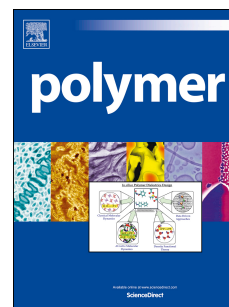


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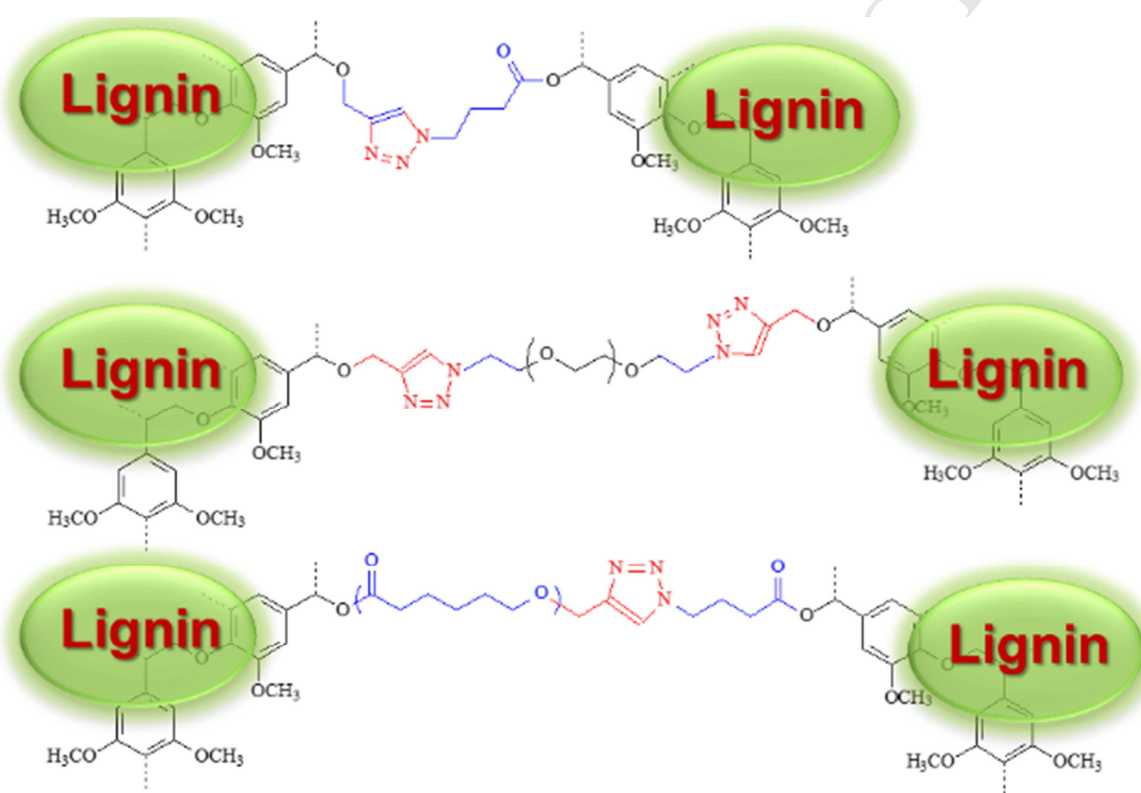
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Graphical Abstract:

Renewable Polymers from Lignin via Copper-free Thermal Click Chemistry

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ABSTRACT: The heterogeneous and multifunctional characteristics of lignin is a paradox for its potential in polymer applications, despite its renewable and aromatic nature. We demonstrate a simple approach to the preparation of renewable lignin-grafted polymers via robust copper-free thermal click chemistry. High lignin content polymers were prepared between polymer pairs containing azide and alkyne groups with tunable compositions including PEG, PCL and PLA.

KEYWORDS: lignin, renewable polymers, click chemistry

INTRODUCTION

The development of renewable polymers is driven by the reduction of our dependence on fossil fuels as organic material feedstocks. Polymers from natural and renewable resources have attracted a lot of attention in recent years, owing to their low cost, easy availability, renewability, unique properties and possible biodegradability[1-10]. Together with hemicelluloses, lignin, a natural polymer, acts as a cementing matrix of cellulose fibers within the structure of plants and trees. It is one of the principal constituents of wood (around 25–35%) and is the second most abundant natural polymer. Lignin has an amorphous, highly branched macromolecular network structure with aromatic nature and complex compositions[11-14].

Only a small portion (about one million tons) of lignin is currently used as feedstocks for low molecular weight chemicals and polymer applications[15-18]. Methods to convert lignin into high valued products would have a positive impact on biorefinery economics[19-21]. The Epps group recently developed model compounds from lignin[22-23]. Several laboratories have explored the use of lignin as an inexpensive filler, surfactant, and additive in materials applications. For example, lignin is used in biobased polymeric composites to modify material properties such as hydrophobicity, stiffness, and crystallinity relative to the neat polymers[24-27]. Hydroxyl groups are the most characteristic functional groups in lignin, thus considerable efforts have been directed toward the development of functional polymeric materials involving these groups, such as esterification and etherification[28-31]. These modified lignin derivatives provide broader applications in composite materials via grafting polymerization, cross-link coupling, etc[32-34]. The Washburn group found that a polymer-grafted strategy significantly enhanced toughness of composites compared to homopolymers[33, 35]. We found that UV-absorbent thermoplastic elastomers could be prepared by grafting polymers from lignin[29]. Novel polyols derived from lignin and fatty acids have been used for polyurethane fabrication[31].

The concept of “click” chemistry was first introduced by Sharpless and coworkers, defined as a reaction that is modular, wide in scope, high in yield, with little side products, which could be easily removed by non-chromatographic methods[36]. Click chemistry is a powerful approach with high fidelity in assembling specially designed building

blocks[37-40]. Through the choice of appropriate building blocks, click chemistry can play an important role in the field of renewable polymers from natural products[41-43]. The most widely studied click reactions is Huisgen cycloaddition between azide and alkyne groups. In most cases, this reaction involves the use of copper catalysts[44-46]. The Bertozzi group introduced a novel strategy for avoiding the use of copper, which is mostly based on strained cyclooctyne[47]. However, the preparation of functional cyclooctynes is still challenging and limited in small scales, making it only applicable for some niche applications. Historically, Huisgen cycloaddition was thermally promoted, and numerous materials have been prepared through the alkyne-azide cyclization at an elevated temperature in the absence of any catalysts[48-50]. Propargylation of phenolic hydroxyl groups using propargyl bromide through nucleophilic substitution mechanism led to modified lignin product which could serve as the reactive building blocks for high molecular weight polymers, as aryl propargyl ether moieties can be used as a prospective component for click chemistry along with an organic azide[51-53].

Herein we report a new approach to the functionalization of lignin via copper-free click chemistry[54-56]. This approach particularly caters the utilization of biomass toward low-cost scalable renewable polymers and composites[57-59]. Specifically, we utilized the concept of thermal click chemistry between azide and alkyne groups. A variety of lignin derivatives (Lignin-Azide, Lignin-Alkyne, Lignin-PCL-Alkyne and Lignin-(PCL-co-PLA)-Alkyne) were synthesized. Composites with high lignin content were prepared via this copper-free thermal click chemistry. While this work primarily aims to demonstrate the application of click chemistry in lignin modifications, the use of biodegradable polyesters also maximizes the sustainability.

EXPERIMENT

Materials

Lignin ($M_n = 1400$ g/mol) was supplied by Hong Kong Laihe Biotechnology Co., Ltd and was dried at 50 °C vacuum for 36 h and stored in a glovebox (N_2) prior to use. The hydroxyl value was 1.9 mmol/g as determined by ^{31}P NMR spectroscopy [60,61]. L-lactide (S,S) (LLA) (Purac Biochem, Netherlands) was used as received and stored in a glovebox under nitrogen. ϵ -Caprolactone (CL, Sigma-Aldrich) was dried over CaH_2 and

vacuum distilled before use. All other chemicals and reagents were purchased from Sigma-Aldrich and used as received. All polymerization reactions were carried out under inert atmosphere (nitrogen).

Characterization

^1H NMR (300 MHz) spectra were recorded on a Varian Mercury 300 spectrometer with tetramethylsilane (TMS) as internal reference. Gel permeation chromatography (GPC) was performed using a Waters GPC system equipped with a 515 HPLC pump, a 2410 refractive index detector, and three Styragel columns (HR1, HR3, HR5E in the effective molecular weight range of 100–5,000 g mol^{-1} , 500–30,000 g mol^{-1} , and 2,000–4,000,000 g mol^{-1} , respectively) with HPLC grade tetrahydrofuran (THF) as the eluent at 30°C and a flow rate of 1.0 mL min^{-1} . GPC samples were prepared by dissolving the sample in THF with a concentration of 3.0 mg/mL and passing through micro-filters with a pore size of 0.2 μm (Nylon, Millex-HN 13 mm Syringes Filters, Millipore, USA). The columns were calibrated against polystyrene standards. Fourier transform infrared spectrometry (FT-IR) spectra of samples were collected on a PerkinElmer spectrum 100 FTIR spectrometer using an attenuated total reflection (ATR) method. Transmission spectra were recorded at 4 cm^{-1} resolution and signal averaged over 32 scans. Thermal properties of polymers were recorded using differential scanning calorimetry (DSC) on a DSC Q2000 calorimeter (TA instruments). Samples were heated from -50 to 180 °C at a rate of 10 °C /min, maintained at 180 °C for 2 min and then cooled to -50 °C at a rate of 10 °C /min. Data were collected from the second heating scan. The average sample mass was about 5 mg, and the nitrogen flow rate was 50 mL/min .

Synthesis of Lignin-Alkyne

For the synthesis of Lignin-Alkyne (Scheme 1), lignin (1.0 g, 1.9 mmol -OH) was firstly dissolved in 20 mL dimethylformamide (DMF) at room temperature. Propargyl bromide (0.6 g, 4.8 mmol) was added to the lignin solution and heated at 75 °C for 12h under continuous stirring in the presence of K_2CO_3 . After cooling down to room temperature, the mixture was precipitated from water and washed with excess deionized water before dried in a freeze dryer. The product Lignin-Alkyne was obtained at ~ 90% yield with an

alkyne concentration ~1.5 mmol/g.

Synthesis of Lignin-Azide

For the synthesis of Lignin-Azide (Scheme 1), lignin (0.8 g, 1.6 mmol -OH) was dissolved in anhydrous THF (40 mL) and mixed with triethyl amine (0.2 g, 2.0 mmol) within a round bottom flask under nitrogen. Bromobutyryl chloride (0.4 g, 2.0 mmol) in anhydrous THF (10 mL) was slowly added to the above mixture at 0 °C for an hour. The reaction ran at room temperature for 24 h. Deionized water (10 mL) was then added slowly to quench any un-reacted bromobutyryl chloride. Solvents were removed by rotary evaporation under vacuum. The product was dissolved in 1,4-dioxane and precipitated into saturated NaHCO₃ solution. Lignin-Br was obtained after filtration followed by repeated washing with water, freeze-drying, washing with diethyl ether, and dried under vacuum at 40 °C until constant weight. The lignin-Br (1.0 g, 1.3 mmol -Br) was dissolved in DMF and treated with sodium azide (0.13 g, 2.0 mmol) at 50 °C for 12 hours. The reaction mixture was then diluted with water and extracted with ethyl acetate to get Lignin-Azide with an azide concentration ~1.3 mmol/g.

Synthesis of azide terminated poly(ethylene glycol) (PEG-N₃)

For the synthesis of PEG-N₃ (Scheme 2), PEG (4.6 g, 2.0 mmol -OH) was azeotropically distilled using toluene and dissolved in anhydrous THF (15 mL). Triethylamine (1.5 mL, 10.0 mmol) was added into the solution before adding 4-toluenesulfonyl chloride (2.9 g, 20.0 mmol) in 10 mL THF drop wisely within 10 mins. The reaction ran at room temperature for 24 h before saturated NaHCO₃ aqueous solution was added and stirred for another 4 hours. The solution was extracted by DCM (50 mL) for 3 times. The combined organic phase was precipitated into ether to get PEG-OTs, which was latter mixed together with NaN₃ (1.5 g, 23 mmol) in 10 mL DMF and stirred for 24 h at 30 °C. DCM (100 mL) was added to dissolve the final product before washing with brine solution for three times. The product was recovered by condensing the solution and precipitating from cold diethyl ether to obtain PEG-Azide with an azide concentration ~0.43 mmol/g.

Synthesis of Lignin-PCL-Alkyne

For the synthesis of Lignin-PCL-Alkyne (Scheme 3), lignin (0.5 g, 1.0 mmol -OH), ϵ -caprolactone (5.0 g) and stannous octoate (1.0 wt %) were weighed into a schlenk flask (25 mL) with a stir bar. The vial was sealed for three cycles of freeze-pump-thaw to degas the solution. After refilling with N₂, the flask was immersed into an oil bath at 125 °C for 3.5 h to reach a conversion ~ 90%. The reaction mixture was then cooled to room temperature and precipitated into cold methanol. The precipitated polymer Lignin-PCL was dried under vacuum to a constant weight, and the molecular weight (M_n) was determined to be 1.23×10^4 g/mol based on GPC. Lignin-PCL (0.5 g, 0.1 mmol -OH) was dissolved in 20 mL DMF at room temperature and propargyl bromide (0.2 g, 0.15 mmol) was added to the solution and heated at 75 °C for 12h under continuous stirring in the presence of K₂CO₃. After cooling down, the product was precipitated from cold methanol to obtain Lignin-PCL-Alkyne with an alkyne concentration ~0.2 mmol/g.

Synthesis of Lignin-(PCL-co-PLA)-Alkyne

For the synthesis of Lignin-(PCL-co-PLA)-Alkyne (Scheme 4), lignin (0.5 g, 1.0 mmol -OH), L-lactide (3.0 g), ϵ -caprolactone (2.0 g) and stannous octoate catalyst (1.0 wt%) were weighed into a schlenk flask (25 mL) equipped with a stir bar. The vial was sealed and degassed by three cycles of free-pump-thaw. After refilling with N₂, the flask was immersed into an oil bath at 125 °C for 3.5 h to reach a conversion ~ 90%. The polymer product Lignin-(PCL-co-PLA) was precipitated from methanol and dried under vacuum to a constant weight. The molecular weight (M_n) was 6.0×10^3 g/mol based on GPC. Lignin-(PCL-co-PLA) (0.5 g, 0.1 mmol -OH) was dissolved in 20 mL DCM and mixed with triethyl amine in a round bottom flask under nitrogen. 5-Hexynoic acyl chloride (0.2 g, prepared from 5-hexynoic acid by reaction with oxalyl chloride, Scheme 4) in anhydrous DCM (10 mL) was slowly added to the above mixture at 0 °C. The reaction was ran at room temperature for 12 h. The solution was concentrated and precipitated from cold methanol to get Lignin-(PCL-co-PLA)-Alkyne with an alkyne concentration ~0.2 mmol/g.

General procedure for click reaction between alkyne and azide

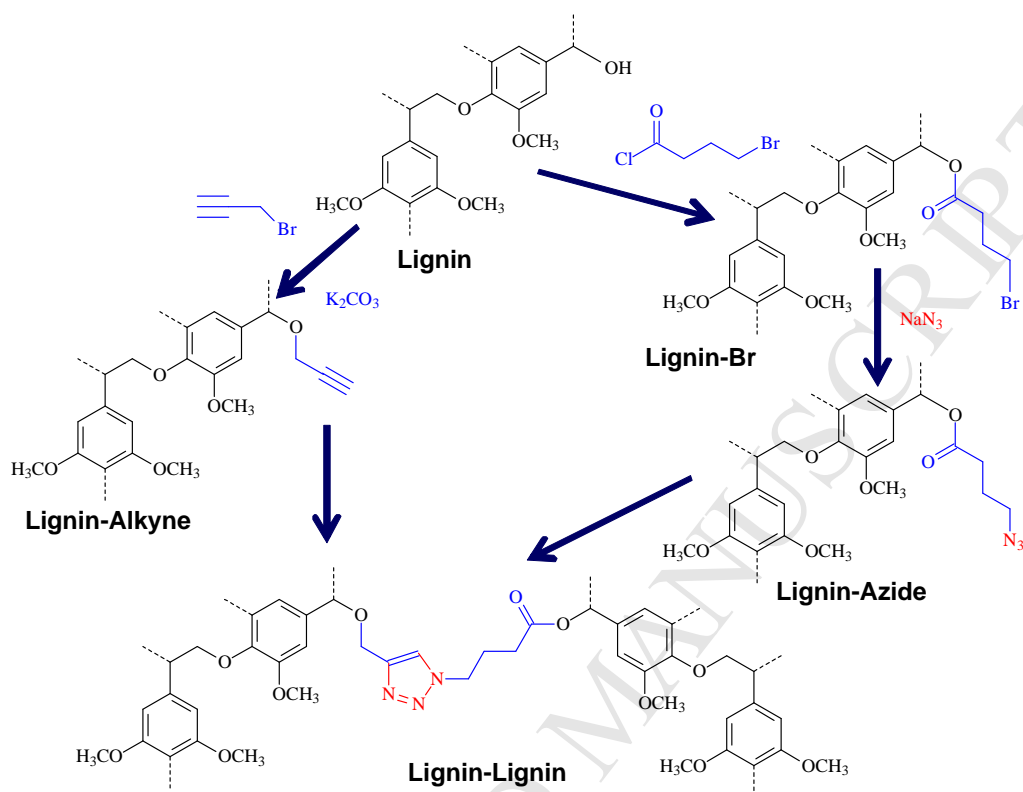
The synthesis of lignin polymers were carried out using alkyne-azide thermal click reaction. Lignin-Lignin polymers were synthesized by Lignin-Alkyne with Lignin-Azide (Scheme 1). Lignin- PEG-Lignin polymers were synthesized by Lignin-Alkyne and PEG-Azide (Scheme 2). Lignin-PCL-Lignin polymers were synthesized by Lignin-PCL-Alkyne and Lignin-Azide (Scheme 3). Lignin-(PCL-co-PLA)-Lignin polymers were synthesized by Lignin-(PCL-co-PLA)-Alkyne and Lignin-Azide (Scheme 4). Azide derivatives and alkyne derivatives were mixed at a 1:1 ratio of azide : alkyne in THF before transferred to a PTFE mold, followed by slow solvent evaporation and vacuum drying for 24 h at room temperature. The reaction mixture was placed in oven and cured at 130 °C for 12 h. The cured product was cooled to room temperature for further characterization.

RESULTS AND DISCUSSION

Synthesis of lignin polymers via click reaction of Lignin-Alkyne with Lignin-Azide

Lignin has plenty of hydroxyl groups that can be functionalized through appropriate modifications such as esterification. Lignin-Br was synthesized through simple esterification reactions between bromobutyryl chloride and phenolic and aliphatic alcohol groups of lignin in the presence of TEA (Scheme 1). Compared with the unmodified lignin, ^1H NMR spectra (Figure 1) confirmed the formation of ester groups on lignin, as there are characteristic peaks at 2.2 ppm, 2.7 ppm and 3.5 ppm, corresponding to the methylene protons of bromobutyryl group. The bromo group in lignin was subsequently converted into azide (Lignin-Azide) and we observed the shift of methylene $-\text{CH}_2\text{Br}$ (peak a) to $-\text{CH}_2\text{N}_3$ (peak d). On the other hand, lignin was directly reacted with propargyl bromide in the presence of potassium carbonate, yielding alkyne-modified lignin (Lignin-Alkyne). The incorporation of propargyl group onto lignin can be evidently seen from the broad peak of the attached methylene group ($-\text{O}-\text{CH}_2-$) (4.3 to 4.9 ppm) and the proton on the alkyne group (2.4 to 2.5 ppm) in the ^1H NMR spectrum (Figure 1).

SCHEME 1. Synthesis of Lignin-Lignin polymers via copper-free click reaction of Lignin-Alkyne with Lignin-Azide.



FT-IR spectra of Lignin-Azide showed a characteristic strong absorption at $\sim 2100\text{ cm}^{-1}$, corresponding to the azide absorption (Figure 2). A few peaks in the range of $1406\text{--}1590\text{ cm}^{-1}$ correspond to the aromatic ring vibration. The azide absorption peak disappeared completely after the thermal click reaction. The FT-IR spectra clearly demonstrated the high fidelity of thermal click reaction between Lignin-Alkyne and Lignin-Azide. Also, after the thermal treatment of mixed Lignin-Alkyne and Lignin-Azide, the product was no longer soluble in any organic solvents, like THF, DCM, and toluene, due to the formation of crosslinked structures.

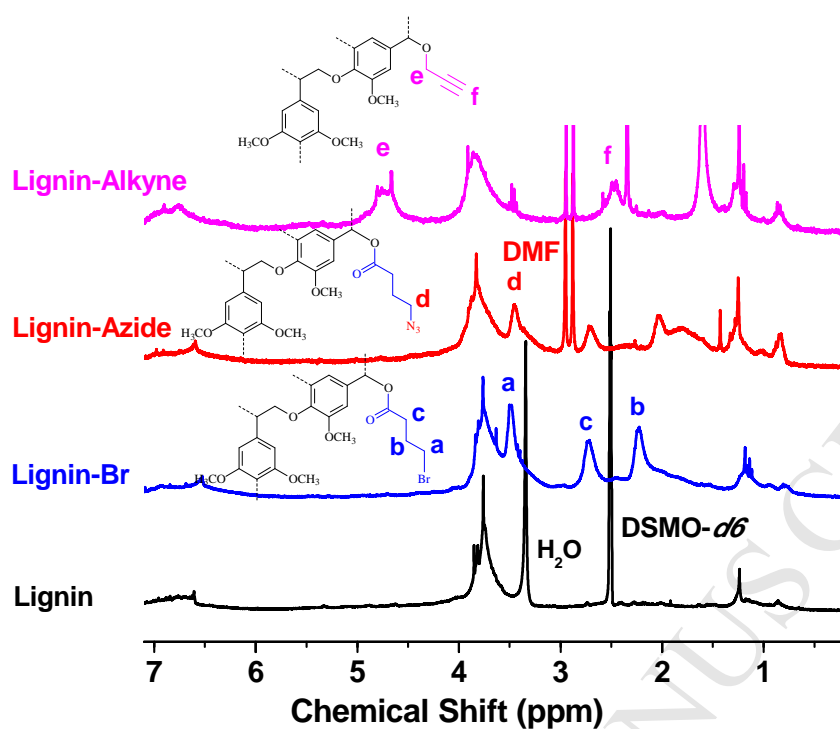


FIGURE 1. ^1H NMR spectra of lignin, Lignin-Br, Lignin-Azide and Lignin-Alkyne.

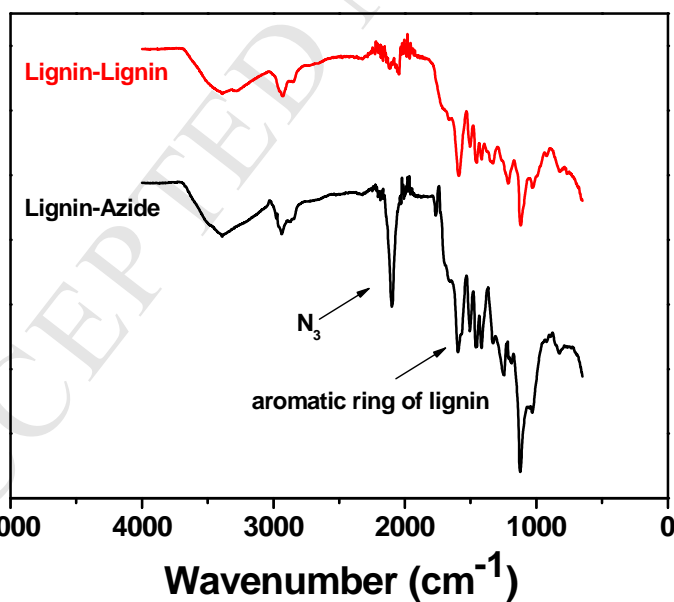
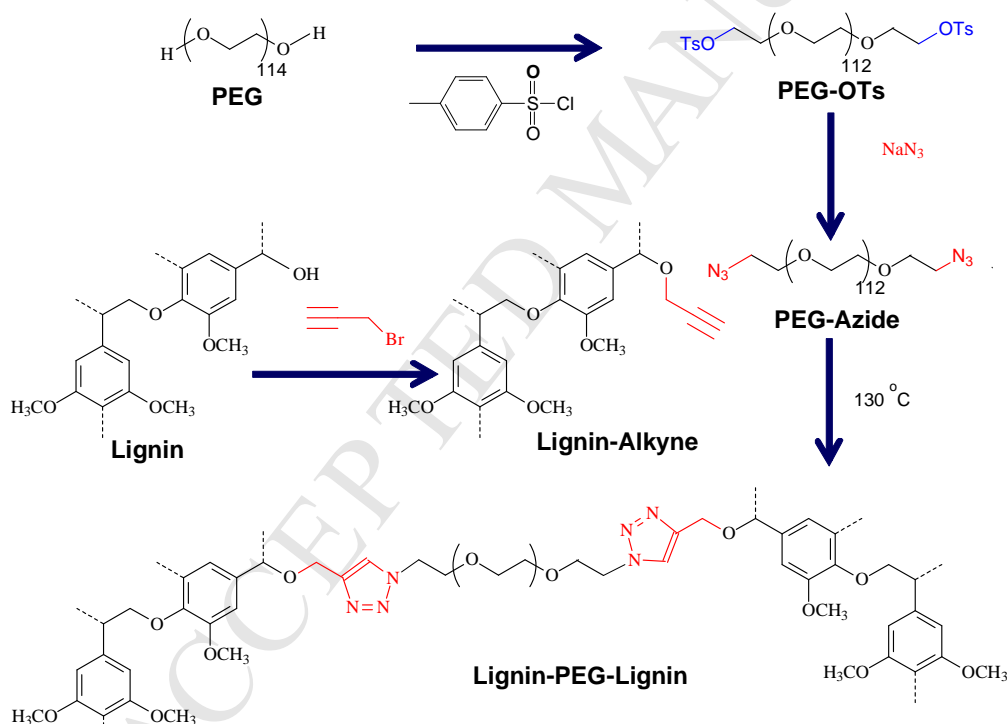


FIGURE 2. FT-IR spectra of Lignin-Azide and lignin polymer after click reaction.

Synthesis of lignin polymers via click reaction of Lignin-Alkyne with PEG-Azide

The above reaction between Lignin-Azide and Lignin-Alkyne proved the possibility to make renewable polymer materials by the thermally-promoted click reaction. We next examined the integration of other components into lignin by introducing azide or alkyne functionalized polymers. Poly(ethylene glycol) (PEG) was functionalized with terminal azide groups (Scheme 2). Tosylation and subsequent azide substitution were used for the modification. ^1H NMR spectra (Figure 3) confirmed the complete tosylation and substitution process. FT-IR spectra of PEG-azide showed a strong absorption at $\sim 2100\text{ cm}^{-1}$, indicating the incorporation of azide group (Figure 4).

SCHEME 2. Synthesis of lignin polymers via click reaction of Lignin-Alkyne with PEG-azide.



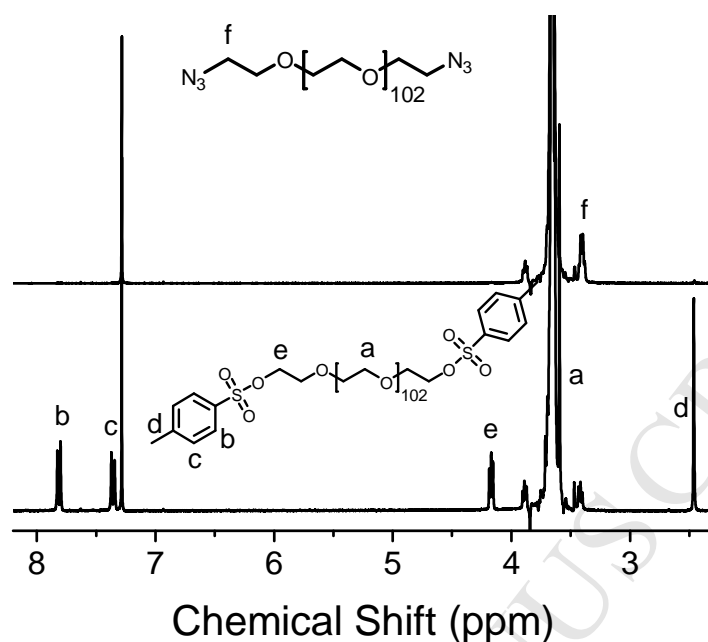


FIGURE 3. ^1H NMR spectra of PEG-OTs and PEG-Azide.

The di-functional PEG-Azide was then used as a cross-linker to react with Lignin-Alkyne (Scheme 2) through a thermal click process. The azide peak at $\sim 2100\text{ cm}^{-1}$ in the FT-IT spectra disappeared completely after the thermal click reaction. The cured product is not soluble in many common organic solvents such as chloroform, THF, and DMF.

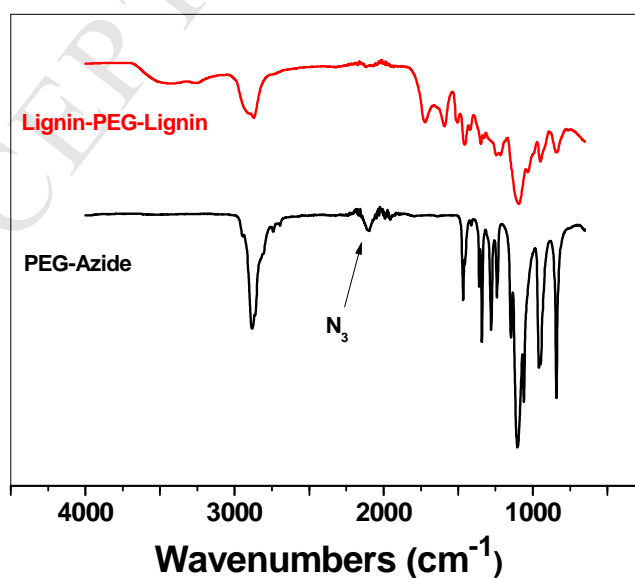
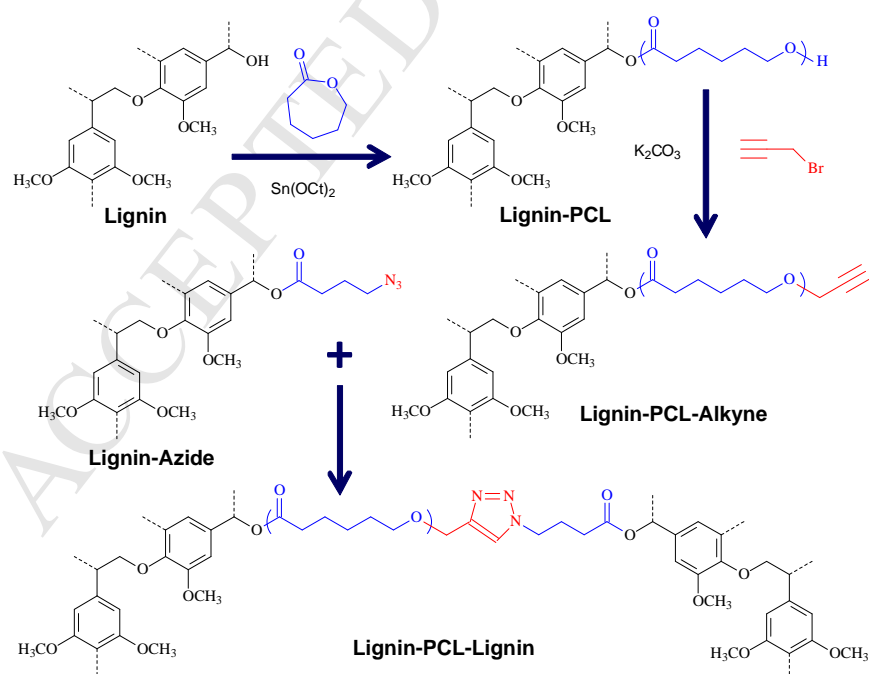


FIGURE 4. FT-IR spectra of PEG-Azide and Lignin-PEG-Lignin after click reaction.**Synthesis of lignin polymers via click reaction of Lignin-PCL-Alkyne with Lignin-Azide**

The presence of hydroxyl groups on lignin would allow the preparation of grafted copolymers from lignin via ring-opening polymerization (ROP). Since polyesters are degradable polymers, incorporation of PCL could add biodegradability to the final product. We carried out ROP of CL using lignin as initiator (10 wt% to monomer) in the presence of stannous octoate (1 wt% to monomer). The obtained polymer Lignin-PCL was further propargylated with propargyl bromide in the presence of K_2CO_3 (Scheme 3). The alkyne-containing polymer Lignin-PCL-Alkyne was then reacted with Lignin-Azide, aiming at the preparation of composite polymer Lignin-PCL-Lignin. FT-IR spectra also demonstrated the successful reaction between Lignin-Azide and Lignin-PCL-Alkyne. The strong azide absorption disappeared completely after the thermal click reaction (Figure 5).

SCHEME 3. Synthesis of lignin polymers via click reaction of Lignin-PCL-Alkyne with Lignin-Azide.

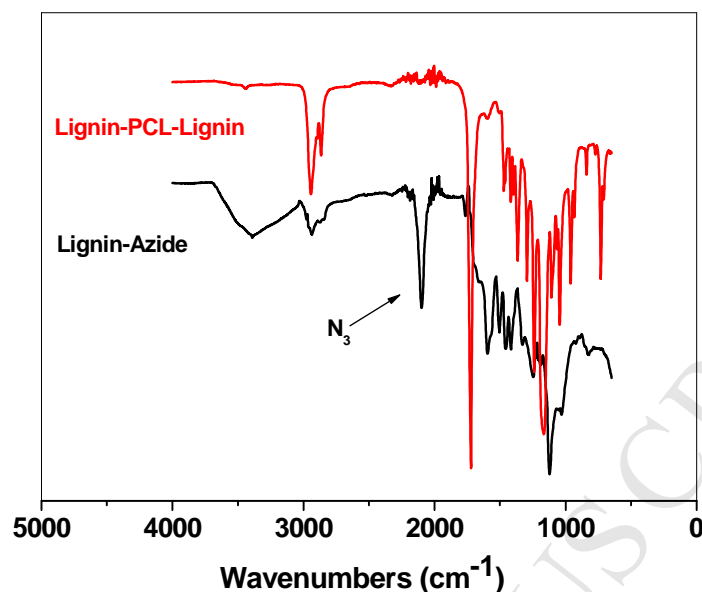


FIGURE 5. FT-IR spectra of Lignin-Azide and Lignin- PCL- Lignin polymer after click reaction.

Synthesis of lignin polymers via click reaction of Lignin-(PCL-co-PLA)-Alkyne with Lignin-Azide

To demonstrate the robustness of this copper-free click reaction, we further applied it to prepare a copolymer grafted lignin. ROP of lactide and caprolactone from lignin catalyzed by stannous octoate resulted in a Lignin-(PCL-co-PLA) copolymer. Propargylation of the –OH end groups in Lignin-(PCL-co-PLA) was carried out by esterification with 5-hexynoic acid (Scheme 4). Incorporation of the propargyl group onto Lignin-(PCL-co-PLA) can be evidently seen the ¹H NMR spectrum (Figure 6).

SCHEME 4. Synthesis of lignin polymers via click reaction of Lignin-(PCL-co-PLA)-Alkyne with Lignin-Azide.

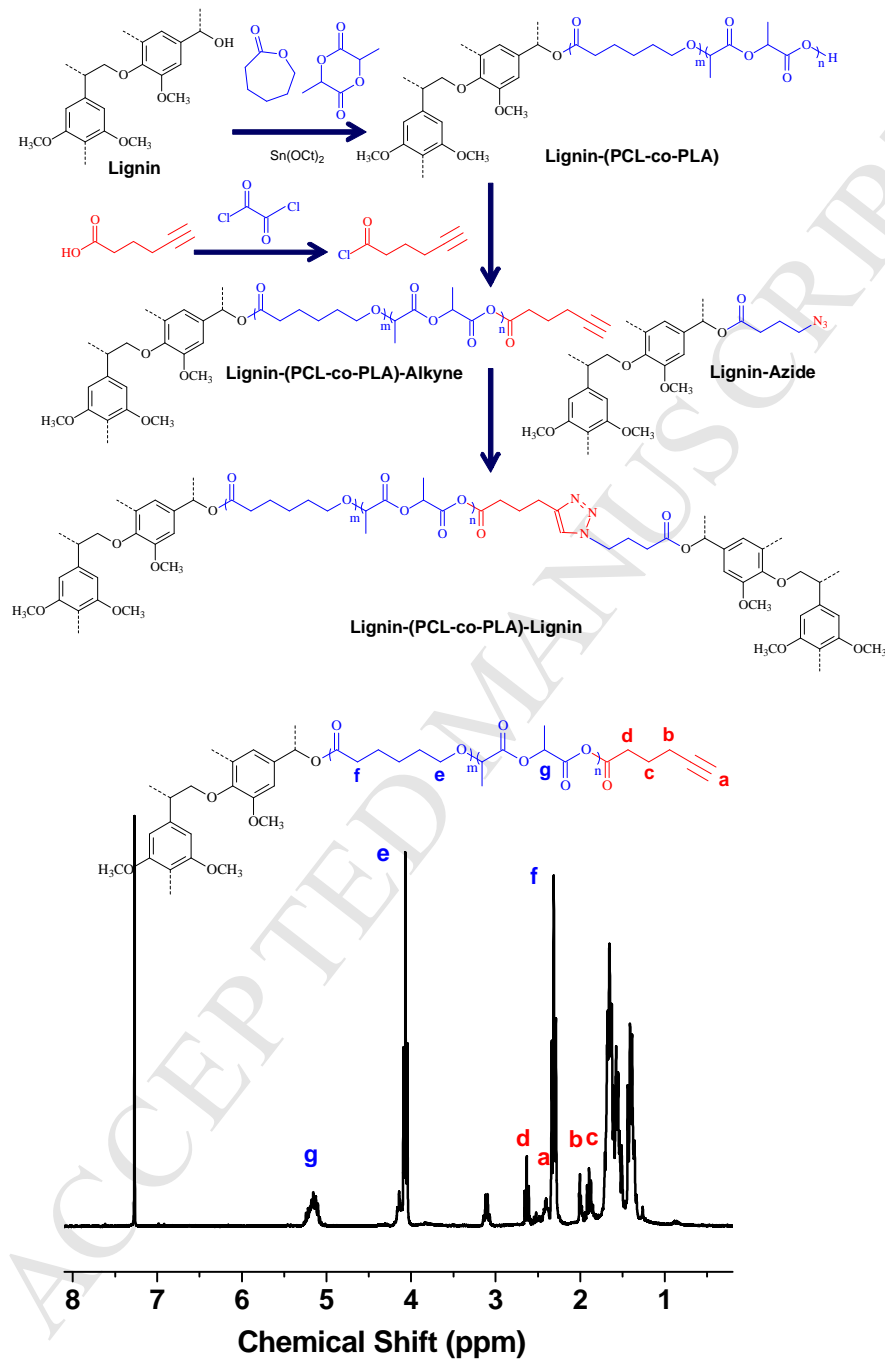


FIGURE 6. ^1H NMR spectrum of Lignin-(PCL-co-PLA)-Alkyne.

Lignin-(PCL-co-PLA)-Lignin was prepared by the thermal click reaction between

Lignin-Azide and Lignin-(PCL-co-PLA)-Alkyne. FT-IR spectra demonstrated the reaction between alkyne groups and azide groups. The peak at $\sim 2100\text{ cm}^{-1}$, corresponding to the azide absorption, disappeared completely after the thermal click reaction (Figure 7). The final product was found to be insoluble in common organic solvents such as THF and DCM.

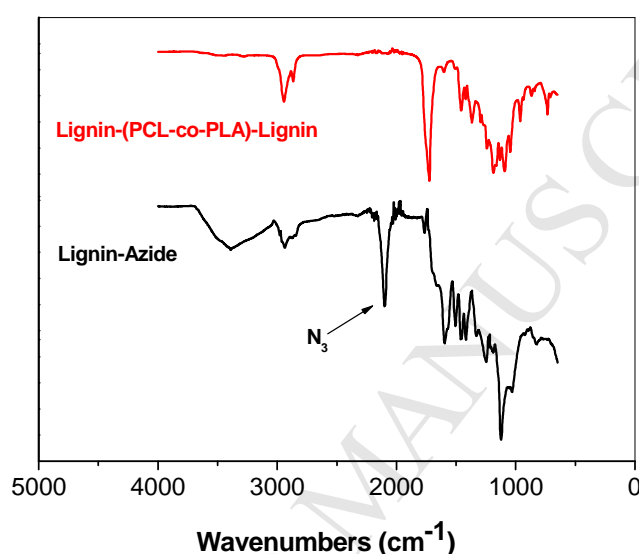


FIGURE 7. FT-IR spectra of Lignin-Azide and Lignin-(PCL-co-PLA)-Lignin polymer after click reaction.

DSC analysis of lignin polymers prepared by thermal click reactions

Lignin has a relatively high glass transition temperature (T_g), as the condensed rigid phenolic moieties and strong intermolecular hydrogen bonding interactions restrict the mobility of lignin molecules. The grafting of PEG, PCL and PCL-co-PLA from lignin is expected to affect their thermal properties. DSC analysis of the lignin polymers clearly shows that the incorporation of PEG, PCL and PCL-co-PLA chains significantly influences the thermal properties of lignin polymers (Figure 8). Depending on the grafted polymer structures, T_g s of lignin polymers varied in the range of $-34\text{ }^{\circ}\text{C}$ and $155\text{ }^{\circ}\text{C}$ with melting temperatures ranging from $38\text{ }^{\circ}\text{C}$ to $55\text{ }^{\circ}\text{C}$.

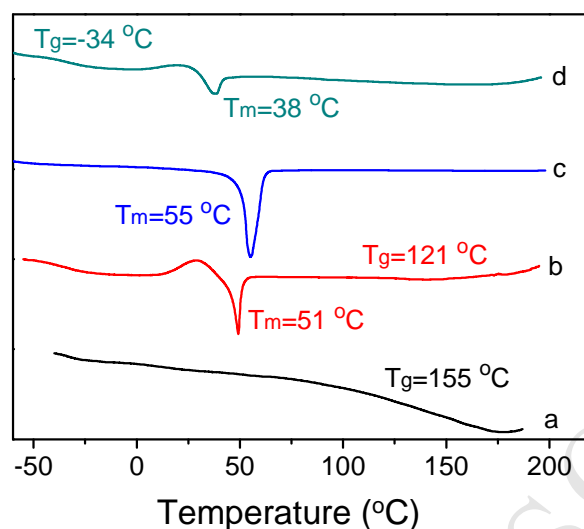


FIGURE 8. DSC curves of different lignin polymers: (a) Lignin-Lignin; (b) Lignin-PEG-Lignin; (c) Lignin-PCL-Lignin; (d) Lignin-(PCL-co-PLA)-Lignin.

CONCLUSIONS

Reactive lignin derivatives with either alkyne or azide group, including Lignin-Azide, Lignin-Alkyne, Lignin-PCL-Alkyne and Lignin-(PCL-co-PLA)-Alkyne, were prepared through facile chemical modifications from lignin. Renewable polymers were prepared by a simple thermal treatment of paired components containing alkyne and azide groups, such as Lignin-Alkyne/Lignin-Azide, Lignin-Alkyne/PEG-Azide, Lignin-Azide/Lignin-PCL-Alkyne and Lignin-Azide/Lignin-(PCL-co-PLA)-Alkyne. The copper-free click coupling between paired polymers were confirmed by FT-IR characterization following the disappearance of characteristic azide absorption peak and the lost solubility in common organic solvent of obtained products (Lignin-Lignin, Lignin-PEG-Lignin, Lignin-PCL-Lignin, Lignin-(PCL-co-PLA)-Lignin). The thermal properties of obtained products exhibited dependence on the pairing components. The copper-free thermal click chemistry could open a new avenue to the preparation of sustainable polymers and composites from a variety of renewable resources.

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Renewable Polymers from Lignin via Copper-free Thermal Click Chemistry

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Highlights:

- Copper-free azide-alkyne click chemistry for sustainable polymers.
- Lignin utilization in combination with biodegradable polyesters.