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Sustainable synthesis methods of lignin-based copolymers: recyclable non-carbodiimide catalytic systems in aqueous solvent

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Lignin is a valuable biopolymer that serves as a raw material for producing functional polymers due to its abundance, low price, sustainability, and high aromatic content. However, conventional lignin modification methods often rely on environmentally harmful reagents, solvents, and catalysts, primarily because these are common in traditional organic and polymer chemistry. Therefore, utilizing more sustainable solvents, reagents, and catalysts for synthesizing biomass-based, biodegradable polymers is crucial for developing more sustainable production methods. In this work, a lignin-containing copolymer, lignin-graft-polycaprolactone (lignin-graft-PCL), was synthesized using more environmentally friendly solvents, reagents, and catalysts. The first innovation focuses on natural lignin modification. While conventional methods use *N,N'*-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) to introduce carboxylic acid functionality into lignin, this study employs 2-chloro-1-methylpyridinium iodide (Mukaiyama reagent), which eliminates the formation of harmful byproducts such as *N,N'*-dicyclohexylurea (DCU) while maintaining high efficiency. Additionally, a tetrahydrofuran (THF)/water cosolvent system was used for lignin modification, replacing the traditionally used dimethylformamide (DMF). The second key innovation is the use of a recyclable catalyst system for lignin-based graft copolymer synthesis, which requires separate synthesis of PCL prior to graft onto lignin through covalent linkage. Unlike conventional approaches, this study presents a new recyclable polymer bound catalyst, 1,3,4,6,7,8-Hexahydro-2*H*-pyrimido[1,2-*a*] pyrimidine, polymer-bound (PS-TBD), for a ϵ -caprolactone polymerization. The PS-TBD catalyst was successfully recycled and demonstrated sustained performance over four consecutive cycles, showing only a gradual reduction in efficiency. Comprehensive spectroscopic analyses confirmed the chemical structures of all synthesized products obtained from the esterification in lignin modification, ring-opening polymerization, and copolymerization, demonstrating high efficiency.

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1. Introduction

The growing effort to diversify raw material sources beyond petroleum-based feedstocks has driven significant research into bio-based alternatives, particularly renewable biomass feedstocks, as viable and sustainable options.¹ One renewable biopolymer that has gained significant attention in recent years is lignin. Lignin, the second most abundant macromolecule globally alongside cellulose, is a cost-effective and widely available resource from various industries, making it a promising candidate for biodegradable/non-biodegradable polymer production.^{2,3} Lignin is found mostly in the cell walls of vascular plants and accounts for 15–30 weight percent of lignocellulosic biomass.^{4,5} The majority of lignin is currently

combusted for energy generation, primarily in the paper and pulp industry, with only a small fraction utilized for real world applications.⁶ Recent research aims have been the utilization of lignin to produce novel and effective materials that are, most importantly, biobased, and sustainable.⁷ Due to its aromatic structure, biodegradability, and ease of chemical modification, lignin has potential applications in bioplastics, adhesives, coatings, and composites, offering a sustainable alternative to petroleum-based materials.

On a chemical level, lignin is a randomly crosslinked phenolic biopolymer network with a variety of functional groups, including hydroxyl, carboxyl, methoxy, and ether groups. The main repeating units found in lignin consist of coumaryl, coniferyl, and sinapyl alcohols. This variety of functional groups leads to difficulties in characterization and modification of lignin, as well as poor and undefined solubility in commonly used solvents in chemical science.^{8,9} However, the presence of large contents of aliphatic and phenolic hydroxyl groups allows for great modification potential within the structure of

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lignin.^{10–12} The extraction method and plant source of lignin strongly influence both chemical structure and solubility. Dealkaline Kraft lignin is obtained as a by-product of alkaline sulfate pulping. Kraft lignins exhibit lower solubility than organosolv or lignosulfonate lignins, owing to their higher degree of condensation and lower content of hydrophilic substituents.^{13,14}

The above-mentioned poor solubility issue presents significant challenges in working with and processing dealkaline Kraft lignin for various applications, including the development of lignin-based polymers. Dimethylformamide (DMF) is one of the most common organic solvents used to solubilize lignin.^{15,16} This solvent is highly polar and possesses high boiling point, making it possible to work with and solubilize dealkaline Kraft lignin.^{17,18} However, DMF is classified as less environmentally friendly due to its toxicity and potential for environmental contamination.¹⁹

One promising, green, solvent alternative for lignin modification is dihydrolevoglucosenone (Cyrene). Cyrene is a cellulose biomass-derived solvent, which can be synthesized in a two-step process.^{20,21} In addition, this solvent is biodegradable, non-mutagenic, and non-toxic. Therefore, cyrene can replace commonly employed dipolar organic solvents such as DMF and NMP. However, cyrene does not dissolve all varieties of lignin efficiently.²² Because of this, it requires intensive additional studies and employing Cyrene on a large scale right now involving lignin would not be advantageous.

Another promising and sustainable solvent is γ -valerolactone (GVL), which is a naturally occurring and non-toxic compound. One of the most attractive properties is its remarkably low vapor pressure, which enhances its safety and usability as a sustainable solvent.²³ Additionally, GVL does not form hazardous peroxides when exposed to air, making it a stable option for various industrial processes.²⁴ These characteristics position GVL as a promising candidate for replacing harmful organic solvents. However, GVL alone cannot dissolve lignin, and thus a cosolvent system is required that typically includes DMF or DMSO.^{25,26} In addition, there is also still a need to develop economical production technologies that can efficiently convert carbohydrate-based biomass into GVL.²⁷ These advancements are crucial for making GVL viable for broader goals of sustainable solvents.

The next sustainable solvent is 2-methyl-tetrahydrofuran (2-MeTHF), which can be derived from renewable resources, such as furfural and levulinic acid.^{28–30} The solvent possesses practically useful physical and chemical properties, including low water miscibility, a moderate boiling point, and remarkable stability compared to other cyclic chemical structure solvents.³¹

The examples provided above represent viable greener solvent alternatives, yet several factors hinder their effective implementation in practice. Economic drawbacks, the current challenges of scaling up for industrial use, and difficulties in solubilizing lignin are among the key obstacles facing these solvents. Therefore, improved solvent systems to facilitate lignin modification and polymerization are required.

Unlike the commonly used lignin solvent, DMF, which has a high boiling point of 153 °C, tetrahydrofuran (THF)'s boiling point is 66 °C.³² The low boiling point of THF provides multiple advantages including easy removal from a reaction mixture, which minimizes energy costs and carbon footprints that produce high heating for purification processes.

Another important synthesis step of the lignin-based polymer production is graft copolymerization to covalently link biomass lignin and other polymers that customize functionalities for advanced applications. For this graft copolymerization, carbodiimide catalysts are widely used due to their ability to facilitate the formation of ester bonds.^{33,34} These catalysts, such as dicyclohexylcarbodiimide (DCC), activate the carboxylic acids, enabling them to react with alcohols. While carbodiimide catalysts are effective and well-known for ester bond linking, they present significant challenges such as the generation of a hazardous byproduct, *N,N'*-dicyclohexylurea (DCU), which is difficult to remove from the reaction product.^{35,36} The potential toxicity and environmental impact of these byproducts make the use of carbodiimide catalysts less desirable in sustainable practices. Hence, finding an alternative route to introduce greener and more efficient esterification catalysts is paramount for advancing sustainable polymer synthesis.

2-Chloro-1-methylpyridinium iodide (Mukaiyama reagent) is a viable replacement for traditional DCC and DMAP reagents used for esterification reactions. This catalyst has been used as a condensation reagent in the creation of esters from carboxylic acids and alcohols, as first reported by Mukaiyama *et al.* in 1975.³⁷ The benefits of using this novel catalyst in place of DCC/DMAP are mainly environmental, as they provide a greener approach to carrying out esterification reactions without the production of the hazardous byproduct, DCU.³⁸

Ring-opening polymerizations (ROP) commonly employ 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP), and 1,5,7-Triazabicyclo [4.4.0] dec-5-ene (TBD) catalysts particularly for lactones and cyclic esters.^{39–43} However, the TBD catalysts are not recoverable and reusable after the polymerization reaction. This not only raises economic concerns but also poses challenges from an environmental standpoint, as the loss of catalyst contributes to waste and increases purification efforts that lead to additional solvent use. Polymer-bound catalysts can solve these outstanding issues. Because these catalysts are immobilized by insoluble or soluble polymer networks or chains, the polymer bound catalyst can be recovered and repeatedly used at the end of the desired chemical reaction, including polymerization. Particularly, the separation of polymer bound catalysts from solution can be easily done by simple filtration, as the polymer support is typically designed to be insoluble and can be easily filtered out, leaving the reaction product in the solution. Depending on the catalyst reactivity, those removed (or recovered) polymer bound catalysts can be reused in other reactions multiple times. Thus, the use of polymer bound catalysts may significantly reduce solvent waste for purification and amount



of catalyst required.^{44–46} Their tunable properties, such as changes in pore size or the hydrophobicity of polymers, also allow for advanced modifications with controllable solubility of the polymer bound catalysts. Therefore, a polymer-bound catalyst could be a good replacement for traditional ROP catalysts and is investigated in this work.

The sustainable PS-TBD presents a promising alternative to traditional TBD catalysts. PS-TBD is a polymer-supported organocatalyst, consisting of a guanidine-based TBD moiety covalently linked to polystyrene resin. It has been successfully applied in a range of reactions, including epoxide ring-opening, aldol-type condensation, Knoevenagel condensation, and Michael additions.^{47,48} While TBD is widely recognized as the most common catalyst for the ROP of cyclic esters, PS-TBD involved ROP is rare with only a few examples.^{49–51}

This report focuses on the synthesis of lignin-based polymers using more sustainable solvent, reagent, and catalyst systems. The model polymer synthesized was lignin-graft-polycaprolactone (lignin-graft-PCL). Although similar lignin-based polyesters were reported previously, this work employed higher sustainable synthesis methods compared to classic methods.^{52,53} The esterification of lignin and the covalent linking of polycaprolactone (PCL) to the modified lignin was achieved using 2-chloro-1-methylpyridinium iodide (Mukaiyama reagent) and a THF/water cosolvent system (Scheme 1, Step 1 and Scheme 3, Step 3). The ROP of PCL was successfully carried out using 1,3,4,6,7,8-Hexahydro-2H-pyrimidine, polymer bound catalyst system (PS-TBD) (Scheme 2, Step 2). The formation of each synthesis step's product is

thoroughly established by multiple spectrometry methods, including ¹H NMR, ¹³C NMR, and FT-IR spectroscopy. Thermal properties of the final copolymer were also investigated in comparison to previously reported lignin-based copolymers.

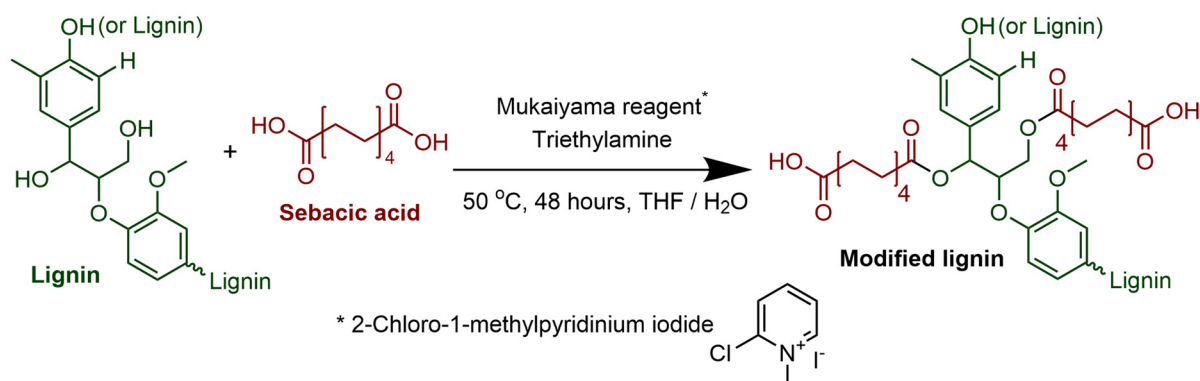
2. Experimental

2.1. Materials

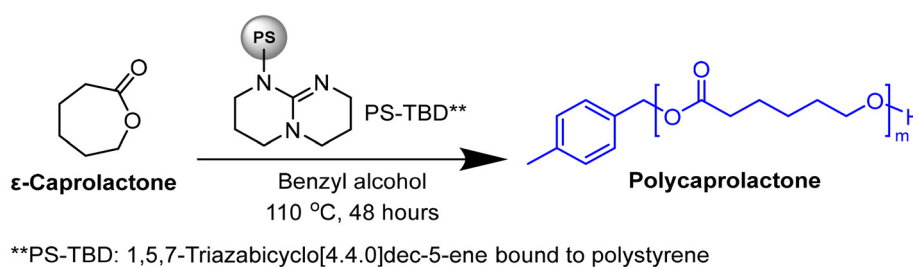
1,3,4,6,7,8-Hexahydro-2H-pyrimido[1,2-*a*] pyrimidine polymer-bound (polystyrene-bound TBD, PS-TBD), 2-chloro-1-methylpyridinium iodide (Mukaiyama reagent), ϵ -Caprolactone, triethylamine, and sebacic acid were purchased from MilliporeSigma. Dealkaline Kraft lignin (product number L0045) and 4-methylbenzyl alcohol were purchased from TCI America. According to the product details in TCI America, the sodium ligninsulfonate was initially obtained from needle-leaved trees and broad-leaved trees through the treatment of sodium sulfite. Then, the dealkaline lignin is attained from sodium ligninsulfonate through the chemical modifications such as partial desulfonation, oxidation, hydrolysis and demethylation. All chemicals were used without further purification unless otherwise stated.

2.2. Synthesis of sebacic acid modified lignin (modified lignin)

Lignin (2.00 g, OH content: 4.5 mmol g⁻¹, 1 equivalent), sebacic acid (1.82 g, 9 mmol, 1 equivalent), and triethylamine (3 mL, 21.4 mmol, 2.4 equivalent) were taken in a 100 mL two-necked round-bottom flask. Then, 20 mL water/tetrahydro-



Scheme 1 Step 1: Synthesis of modified lignin for further graft copolymerization.



Scheme 2 Step 2: Synthesis of PCL *via* ring-opening polymerization.



THF) cosolvent system (1:1 volume ratio) was added into the flask and stirred to obtain the homogeneous mixture solution. Subsequently, a separate solution of Mukaiyama reagent (2.53 g, 9.9 mmol, 1.1 equivalent) in 20 mL water/THF cosolvent was prepared by stirring at room temperature. Both reaction solutions were degassed under continuous argon atmosphere for 15 minutes. Afterwards, the solution of Mukaiyama reagent was added slowly to the initial solution of lignin and sebacic acid. The final reaction mixture was continuously stirred at 50 °C for 48 hours. The resulting dark solution was precipitated in 1 M HCl solution at 0 °C. The precipitation was filtered under vacuum and rinsed multiple times with de-ionized water. Finally, a brown solid product was obtained after drying under vacuum. Yield: 82 wt% (3.14 g).

2.3. Synthesis of polycaprolactone (PCL)

ϵ -Caprolactone (4.0 mL, 36.10 mmol, 1 equivalent), PS-TBD (139 mg, 0.361 mmol, 0.01 equivalent), and 4-methylbenzyl alcohol (44.1 mg, 0.361 mmol, 0.01 equivalent) were added to a glass vial and degassed under an argon atmosphere. The reaction mixture was stirred at 110 °C for 48 hours. Then, the mixture was precipitated with cold methanol and precipitation allowed to settle down for 10 minutes. Afterwards, a vacuum filtration was used to separate the solid components (polymer precipitation and polymer bound catalyst) from the methanol. Then, dichloromethane (DCM) was added to the solid products, where the synthesized PCL polymer dissolved in DCM, while the PS-TBD remained insoluble in DCM. The polymer dissolved in DCM solution and the solid yellow PS bound catalyst were collected separately. Lastly, solid PCL polymer was obtained by evaporating DCM under vacuum. Notably, the recovered solid polymer-bound catalyst (PS-TBD) was reused in new polymerization reactions. Yield: 80 wt% (3.3 g).

2.4. Synthesis of lignin-graft-polycaprolactone

Modified lignin (0.33 g, OH content: 4.5 mmol g⁻¹, 1.492 mmol, 1 equivalent), PCL (1.0 g), and triethylamine (0.36 g, 3.58 mmol, 2.4 equivalent) were taken in a two-necked round bottom flask. 14 mL of THF/water cosolvent (1:1 volume ratio) was added to the flask and stirred until dissolved. Simultaneously, a second reaction solution of Mukaiyama reagent (0.46 g, 1.79 mmol, 1.2 equivalent) in 14 mL of THF/water cosolvent was prepared by stirring at room temperature under continuous argon flow for 15 minutes. At this time, the second solution of Mukaiyama reagent was added slowly to the initial mixture of modified lignin, PCL, and triethylamine. The combined mixture solution was continuously stirred at 50 °C for 48 hours. The final reaction mixture was poured into the 1 M HCl solution at 0 °C. The brown solid product was ultimately obtained by vacuum filtering the mixture and rinsing it several times with deionized water. Yield: 80 wt% (1.06 g).

2.5. Instrumentation

2.5.1. Nuclear magnetic resonance analysis. Nuclear Magnetic Resonance (NMR) tests were carried out on Bruker

600 MHz and 500 MHz spectrometers. ¹H and ¹³C NMR were used for structural characterization. Acquisition parameters of each spectrum are as follows: ¹H NMR spectral width: 12020, acquisition time: 2.72, relaxation delay: 1 s, digital resolution: 0.09. ¹³C NMR spectral width: 36232, acquisition time: 0.90, relaxation delay: 2 s, digital resolution: 0.55. DMSO-d₆ was used as the NMR solvent to dissolve the unmodified lignin, modified lignin and modified lignin-graft-PCL at room temperature. CDCl₃ was used as the NMR solvent for PCL samples at room temperature.

2.5.2. Gel permeation chromatography analysis. The molecular weight of polymers and PDI values were determined on an Agilent–Wyatt combination gel permeation chromatography (GPC) instrument containing three successive Agilent PLgel Mixed-C columns, an Agilent 1260 infinity series pump, a degasser, and an autosampler. The Wyatt detection unit hosts the Optilab TrEX refractive index detector. The GPC system was initially calibrated using polystyrene (PS) standards with a molecular weight from 3 022 000 to 580 Da. The calibration curve is utilized to determine the molecular weight of the samples. GPC measurements of the PCL samples were carried out using tetrahydrofuran as the eluent at a flow rate of 1 mL min⁻¹ at room temperature. An injection volume of 50 μ L and a sample concentration of 10 mg mL⁻¹ were used.

2.5.3. Fourier transform-infrared spectroscopy (FT-IR). Fourier Transform-Infrared spectra were obtained from a JASCO 6800 FT-IR Spectrometer in the mode of attenuated total reflectance. A scan number of 200 and a resolution of 4 cm⁻¹ were used for each spectrum.

2.5.4. Thermal properties. The decomposition temperature was analyzed by thermal gravimetric analysis (TGA) data. TGA experiments were performed in TA Instruments simultaneous thermal analyzer (SDT, Model: Q600), where the samples were heated up to 600 °C at a heating rate of 10 °C min⁻¹ under constant argon gas flow (100 mL min⁻¹). $T_{d5\%}$ represents the temperature at which the polymers experience 5% weight loss.

3. Results and discussion

In this current study, the key features are (1) the utilization of a more sustainable water based cosolvent THF/water, (2) the use of the environmentally friendly Mukaiyama reagent for lignin modification, and (3) exploring the multiple recyclable nature of the PS-TBD catalyst during the ROP of ϵ -caprolactone (Table 1). This lignin modification reaction has previously been conducted using DCC and DMAP along with high boiling point DMF (153 °C) as the choice solvent.⁵⁴ The primary focus of this research was the replacement of all three of these chemicals (DCC, DMAP, and DMF) for a more effective and less environmentally impactful alternative without changing the overall chemistry and mechanism of the lignin modification. Overall, lignin-graft-PCL copolymer, is synthesized by three steps: modification of natural lignin, synthesis of PCL, and the covalent integration of modified lignin and PCL. The spectroscopic evidence (¹H NMR and ¹³C NMR) of synthesized



Table 1 Summary table of this work compared with conventional methods

| Aspect | This work (improved sustainable methods) | Conventional methods (non-sustainable methods) | Sustainability benefits of this work |
|------------------------|--|---|--|
| Solvent system | Water/tetrahydrofuran (THF) cosolvent system (50 : 50 ratio) | Dimethylformamide (DMF) ⁵⁵ | Reduces toxicity: Reduces the need for organic solvents and toxicity associated with DMF. ¹⁹ Lower boiling point: Easier removal of solvent and less energy consumption. ⁵⁴ |
| Esterification reagent | Mukaiyama reagent (2-chloro-1-methyl pyridinium iodide) | 4-Dimethylamino pyridine (DMAP) and <i>N,N'</i> -dicyclohexyl carbodiimide (DCC), generates toxic <i>N,N'</i> -dicyclohexylurea (DCU) ⁵⁶ | Reduces toxicity: The Mukaiyama reagent eliminates the formation of the toxic byproduct DCU, which is harmful to both the environment and human health. ^{35,38} |
| ROP catalyst recycling | Polymer-supported TBD (PS-TBD) catalyst | Single-use TBD catalyst ⁵⁷ | Waste reduction: The ability to recycle the PS-TBD catalyst significantly reduces material waste. ⁴⁸ Cost-effective: Recycling the catalyst eliminates the need for purchasing new catalyst with each cycle, making the process more cost-effective. |

products (modified lignin, ϵ -caprolactone, PCL, lignin-graft-PCL, and "Model Product"), photos of various modified lignins, solubility visuals of raw and modified lignin, and degree of modified lignin acid modification calculations are displayed in Fig. S1–18 in the SI. The schematic representations of these reaction steps can be found in Schemes 1–3, Steps 1–3 and Fig. S12, 15, and 18.

3.1. Cosolvent system for lignin modification and graft copolymerization

In previous reports, lignin modification commonly used DMF, a solvent with low sustainability. In this study, we established a more sustainable lignin modification method using a THF/

water cosolvent system in place of traditional DMF solvent. The synthesis scheme is shown in (Scheme 1, Step 1). While the THF/water mixture represents an improvement over DMF, it should be noted that 50% THF is not a fully green solvent since THF is petroleum-derived. A promising future direction would be to explore 2-methyltetrahydrofuran (2-MeTHF), which can be produced from bio-based raw materials and offers a more sustainable alternative to THF.^{28–30} The efficiency of Scheme 1, Step 1 reaction was compared with the product obtained using the traditional solvent, DMF, *versus* the product obtained using the new and more sustainable THF/water cosolvent. It is important to note that neither THF nor water can dissolve the lignin on their own as seen in

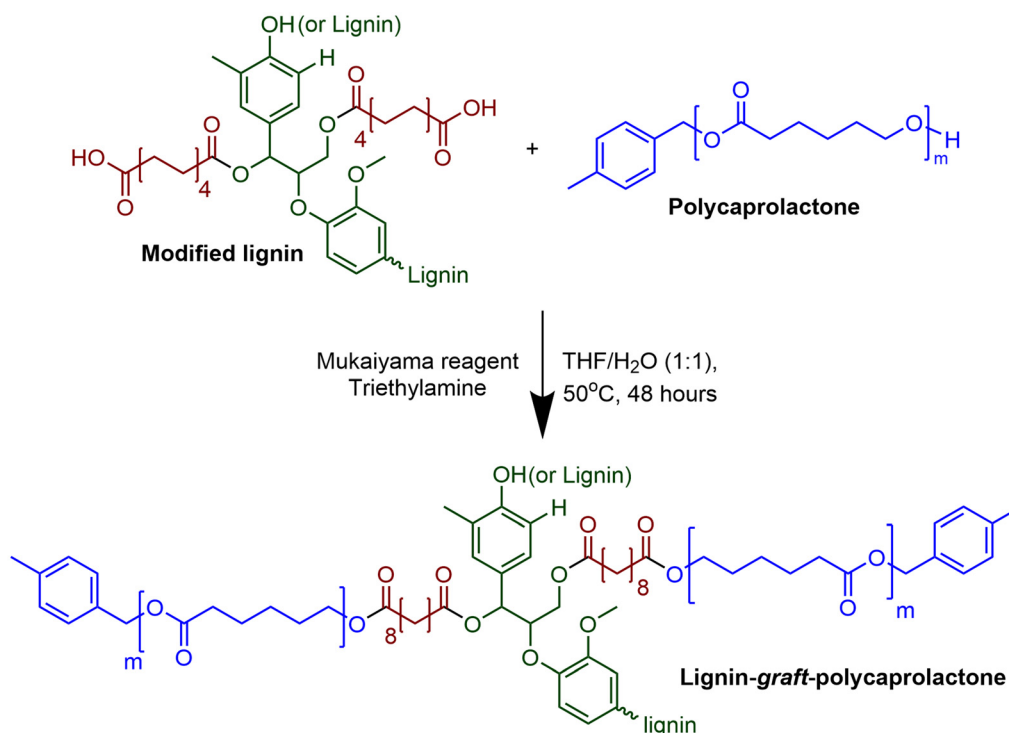
**Scheme 3** Step 3: Synthesis of the copolymer lignin-graft-PCL.

Fig. S5a and S5b found in the SI. To solve this issue, a cosolvent system was employed using THF and water in a 50:50 volume ratio. In Fig. S3, found in the SI, a noticeably darker color was observed in the modified lignin reaction using DMF as the solvent. The product was stickier and more viscous than the product found using the novel THF/water cosolvent system, which was a much lighter brown color and was more of a powder with a much lower viscosity. Another metric used to analyze the effectiveness of each reaction is a weight yield. The conventional lignin modification using DMF resulted in a 62 wt% yield (Table S1). In contrast, performing the same reaction in a THF/water cosolvent increased the yield to 71 wt% (Table S1). This reaction scheme and ^1H and ^{13}C NMR can be found in the SI in Fig. S12–14. Note that these solvent comparison tests were conducted using DCC/DMAP catalysts, not the Mukaiyama reagent. These results additionally highlight not only the increased sustainability of our novel scheme, but also the surprisingly superior effectiveness of the method employed, and the quality of the novel product acquired.

Additionally, this new cosolvent system was tested on a basic esterification reaction using DCC/DMAP (Fig. S18). While this reaction did not proceed, the focus of this research remains on lignin, leaving this reaction open for future work.

For Scheme 3, Step 3, the graft copolymerization step, the cosolvent system using THF and water in a 50:50 ratio was also employed.

3.2. Sustainable catalyst for lignin modification

The first step to prepare the lignin-*graft*-copolymer is the modification of natural lignin. A new and sustainable catalytic system, (Mukaiyama reagent), was utilized to modify lignin.³⁷ The Mukaiyama reagent facilitated the esterification reaction between the hydroxyl groups in natural lignin and the carboxylic acid groups of sebacic acid, as demonstrated in Scheme 1, Step 1. The terminal carboxylic acid groups of the modified lignin were later used for the graft copolymerization with PCL. The successful completion of the reaction in Scheme 1, Step 1 was confirmed using both ^1H and ^{13}C NMR (Fig. 1 and 2). The degree of acid modification was found to be $5.1532\text{ mmol g}^{-1}$ for the modified lignin. Details of the calculations are available in SI 6, and the SI ^1H NMR spectrum is also provided in Fig. S6.

The appearance of a small and broad peak in Fig. 1 around 12.00 ppm, labeled “a”, appeared from the end carboxylic acid groups’ hydrogen in the modified lignin after the reaction between lignin and sebacic acid.⁵² The presence of methoxy groups can be confirmed by the peak labeled “e” at 3.40 ppm. The peaks labeled “b, c, and d” correspond to the aliphatic carbon chains found within the structure of the attached sebacic acid that subsequently forms the modified lignin.⁵² The range of peaks found between 6.00 ppm and 9.00 ppm correspond to the various protons found within the unmodified structure of lignin.^{58,59} According to the ^1H NMR data, the

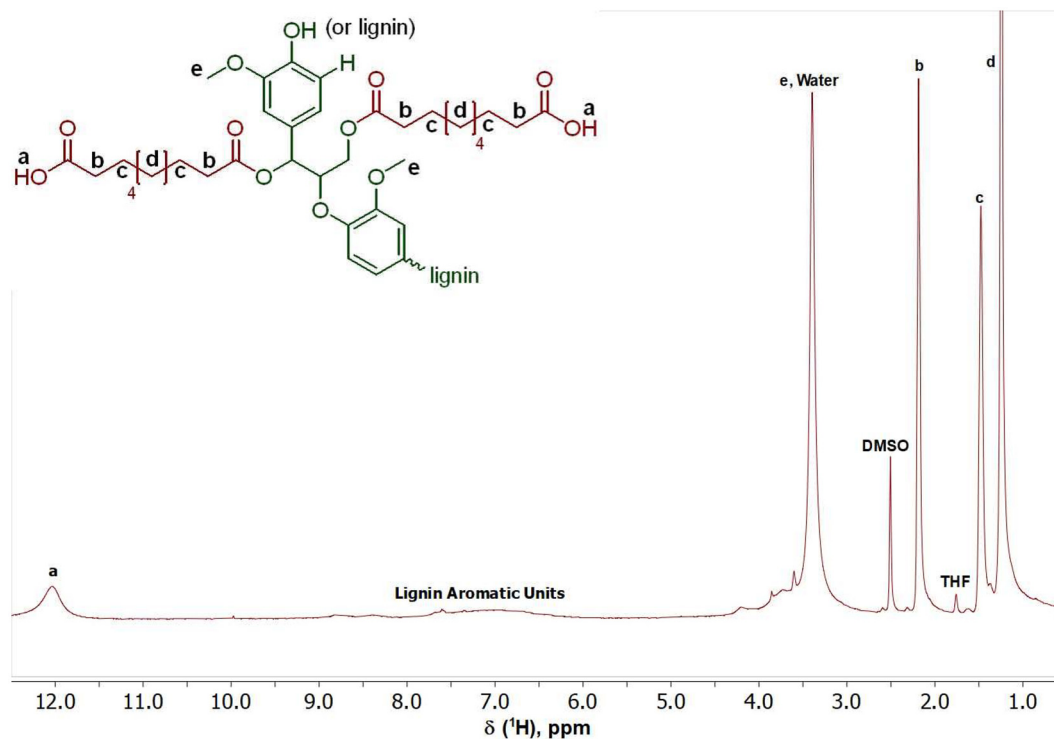


Fig. 1 ^1H NMR of Modified Lignin; hydroxyl groups on lignin were consumed through esterification. The presence of sebacic acid end groups can be seen in the peak labeled “a”. The presence of lignin can also be observed in the aromatic region between 7.0–8.0 ppm.



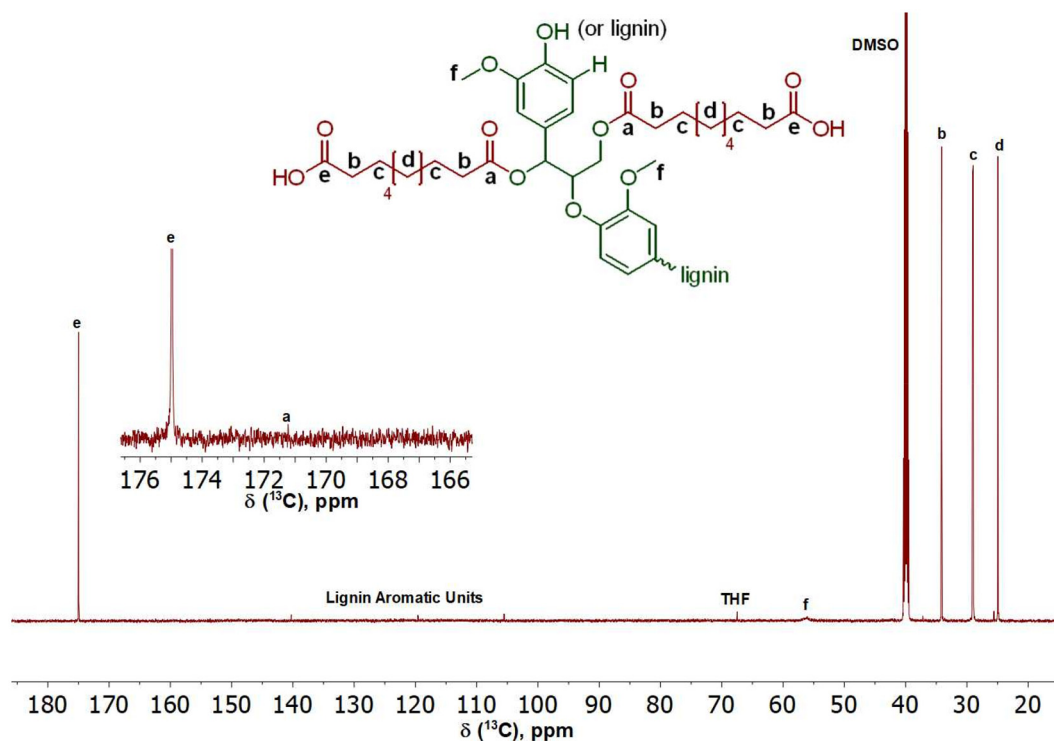


Fig. 2 ^{13}C NMR of Modified Lignin; hydroxyl groups on lignin were consumed through esterification. New ester linkages of the modified lignin can be seen in peak "a".

modification of natural lignin to introduce carboxylic acid functionalities was successfully occurred, as illustrated in Scheme 1, Step 1, using a more effective and sustainable esterification route.

In ^{13}C NMR (Fig. 2), the presence of a small peak at 172.82 ppm in Fig. 2, labeled "a", confirms the successful grafting of sebacic acid onto the natural lignin and the presence of an ester within the final structure.⁵² The larger peak at 175.03 ppm, labeled "e", represents the carboxylic end groups of the introduced sebacic acid present in the final product.⁵² Additionally, peaks "b, c, and d" of the chemical structure of the modified lignin in Fig. 2 can be seen between 25.00 ppm and 35.00 ppm.⁵² These peaks represent the aliphatic carbon chains found within the structure of the attached sebacic acid that subsequently forms the modified lignin. The central and unmodified lignin structure appears between 105.00–140.00 ppm.

The 2D HSQC (^1H - ^{13}C) NMR spectra shown in Fig. 3(a–c) offer detailed insights into the structural differences between the unmodified lignin and modified lignin. In Fig. 3(a), the characteristic signals corresponding to hydroxyl groups at the α , β , and γ positions of unmodified lignin are observed at $\delta_{\text{H}}/\delta_{\text{C}} = 3.2\text{--}4.9$ ppm/59–78 ppm.^{52,60–62} The methoxy group ($-\text{OCH}_3$) signal displayed at $\delta_{\text{H}}/\delta_{\text{C}}: 3.80$ ppm/56 ppm.^{52,60,62} Altogether, the HSQC NMR spectrum of unmodified lignin showed the typical chemical structure of lignin with abundant hydroxyl groups (Fig. 3(a)). After modification, the signals corresponding to the α and γ hydroxyl groups disappeared in the HSQC NMR spectrum of the modified lignin (Fig. 3(b)).

Moreover, the signals of the methylene unit ($-\text{CH}_2-$) from the sebacic acid segment appeared at $\delta_{\text{H}}/\delta_{\text{C}}: 2.18\text{--}2.20$ ppm/28–40 ppm in Fig. 3(b).⁵² Thus, the consumption of α and γ hydroxyl groups after the reaction, along with the appearance of methylene signals in the modified lignin (Fig. 3(b)), confirms the successful incorporation of the sebacic acid unit into lignin.

To test the effectiveness of the new Mukaiyama reagent system as a replacement for DCC/DMAP, both DMF and the THF/Water cosolvent system were applied in the catalyst reactions. The reaction scheme and ^1H and ^{13}C NMR for the reaction using the Mukaiyama reagent and DMF can be found in the SI in Fig. S15–17. The Mukaiyama reagent in DMF resulted in a yield of 69 wt% of the initial reactant mass (Table S1) and when the reaction was performed in the co-solvent system, the yield increased to 82 wt% of the initial reactant mass (Table S1). These findings, paired with detailed ^1H and ^{13}C NMR spectroscopy, demonstrate that the combined use of the new cosolvent system with the Mukaiyama reagent enhances the yield when compared to either system by itself.

Both natural and synthesized modified lignin demonstrated excellent solubility in the THF/water cosolvent, dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), and *N*-methylpyrrolidone (NMP) as displayed in Fig. S5c and S5d (SI). The modified lignin produced using the THF/water cosolvent system retained a solubility profile similar to that of natural lignin because of the preserved aromatic lignin core. This comparable solubility of modified lignin is utilized to



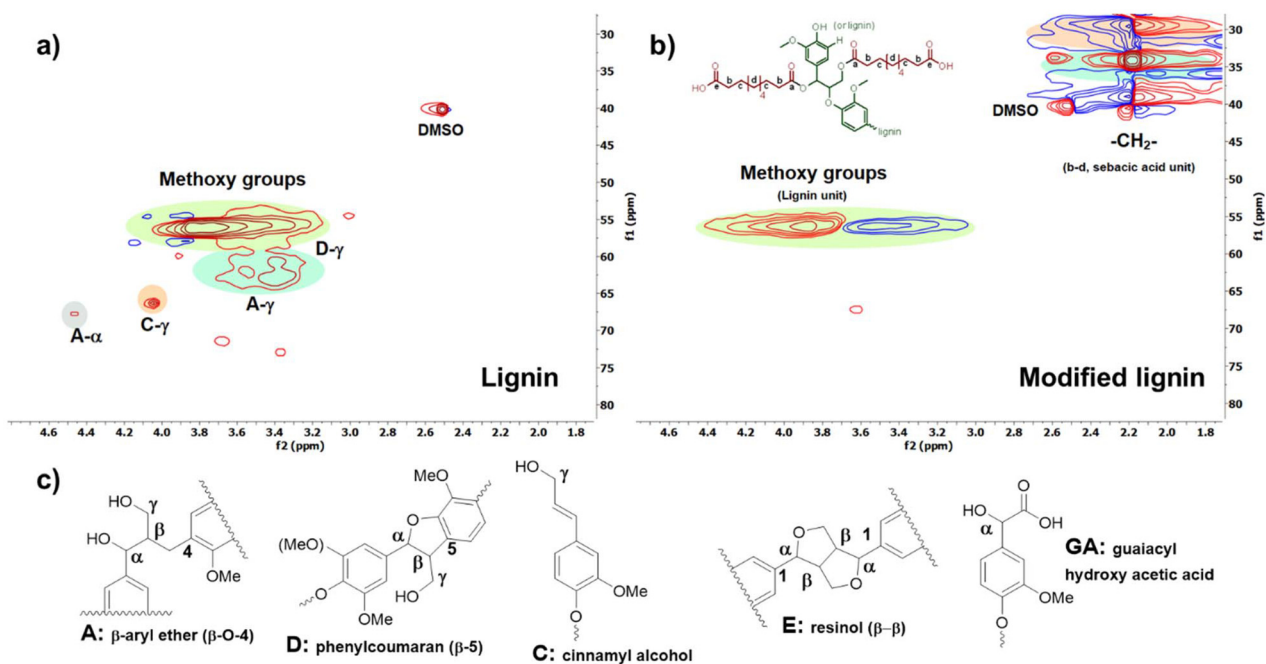


Fig. 3 (a) 2D HSQC (^1H - ^{13}C) NMR spectrum of raw lignin. (b) 2D HSQC (^1H - ^{13}C) NMR spectrum of modified lignin. (c) Major chemical structural units of lignin.

perform the esterification reaction in THF/water cosolvent using the Mukaiyama reagent in the graft polymerization (Scheme 3, Step 3).

3.3. Sustainable and recyclable polymer-bound catalyst for ring-opening polymerization

The second step in preparing the lignin-graft-copolymer was to synthesize the aliphatic polymer, PCL. In this work, we established a new sustainable catalytic system, using the PS-TBD catalyst to carry out a ROP of ϵ -caprolactone according to Scheme 2, Step 2. ϵ -Caprolactone was chosen for its simple lactone structure, ease of availability, degradability, and cost-effectiveness.⁶³ The initiator, 4-methylbenzyl alcohol, was also used in conjunction with the catalyst. Although the ROP of ϵ -caprolactone is a well-established polymerization, the use of polymer-bound catalyst, PS-TBD is rare. The ROP was conducted under bulk conditions without a solvent. PS-TBD is easily separated from the polymer product solution by filtration during purification, as PS-TBD is not soluble in the solvent. The ^1H NMR spectra in Fig. 4 confirms the successful ROP, validating the precise chemical structure of the synthesized PCL through specific proton assignments. For comparison, the ROP of ϵ -caprolactone was also conducted without the PS-TBD catalyst, while keeping all other conditions identical, to assess the catalytic role of PS-TBD. Although the PCL synthesis procedure still employs non-green solvents such as methanol, dichloromethane (DCM), and initiator (4-methylbenzyl alcohol), greener alternatives have been explored in the literature.^{64,65} Including ethanol to replace methanol; ethyl acetate could substitute for DCM; and bio-based alcohol could replace 4-methylbenzyl alcohol. Incorporating such alterna-

tives would further enhance the sustainability of the synthesis and represent a promising direction for future work. It is also worth noting that while PS-bound TBD is effective for laboratory-scale demonstrations, industrial separation/recycling processes should be designed and evaluated for a large-scale application, while still preserving the key principles of the synthesis. The corresponding ^1H and ^{13}C NMR spectra of the resulting polymer products are presented in Fig. S9 and S10. Although polymer formation was observed, the yield was extremely low (<14%) compared to the ROP conducted with PS-TBD, which consistently achieved yields above 90% in repeated experiments. These outcomes show that PS-TBD is key to efficient polymerization.

The recycled catalyst was used in four separate and repeated polymerizations, as shown in the four spectra in Fig. 4. More specifically, a single batch of PS-TBD catalyst is repeatedly used for conducting four separate ROP reactions in order to test the recyclability of PS-TBD. The reactions followed the same procedure and scheme, with the only variation being the use of the same catalyst in four consecutive runs to assess its durability and effectiveness after repeated use. The amount of catalyst recovered after each reaction was greater than 90% by weight, and the main reason for this minor weight loss can be attributed to physical loss (fractionation of PS resin solid and its bound catalysts) through handling and moving the catalyst. These ^1H and ^{13}C NMR spectra demonstrated that the polymerization of ϵ -caprolactone proceeded according to Scheme 2, Step 2.

In Fig. 4, one of the key peaks to focus on in this ^1H NMR spectrum is the small peak labeled "b" at 5.04 ppm. This peak corresponds to the benzyl carbon found between the ester and



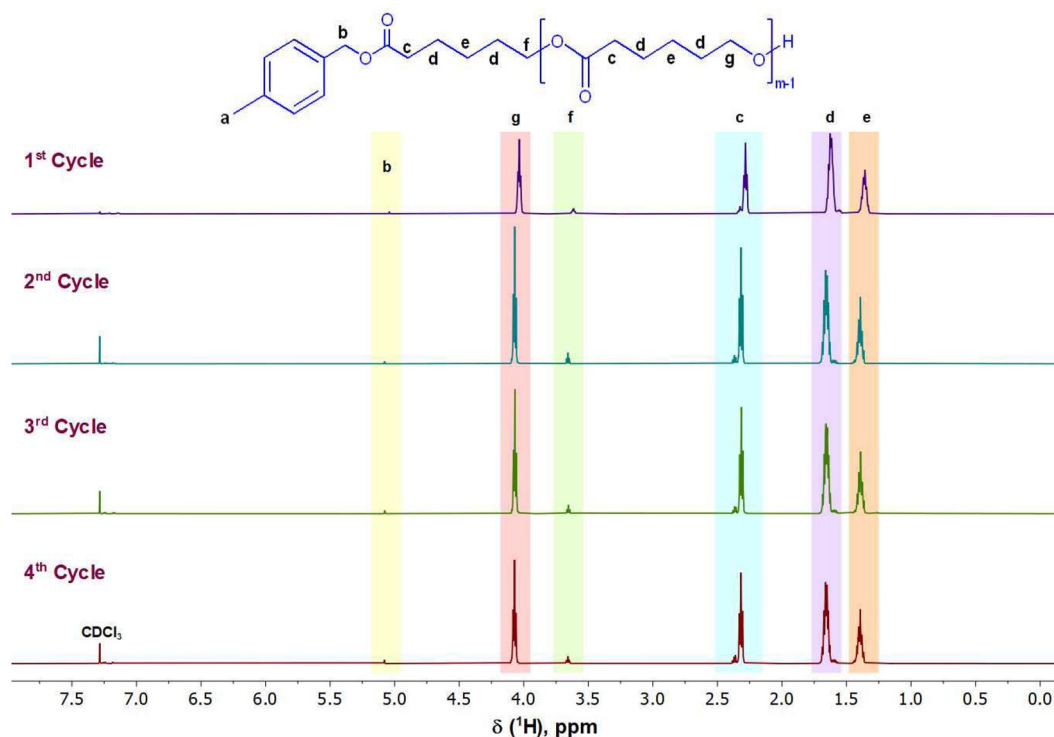


Fig. 4 Stacked ^1H NMR of PCL synthesized using identical PS-TBD in four consecutive trials. Each cycle represents a trial. The ester linkage of benzyl alcohol with the ring-opened PCL is observed in peak "b" for all trials. The magnitude difference and shift between peaks "f" and "g" is clearly observed for the final carbon in each repeating ring-opened monomer unit of PCL.

the benzyl ring of the initiator.^{66,67} The inclusion of this peak demonstrates the integration of both the initiator and the ϵ -caprolactone within the final PCL structure. The other significant peak is labeled "g" found at 3.61 ppm.^{66,67} This proton is found at the hydroxyl-terminating end of PCL and confirms the successful ROP of ϵ -caprolactone into PCL. Other peaks present include "c, d, e, and f". These four peaks correspond to the aliphatic carbon chains found within the repeating structure of the ring-opened ϵ -caprolactone.^{66,67}

One of the key peaks to focus on in the ^{13}C NMR spectrum, in Fig. 5, is the presence of peak "c" at 173.66 ppm. This peak indicates ester groups found within the PCL structure.^{66,67} Peak "b" at 66.11 ppm represents the benzyl carbon found between the ester and the benzyl ring of the initiator.^{66,67} Other peaks within the ^{13}C NMR spectra include "d, e, f, g, and h" which are the aliphatic carbon chains found within the repeating unit of PCL.^{66,67} The aromatic unit of the initiator is observed between 125.00–130.00 ppm.

Another notable transformation is the slight shift between the cyclic structure of the ϵ -caprolactone and the aliphatic region of the PCL after ring-opening, indicating a change in the proton environment. The spectra of monomer, ϵ -caprolactone, can be found in Fig. S7 and S8 within the SI. A final point to consider is the height difference in Fig. 5, where the peaks of the repeating aliphatic unit are significantly larger than those of the terminating units at the ends of the PCL

chain.^{66,67} This indicates the successful formation of multiple successive repeating units that make up the PCL chain.

Table 2 shows the molecular weights and molecular weight distribution (PDI: Polydispersity index) of the synthesized polymers. The molecular weight and PDI data (Table 2) demonstrate that the polymer-bound PS-TBD catalyst remains highly recyclable and retains substantial catalytic activity over multiple reuse cycles. A gradual decrease in molecular weight from 3.78 to 2.37 kDa is observed with each successive cycle, corresponding to a 37% reduction in PCL molecular weight over the four cycles. This trend indicates a modest decline in catalytic efficiency with reuse. However, even in cycle 4, the reaction continues to produce polymer with a well-defined molecular weight (2.37 kDa) and a narrow molecular weight distribution (PDI = 1.11). This conclusion is further reflected by the consistently high product yields of 80 wt%, 78 wt%, 87 wt%, and 82 wt% for cycles 1–4, respectively. Further analysis of its recyclability beyond four cycles is currently underway, and the results will be reported in future work.

3.4. Sustainable catalyst for graft copolymerization

After lignin modification and PCL preparation *via* ROP, the final copolymer, lignin-*graft*-PCL, was synthesized. The final graft copolymerization step, an esterification reaction, was successfully accomplished using the THF/Water cosolvent system and 2-chloro-1-methylpyridinium iodide (Mukaiyama



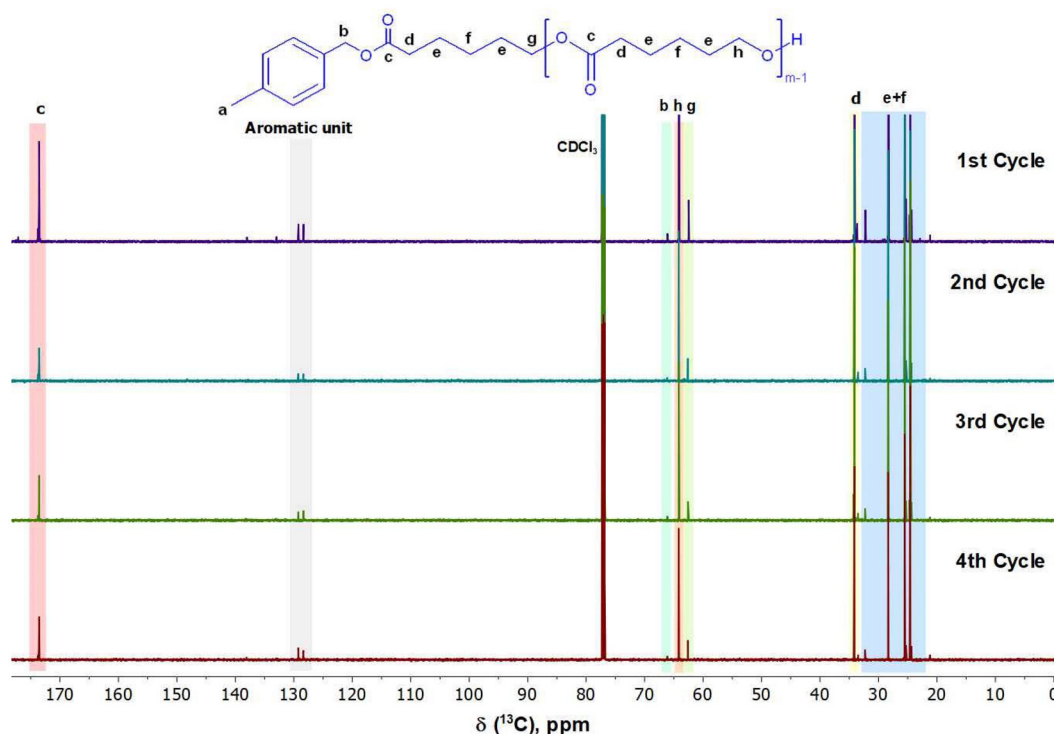


Fig. 5 Stacked ^{13}C NMR of PCL synthesized using identical PS-TBD in four consecutive trials (ROP Reaction). Each cycle represents a trial. The ester linkage of benzyl alcohol with the ring-opened PCL is observed in peak "a" for all trials. The magnitude difference and shift between peaks "f" and "g" is clearly observed for the final carbon in each ring-opened repeating unit of PCL.

Table 2 Molecular weights and molecular weight distribution (PDI: Polydispersity index) from repeated polymerizations of ROP in the presence of PS-TBD catalysts

| Cycle ^a (#) | M_w , GPC ^b (kDa) | PDI ^c |
|------------------------|--------------------------------|------------------|
| Cycle 1 | 3.78 | 1.13 |
| Cycle 2 | 3.05 | 1.08 |
| Cycle 3 | 2.44 | 1.18 |
| Cycle 4 | 2.37 | 1.11 |

^a Each cycle represents a trial. ^b The M_w , GPC, measured in kDa, is the number-average molecular weight of each PCL product. ^c PDI represents the polydispersity index (molecular weight distribution) of each PCL as measured by GPC in THF solvent.

reagent).³⁷ This sustainable esterification route forms ester linkages between the carboxylic acid groups of the modified lignin and the terminal hydroxyl groups of PCL. The yield of the final copolymer (lignin-graft-PCL) was 80 wt% of the initial reactant mass. This represents the highest yield obtained in the study, attributed to the complementary effects of the cosolvent system and the Mukaiyama reagent found in the lignin modification step.

Fig. 6 displays the FT-IR spectra of PCL, modified lignin, and the final copolymer, lignin-graft-PCL. The strong bands at 1730 cm^{-1} attributed to C=O stretching vibration of the ester groups, which were present in PCL (black), modified lignin (red), and lignin-graft-PCL (blue, Fig. 6).^{52,58,68} The ester lin-

kages in the PCL correspond to the repeating ester units that originated after the ring-opening of ϵ -caprolactone. The ester bonds in the modified lignin correspond to the incorporated sebacic acid unit within the structure. The lignin-graft-PCL exhibited two peaks for the C=O stretching band within the region of $1710\text{--}1730\text{ cm}^{-1}$, signifying the presence of two distinct types of ester linkages from PCL and modified lignin units.^{52,58,68} The characteristic C-H stretching peaks from the aliphatic linkages were found between $2800\text{--}3000\text{ cm}^{-1}$ (highlighted in gray, Fig. 6). Moreover, the characteristic peak of C-O stretching from the ester group was observed at 1040 cm^{-1} (highlighted in green, Fig. 6).^{52,58,68} Thus, the results confirm the successful integration of PCL and modified lignin into the graft copolymer, lignin-graft-PCL.

As shown in Fig. 7 and 8, ^1H NMR and ^{13}C NMR were performed to analyze the chemical structure of the lignin-graft-PCL. For the ^1H NMR (Fig. 7), the peak labeled "f" located at 3.98 ppm corresponds to the linkage of PCL with the modified lignin to create the copolymer structure.^{52,59,66} The inclusion of the protons found on the benzyl carbon between the ester and the benzyl ring of the initiator can be seen in peak "a" located at 5.04 ppm.^{66,67} The range of peaks found between 6.00 ppm and 9.00 ppm correspond to the various protons found within the unmodified lignin structure of lignin along with the methoxy groups seen in peak "o" at 3.39 ppm.^{52,59} A large number of protons on aliphatic carbon chains are also found in the final copolymer structure, labeled "b-n".^{52,66}



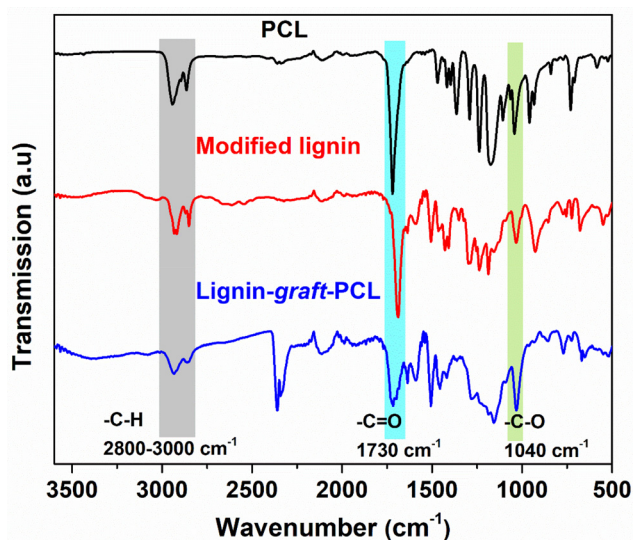


Fig. 6 FT-IR spectra of PCL (black), modified lignin (red), and lignin-graft-PCL (blue); the absorption band of the C=O bond found in the synthesized ester linkage is observed in the light blue box (1730 cm^{-1}). The absorption band of the C-O bond found in the synthesized ester linkage is observed in the light green box (1040 cm^{-1}).

In the ^{13}C NMR (Fig. 8), the linkage between the PCL and modified lignin can also be seen at 63.96 ppm in peak “g”.^{52,59,66} The peak at 63.96 ppm contains the signal for the benzyl carbon “a”, located between the ester and the benzyl

ring of the initiator in the PCL, further confirming the successful synthesis of lignin-graft-PCL.^{66,67} Peaks “b” and “b*” represent the ester linkages found within the copolymer. Peak “b*” represents the ester linkage between sebacic acid and natural lignin present in the modified lignin.^{52,59,66} The unmodified lignin appears in the range of $70.00\text{--}140.00\text{ ppm}$, but high baseline noise prevents clear resolution of distinct peaks. The inset in Fig. 8 shows the carbons of the aliphatic chain present in the copolymer. These include peaks “c-f” and “h-o” between 24.00 and 34.00 ppm .^{52,59,66}

Fig. 9 presents the 2D HSQC ($^1\text{H}\text{--}^{13}\text{C}$) NMR spectrum of lignin-graft-PCL. The signals of the PCL segment are observed at $\delta_{\text{H}}/\delta_{\text{C}} = 4.00\text{ ppm}/64\text{ ppm}$ ($-\text{OCH}_2-$) and $3.37\text{ ppm}/61\text{ ppm}$ ($-\text{CH}_2-$). The methoxy group signal from the lignin unit appears at $\delta_{\text{H}}/\delta_{\text{C}} = 3.78\text{ ppm}/56\text{ ppm}$ (Fig. 9). In addition, signals corresponding to the sebacic acid segment are detected at $\delta_{\text{H}}/\delta_{\text{C}} = 2.18\text{--}2.22\text{ ppm}/28\text{--}40\text{ ppm}$, consistent with those of the modified lignin. Hence, the overall results confirm the inclusion of all structural components within the lignin-graft-PCL copolymer.

3.5. Thermal properties of lignin-graft-PCL

Thermal property analysis was performed on the final copolymer to confirm its structure and assess thermal stability. The results showed a significant improvement in the thermal stability of modified lignin after incorporation of PCL into the copolymer. As shown in Fig. 10, the temperature ($T_{\text{d}5\%}$) at

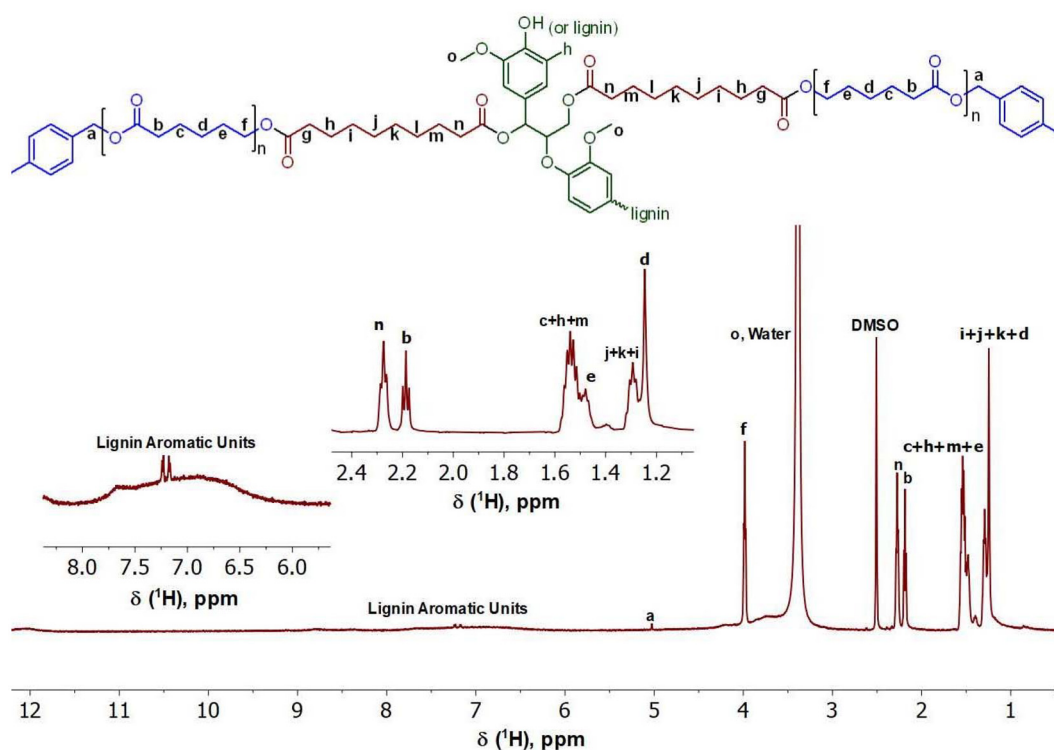


Fig. 7 ^1H NMR of lignin-graft-PCL; The ester bond newly formed between lignin and PCL is observed at peak “f”. Peak “a” represents the linkage found between PCL and the initiator benzyl alcohol as shown in the chemical structure.



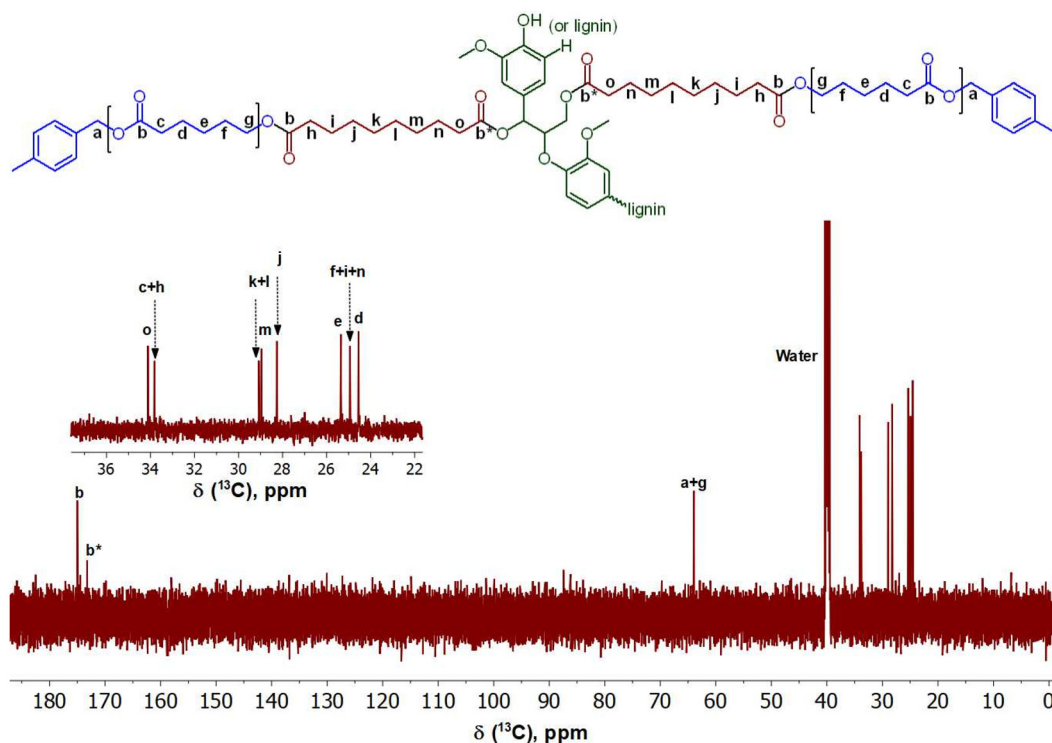


Fig. 8 ^{13}C NMR of lignin-graft-PCL; The newly formed ester bonds between lignin and PCL, as well as the PCL terminal's ester, are observed at peak "a + g".

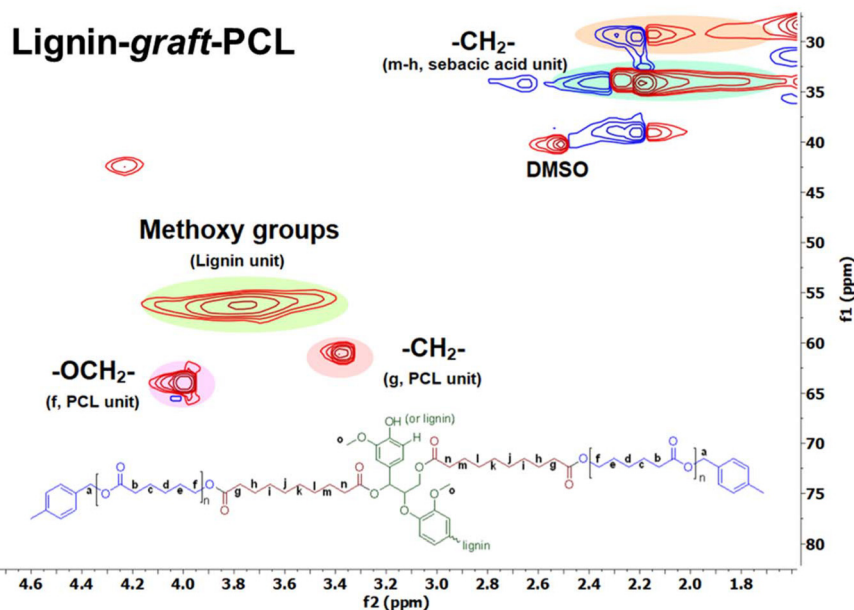


Fig. 9 2D HSQC (^1H - ^{13}C) NMR spectrum of lignin-graft-PCL.

which 5% of the total mass degraded was calculated for all three samples, PCL, modified lignin, and lignin-graft-PCL. The $T_{d5\%}$ was found to be 213 °C for modified lignin, 334 °C for PCL, and 282 °C for lignin-graft-PCL.⁶⁹ It is worthwhile to compare the copolymer's thermal behavior with that of similar

lignin-based structures to better assess the potential of the proposed green alternatives. According to previous reports, the $T_{d5\%}$ for lignin-graft-poly(lactide) is near 300 °C and that of lignin-graft-polyethylene brassylate is found to be around 350 °C.^{52,70} These similar polymers exhibit slightly higher



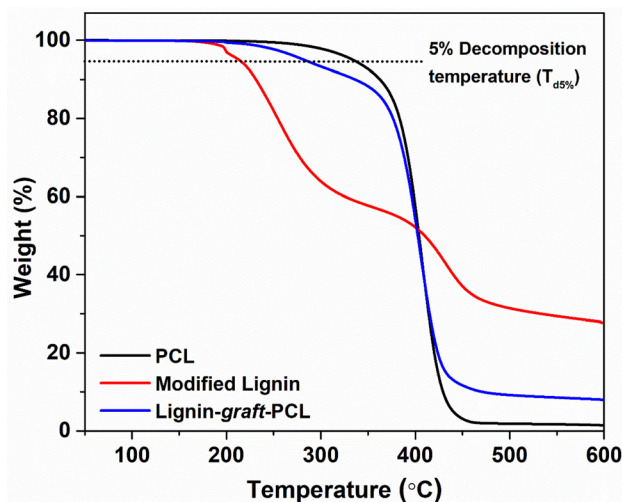


Fig. 10 TGA traces of lignin-graft-PCL (blue line), PCL (black line), and modified lignin (red line). The 5% degradation temperatures are 282 °C for lignin-graft-PCL, 334 °C for PCL, and 213 °C for modified lignin.

thermal stability than PCL-graft-lignin, which can be attributed to the use of ϵ -caprolactone as the monomer building block for the copolymer. The observed thermal stability of lignin-graft-PCL suggests it can be processed under conventional melt-processing conditions and could be suited for applications such as biodegradable films or thermally stable composite materials, owing to its ability to efficiently absorb and release thermal energy.⁶⁹ This research enables the selection of monomers to be tailored to the specific requirements of the intended application. Incorporating different monomers into the lignin copolymer structure can result in a range of thermal properties.

4. Conclusions

In this work, we report a similar lignin-based polyester to that of previous research, using the Mukaiyama reagent and a THF/water cosolvent system as an effective replacement for a DMF solvent, and DCC and DMAP reactant system. The modified lignin component of the reaction was found in higher yields using the Mukaiyama reagent and a THF/water cosolvent in place of conventional DMF. As a grafting polymeric unit, PCL was created by the ring-opening polymerization of ϵ -caprolactone using a novel PS-TBD catalyst in the presence of an initiator. The new catalyst shows evidence of reasonably high effectiveness through multiple recycles during the ROP reaction. Finally, both the modified lignin and PCL are utilized in the synthesis of lignin-graft-PCL resulting in a yield 80 wt% of the initial reactant mass. Subsequently, chemical structures were confirmed using ¹H NMR, ¹³C NMR, and FT-IR spectroscopy. The thermal property studies of lignin-graft-PCL showed comparable thermal stability to copolymers of similar size and composition, with a $T_{d5\%}$ of 283 °C. Therefore, this research is a step forward in the field of green and sustainable

biomass-based polymer chemistry and leaves the door open to potential improvements and further research, specifically by investigating the recyclability of polymer-bound catalysts.

Conflicts of interest

There are no conflicts to declare.

Data availability

All characterization data of the synthesized compounds are included in the manuscript and supplementary information. Additional information, such as extremely detailed experimental procedures, optimized reaction conditions, and data not discussed in the article, are available from the corresponding author upon reasonable request.

Supplementary information (SI): characterization data for all synthesized compounds, are provided in the Figures, Tables, SI, and Experimental section. See DOI: <https://doi.org/10.1039/d5lp00387c>.

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