheme 1. Telomerisation reaction with Kraft lignin – simplified representation of the material (source : ref 21)

Table 1. Comparison of elemental analysis of modified kraft lignin and native lignin

Element	Kraft Lignin	Telomerised Lignin
Carbon	64.3 %	72.9 %
Hydrogen	5.8 %	7.3 %
Nitrogen	1.0 %	0.8 %
Sulfur	1.5 %	1.0 %

Elemental analysis of the precipitate evidenced the presence of a higher content of carbon and hydrogen than in the starting material thus indicating that alkyl chains have been introduced in the material (See Table 1). The comparison of the IR spectra of the lignin before and after reaction clearly evidences a decrease of the characteristic broad band of the hydroxyl groups at 3500 cm^{-1} and an increase of the C-H stretching bands at $2700 - 3100\text{ cm}^{-1}$ (Figure 1). The new signals in telomerized Kraft lignin at 991 and 911 cm^{-1} on the one hand, and at 970 cm^{-1} on the other hand, are assigned to alkene sp^2 C-H bending patterns for monosubstituted and *trans*-disubstituted olefin functions.

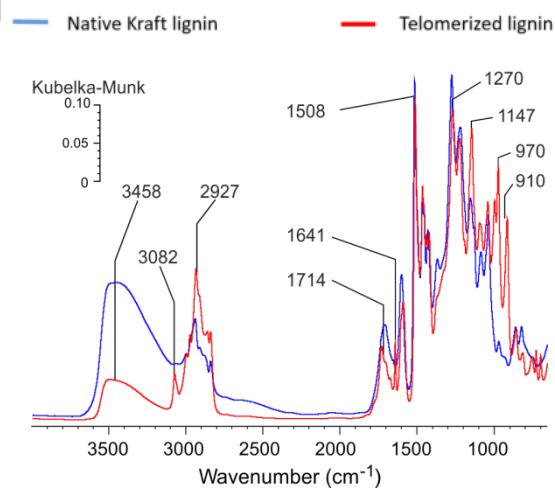


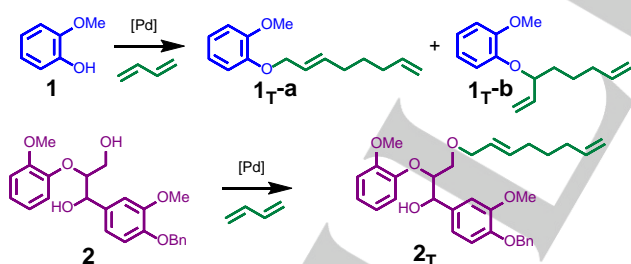
Figure 1. Comparison of infrared spectra of native (blue) and modified (red) Kraft lignin.

This assignment is also confirmed by the comparison of the IR spectra of *gaia*col 1 with that of telomerized derivatives **1T-a** and **1T-b**, where similar bands are observed at 992 , 970 and 911 cm^{-1} in the modified phenol (see supporting

information Figure S13). The ^1H NMR spectrum indicated the presence of new signals that are characteristic of the octadienyl moieties (see ESI). It is noteworthy that the ^1H NMR spectrum of the isolated product remained unchanged after several washings with pentane, thus showing that the octadienyl tails are chemically bonded on the polymer. The structure of Kraft lignin ^[21] bears three types of nucleophilic centers that can be potentially involved in the telomerisation reaction, namely aliphatic primary and secondary alcohols, phenolic alcohols and carboxylic groups.

The different types of hydroxyl groups in the industrial grade Kraft lignin used for this study have been titrated before and after chemical functionalization according to a standard method based on ^{31}P NMR analysis performed after the derivatisation of the hydroxyl groups with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane.^[22] This study demonstrates the partial alkylation of phenols and aliphatic alcohols and the full alkylation of the carboxylic groups (see Table 2, Entry 2).

In order to get more insights concerning the chemical modification of the hydroxyl groups of lignin, the reaction has been performed on model substrates that bear hydroxyl groups found in the biopolymer (phenols, aliphatic primary and secondary alcohols). *o*-methoxyphenol **1** and compound **2**^[23] have been reacted according to similar reaction conditions (Scheme 2). Purification by chromatography on silica gel column has allowed the separation of pure products, which were fully characterized by ^1H , ^{13}C NMR and HRMS analysis (See Supporting Information). From phenol **1**, the linear isomer **1_{T-a}** was obtained as the main product with 32 % isolated yield and the branched isomer **1_{T-b}** with 16 % yield.



Scheme 2: Telomerisation reaction with model substrates

The derivative **2_T** obtained from diol **2** was isolated as sole product of reaction with 53 % yield and the ^1H NMR of the crude of reaction evidenced the formation of less than 2 % of the branched isomer. These results evidence rather different regioselectivity of the telomerisation reaction with phenols and aliphatic alcohols. While aliphatic alcohols yield linear octadienyl ethers with a high selectivity, the use of phenols as substrate leads to the formation of high amounts of branched structures.²⁰

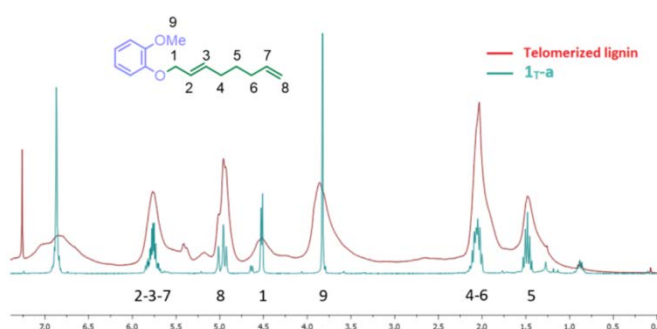


Figure 2 : Comparison of ^1H NMR spectra of modified lignin and **1_{T-a}**

Moreover, the result obtained from the conversion of the diol **2** (See ESI Figure S2) evidences that primary alcohols are much more reactive than the secondary ones, most probably for steric reasons, and this is very likely also the case with Kraft lignin. The ^1H NMR spectra obtained for the products **1_{T-a}** and **1_{T-b}** were compared to those obtained for the telomerized lignin (Figures 2 and 3). As the ^1H NMR spectrum of **2_T** is rather complex, only the comparison of the ^1H NMR spectra of **1_{T-a}** and **1_{T-b}** with the ^1H NMR spectrum of the telomerized kraft lignin are shown in Figures 1 and 2. The signals in the aliphatic part of the spectrum and the similarity with the signals obtained for **1_{T-a}** and **1_{T-b}** further demonstrate that octadienyl tails are grafted on the lignin material. Intense signals at 4.8 ppm and 5.5-6.0 ppm clearly indicate the presence of olefinic protons in the chemically modified lignin. The signal at 4.5 ppm is characteristic of the OCH_2 protons in the octadienyl chain. If linear structures are predominating, signals at 5.15 ppm on the ^1H NMR spectrum evidence the presence of branched structures.

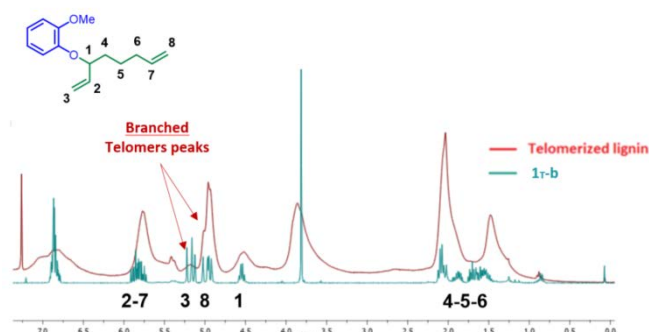


Figure 3 : Comparison of ^1H NMR spectra of modified lignin and **1_{T-b}**

Thus, the NMR study based on the derivatives **1_{T-a}**, **1_{T-b}**, **2_T** and additional HSQC 2D NMR experiments further confirm the presence of branched phenyl ether structures within modified Kraft lignin (See ESI).

Table 2 : Optimization of butadiene telomerisation with Kraft lignin ^a

Entry	Pd (eq per OH)	Temp. (°C)	Butadiene (eq per OH)	Time (h)	Conv. OH _{total} [%] ^b	Conv. OH _{aliph} [%] ^b	Conv. OH _{phen} [%] ^b	Conv. COOH [%] ^b	Polybutadiene (eq per OCH ₃) ^c
1	1.1%	80	5	6	45	0	62	100	-
2	1.1%	80	5	21	56	45	60	100	-
3	1.1%	80	5	48	35	54	28	70	-
4	1.1%	80	5	74	21	39	15	80	-
5	0.6%	80	5	48	69	39	80	100	-
6	0.6%	60	5	21	0	0	0	0	-
7	0.6%	80	5	21	28	25	30	100	-
8	0.6%	100	5	21	44	33	49	100	3%
9	0.6%	120	5	21	34	34	33	91	9%
10	0.6%	80	2,5	21	3	12	0	90	-
11	0.6%	80	5	21	28	25	30	100	-
12	0.6%	80	12	21	41	38	42	100	2%

a) Conditions : PPh₃ (6 eq / Pd), 10 mL THF; b) conversion of total, aliphatic and phenolic OH groups, respectively, and of acid groups, determined by ³¹P NMR; c) determined by ¹H NMR

Solubility properties of the telomerised Kraft lignin are consistent with the chemical functionalization of the hydroxyl groups. It is noteworthy that the material obtained after the telomerisation reaction has a higher solubility in apolar organic solvents such as CHCl₃ than the starting lignin. On the contrary to Kraft lignin, the product is not soluble in water in the presence of a base such as sodium hydroxide. The catalytic reaction with lignin has been further optimized by varying reaction conditions. A shorter reaction time led to a lower substitution degree with the aliphatic alcohols almost untouched (compare Table 2 entries 1 and 2). It is important to notice that reaction times higher than 21 h reproducibly lead to lower substitution degrees (Entries 2-4). In these experiments, the conversions of the phenols and carboxylic acids are drastically lower (compare entry 2 with entries 3 and 4). GC-MS and ¹H NMR analyses of the pentane used for the precipitation of the material evidenced the formation of octatrienes formed during the reaction (See ESI).

This observation is in line with the results obtained by Klein Gebbink ^[20] and Tsuji ^[19m] when studying the telomerization reaction on phenols. Longer reaction times are needed if lower catalyst charges are used (entry 5). The influence of the reaction temperature was probed (entries 6-9). While no conversion occurs at 60°C (entry 6), lower substitution degrees are obtained at temperatures higher than 100 °C, which is largely explained by the formation of octatrienes. Moreover, it should be mentioned that the ¹H NMR spectra of the materials obtained at high temperature evidenced the formation of polybutadiene (Entries 8 and 9, see ESI). This polymer obtained from the thermal polymerization of butadiene ^[24,25] could not be separated from the modified lignin after several pentane washings. The number of equivalents of butadiene also impacts the substitution

degree of the material. High butadiene loadings lead to improved substitution degrees and low amounts of polybutadiene at 80° after 21 h of reaction (Entries 10-12).

The number of equivalents of phosphine used to stabilize the homogeneous catalyst is a key parameter. With 6 equivalents of phosphine, the functionalization of the hydroxyl groups is limited to 19 % (Table 3, entry 1). Higher substitutions degrees are obtained as the number of equivalents of phosphine is increased with only 0.4 mol% of palladium. This contrasts with the case of the telomerisation reaction with simple alcohols, where reaction rates are typically reduced with the increase of the number of equivalents of phosphine, as the ligand stabilizes the metal in solution but also competes with the coordination of the diene reagent.

In order to rationalize this observation, we initiated a study on the fate of the ligand in the presence of Kraft lignin. ³¹P NMR spectra of PPh₃ and lignin THF solutions were recorded under inert conditions, with increasing amounts of triphenylphosphine with respect to a constant amount of lignin.

Table 3: Influence of the phosphine-to-metal to ratio on lignin telomerisation ^a

Entry	PPh ₃ /Pd ^b	Conv. OH _{total} [%] ^c	Conv. OH _{aliph} [%] ^c	Conv. OH _{phen} [%] ^c	Conv. COOH [%] ^c
1	6	5	19	0	63
2	12	43	24	50	100
3	18	39	34	40	87
4	24	50	53	49	88

a) 1.25 g Kraft lignin, 0.4% of Pd per OH group, 5 eq. butadiene per OH group, 10 mL THF, 80 °C, 48h; b) molar ratio between PPh₃ and Pd; c) conversion of total, aliphatic and phenolic OH groups, respectively, and of acid groups, determined by ³¹P NMR .

Interestingly, new signals assigned to triphenylphosphine oxide and triphenylphosphine sulfide were observed after 1 hour at 80 °C, as confirmed by comparison to authentic samples. Composition of the mixtures was assessed by integration of the signals (Table 4 and Figure 4). If low amounts of PPh_3 are used, the ligand is essentially converted into the corresponding triphenylphosphine oxide and triphenylphosphine sulfide (Table 4, entries 1 and 2). Higher triphenylphosphine to lignin ratio are needed to observe unreacted triphenylphosphine (Entries 3 to 6 and Figure 4). This clearly evidences the presence of contaminants in industrial grade Kraft lignin that readily oxidize (and sulfidize) the phosphines early in the course of the reaction, even under significantly milder conditions than catalytic conditions. The presence of molecular sulfur in Kraft lignin^[26] is known and probably explains the formation of triphenylphosphine sulfide. However, the exact nature of the oxidant remains unknown. The plateaux obtained for the formation of triphenylphosphine oxide and triphenylphosphine sulfide (Figure 4) allow to determine that 20 mg of triphenylphosphine is oxidized (and sulfidized) per gram of lignin involved in the reaction. Thus, the excess of ligand needed to achieve efficient lignin conversion is required to compensate for this ligand degradation, by scavenging the impurities contained in the agro-material.

Table 4: Reactivity of PPh_3 in the presence of Kraft lignin ^a

Entry	PPh_3^b (mg)	PPh_3^c (μmol)	OPPh_3^c (μmol)	SPPh_3^c (μmol)
1	7	0	9	17
2	14	0	17	37
3	21	8	32	40
4	28	23	34	49
5	56	120	43	53
6	84	230	42	51

a) Conditions: 1.25 g Kraft lignin with PPh_3 in 10 mL of degassed THF after 1h at 80 °C; b) Amount of PPh_3 initially added to the solution of lignin; c) Amount of PPh_3 , OPPh_3 and SPPh_3 titrated by ^{31}P NMR.

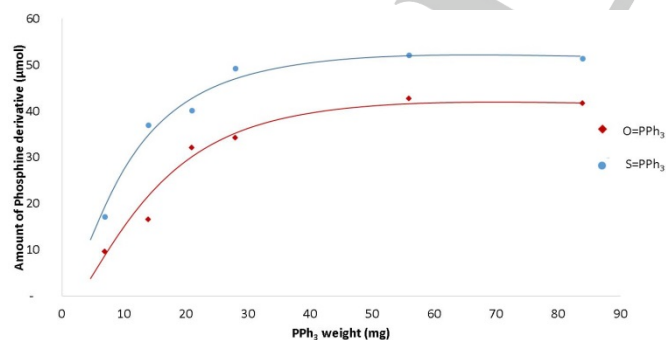


Figure 4: Amount of triphenylphosphine oxide and triphenylphosphine sulfide formed in the presence of lignin (see Table 3 for the data)

In a preliminary study, we investigated the thermal properties of the telomerized Kraft lignin. As expected, the

functionalization of the Kraft lignin with octadienyl chains has a strong impact on its glass transition temperature (T_g) that has been determined from DSC experiments.

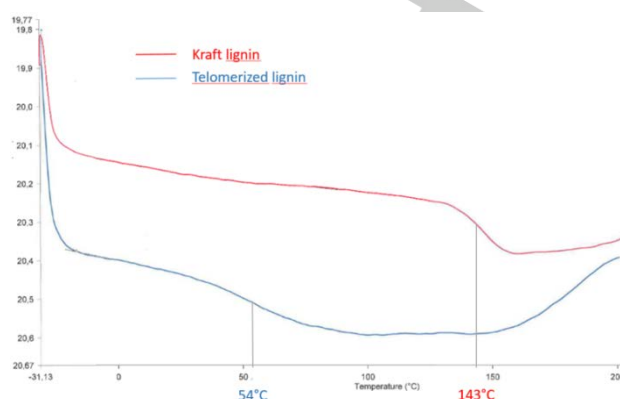


Figure 5. Comparison of DSC traces of modified lignin vs. Kraft lignin.

Indeed, T_g values for the modified lignin (prepared from conditions described in Table 1, entry 5) are close to 50 °C, while the starting material features a T_g of 144 °C (Figure 5)^[27]. The functionalization has thus a major impact on the thermal properties of the new material. Indeed, the telomerized lignin is a malleable material at higher temperatures than 50 °C and can thus easily be shaped as exemplified on Figure 6. This property is more particularly observed with highly substituted lignins whereas lignins with substitution degrees lower than 50 % give more brittle materials at room temperature. The malleability arises from the introduction of aliphatic tails in the structure of lignin that suppresses intramolecular hydrogen bonding, in line with similar observations made with esterified lignins.^[28] In contrast to these latter materials, the modified lignins are significantly more robust towards water, as the ether group is more reluctant to hydrolysis than the ester function, even in the presence of bases.



Figure 6. Pictures of telomerized lignin with 69 % substitution degree

Conclusions

The telomerisation reaction proved to be an efficient and clean synthetic methodology for the functionalization of lignin with ether functions from 1,3-butadiene, a reactant

industrially available from fossil carbon or bioethanol.^[29] The characterization of the products was achieved by combination of spectroscopic methods and elemental analysis. Moreover, assignments were confirmed and refined thanks to comparative studies on model substrates. In sharp contrast to other preparative pathways, for example based on the Williamson reaction, no salt is released during the synthesis of these ether moieties, and the gaseous butadiene used as reagent can be easily removed from the product by simply venting the reactor. The thus-obtained materials can be efficiently processed into shaped objects. Most interestingly, the telomerisation of butadiene affords chains featuring unsaturations that are most convenient handles for further chemical modifications: This paves the way for a wide range of applications of these materials, as fillers, macromonomers or compatibilizing agents. Deeper studies on the telomerisation reaction with lignin allowed delineating some important aspects, that hold significant impact in the field of homogeneous catalytic conversion of this biopolymer. Particularly relevant is the fact that industrial grade Kraft lignins contain contaminants that interfere with the catalytic system. In the present case, the Kraft lignin contained impurities that convert the phosphine used as ligand in the corresponding phosphine oxide and sulphide. Such a phenomenon must be taken into account while contemplating the development of lignin functionalization through homogeneous catalysis, in particular if low catalyst loadings were to be targeted.

Experimental Section

General Considerations

Kraft lignin was provided by UPM Biochemicals, Finland. Due to the high water uptake, neat kraft lignin was dried at reduced pressure at 60°C for 48h before use. Chemicals were purchased from Aldrich, Alfa Aesar, Acros and Strem. Butadiene was purchased from Linde Gas France. Tetrahydrofuran was obtained from a MBraun SPS-800 solvent purification system. DSC measurements were carried out using a Perkin-Elmer DSC 4000 differential scanning calorimeter.³¹ The measurements were done with a heating rate of 10 K/min in the temperature range from 243 K to 473 K, under nitrogen flow (20 ml/min). Diffuse reflectance infrared spectra were collected with a Harrick cell on a Nicolet Avatar spectrometer fitted with a MCT detector. Typically, 64 scans were accumulated for each spectrum (resolution of 4 cm⁻¹).

General procedure for the telomerisation of butadiene with Kraft lignin

Lignin (500 mg), Pd(OAc)₂ (0,027 mmol, 6 mg) and the triphenylphosphine (0,16 mmol, 42 mg) were introduced into a Schlenk tube closed with a Rotaflo stop cock and flushed under nitrogen. Degassed THF (10 mL) was added. The tube was cooled down to -40°C. Butadiene (22.2 mmol, 1,2 g, 2 mL) was condensed in a Schlenk tube cooled with an acetone/dry ice mixture and transferred into the Schlenk tube containing the catalyst and the lignin. The reactor was closed, heated at 80°C and stirred with a magnetic stirrer overnight. After the

reaction, the system was cooled to room temperature and excess gaseous butadiene was vented. The mixture was precipitated on pentane and filtered. The resulting brown powder was dried at 60°C under reduced pressure for 24h.

Titration of the hydroxyl groups in the Kraft lignin and telomerized lignin

³¹P NMR experiments were carried out following a previously reported method^[30]: Lignin(30 mg) was dissolved in a CDCl₃ / Pyridine mixture (1:1.6 v/v, v/v 0,5 mL). The phosphorylation reagent, 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (150 μL), and the internal standard N-hydroxy-6-norbornene-2,3-dicarboximide (100 μL of 0.1 M solution in 1:1.6 v/v CDCl₃ / Pyridine mixture) were added successively. Chromium(III) acetylacetonate (100 μL of 0.014M solution) in the same CDCl₃ / Pyridine mixture was added to the solution in order to homogenize and accelerate phosphorus relaxation. Spectra were recorded with a 15 sec relaxation time and an average numbers of 512 scans. Chemical shifts are relative to the signal of the phospholane hydrolysis product at 132.2 ppm. The integral value of the internal standard was used for calculation of the absolute amount of each functional group.

Comparison between amount of native Kraft lignin functional group (Table SI1) and amount of telomerized lignin functional groups give the substitution ratio of hydroxyl groups.

Acknowledgements

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Keywords: telomerisation • butadiene • Kraft lignin • allylation • ether

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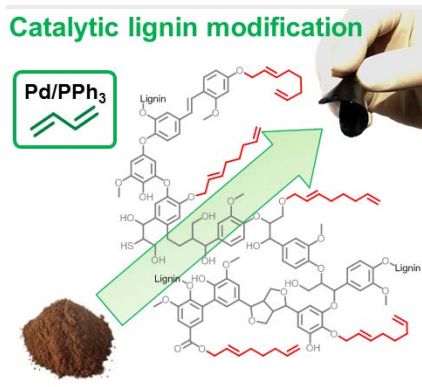
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Kraft lignin was functionalized with octadienyl ether linkages thanks to palladium-catalyzed telomerisation of 1,3-butadiene, affording a processable material. Studies on model compounds were performed to refine understanding of this atom-economical process.



C. Dumont, R. M. Gauvin, F. Belva, M. Sauthier*

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**Palladium-Catalyzed
Functionalization of Kraft Lignin:
Ether Linkages through the
Telomerisation Reaction**

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