UV Protection

Laccase-Catalyzed Synthesis of Low-Molecular-Weight Lignin-Like Oligomers and their Application as UV-Blocking Materials

Jieyan Lim,[a] Barindra Sana,[b] Ranganathan Krishnan,[c] Jayasree Seayad,[a] Farid J. Ghadessy,[b] Satyasankar Jana,*[c] and Balamurugan Ramalingam*[a]

Abstract: The laccase-catalyzed oxidative polymerization of monomeric and dimeric lignin model compounds was carried out with oxygen as the oxidant in aqueous medium. The oligomers were characterized by using gel permeation chromatography (GPC) and matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF MS) analysis. Oxidative polymerization led to the formation of oligomeric species with a number-average molecular weight (M_n) that ranged from 700 to 2300 Da with a low polydispersity index. Spectroscopic analysis provided insight into the possible modes of linkages present in the oligomers, and the oligomerization is likely to proceed through the formation of C—C linkages between phenolic aromatic rings. The oligomers were found to show good UV light absorption characteristics with high molar extinction coefficient (5000–38000 $M^{-1}cm^{-1}$) in the UV spectral region. The oligomers were blended independently with polyvinyl chloride (PVC) by using solution blending to evaluate the compatibility and UV protection ability of the oligomers. The UV/Vis transmittance spectra of the oligomer-embedded PVC films indicated that these lignin-like oligomers possessed a notable ability to block UV light. In particular, oligomers obtained from vanillyl alcohol and the dimeric lignin model were found to show good photostability in accelerated UV weathering experiments. The UV-blocking characteristics and photostability were finally compared with the commercial low-molecular-weight UV stabilizer 2,4-dihydroxybenzophenone.

Introduction

Materials produced by enzymatic reactions constantly receive notable attention by chemical industries due to increasing public awareness, legal restrictions, environmental concerns, and interest in overcoming the limitations of conventional chemical methods.[1] Oxidative polymerization by oxidases, such as laccase and peroxidases, is an elegant, sustainable approach to produce polymers or oligomers that are difficult to obtain by using conventional chemical polymerization methods.[2] Indeed, biotechnological advancements have shown that laccase is involved in the biosynthesis of lignin in nature.[3] Lignin, a readily available natural polymer, has a high carbon content, high thermal stability, antioxidant properties, and biodegradability, all of which stimulate its use as a performance material.[4,5] However, the inconsistent structure of native lignin (which varies according to its source)[6] and its high molecular weight, brittleness, and incompatibility with conventional polymers hinder[7] its use as a renewable material for wider applications. Modifications of lignin by using either chemical methods[8] or graft polymerization approaches[9] have been shown to increase the use of lignin as a performance material. For example, polypropylene/lignin blends[10] and polypropylene/corn fiber composite[11] showed antioxidant properties comparable to commercial antioxidants. Moreover, addition of 10 to 40 wt% of steam-explosion lignin into polycaprolactone considerably improved the UV stabilization of the resulting polymer blend.[12] A nanocomposite coating consisting of cellulose nanocrystals (CNCs) and fractionated lignin exhibited high transmittance in the visible region and high blocking in the UV spectrum.[13] However, the existence of weaker hydrogen bonds and hydrophobic interactions between the cellulose rods and lignin stimulated disaggregation. In another study, modified bio-butanol lignin (BBL; a byproduct of lignocellulose butanol production) was copolymerized with n-butyl acrylate (BA) and methyl methacrylate (MMA) to obtain the BBL graft copolymer. The copolymer film showed excellent absorption capacity in the UV region, even after continuous UV radiation for 75 min.[14] Recently, blending of lignin into commercial sunscreen products was reported to improve the UV absorb-

[a] J. Lim, Dr. J. Seayad, Dr. B. Ramalingam
Organic Chemistry, Institute of Chemical and Engineering Sciences, #07-01/02 Neuros, 8 Biomedical Grove, Singapore 138665 (Singapore)
E-mail: balamurugan_ramalingam@ices.a-star.edu.sg

[b] Dr. B. Sana, Dr. F. J. Ghadessy
P53 Laboratory, #06-04/05 Neuros/Immunos, 8A Biomedical Grove, Singapore 138648 (Singapore)

[c] Dr. R. Krishnan, Dr. S. Jana
Polymer Engineering & Characterization, Institute of Chemical and Engineering Sciences, 1 Pesek road, Jurong Island, Singapore 627833 (Singapore)
E-mail: satyasankar_jana@ices.a-star.edu.sg

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ance significantly upon UV irradiation.[15] This superior performance was correlated to the synergistic effect of the antioxidant property of the lignin and the presence of sunscreen actives. However, the incorporation of higher-molecular-weight lignin or modified lignin into polymers is often hindered by 1) the inherent insolubility of lignin in common solvents and 2) the poor dispersion of high-molecular-weight native lignin into polymers due to reduced interfacial binding. We hypothesize that low-molecular-weight lignin-like materials with characteristics similar to lignin would, therefore, improve dispersibility and compatibility with the synthetic commercial polymers used for different applications, such as packaging materials.

Consequently, the objective of this study was to obtain low-molecular-weight lignin-like oligomers and to evaluate their UV-blocking characteristics after blending with polymers. Herein, two approaches (Scheme 1) were used to obtain oligo-
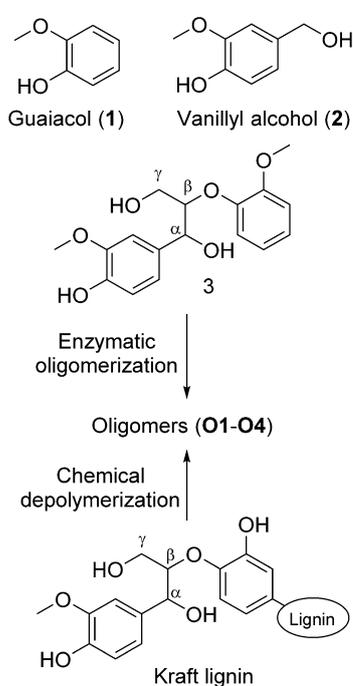
Scheme 1. Approaches to obtain oligomers from lignin model compounds and lignin.

mers, 1) laccase-catalyzed oxidative oligomerization[16] of guaiacol-based monomeric and dimeric lignin model compounds and 2) oxidative depolymerization[17] of commercially available kraft lignin by using chemical methods, because a reduction in lignin molecular weight and hydroxyl content has been reported[10,18] to increase its dispersion and compatibility with polymers. The oligomers are termed as lignin-like oligomers[19] because they were derived from lignin models. Given that their applications have not elicited much attention so far, we envision that these lignin-like oligomers could potentially be used for UV light protection applications, similar to lignin yet with better dispersion for wider applications.

Results and Discussion

Herein, readily available monomeric lignin model compounds, such as guaiacol (**1**), vanillyl alcohol (**2**), and dimeric lignin model compound (**3**), which contain β-*O*-4 linkages and closely mimic native lignin, were chosen as substrates for the laccase-catalyzed oligomerization, whereas kraft lignin, a natural feedstock that is generally considered a low-value fuel in the paper industry, was used as the substrate for depolymerization. Guaiacol is a naturally occurring compound derived from guaiacum and could also be obtained by lignin pyrolysis. In petrochemical industries, guaiacol is produced from phenol or catechol.[20] Vanillyl alcohol is a hydrogenated analogue of vanillin, a natural compound derived from the vanilla plant or chemically synthesized from guaiacol.[21] For the synthesis of oligomers from monomeric and dimeric lignin model compounds **1–3**, we adopted similar reaction conditions as reported previously by us[22] and by Rittstieg et al.,[23] with commercially available *Trametes versicolor* laccase (TVL) as an environmentally benign oxidation catalyst and oxygen as an oxidant. Laccase catalyzes the one-electron oxidation of phenol-containing monomers to phenoxy radicals, which further undergo radical polymerization.[3,24] Model compounds **1–3** were dissolved in an acetate buffer (pH 5.2) that contained 20% DMSO or acetone, and the appropriate amount of laccase was added. After the mixture was stirred at room temperature under oxygen for 3 h, a precipitate formed in the flask and was collected and dried to afford oligomers **O1–O3** in 83 to 95% yield from compounds **1–3** respectively. Analysis of the oligomers by using high-performance liquid chromatography (HPLC) indicated the complete utilization of monomers during the polymerization (see Figures S1 and S2 in the Supporting information).

Low-molecular-weight lignin **O4** was obtained from kraft lignin by using an oxidative depolymerization method developed in-house.[25] Kraft lignin was treated with oxygen (10–20 bar) in the presence of $MeReO_3$ at 160 °C in propylene carbonate as the solvent to obtain **O4** with M_n and M_w values of 890 and 1390 Da, respectively. Comparable low-molecular-weight lignin could also be obtained by other lignin depolymerization methods. For example, a similar weight average molecular weight (M_w) of 1200 to 1500 Da was observed[26] in the depolymerization of alkali lignin in aqueous ionic liquid. Fenton catalyst[27] was reported to promote the depolymerization of organosolv lignin in the presence of hydrogen peroxide, to afford low-molecular-weight lignin oil with an average molecular weight of less than 700 Da. Sequential fractionation of Kraft-AQ pulping lignin by simple extraction with organic solvents[28] at elevated temperatures and extraction of lignin from Douglas fir by using deep eutectic solvents[29] were also found to give fractions that contained lignin materials with an average molecular weight that ranged from 490 to 2600 Da.

Oligomers **O1–O4** were analyzed by using GPC (Figures S3–S6) and showed a number average molecular weight (M_n) of

1800 to 2200 Da. Moreover, the polydispersity index (PDI) of oligomers **O1–O3** indicated that the oligomers were uniformly formed from the monomers. Oligomer **O4,** which was obtained by depolymerization, showed a lower PDI value than that of native kraft lignin (PDI 1.97) due to the reduction in molecular weight. MALDI-TOF MS was next used to enable a reliable determination of the number of repeating units present in each oligomer chain, their composition, the average molecular weight and distribution, and the polymer chain length. MALDI-TOF MS analysis of oligomer **O1** indicated the formation of oligomers with a M_n value of 1260 Da and a low PDI ($M_w/M_n=$ 1.21). The repeating molecular mass corresponded to 122.1 Da (Figure 1), which indicated that the repeating unit is dehydro-
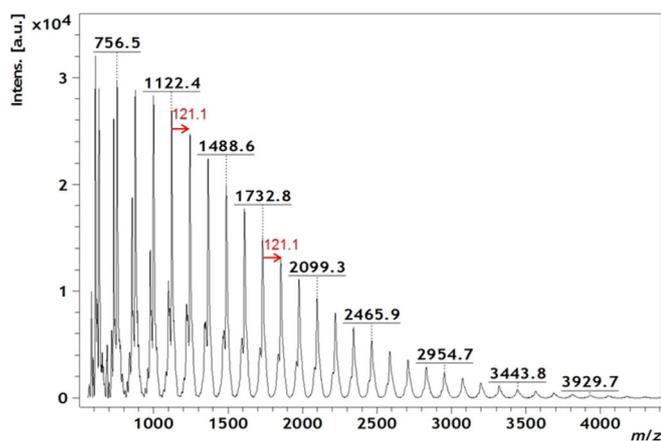

Figure 1. MALDI-TOF MS spectra of oligomers **O1**.

guaiacol [$M-2H$] formed by the removal of two hydrogen atoms from **1**. A M_n value of 7000 to 9000 Da, as determined from a GPC analysis, was reported[30] for the oligomer obtained from guaiacol when fungal laccase was used as the oxidation catalyst. Similarly, by using a high concentration of *T. hirsuta* laccase (1.1 nKat for 1 µmol of guaiacol), a M_n value of 4000 to 5500 Da was observed.[23a] The lower M_n values observed by us could possibly be due to differences in the enzyme source, concentration, reaction time, and method of analysis. Fourier-transform IR (FTIR) spectra of **1** and **O1** (Figure S7) provided valuable information on the possible mode of linkages present in oligomer **O1**: 1) The sharp IR absorption for **1** at 743 cm^{-1} from C—H bending vibrations decreased significantly in **O1**,
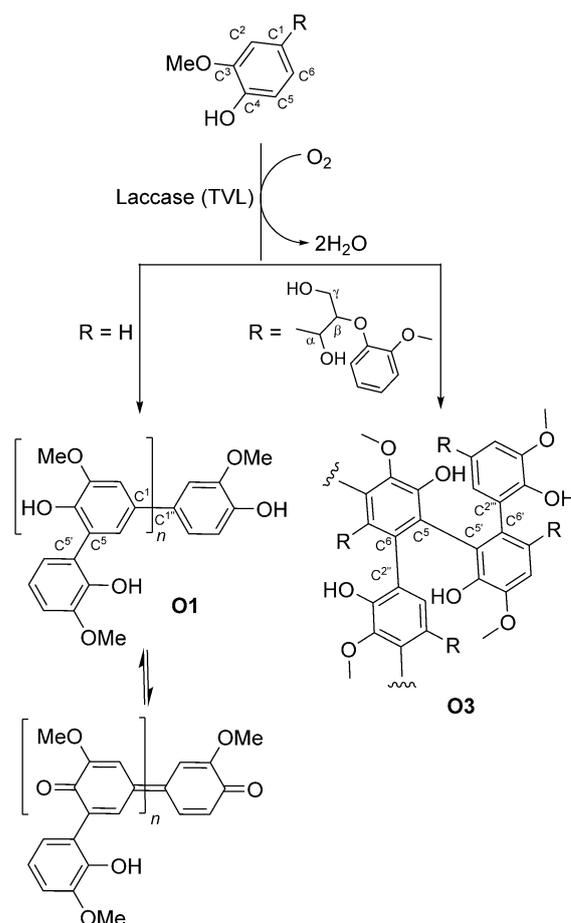
Scheme 2. Proposed possible linkages present in oligomers **O1** and **O3**. Linkages were predicted based on MALDI-TOF MS and IR data. Possible resonance structures and pathway for the formation of **O3** are presented in Schemes S1 and S2.

which suggested that oligomerization may have proceeded through aromatic C—C coupling; 2) the phenolic O—H in-plane bending vibration (1360 cm^{-1}) for guaiacol also decreased considerably after oligomerization; and 3) the absorption at 1662 cm^{-1} for **O1** suggested the presence of quinone-type functional groups in the oligomer, which is clearly absent in the IR spectrum of **1**. The above interpretation was supported by the UV/Vis absorption behavior of **O1**. The strong absorption at $\lambda=480$ nm (Table 2, entry 2) displayed by **O1** in the visible region indicated the possible presence of conjugation in the resulting oligomer. Based on the above experimental ob-

Table 1. GPC and MALDI-TOF MS data for the oligomers.[a]

Entry	Monomers/lignin	Oligomers	GPC[b]			MALDI-TOF MS[c]			Yield [wt%]
			M_n [Da]	M_w [Da]	M_w/M_n	M_n [Da]	M_w [Da]	M_w/M_n	
1	**1**	**O1**	2230	4030	1.80	1260	1530	1.21	93±2
2	**2**	**O2**	1790	1940	1.09	700	720	1.03	77±4
3	**3**	**O3**	2150	2360	1.06	1120	1170	1.04	85±3
4	kraft lignin[d]	**O4**	890	1390	1.56	1230	1420	1.15	78±8

[a] Reaction conditions: **1–3** (0.6 mmol) and acetone (1.2 mL) in sodium acetate buffer (4.8 mL); reaction time: 3 h, reaction temp.: 25 °C. [b] PMMA was used for calibration. [c] DCTB matrix with NaTFA cationic salt. [d] GPC data for kraft lignin: M_n, 2560 Da; $M_w=5020$ Da; $M_w/M_n=1.97$.

servations, the possible linkages present in **O1** are depicted in Scheme 2.

The presence of higher-molecular-weight species was evident (Table 1, entry 2) from the MALDI-TOF MS spectrum of **O2**
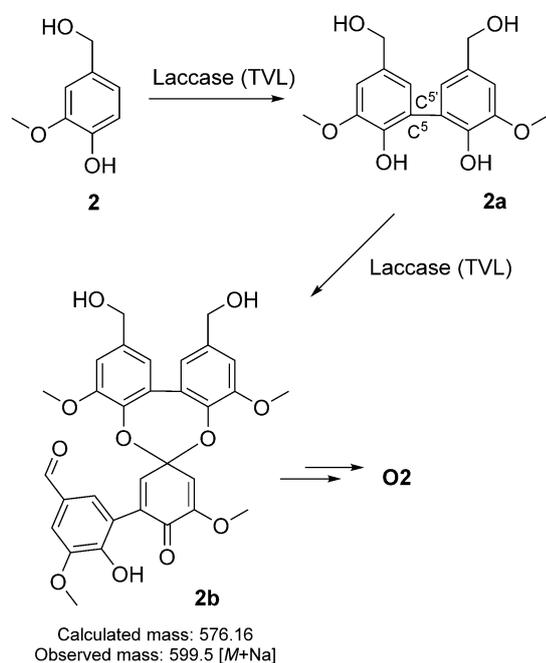
Scheme 3. Proposed reaction pathway for the formation of oligomer **O2** based on the observations herein and literature reports.[31,32]

(Figure S11). Monomer **2** is expected to undergo dimerization first through the C^5–$C^{5'}$ linkage (**2a**, Scheme 3) predominantly upon treatment with laccase.[31] Subsequently, the resulting dimers may form a complexed product that consists of aldehyde or quinone moieties (Scheme 3). The observed mass of 599.5 Da ([M+Na]) in the MALDI-TOF MS study confirmed the presence of a complex structure (**2b**) that was proposed by Lahtinen et al.[32] The higher-molecular-weight peaks at 721.3 and 872.8 Da (Figure S11) may have originated from the addition of guaiacol (121.8 Da, [M−2H]) and vanillin (151.5, [M−H]), respectively. The IR spectrum (Figure S8) of **O2** showed a sharp absorption band at 1674 cm^{-1}, which suggested the presence of quinone-type functional groups. Furthermore, the existence of signals between $\delta = 9.76$ and 9.84 ppm in the ^{1}H NMR spectrum (Figure S13) clearly indicated the presence of aldehyde-type functional groups in resulting oligomer **O2**.

The observed mass value of 1612.4 Da in the mass spectrum of oligomer **O3** (Figure 2) clearly indicated the formation of decamers comprised of five units of dimeric model compound **3** ([M−2H+Na]). Analysis of the mass peaks showed that the oligomers retained a repeating unit mass of 317.8 Da ([M−2H]). Recently, we established[22] the linkages present in the early stage laccase-catalyzed oligomerization products of dimeric model compound **3** by isolating and characterizing them. The formation of biphenyl linkages (C^5–$C^{5'}$) was found to be predominant in the tetramers. DFT calculations of relative free energies of higher-molecular-weight products also indicat-
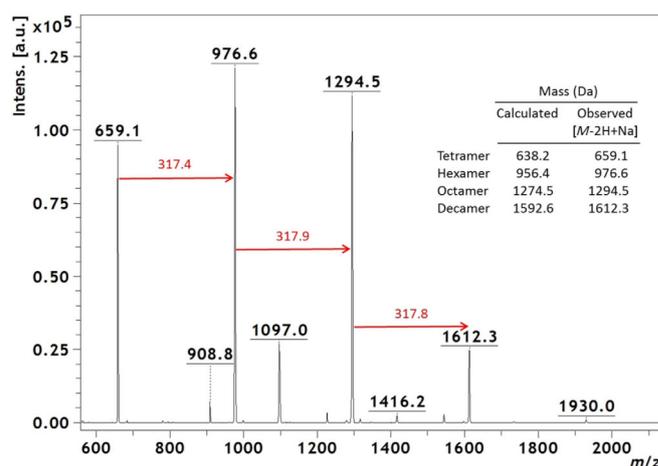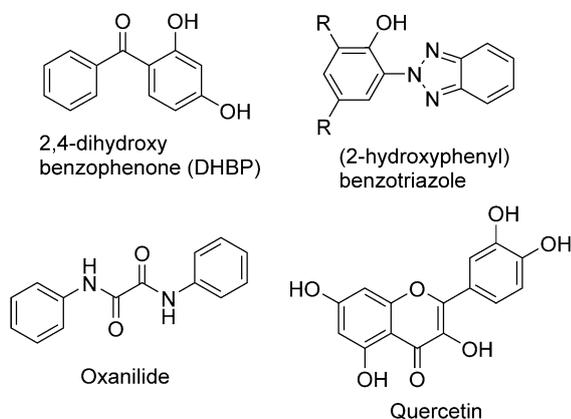

Figure 2. MALDI-TOF MS spectra of oligomers **O3**.

ed that the formation of C—C bonds is more thermodynamically favored over C—O and O—O linkages by 10 and 71.4 kcal mol^{-1}, respectively. Thus, it is probable that the oligomerization of **3** proceeds through the formation of more stable C—C type linkages. The FTIR spectrum of **O3** (Figure S9) showed that the characteristic aromatic ring C—C stretching vibrations in the 1400 to 1650 cm^{-1} region for **O3** became more intense compared with **3**. The C—O stretching absorption band of **3** at 1253 and 1027 cm^{-1} were unaffected after oligomerization. Moreover, the presence of four distinct ^{1}H/^{13}C NMR signals from $\delta = 3.67$ to 3.79 and 55.4 to 55.7 ppm (Figure S14) that arose from the guaiacyl methoxy groups of **O3** indicated the possible presence of oligomers with varying chain lengths of **3**. The above observations are consistent with MALDI-TOF MS analysis. The possible structure and linkages for **O3** are depicted in Scheme 2 based on the hypothetical radical resonance possibilities described in the Supporting Information (Schemes S1 and S2). It is highly possible that the oligomerization proceeds through the carbon center that is relatively more resonance stabilized. Although the mass of the repeating unit remains the same, each regioaddition of **O3** to its higher-molecular-weight compound might possibly have occurred through different carbon centers (C2, C5, and C6, Scheme 2) of the aromatic ring. Thus, it is apparent that oligomers **O3** have both C^5–$C^{5'}$ and β-O-4 linkages that are present in the lignin.

Analysis of oligomers **O4** by using MALDI-TOF MS (Figure S12) indicated notable mass peaks at 749.9, 879.9, 1129.8, and so on. Although two repeated unit masses (120.8 and 130.6 Da) were observed, it was too intricate to deduce possible linkages present in **O4**. Analysis of the heteronuclear single quantum coherence (HSQC) NMR spectra[33] of kraft lignin and **O4** provided insight into the possible types of linkages present in **O4**. The C^α–H^α correlations for kraft lignin observed at $\delta_C/\delta_H = 71.0/4.8$, 85.0/4.6, and 86.7/5.5 ppm were assigned to β-O-4 aryl ether linkages, resinol structures, and phenylcoumaran units, respectively (Figure S17). The above signals were found to be absent in the HSQC spectra of **O4**, which suggested the absence of β-O-4 type bond after oxidative depolymerization. The low bond dissociation energies (54–69 kcal mol^{-1}) of β-O-4

linkages likely cause them to be susceptible to bond cleavage.[34] Essentially, the oligomer obtained after depolymerization possibly possesses mainly biphenyl-type linkages (bond dissociation energy 115–118 kcal mol^{-1}) that are relatively harder to cleave under the reaction conditions. The C^2–H^2 correlation for **O4** observed at $\delta_C/\delta_H = 55.5/3.82$ and $115.0/6.85$ ppm (Figure S16) indicated the presence of methoxy-containing aromatic groups. The FTIR spectra of **O4** showed a strong absorption at 1716 cm^{-1}, which suggested the possible presence of carbonyl groups. Spruce and bamboo milled-wood lignin were reported to show absorption in the 1738 to 1709 cm^{-1} region for the presence of such functionalities.[35] The above observations suggest that the oligomers possibly consist of C–C type linkages through the aromatic rings, which likely make them intrinsically robust as observed by thermogravimetric analysis (TGA). TGA curves at a heating rate of 20 °C min^{-1} under N$_2$ indicated that oligomers **O1**, **O2**, and **O3** lost 5 wt%$^{-1}$ at temperatures of 260, 250, and 225 °C, respectively (Figures S18–S20), which suggested that the oligomers are thermally stable. Oligomer **O4** was found to be thermally unstable and weight loss was observed linearly with temperature (Figure S21). The thermal stability of the oligomers is one of the important criteria for their blending as additives into commercial polymers by melt processing.

Lignin and modified lignin have been incorporated into a wide range of materials as UV blockers.[12–15] We predicted that the lignin-like oligomers should also possess UV-blocking characteristics similar to lignin. To our knowledge, the application of lignin-like oligomers for UV-blocking purposes has not been reported in the literature before. UV blockers are added to polymers during formulation to protect them from sunlight and/or artificial UV radiation.[36] Commercially available synthetic small molecule UV stabilizers, such as 2,4-dihydroxybenzophenone (DHBP), 2-(2-hydroxyphenyl)-1,3,5-triazines, and 2-(2-hydroxyphenyl)benzotriazole (Scheme 4) show exceptional photostability and are extensively used as additives to polymers and personal care products. For a molecule to be a good

UV stabilizer, the molecule should absorb UV light faster than the polymer and should show excellent photostability. As an initial evaluation, the UV/Vis absorption spectra of oligomers **O1**–**O4** (Figures S22–S25) were measured in DMF. All the oligomers showed an intense band in the UV region with a high molar extinction coefficient (Table 2). High ε values for oligomers **O1** (37 700 M^{-1} cm^{-1}, $\lambda = 294$ nm), **O2** (22 350 M^{-1} cm^{-1}, $\lambda = 309$ nm), and **O3** (30 550 M^{-1} cm^{-1}, $\lambda = 279$ nm) suggested that the oligomers are capable of absorbing UV light effectively. The UV/Vis absorption data for DHBP, a commercially available synthetic UV stabilizer, is provided for comparison (Table 2, entry 9).
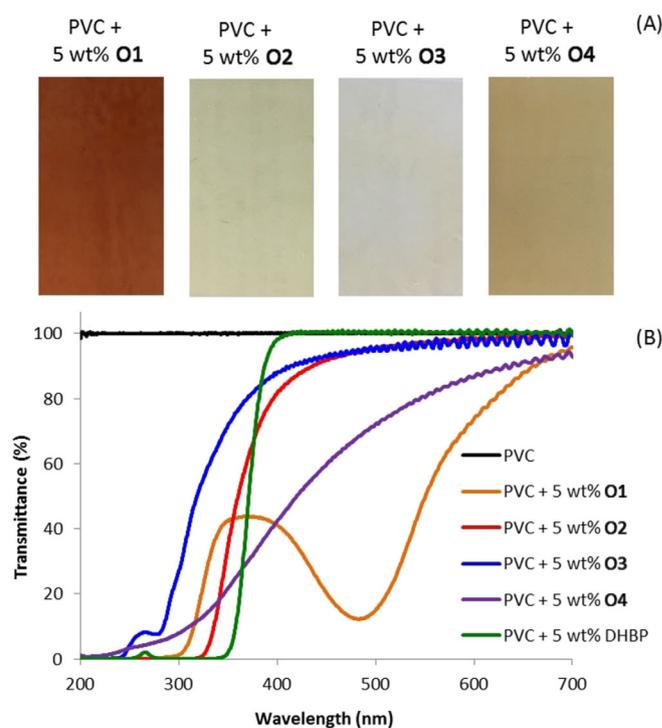
Table 2. UV/Vis absorption data for the monomers and oligomers.[a]

Entry	Monomers/lignin/oligomers	λ [nm] (ε [M^{-1} cm^{-1}])[b]
1	guaiacol (**1**)	277 (2700)
2	**O1**	480 (11 100), 294 (37 700), 270 (48 950)
3	vanillyl alcohol (**2**)	281 (3050)
4	**O2**	353 (23 750), 309 (22 350), 266 (27 200)
5	**3**	279 (4940)
6	**O3**	279 (30 550)
7	kraft lignin[d]	280 (23),[c] 214 (10)[c]
8	**O4**[e]	268 (35)[c]
9	DHBP	337 (4860), 262 (14 000)

[a] Measured in DMF. [b] Molar extinction coefficients (ε) were calculated based on the M_n value of the oligomers obtained by using MALDI-TOF MS. [c] ε values are given in g^{-1} cm^{-1}. [d] Conditions: lignin (0.022 g) in DMF (1 L). [e] Conditions: **O4** (0.018 g) in DMF (1 L).

Scheme 4. Representative structural motifs of commercial UV stabilizers.

Figure 3. A) Oligomeric UV stabilizers incorporated in PVC films. B) UV/Vis transmittance spectra of oligomer-embedded PVC films.

Oligomers **O1**–**O4** (5 wt %) were incorporated into polyvinyl chloride (PVC) by using the solvent blending method and an embedded film (Figure 3A) was prepared by using a film applicator. The films obtained from oligomers **O1** and **O4** were partially opaque, whereas the **O2**- and **O3**-embedded films were nearly transparent. All the oligomer-embedded films exhibited UV absorption characteristics similar to the oligomers in solution. The UV/Vis transmittance spectra of oligomers **O1**–**O4**-embedded PVC films are provided in Figure 3B and all showed light-blocking behavior in the UV region below $\lambda = 300$ nm. The UV/Vis transmittance spectrum of a blank PVC film (without any UV blockers) indicated that all the UV and visible light passed through the film (Figure 3B). The transmittance behavior of a known synthetic UV stabilizer (DHBP) is provided for comparison. The DHBP-embedded film showed the transmission of nearly all visible light ($\lambda = 700$–400 nm), began blocking UV light at $\lambda = 400$ nm, and blocked it completely below $\lambda = 345$ nm. Of the four oligomers incorporated into PVC, **O2** was found to show transmittance characteristics (Figure 3B) similar to those of the DHBP-embedded film. The above observations indicated that the lignin-like oligomers could potentially be used as UV blockers depending on the UV region and the application requirements.

Next, the photostability of the oligomers in their blended form was evaluated. The embedded films were exposed to UV light with an irradiance of 100 W m^{-2} (about 65–70 times stronger than the UV radiation that reaches the earth's surface from the Sun). The estimated annual UV irradiance that reaches the earth from the sun is 1.2 to 1.5 W m^{-2}.[37] The transmittance spectra of the films were measured before and after exposure of the films to UV light for different time periods (Figure 4). The **O1**-embedded PVC film showed a distinct color change from brown to colorless. This was reflected in the disappearance of the absorption band ($\lambda_{max} = 480$ nm) in the visible region and the film showed different UV-blocking characteristics after UV exposure. The difference in UV-blocking behavior might be due to a quinone–phenol-type equilibrium (Scheme 2) that occurs in **O1** upon UV exposure.

When lignin was added to sun-screen lotions, an improvement in the UV-blocking characteristics was reported[15] upon UV irradiation. Oligomers **O2** (Figure 4) and **O3** (Figure S26) showed noticeable photostability over 24 h without a significant change in their UV/Vis transmittance spectra. Although it is too premature to predict the mechanism behind the UV protection by the oligomers in PVC material, the presence of polyphenolic groups in the oligomers could potentially act as antioxidants by scavenging radicals formed during irradiation. The above studies indicate that the oligomeric materials could potentially be used as UV light blockers to protect polymers and plastics. However, for practical applications, the mechanical properties of the film-forming polymers need to be evaluated before and after exposure of the oligomer-embedded film to the sunlight or artificial UV radiation.
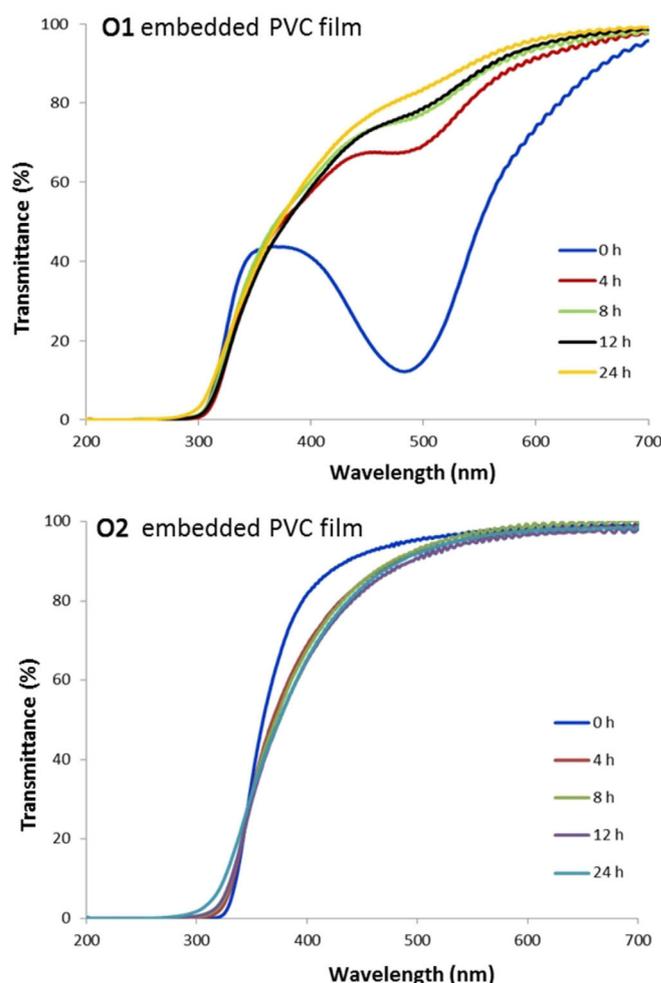
Figure 4. UV/Vis transmittance spectra of oligomer-embedded PVC before (0 h) and after UV light exposure at different time intervals.

Conclusions

Oligomers were successfully synthesized from lignin monomers and dimers by using an environmentally benign laccase-catalyzed oxidative polymerization. The nature of possible linkages present in the oligomers was predicted based on MALDI-TOF MS, NMR spectroscopy, and FTIR studies. The oligomers were found to possess primarily C—C type linkages, analogous to the C^5–$C^{5'}$ linkages in native lignin, that are more thermodynamically stable than the other possible C—O and O—O type linkages. A potential application of the low-molecular-weight lignin-like oligomers as a UV-blocking material was evaluated for the first time. The UV-blocking characteristics shown by the oligomers are promising and encouraged us to formulate them for applications, such as antioxidants in functional foods and UV blockers for sunscreen lotions. The current study becomes particularly important as significant progress[27,38] is being made in the area of lignin depolymerization to form guaiacol- and syringol-based monomers, and difficulties still persist in the isolation of individual monomers for specific applications. The current study paves the way towards the potential utilization of a mixture of lignin-derived monomers and

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other phenolic products as a feedstock for the synthesis of performance materials. Additionally, oligomers are attractive alternatives to synthetic UV stabilizers that have increasingly been shown to be toxic to humans and the environment.[39] The oligomeric UV blockers herein would potentially be less vulnerable to leaching from polymers or plastics into the environment. Moreover, it has been demonstrated that macromolecular and polymeric UV stabilizers exhibit improved light-protection characteristics relative to small-molecule UV stabilizers.[40] Currently we are investigating the incorporation of these oligomers into other polymers, such as polystyrene and polyethylene terephthalate, to evaluate their compatibility, processability, and UV-stabilizing potential in these commercial polymers.

Experimental Section

General procedure for laccase-catalyzed oligomerization

Lignin model compounds (0.6 mmol) were dissolved in dimethyl sulfoxide or acetone (1.2 mL) and sodium acetate buffer (4.8 mL, 50 mM, pH 5.2) was added. The reaction mixture was purged by using an O_2 balloon for 5 minutes. A solution of laccase (100 µL, 400 U mL^{-1}) was added and the mixture was stirred for 3 h at 25 °C under an O_2 atmosphere. The precipitate formed was collected by using centrifugation and dried under vacuum at 50 °C for 24 h. The isolated yields of the oligomers are presented in Table 1.

Chemical depolymerization of kraft lignin

A suspension of kraft lignin (4 g) in propylene carbonate (100 mL) was treated with molecular oxygen (10–20 bar) at 160 °C in the presence of $MeReO_3$ (1.5 wt %) as a catalyst. After 3–6 h, the reaction mixture was filtered and the solvent was distilled under vacuum. The resulting lignin oil was extracted with dichloromethane to leave behind solid oligomer residue **O4**.

Incorporation of oligomer into PVC for the preparation of thin films

Polyvinyl chloride (PVC, 400 mg) and the oligomer (20 mg, 5 wt %) were dissolved in THF (2 mL). The solution was stirred and the solvent was allowed to evaporate until a moderately viscous solution was obtained. The solution was spread uniformly onto a glass plate by using a film applicator. After drying, the film was gently peeled from the plate.

Photostability studies

Photostability experiments were carried out by using an Omni UV curing S2000 system equipped with a high-power light guide. An adjustable collimating adaptor was coupled with the light guide to provide uniform light distribution. The working distance between the adaptor and the film samples was adjusted to obtain a constant irradiance of 100 W m^{-2}. Irradiance was measured at the curing spot by using a handheld UV radiometer. The oligomer-embedded films were exposed to UV light for a total of 24 h and the transmittance spectra of the films were recorded at different time intervals, as shown in Figure 4.

Conflict of interest

The authors declare no conflict of interest.

[1] a) S. Rodríguez Couto, J. L. T. Herrera, *Biotechnol. Adv.* **2006**, *24*, 500–513; b) J. Liu, Y. Cai, X. Liao, Q. Huang, Z. Hao, M. Hu, D. Zhang, Z. Li, *J. Cleaner Prod.* **2013**, *39*, 154–160.

[2] a) S.-I. Shoda, H. Uyama, J.-i. Kadokawa, S. Kimura, S. Kobayashi, *Chem. Rev.* **2016**, *116*, 2307–2413; b) S. Kobayashi, H. Uyama, S. Kimura, *Chem. Rev.* **2001**, *101*, 3793–3818.

[3] a) J.-R. Jeon, P. Baldrian, K. Murugesan, Y.-S. Chang, *Microbial Biotechnol.* **2012**, *5*, 318–332; b) J. M. Humphreys, C. Chapple, *Curr. Opin. Plant Biol.* **2002**, *5*, 224–229.

[4] a) D. Kai, M. J. Tan, P. L. Chee, Y. K. Chua, Y. L. Yap, X. J. Loh, *Green Chem.* **2016**, *18*, 1175–1200; b) W.-J. Liu, H. Jiang, H.-Q. Yu, *Green Chem.* **2015**, *17*, 4888–4907; c) A. Duval, M. Lawoko, *React. Funct. Polym.* **2014**, *85*, 78–96.

[5] Use of lignin as low cost metal absorbent: a) P. J. M. Suhas, M. M. L. Carrott, *Bioresour. Technol.* **2007**, *98*, 2301–2312; See also, b) Y. Wu, S. Zhang, X. Guo, H. Huang, *Bioresour. Technol.* **2008**, *99*, 7709–7715; c) D. Mohan, C. U. Pittman Jr, P. H. Steele, *J. Colloid Interface Sci.* **2006**, *297*, 489–504.

[6] A. J. Ragauskas, G. T. Beckham, M. J. Biddy, R. Chandra, F. Chen, M. F. Davis, B. H. Davison, R. A. Dixon, P. Gilna, M. Keller, P. Langan, A. K. Naskar, J. N. Saddler, T. J. Tschaplinski, G. A. Tuskan, C. E. Wyman, *Science* **2014**, *344*, 709–720.

[7] A. Vishtal, A. Kraslawski, *BioResources* **2011**, *6*, 3547–3568.

[8] S. Laurichesse, L. Avérous, *Prog. Polym. Sci.* **2014**, *39*, 1266–1290.

[9] A summary of lignin modification by using graft polymerization is provided in Ref. [4a].

[10] C. Pouteau, P. Dole, B. Cathala, L. Averous, N. Boquillon, *Polym. Degrad. Stab.* **2003**, *81*, 9–18.

[11] A. A. Morandim-Giannetti, J. A. M. Agnelli, B. Z. Lancas, R. Magnabosco, S. A. Casarin, S. H. P. Bettini, *Carbohydr. Polym.* **2012**, *87*, 2563–2568.

[12] R. Pucciariello, C. Bonini, M. D'Auria, V. Villani, G. Giammarino, G. Gorrasi, *J. Appl. Polym. Sci.* **2008**, *109*, 309–313.

[13] A. Hambardzumyan, L. Foulon, B. Chabbert, V. Augié-Béghin, *Biomacromolecules* **2012**, *13*, 4081–4088.

[14] X. Liu, J. Wang, S. Li, X. Zhuang, Y. Xu, C. Wang, F. Chu, *Ind. Crops Prod.* **2014**, *52*, 633–641.

[15] Y. Qian, X. Qiu, S. Zhu, *Green Chem.* **2015**, *17*, 320–324.

[16] For general reports on laccase mediated oxidative oligomerization, see Ref. 2 and a) M. Lahtinen, L. Viikari, P. Karhunena, J. Asikkalaa, K. Kruusc, I. Kilpeläinena, *J. Mol. Catal. B* **2013**, *85–86*, 169–177; b) N. Mita, S.-i. Tawaki, H. Uyama, S. Kobayashi, *Macromol. Biosci.* **2003**, *3*, 253–257; c) N. Akta, A. Tanyolaç, *J. Mol. Catal. B* **2003**, *22*, 61–69; d) R. Ikeda, H. Uyama, S. Kobayashi, *Macromolecules* **1996**, *29*, 3053–3054.

[17] For recent reports on lignin deploymerization, see a) S. Gillet, M. Aguedo, L. Petitjean, A. R. C. Morais, A. M. da Costa Lopes, R. M. Łukasikd, P. T. Anastas, *Green Chem.* **2017**, *19*, 4200–4233; b) A. R. C. Morais, J. V. Pinto, D. Nunes, L. B. Roseiro, M. C. Oliveira, E. Fortunato, R. Bogel-

Łukasik, *ACS Sustainable Chem. Eng.* **2016**, *4*, 1643–1652; c) R. Rinaldi, R. Jastrzebski, M. T. Clough, J. Ralph, M. Kennema, P. C. A. Bruijnincx, B. M. Weckhuysen, *Angew. Chem. Int. Ed.* **2016**, *55*, 8164–8215; *Angew. Chem.* **2016**, *128*, 8296–8354; d) C. Xu, R. Arneil, D. Arancon, J. Labidid, R. Luque, *Chem. Soc. Rev.* **2014**, *43*, 7485–7500; e) X. Huang, T. I. Korányi, M. D. Boot, E. J. M. Hensen, *ChemSusChem* **2014**, *7*, 2276–2288.

[18] C. Pouteau, B. Cathala, P. Dole, B. Kurek, B. Monties, *Ind. Crops Prod.* **2005**, *21*, 101–108.

[19] In the literature, the oligomers from lignin model compounds were called low-molecular-weight lignin or lignin model polymer, see a) L. Pistone, G. Ottolina, S. De, A. A. Romero, L. O. Martins, R. Luque, *ChemSusChem* **2016**, *9*, 756–762; b) R. L. Crawford, L. E. Robinson, R. D. Foster, *Appl. Environ. Microbiol.* **1981**, *41*, 1112–1116.

[20] Z. Fu, Y. Yu, D. Yin, Y. Xu, H. Liu, Q. Xu, F. Tan, J. Wang, *J. Mol. Catal. A* **2005**, *232*, 69–75.

[21] H. Wynberg, E. W. Meijer in *Organic Reactions* Vol. 28, John Wiley & Sons, Inc., **1982**, pp 1–36.

[22] B. Ramalingam, B. Sana, J. Seayad, F. J. Ghadessy, M. B. Sullivan, *RSC Adv.* **2017**, *7*, 11951–11958.

[23] a) K. Rittstieg, A. Suurnäkki, T. Suortti, K. Kruus, G. M. Guebitz, J. Buchert, *Enzyme Microb. Technol.* **2002**, *31*, 403–410; b) K. Rittstieg, A. Suurnäkki, T. Suortti, K. Kruus, G. M. Guebitz, J. Buchert, *Biotechnol. Prog.* **2003**, *19*, 1505–1509.

[24] a) J. F. D. Dean, K.-E. L. Eriksson, *Holzforschung* **1994**, *48*, 21–33; b) D. M. O'Malley, R. Whetten, W. Bao, C.-L. Chen, R. Sederoff, *Plant J.* **1993**, *4*, 751–757.

[25] J. Seayad, G. Saravanan, B. Ramalingam, WO 2017/171652 A1.

[26] L. Das, S. Xu, J. Shi, *Front. Energy Res.* **2017**, 5:21 https://doi.org/10.3389/fenrg.2017.00021.

[27] J. Zeng, C. G. Yoo, F. Wang, X. Pan, W. Vermerris, Z. Tong, *ChemSusChem* **2015**, *8*, 861–871.

[28] K. Wang, F. Xu, R. Sun, *Int. J. Mol. Sci.* **2010**, *11*, 2988–3001.

[29] C. Alvarez-Vasco, R. Ma, M. Quintero, M. Guo, S. Geleynse, K. K. Ramasamy, M. Wolcottc, X. Zhang, *Green Chem.* **2016**, *18*, 5133–5141.

[30] T. Tanaka, M. Takahashi, H. Hagino, S.-I. Nudejima, H. Usui, T. Fujii, M. Taniguchi, *Chemical Engg Sci.* **2010**, *65*, 569–573.

[31] M. Lahtinen, P. Heinonen, M. Oivanen, P. Karhunen, K. Kruus, J. Sipilä, *Org. Biomol. Chem.* **2013**, *11*, 5454–5464.

[32] M. Lahtinen, K. Kruus, P. Heinonen, J. Sipila, *J. Agric. Food Chem.* **2009**, *57*, 8357–8365.

[33] a) S. Constant, H. L. J. Wienk, A. E. Frissen, P. de Peinder, R. Boelens, D. S. van Es, R. J. H. Grisel, B. M. Weckhuysen, W. J. J. Huijgen, R. J. A. Gosselink, P. C. A. Bruijnincx, *Green Chem.* **2016**, *18*, 2651–2665; b) M. Sette, H. Lange, C. Crestini, *Comput. Struct. Biotechnol. J.* **2013**, *6*, e201303016; c) J. Rencoret, G. Marques, A. Gutiérrez, L. Nieto, J. Jiménez-Barbero, Á. T. Martínez, J. C. del Río, *Ind. Crops Prod.* **2009**, *30*, 137–143.

[34] L. Munk, A. K. Sitarz, D. C. Kalyani, D. Mikkelsen, A. S. Meyer, *Biotechnol. Adv.* **2015**, *33*, 13–24.

[35] O. Faix in *Methods in Lignin Chemistry* (Eds.: S. Y. Lin, C. W. Dence), Springer, Heidelberg, **1992**, pp. 83–109.

[36] a) M. Zayat, P. Garcia-Parejo, D. Levy, *Chem. Soc. Rev.* **2007**, *36*, 1270–1281; b) P. Garcia-Parejo, M. Zayat, D. Levy, *J. Mater. Chem.* **2006**, *16*, 2165–2169.

[37] a) J. Lean, *Science* **1989**, *244*, 197–200; b) http://solargis.com/products/imaps/useful-resources/.

[38] a) A. Rahimi, A. Ulbrich, J. J. Coon, S. S. Stahl, *Nature* **2014**, *515*, 249–252; b) J. D. Nguyen, B. S. Matsuura, C. R. J. Stephenson, *J. Am. Chem. Soc.* **2014**, *136*, 1218–1221.

[39] H. Nagayoshi, K. Kakimoto, S. Takagi, Y. Konishi, K. Kajimura, T. Matsuda, *Environ. Sci. Technol.* **2015**, *49*, 578–587.

[40] a) M. L. Binet, S. Commereuc, P. Lajoie, J. Lacoste, *J. Photochem. Photobiol.* **2000**, *137*, 71–77; b) J. Malík, G. Ligner, L. Avar, *Polym. Degrad. Stab.* **1998**, *60*, 205–213.

FULL PAPER

Block out the sun: Materials produced by the laccase-catalyzed oxidative oligomerization of lignin model compounds were revealed to exhibit promising UV-blocking characteristics (see figure). The photostability and transmittance properties were compared with commercial UV blockers under accelerated experimental conditions.
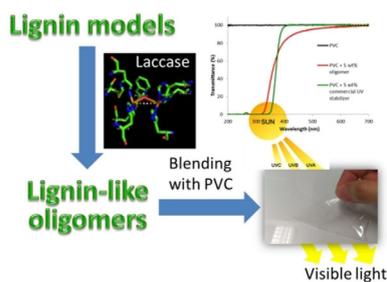
UV Protection

Jieyan Lim, Barindra Sana, Ranganathan Krishnan, Jayasree Seayad, Farid J. Ghadessy, Satyasankar Jana,* Balamurugan Ramalingam*

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Laccase-Catalyzed Synthesis of Low-Molecular-Weight Lignin-Like Oligomers and their Application as UV-Blocking Materials