Acetylated Lignins: A Potential Bio-Sourced Photosensitizer

Marchand, G.; Calliste, C.A.; Williams, R.M.; McLure, C.; Leroy-Lhez, S.; Villandier, N.

DOI
10.1002/slct.201801039
Publication date
2018
Document Version
Final published version
Published in
ChemistrySelect

ChemPubSoc Europe

DOI: 10.1002/slct.201801039

Chemistry SELECT Communications

Electro, Physical & Theoretical Chemistry

Acetylated Lignins: A Potential Bio-Sourced Photosensitizer

Guillaume Marchand,[a] Claude A. Calliste,[a] René M. Williams,[b] Charlotte McLure,[b] Stéphanie Leroy-Lhez,[a] and Nicolas Villandier*[a]

Nowadays, lignins are receiving an increasing interest from the scientific community. Indeed, this biopolymer, formerly considered a waste-product of the paper industry, appears today as an interesting oil equivalent in many fields. In this context, many chemical modifications of lignins have been presented to valorize this attractive feedstock. However, spectroscopic properties of these modified materials remain poorly studied, in particular their capacity to produce reactive oxygen species (ROS) under light irradiation. Thus, the purpose of this work is to monitor the production of singlet oxygen and superoxide anion under light irradiation of three different acetylated lignins. The results obtained show that those modified lignins can generate ROS levels, allowing to consider a use of these materials as photosensitizers for applications such as photodynamic treatments.

The increase of global environmental problems and overexploitation of the planet's resources is of growing concern. The replacement of non-renewable sources of energy and raw material by more sustainable options is therefore one of the major challenges of the 21st century. In this context, lignocellulosic biomass appears as one of the most attractive alternative to fossil fuels in the production of energy[1] and chemicals.[2] Lignins represent a large part of this biomass being the highly abundant biopolymer after cellulose and the main aromatic renewable source.[3]

However, out of the 55–70 million tons of lignins extracted annually, 98% are directly combusted for energy production.[4] Only the remaining 2% are used for the production of value-added products, either directly, (as binder, filler, additive, dispersant, adsorbent, surfactant or precursors for carbon materials)[3b,5] or after chemical modification. Indeed, the presence of aliphatic and phenolic hydroxyl groups on the polymer's surface allows multiple functionalizations of the material thanks to various chemical modifications.[3b,5b,6] One of the most commonly described in the literature is their acetylation, usually to integrate subsequently the modified biopolymer into a plastic matrix[7] or for structural analysis.[8] Therefore, the synthesis and the study of the physicochemical properties of acetylated lignins are very well described,[6a,9] whereas spectroscopic properties, and in particular radical production capacity and processes undergone after the photoactivation of this esterified biopolymer, have received very little attention.

Indeed, the antioxidant properties of lignins are widely described by many works,[10] and a significant amount of studies have also shown that lignins are able to photochemically generate stable organic radicals responsible for the degradation and thus the aging of lignin-based materials.[11] Contrariwise, the excited state properties of acetylated lignins are poorly described, especially the consequence of acetylation on radical production under light irradiation.

However, since the mid-40's, works on photo-yellowing of wood and wood-based materials have focused on the radical behavior of acetylated lignins.[12] Authors have shown that after protection of their alcohol functions by acetyl groups, lignins no longer produce quinone-type radicals, thus preventing the material containing them (wood or paper) from photo-yellowing. These observations were later confirmed by further works.[13] Moreover, a recent study shows that raw lignins were found to have a higher antioxidant activity than acetylated ones.[10a] It therefore seems that lignins' acetylation significantly modifies its radical behavior.

Taking into account these results, and in line with our previous work on the one hand the design of photosensitizers,[14] and on the other hand biopolymers' valorization,[15] we wonder if acetylated lignins could be considered as a new bio sourced photosensitive material that could be used in photodynamic treatment for eradication of bacteria, fungi and so on. Special focus will thus be given to their reactive oxygen species (ROS) production under and without light irradiation.

For that purpose, three different lignins were used. Each one was obtained from a different process. The two first were both Kraft softwood lignins industrially removed from alkaline black liquors by acidification. The first one (KL-1) was obtained by classical addition of an acidic solution and the second one (KL-2) by using the Lignoboost process.[16] The third one (OL) were extracted from chestnut tree sawdust by a classical ethanol/water organosolv process.[17] Two Kraft lignins were used because they are obtained from the most used process by the paper industry and therefore available in large quantities.

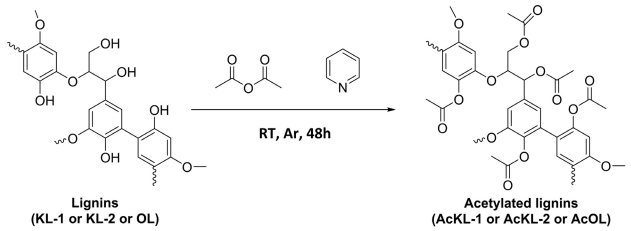
[a] G. Marchand, Dr. C. A. Calliste, Dr. S. Leroy-Lhez, Dr. N. Villandier
Laboratoire PEIRENE, EA7500, Faculté des Sciences et Techniques, 123 avenue Albert Thomas, 87060 Limoges, France
E-mail: nicolas.villandier@unilim.fr

[b] Dr. R. M. Williams, C. McLure
Molecular Photonics group, Van't Hoff Institute for Molecular Sciences (HIMS), Universiteit van Amsterdam, Science Park 904, 1098 XH Amsterdam, Netherlands

Supporting information for this article is available on the WWW under https://doi.org/10.1002/slct.201801039

An organosolv lignin has also been chosen because this delignification technique takes advantage of being used in the laboratory, thus making it possible to ensure no external pollution during the various extraction steps. The influence of the extraction mode and of the biological origin of lignins can thus be discussed.

These three raw lignins were then conventionally acetylated according to the literature (Scheme 1).[18] Acetylated lignins were respectively named AcKL-1, AcKL-2 and AcOL.



Scheme 1. Lignins acetylation.

Firstly, these three lignins were widely characterised, following this, the structure of the acetylated lignins was confirmed by different physical-chemical characterizations, the results of which will be displayed below. Secondly, the capacity of ROS production by these different compounds will be discussed.

The elemental compositions of KL-1, KL-2 and OL are shown in Table 1. KL-2 was found to contain the higher amount of carbon with 69.49%. Both Kraft lignins contain similar oxygen and sulfur rates whereas in OL samples, no sulfur was detected and a higher oxygen percentage was observed. Low amounts of nitrogen were detected in KL-1 and OL, while KL-2 are nitrogen-free lignins. In parallel, the quantity of methoxy groups present on each initial lignin was evaluated.[19] The methoxy content is of 10.7%, 15.30% and 18.80% in KL-1, KL-2 and OL samples, respectively. KL-1 and KL-2 therefore differ mainly in their methoxy rates, and consequently in their carbon rate, whereas OL are relatively different from the other two Kraft lignin by their elementary compositions. These variations observed can be explained by the differences in the plant origin of lignins and/or by the extraction protocols used. From all these data, the C9 formula of each lignin was calculated (Table 1).

Table 1. Elemental composition and C9 formulae of raw lignins

	C (%)	H (%)	O (%)	N (%)	S (%)	C9 formulae
KL-1	59.14	5.41	27.04	0.80	1.39	$C_9H_{8.5}O_{2.6}N_{0.1}S_{0.1}(OMe)_{0.7}$
KL-2	69.49	5.80	26.54	0.00	1.40	$C_9H_{7.3}O_2S_{0.1}(OMe)_{0.8}$
OL	55.35	5.65	33.20	0.21	0.00	$C_9H_{8.5}O_3N_{0.03}(OMe)_{1.4}$

The chemical composition of the starting lignins used is presented in Table 2. KL-1 and KL-2 exhibit similar total lignin levels and about ten percent higher than OL ones. According to results, OL shows a lower amount of acid insoluble lignins (AIL) than KL-1 and KL-2. On the other hand, acid insoluble lignins (ASL) are more important in organosolv sample than in Kraft lignins. KL-2 exhibits a very low level of inorganics (0.38%, w/w) whereas a low level (2.53 and 1.65%, w/w) were determined respectively for KL-1 and OL. These results being in line with those described in the literature for each kind of extracted lignin.[16a,20] These analyses consequently reveal that OL sample contains a higher non-lignin organic fractions than in both KL-1 and KL-2. Here, the extraction method used is probably responsible for this difference.

Table 2. Chemical composition of raw lignins

	AIL[a] (%)	ASL[b] (%)	Ash Content (%)	Total lignins[c] (%)	Total[d] (%)
KL-1	87.97	4.83	2.53	92.8	95.33
KL-2	92.60	2.33	0.38	94.9	95.31
OL	74.99	7.40	1.65	82.4	84.04

[a] Acid Insoluble Lignin. [b] Acid Soluble Lignin. [c] AIL + ASL. [d] AIL + ASL + Ash Content

The weight-average (M_w), number-average (M_n) molecular weights, and polydispersity indexes (PDI, M_w/M_n) of previously acetylated KL-1, KL-2 and OL lignins were measured by gel permeation chromatography (GPC) and calculated from the GPC curves (relative values related to polystyrene).[21] AcOL has a M_n of 3900 g mol^{-1} and a M_w of 7700 g mol^{-1} (PDI = 1.5) which is rather close to the value described by Constant et al. (2015).[17b] The M_n of AcKL-1 (4300 g mol^{-1}) is comparable to that of AcKL-2 (4200 g.mol^{-1}). AcKL-1 has a M_w and PDI of 9900 g mol^{-1} and 2.3 respectively, which is lower than AcKL-1 (Mw = 13 100 g mol^{-1}, and PDI = 3.1). These values are quite high but close[22] and upper values[21a] have already been reported in the literature on acetylated Kraft softwood lignins.

Fourier transform infrared (FT-IR) spectra of OL, AcOL, KL-1, AcKL-1, KL-2 and AcKL-2 were also recorded (Figure 1) in order

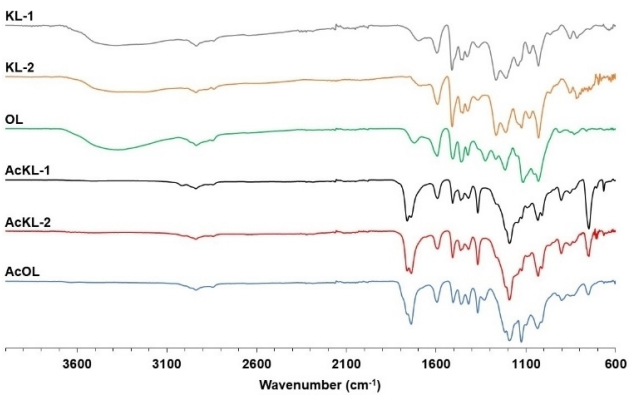


Figure 1. FT-IR spectra of lignins before and after acetylation.

to further characterize these materials and to monitor their acetylation. As expected, OL, like KL-1 and KL-2 lignins, present typical lignin bands that are characteristic of O-H bond stretching (3650-3100 cm^{-1}), of C–H bond stretching (3000-2800 cm^{-1}), of aromatic skeleton vibrations (1592, 1508, 1460 and 1420 cm^{-1}) and of guaiacyl ring breathing (1266 cm^{-1}).[23] Unambiguous evidence of acetylation appears in the spectra of AcOL, AcKL-1 and AcKL-2 with new major bands at 1761, 1739 and 1190 cm^{-1} which correspond respectively to C=O aromatic ester bond stretching, C=O aliphatic ester bond stretching and C–O ester bond bending.[24] Moreover, the disappearance of the O–H stretching band on the spectra of modified lignins was observed, evidencing the esterification of hydroxyl groups in lignins.

Aliphatic and phenolic alcohol groups were quantified on starting and acetylated lignins by quantitative ^{31}P NMR analysis after phosphitylation with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) according to the method described by Granata and Argypopoulos.[25] As shown in Figure 2,

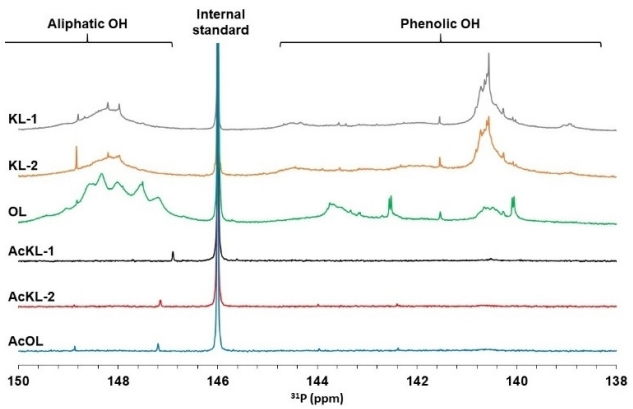


Figure 2. Quantitative ^{31}P NMR spectra of TMDP-derivatized lignins before and after acetylation with signal assignments.

unmodified Kraft and organosolv lignin's spectra exhibit typical signals of phosphitylated aliphatic and phenolic alcohols. Both KL-1 and KL-2 have a higher phenolic hydroxyl content (respectively 3.65 and 3.20 mmol g^{-1}) and a lower aliphatic hydroxyl content (respectively 1.93 and 1.22 mmol g^{-1}) than OL which exhibit 1.83 mmol g^{-1} of phenolic alcohols and 2.61 mmol g^{-1} of aliphatic alcohols. On AcKL-1, AcKL-2 and AcOL spectra no corresponding signals were observed. These results, already described in the literature[26] confirm that all the alcohol groups originally present on OL, KL-1 and KL-2 have been acetylated. This result is consistent with the amount of acetic anhydride used (24 equiv.). Indeed it is much higher than the minimum amount needed to fully acetylate lignins as recently described by Buono et al.[26b]

The ability of KL-1, KL-2, OL, AcKL-1, AcKL-2 and AcOL lignins to produce ROS was then investigated under dark and light exposure. Indeed, under light irradiation, so-called photosensitizer compounds might undergo either a photoinduced electron transfer (Type I process) implying surrounding molecular oxygen or other substrate species, generating radicals such as the superoxide anion ($O_2^{\bullet -}$) and hydroxyl radical ($^{\bullet}OH$), or energy transfer to dioxygen (Type II process), producing singlet oxygen ($^1O_2$).[14a] To detect $O_2^{\bullet -}$ (type I process) and $^1O_2$ (type II process), electron paramagnetic resonance (EPR) spectroscopy was used. But, as the non-radical nature of singlet oxygen and small lifetime of both ROS studied prevented their direct observation, 2,2,6,6-tetramethyl-4-piperidone (TEMP) and 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) were used as specific scavengers of $^1O_2$ (giving TEMPO) and $O_2^{\bullet -}$ (giving DMPO-OOH), respectively. The production of TEMPO and DMPO-OOH can then be monitored by EPR over time. The influence of acetylation and light irradiation on ROS production of the different lignins' sources was investigated. Results are summarized in Figure 3.

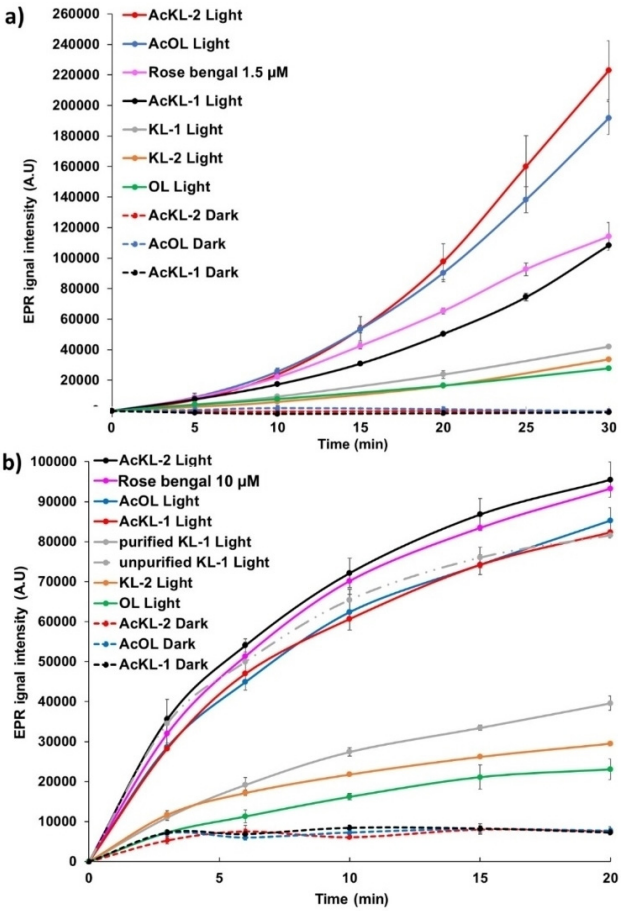


Figure 3. a) EPR signal of TEMPO generation under and without light irradiation for KL-1, KL-2, OL, AcKL-1, AcKL-2, AcOL and Rose bengal**. b)** EPR signal of DMPO-OOH generation under and without light irradiation for KL-1, KL-2, OL, AcKL-1, AcKL-2, AcOL and Rose bengal.

Concerning the production of $^1O_2$ (Figure 3a), under dark conditions, no EPR signal was detected neither for KL-1, KL-2 and OL nor for AcKL-1, AcKL-2 and AcOL, which is not surprising as the formation of singlet oxygen can only be

photoinduced. According to previous studies, lignins KL-1, KL-2 and OL are able to undergo a type II mechanism and thus generate singlet oxygen under light exposure.[27] More surprisingly, and even if a signal was also observed for starting lignin, an important increase in singlet oxygen production was recorded in the case of acetylated analogues. Indeed, this production is ten times higher for AcKL-2 and AcOL and five time higher for AcKL-1 than the one obtained for KL-1, KL-2 or OL. Acetylation thus appears to have a key role here. Indeed, lignins are known to possess antioxidant activity, especially thanks to their phenol groups. KL-1, KL-2 and OL are therefore capable to trap a large part of the singlet oxygen formed, thus preventing is detection by EPR. On the other hand, as AcKL-1, AcKL-2 and AcOL have their phenolic functions blocked by the acetyl groups, $^1O_2$ can diffuse without hindrance into the environment. These observations are in accordance with those previously made by Barclay et al.[28] and Fischer et al.[27b,29] Indeed, these author have shown that 1-(3,4-dimethoxyphenyl-2-(2-methoxyphenoxy)-1-propanone, a molecular model of lignins with methylated phenolic functions, is able to generate singlet oxygen under light irradiation. The singlet oxygen production of acetylated lignins was compared with that obtained in the presence of Rose bengal which is a well-described photosensitizer.[30]

As shown on Figure 3a, the acetylated lignins produce a quantity of singlet oxygen similar to a Rose bengal solution at 1.5 μM. For the sake of comparison, this result make the acetylated lignins suitable for Antimicrobial PhotoDynamic Treatment (APDT) applications as other well-known photosensitizers,[14a,31] in addition to Rose bengal, such as porphyrin derivatives or methylene blue.

In order to get further insight, the capacity of acetylated lignins to produce ROS, the direct observation of $^1O_2$ luminescence was also monitored for AcOL (as well as UV-Visible absorption and emission for this compound, see ESI). This allowed to determine the quantum yield of singlet oxygen emission (Φ_Δ) at 1270 nm due to $^1O_2$ formation upon acetylated lignins excitation to be $\Phi_\Delta = 0.17 \pm 0.03$ in DMF ($\lambda_{ex} = 350$ nm). Zinc phthalocyanine (ZnPC) in DMF was used as a reference ($\Phi_\Delta = 0.55$ in DMF).[32] Upon excitation at 603 or 669 nm however, no singlet oxygen emission was observed (see ESI).

Concerning the production of $O_2^{\bullet-}$ (Figure 3b), i.e. the capacity of lignins to undergo a photoinduced radical process, an increase in signal was observed for all compounds under light irradiation. This is not a surprising result as free radical formation during the photodegradation of lignin-based material is already well described in the literature.[13b] More specifically, Humar et al.[33] have shown, thanks to EPR, that hydroxy and hydroperoxide anions, species that can be formed from superoxide anion, are generated when lignins are exposed under light irradiation. Whatever, it should be noted that the superoxide anion radical production is three times higher in the case of acetylated lignins than in the case of the starting ones, except for AcKL-1 / KL-1. Indeed, in this case, the initial lignin shown a signal as high as the acetylated one. To rule out that this behavior could be due to impurities from the industrial extraction process, this compound was purified. Then the production of $O_2^{\bullet-}$ was monitored once again. The EPR signal intensity was then comparable to that of the other non-acetylated lignins (KL-2 and OL), evidencing that the previous production was partly due to a pollution of the material. As shown on the Figure 3b, this production of superoxyde anion by acetylated lignins is comparative to a 10 μM solution of Rose bengal. Here, like for singlet oxygen, the acetylation of lignins' antioxidant functions prevent the trapping of radical species and so seems to greatly facilitate the diffusion of $O_2^{\bullet-}$ in the surrounding environment. Moreover, for non-acetylated lignins, without light irradiation, no EPR signal corresponding to superoxide anion was detected whereas low EPR signals are detected for AcKL-1, AcKL-2 and AcOL. This supports the theory that the formation of $O_2^{\bullet-}$ seems here mostly photoinduced. Indeed, under dark conditions, stable organic radicals persist in lignins[11] and so are able to lead to a low amount of $O_2^{\bullet-}$ production/detection. In the case of initial linins, KL-1, KL-2, and OL, these radicals are probably trapped by reaction with phenolic groups, which explains the absence of $O_2^{\bullet-}$ EPR signal. But, for AcKL-1, AcKL-2 and AcOL this radical quenching path is no longer possible, explaining the dark signal recorded.

In conclusion, blocking the antioxidant functions of lignins by acetylation greatly increases the amount of ROS that they will be able to release under light irradiation. Given the results, this property seems to be very little impacted by the lignins' origin and/or their extraction process. Indeed AcKL-2 and AcOL, which were obtain from a different biological origin and a different extraction method, have a very similar singlet oxygen production. However, AcKL-1 exhibits a lower singlet oxygen production. Concerning the superoxide anion production, all acetylated lignins (AcKL-1, AcKL-2 and AcOL) have very similar behavior. Acetylated lignins therefore appear as a potential photosensitizer, which opens the scope of their use in many areas such as, for instance, the eradication of harmful micro-organisms. It represents a breakthrough in photodynamic treatment domains. Indeed, as it could be used alone in organic media or, thanks to its capacity to form nanoparticles,[22b] in aqueous ones. Moreover, as for lignin-based nanospheres,[34] these nanoparticles should be able to encapsulate active compounds. Covalent bonds through further chemical modifications can also be envisaged.

Supporting Information Summary

More information on the origin, acetylation and characterization of lignins are given in the supporting information. Details on the EPR analyses and the determination of quantum yield of singlet oxygen are also provided.

Acknowledgements

We thank the "Conseil Régional du Limousin" and European Union for their financial support. Indeed, this work is a part of the ITN-EJD-2017 project POLYTHEA which has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement

n°764837. The authors are indebted to Dr. Yves Champavier for NMR analysis. The authors gratefully acknowledge Pr Daniel Montplaisir for lignins donation and Dr. Yves Champavier for NMR analysis.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Acetylated lignins · EPR spectroscopy · Photosensitizer · Singlet oxygen · Superoxide anion

[1] a) G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.* **2006**, *106*, 4044–4098; b) G. W. Huber, A. Corma, *Angew. Chem., Int. Ed.* **2007**, *46*, 7184–7201.

[2] a) J. S. Luterbacher, D. M. Alonso, J. A. Dumesic, *Green Chem.* **2014**, *16*, 4816–4838; b) F. H. Isikgor, C. R. Becer, *Polymer Chemistry* **2015**, *6*, 4497–4559; c) D. M. Alonso, S. G. Wettstein, J. A. Dumesic, *Chem. Soc. Rev.* **2012**, *41*, 8075–8098.

[3] a) R. J. A. Gosselink, E. de Jong, B. Guran, A. Abächerli, *Ind. Crop. Prod.* **2004**, *20*, 121–129; b) F. G. Calvo-Flores, J. A. Dobado, *ChemSusChem* **2010**, *3*, 1227–1235.

[4] a) S. Salentinig, M. Schubert, *Biomacromolecules* **2017**, *18*, 2649–2653; b) J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius, B. M. Weckhuysen, *Chem. Rev.* **2010**, *110*, 3552–3599; c) T. Aro, P. Fatehi, *ChemSusChem* **2017**, *10*, 1861–1877.

[5] a) A. Naseem, S. Tabasum, K. M. Zia, M. Zuber, M. Ali, A. Noreen, *Int. J. Biol. Macromol.* **2016**, *93*, 296–313; b) A. Duval, M. Lawoko, *React. Funct. Polym.* **2014**, *85*, 78–96.

[6] a) C. Wang, S. S. Kelley, R. A. Venditti, *ChemSusChem* **2016**, *9*, 770–783; b) S. Sen, S. Patil, D. S. Argyropoulos, *Green Chem.* **2015**, *17*, 4862–4887; c) D. Kai, M. J. Tan, P. L. Chee, Y. K. Chua, Y. L. Yap, X. J. Loh, *Green Chem.* **2016**, *18*, 1175–1200; d) S. Laurichesse, L. Avérous, *Prog. Polym. Sci.* **2014**, *39*, 1266–1290.

[7] a) H. Jeong, J. Park, S. Kim, J. Lee, N. Ahn, H.-g. Roh, *Fibers Polym* **2013**, *14*, 1082–1093; b) H. Jeong, J. Park, S. Kim, J. Lee, J. W. Cho, *Fibers Polym* **2012**, *13*, 1310–1318; c) O. Gordobil, R. Delucis, I. Egüés, J. Labidi, *Ind. Crop. Prod.* **2015**, *72*, 46–53; d) C. Vila, V. Santos, B. Saake, J. C. Parajó, *BioResources* **2016**, *11*, 5322–5332; e) Y. Teramoto, S.-H. Lee, T. Endo, *Polym. J. (Tokyo, Jpn.)* **2009**, *41*, 219; f) Y. Teramoto, S.-H. Lee, T. Endo, *J. Appl. Polym. Sci.* **2012**, *125*, 2063–2070; g) O. Gordobil, I. Egüés, R. Llano-Ponte, J. Labidi, *Polym. Degrad. Stab.* **2014**, *108*, 330–338.

[8] G. Brunow, in *Biopolymers Online*, Wiley-VCH Verlag GmbH & Co. KGaA, **2005**.

[9] a) S. C. Fox, A. G. McDonald, *BioResources* **2010**, *5*, 990–1009; b) J. Sameni, S. Krigstin, M. Sain, *BioResources* **2017**, *12*, 1548–1565; c) H. F. Lewis, F. E. Brauns, US Patent 2,429,102, **1947**

[10] a) R. Kaur, S. K. Uppal, P. Sharma, *Sugar Tech* **2017**, *19*, 675–680; b) G. L. Catignani, M. E. Carter, *J. Food Sci.* **1982**, *47*, 1745–1745; c) J. L. Espinoza-Acosta, P. I. Torres-Chávez, B. Ramírez-Wong, C. M. López-Saiz, B. Montaño-Leyva, *BioResources* **2016**, *11*, 5452–5481.

[11] S. V. Patil, D. S. Argyropoulos, *ChemSusChem* **2017**, *10*, 3284–3303.

[12] a) P. L. D. Peill, *Nature* **1946**, *158*, 554; b) H. J. Callow, *Nature* **1947**, *159*, 309; c) G. Leary, *Nature* **1968**, *217*, 672–673.

[13] a) M. Paulsson, J. Parkås, *BioResources* **2012**, *7*, 5995–6040; b) S. Grelier, A. Castellan, D. P. Kamdem, *Wood Fiber Sci.* **2000**, *32*, 196–202; c) M. Paulson, R. Simonson, in *Chemical Modification, Properties, and Usage of Lignin* (Ed.: T. Q. Hu), Springer-Verlag, New York, USA, **2002**, pp. 221–243.

[14] a) C. Riou, C. A. Calliste, A. D. Silva, D. Guillaumot, O. Rezazgui, V. Sol, S. Leroy-Lhez, *Photochem. Photobiol. Sci.* **2014**, *13*, 621–625; b) A. Jiblaoui, J. Brevier, G. Ducourthial, H. González-Núñez, C. Baudequin, V. Sol, S. Leroy-Lhez, *Tetrahedron* **2015**, *71*, 2428–2434; c) A. Jiblaoui, S. Leroy-Lhez, T.-S. Ouk, K. Grenier, V. Sol, *Bioorg. Med. Chem. Lett.* **2015**, *25*, 355–362.

[15] a) C. Klein-Koerkamp, R. Granet, R. Zerrouki, N. Villandier, F. Jérôme, J. Barrault, P. Krausz, *Carbohydr. Polym.* **2009**, *78*, 938–944; b) C. Martias, N. Villandier, E. Thune, A. Glomot, V. Gloaguen, A. Smith, *Appl. Clay Sci.* **2015**, *114*, 609–616; c) N. Villandier, A. Corma, *ChemSusChem* **2011**, *4*, 508–513.

[16] a) W. Zhu, G. Westman, H. Theliander, *J. Wood Chem. Technol.* **2014**, *34*, 77–97; b) M. Nagy, M. Kosa, H. Theliander, A. J. Ragauskas, *Green Chem.* **2010**, *12*, 31–34.

[17] a) X. Pan, N. Gilkes, J. Kadla, K. Pye, S. Saka, D. Gregg, K. Ehara, D. Xie, D. Lam, J. Saddler, *Biotechnol. Bioeng.* **2006**, *94*, 851–861; b) S. Constant, C. Basset, C. Dumas, F. Di Renzo, M. Robitzer, A. Barakat, F. Quignard, *Ind. Crop. Prod.* **2015**, *65*, 180–189.

[18] K. Lundquist, in *Methods in Lignin Chemistry* (Eds.: S. Y. Lin, C. W. Dence), Springer-Verlag, Berlin Heidelberg, Germany, **1992**, pp. 242–249.

[19] H. D. S. Abreu, M. D. F. I. Freire, *An. Bras. Ci.* **1995**, *67*, 379–382.

[20] N.-E. E. Mansouri, J. Salvadó, *Ind. Crop. Prod.* **2006**, *24*, 8–16.

[21] a) F. Kong, S. Wang, J. T. Price, M. K. R. Konduri, P. Fatehi, *Green Chem.* **2015**, *17*, 4355–4366; b) S. Baumberger, A. Abaecherli, M. Fasching, G. Gellerstedt, R. Gosselink, B. Hortling, J. Li, B. Saake, E. de Jong, *Holzforschung* **2007**, *61*, 459–468.

[22] a) A. Tejado, C. Peña, J. Labidi, J. M. Echeverria, I. Mondragon, *Bioresour. Technol.* **2007**, *98*, 1655–1663; b) Y. Qian, Y. Deng, X. Qiu, H. Li, D. Yang, *Green Chem.* **2014**, *16*, 2156–2163.

[23] F. G. Calvo-Flores, J. A. Dobado, J. I. García, F. J. Martin-Martinez *Lignin and Lignans as Renewable Raw Materials: Chemistry, Technology and Applications*, Wiley-Blackwell, Chichester, West Sussex, UK, **2015**.

[24] L. Dehne, C. Vila Babarro, B. Saake, K. U. Schwarz, *Ind. Crop. Prod.* **2016**, *86*, 320–328.

[25] A. Granata, D. S. Argyropoulos, *J. Agric. Food Chem.* **1995**, *43*, 1538–1544.

[26] a) F. Monteil-Rivera, L. Paquet, *Ind. Crop. Prod.* **2015**, *65*, 446–453; b) P. Buono, A. Duval, P. Verge, L. Averous, Y. Habibi, *ACS Sustainable Chem. Eng.* **2016**, *4*, 5212–5222.

[27] a) L. R. Barclay, M. C. Basque, M. R. Vinqvist, *Can. J. Chem.* **2003**, *81*, 457–467; b) K. Fischer, M. Beyer, *Lenzinger Ber.* **2000**, *79*, 25–31.

[28] L. R. C. Barclay, J. K. Grandy, H. D. MacKinnon, H. C. Nichol, M. R. Vinqvist, *Can. J. Chem.* **1998**, *76*, 1805–1816.

[29] K. Fischer, M. Beyer, H. Koch, *Holzforschung* **2009**, *49*, 203–210.

[30] a) D. C. Neckers, *Journal of Photochemistry and Photobiology A: Chemistry* **1989**, *47*, 1–29; b) T. Theodossiou, J. S. Hothersall, E. A. Woods, K. Okkenhaug, J. Jacobson, A. J. MacRobert, *Cancer Res.* **2003**, *63*, 1818–1821.

[31] a) S. Mathai, T. A. Smith, K. P. Ghiggino, *Photochem. Photobiol. Sci.* **2007**, *6*, 995–1002; b) A. Ormond, H. Freeman, *Materials* **2013**, *6*, 817; c) J. C. Gonzales, G. T. P. Brancini, G. B. Rodrigues, G. J. Silva-Junior, L. Bachmann, M. Wainwright, G. Ú. L. Braga, *Journal of Photochemistry and Photobiology B: Biology* **2017**, *176*, 54–61.

[32] W. Spiller, H. Kliesch, D. Wöhrle, S. Hackbarth, B. Röder, G. Schnurpfeil, *J. Porphyrins Phthalocyanines* **1998**, *02*, 145–158.

[33] M. Humar, M. Sentjurc, M. Petrič, *Drvna Industrija* **2002**, *53*, 197–202.

[34] a) M. Tortora, F. Cavalieri, P. Mosesso, F. Ciaffardini, F. Melone, C. Crestini, *Biomacromolecules* **2014**, *15*, 1634–1643; b) P. Figueiredo, K. Lintinen, A. Kiriazis, V. Hynninen, Z. Liu, T. Bauleth-Ramos, A. Rahikkala, A. Correia, T. Kohout, B. Sarmento, J. Yli-Kauhaluoma, J. Hirvonen, O. Ikkala, M. A. Kostiainen, H. A. Santos, *Biomaterials* **2017**, *121*, 97–108.

Submitted: April 9, 2018
Revised: May 9, 2018
Accepted: May 13, 2018