

CO₂ and Lignin-Based Sustainable Polymers with Closed-Loop Chemical Recycling

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This work highlights the conversion method of chaining up greenhouse gas CO₂ with biomass lignin to develop new sustainable, recyclable polymers from abundant and non-food based renewable resources. A cyclic carbonate monomer has synthesized using a cost-effective, non-phosgene-based, and greener approach under atmospheric pressure and room temperature. The fully programmable ring-opening polymerization is accomplished by varying the catalyst (DBU and TBD), catalyst loading (0.5–5.0%) and reaction time (2–40 min). The best polymer is obtained in 1% TBD with a 30-min reaction. The precise characterization of the synthesized cyclic carbonate monomer and polymers' structure are established using spectroscopic analyses including ¹H, ¹³C, and 2D HSQC NMR, FT-IR, and GPC. The new polymers exhibit high molecular weights (M_n : 120.34–154.58 kDa) and adequate thermal stabilities ($T_{d5\%}$: 244–277 °C from TGA and T_g : 33–52 °C from DSC), rendering them advantageous for practical applications. Significantly, the CO₂ and lignin-based polymers have successfully recycled to the monomer for a circular plastic economy by heating at 90 °C for 12 h in the presence of DBU. This process yields original monomers for another polymerization without unwanted changes in chemical structures, presenting an ultimate sustainable solution.

their bio-renewable raw materials and degradability.^[7,8] Moreover, a variety of chemical functionalities that are readily available through bio-based structural units might be incorporated into polymers and confer unique characteristics on the resultant polymer structures.^[9,10] However, the a section of bio-based monomers commonly employed in polymer synthesis are primarily sourced from human food. For instance, maize starch can be converted into glucose, further leading to the production of lactic acid and subsequently forming poly(lactic acid). Similarly, sugar can undergo a transformation into glucose, serving as a precursor for polycarbonate.^[2,11] These bio-based monomers, which are important food resources, compete with each other to be used for making polymers. Nevertheless, another class of biomass-derived monomers, including cellulose, lignin, terpenes, and other plant oils, not intended for human consumption, were utilized to develop functional polymers.^[12–14] Thus, monomers derived from non-food resources

are considered a viable option for the developing sustainable polymers. In an ideal scenario, employing a moderate chemical recycling approach for the bio-based polymer allows the conversion of polymers back into their original monomers. This not only enhances the sustainability of the bio-based polymer but also transforms polymer waste into valuable raw resources for creating a new polymer. This novel chemistry maintains the material properties, distinguishing it from conventional polymer recycling methods.

Lignin is a sustainable raw resource and the second-most abundant plant-based biopolymer after cellulose.^[15,16] Constituting one-third of a tree's mass, lignin serves as a vital structural component, deriving its mechanical strength from high aromatic contents.^[17] Lignin, often deemed an undesired by-product primarily from the paper industry, generates over 50 billion tons of material annually.^[18] Despite its origin, lignin boasts numerous advantageous features, including biodegradability, antioxidant activity, high carbon content, high thermal stability, and rigidity. Moreover, it is readily available and cost-effective.^[19,20] As a compelling substitute for components like maize, soy, sugar, and gelatin in the production of biodegradable polymers, lignin finds applications in various industrial, food, and agricultural fields.^[17,18,21,22] Notably, lignin's mass production cost ranges between \$250 and \$500 per ton, significantly more economical

1. Introduction

The sustainability of the petroleum-based plastic industry has become a significant aspect of contemporary global development.^[1] The petroleum-based resources will ultimately run out due to a natural constraint on petroleum supplies.^[2] Moreover, it is anticipated that 11 billion metric tons of plastic would have accumulated by 2025 in landfills and the environment, leading to a serious impact on the environment on lands and ocean.^[3,4] Hence, sustainable and renewable alternatives to petroleum-based polymers has become an urgent and critical issue for human being.^[5,6] In contrast to conventional polymers derived from petroleum, bio-based (e.g., plant-based) polymers are gaining momentum in the category of sustainable materials due to

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compared to other food-grade biomass-based monomers. For instance, lactic acid commands a market price of \$1600 to \$1900 per ton.^[23–25] Beyond cost consideration, lignin, a pivotal raw resource for polymers, can be covalently linked to CO₂, contributing to its removal from the atmosphere.

CO₂, the predominant greenhouse gas, has seen a continuous rise in the atmospheric concentration due to the expansion of the economy, contributing to an annual temperature increase of over 1 K since 1900. This rise has led to various challenges, including erratic weather patterns, ecological disruptions, desertification, elevated seawater temperature, rising sea levels, and food shortages.^[26,27] Consequently, the imperative to reduce of CO₂ emissions has gained paramount importance. Efficient systems for CO₂ management are crucial for transitioning to a reliable and low-carbon economy to address climate change concerns.^[28,29] The transformation of CO₂ into valuable compounds aligns with the principles of a circular and low-carbon economy, yet the high chemical stability of CO₂ poses significant challenges to this process.^[30] Despite these challenges, CO₂ remains a sustainable, renewable, non-toxic, and non-flammable C1 feedstock with the potential for diverse chemical conversions.

Investigations were conducted on the use of CO₂ as a raw material in the synthesis of ureas,^[31] organic carbonates,^[32] carbamates,^[33] and polycarbonates.^[34–36] To synthesize aliphatic polycarbonates from CO₂, four well-developed synthetic routes were explored, including polycondensation of aliphatic diols with phosgene derivatives or dialkyl carbonates,^[34] copolymerizations of CO₂ with epoxides,^[37–39] direct polymerization of CO₂,^[36,40–42] and ring-opening polymerization of cyclic carbonate monomers.^[34,35,43] Moreover, the utilization of carbonyl sulfide (COS) as a C1 monomer in the synthesis of sulfur-containing polymers was recently investigated in the field of polymer science.^[44,45] Conventionally, hazardous phosgene was used as a raw material in industrial processes to prepare polycarbonates, which produce a lot of salt waste.^[40] Although copolymerization of epoxides or oxetanes with CO₂ was investigated previously, direct polymerization from CO₂ as a carbonyl source will be ideal. These processes have several disadvantages, including high cost, unstable chemical properties, and a restricted range of epoxides and oxetanes.^[46] However, many challenges persist in this endeavor, such as managing the high CO₂ pressure, utilizing specialized of reactors like autoclave, regenerating dehydrating agents, and addressing side reactions associated with these dehydrating agents. In response to these challenges, researchers have accomplished a significant milestone by directly performing ring-opening polymerization of cyclic carbonate monomers. This approach allows for the synthesis of aliphatic polycarbonates,^[35,47–50] with the advantage that cyclic carbonate monomers can be prepared under mild reaction conditions. This preparation involves using CO₂ as a raw resource at room temperature and atmospheric pressure, offering a more accessible, safe, and environmentally friendly route.^[51–53]

The overarching goal of this study is to synthesize recyclable polymer from biomass and CO₂ under atmospheric pressure, contributing to the circular plastic economy for ultimate sustainability (Figure 1). Building on prior research, it is observed that polymers are typically prepared either from biomass or CO₂.^[43,47,48,52,54] Notably, a significant portion of the CO₂-based polymers has been synthesized under high atmospheric

pressure^[35,36,38,40,55] with limited studies demonstrating polymer synthesis under atmospheric pressure.^[53,56] This presents a notable opportunity to develop a variety of polymers based on biomass lignin, utilizing CO₂ under atmospheric pressure as sustainable alternatives to traditional petroleum-derived polymers, addressing environmental concerns.

In the present work, we have successfully developed 100% biomass-based recyclable polymers using both CO₂ and lignin. The synthesized cyclic carbonate monomer and polymer structures are precisely elucidated through spectroscopic techniques, including ¹H, ¹³C, and 2D heteronuclear single quantum coherence (HSQC) nuclear magnetic resonance (NMR), Fourier-transform infrared (FT-IR) spectroscopy and Gel permeation chromatography (GPC). The organocatalytic polymerizations have further explored by synthesizing different polycarbonate through the manipulation of the reaction conditions. Thorough assessment of the thermal properties using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) enhances our understanding of the structure-property relationships and potential applications. Furthermore, the prepared polycarbonate undergoes systematically depolymerization to the original monomer, enabling the synthesis of polymers multiple times again. The synthetic methodology advances a complete circular economy (biomass/CO₂ → monomer → polymer → upcycle to the original monomer → polymer production), eliminating plastic and chemical waste.

2. Results and Discussion

2.1. Synthesis of Cyclic Carbonate Monomer from CO₂ and Lignin

Abundant and inexpensive biomass lignin was reacted with CO₂ gas to prepare the 100% biomass-based cyclic carbonate monomer at atmospheric pressure (Figures 1; Figure S1, Supporting Information). The synthesis process consisted of two moderate chemical reaction steps (Figure 2a). Initially, the addition of DBU led the generation of an ionic salt intermediate by capturing the CO₂ in the less sterically hindered primary hydroxyl groups of lignin.^[57,58] In the second step, the ring-closing process occurred through the nucleophilic addition-elimination process, where the introduction of the tosyl chloride leaving group facilitated the formation of cyclic carbonate monomer. The reaction was performed in highly diluted condition (0.1 mol L⁻¹) and at low temperature to accomplish the targeted unimolecular cyclization over competing dimerization processes.^[57] Finally, a deep brown viscous liquid product, namely cyclic carbonate monomer, was obtained (Figure S2a–d, Supporting Information). Notably, in contrast to unmodified lignin, which was insoluble in dichloromethane (DCM), the synthesized cyclic carbonate monomer demonstrated excellent solubility in DCM (Figure 2b). The alternation in solubility serves as a promising indicator for identifying a successful chemical modification before proceeding to the spectrometric characterizations.

In line with our main hypothesis for this research, which centers on the synthesis of a cyclic carbonate monomer from CO₂ and natural lignin, the chemical structure of the monomer was systematically elucidated through a series of diverse spectroscopic analyses. After successfully synthesizing the cyclic carbonate monomers, our hypothesis extends to the potential

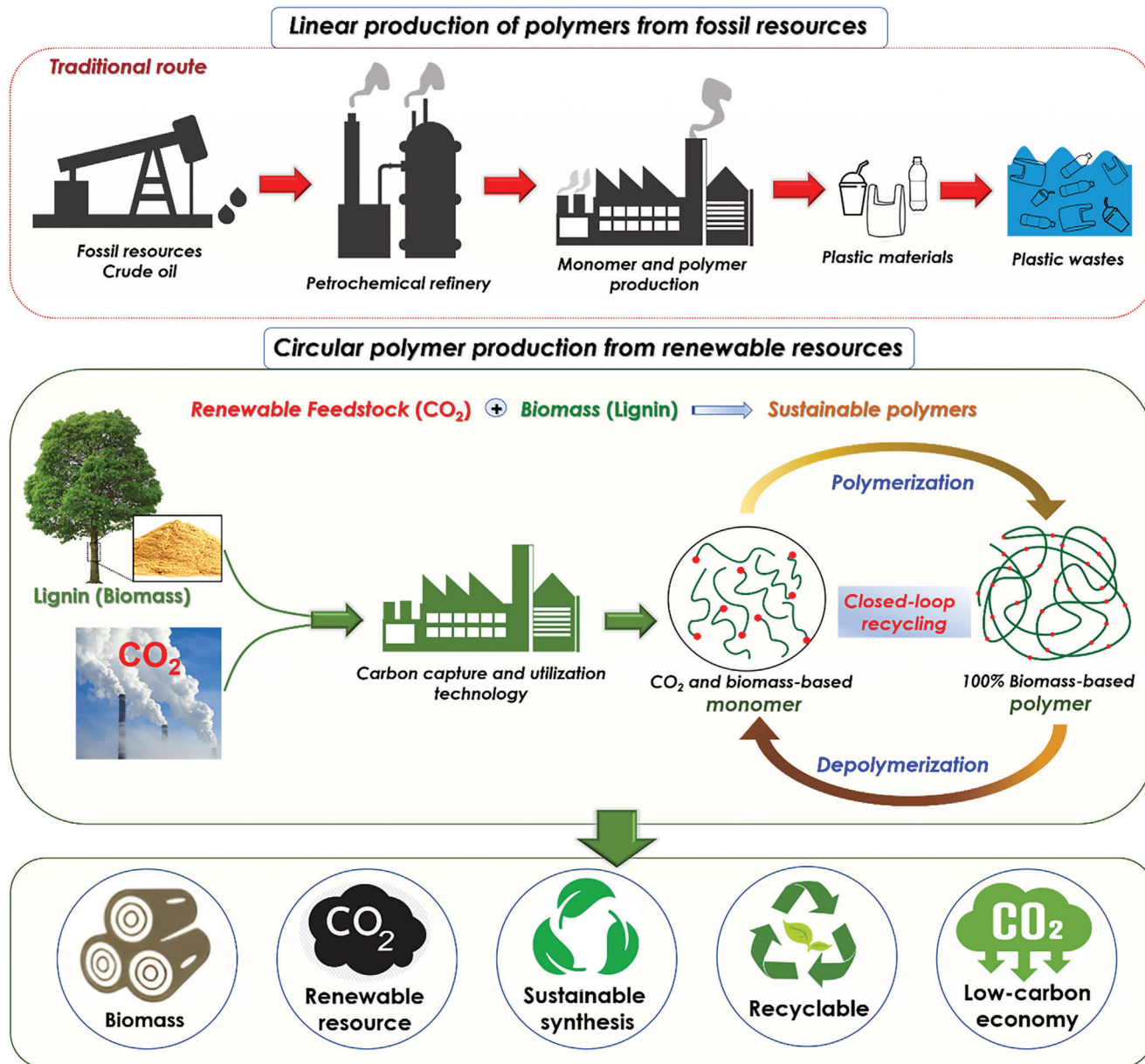


Figure 1. Conceptual framework illustrating the synthesis of polymers (bottom) using CO₂ (renewable resource/greenhouse gas) and lignin (biomass) through carbon capture and utilization (CCU), offering an alternative to the petroleum-based polymer production (top).

synthesis of a polycarbonate that possesses remarkable sustainability for complete depolymerization and following polymerization recycling loop. During the first step of verifying our hypothesis regarding novel monomer synthesis, the 2D HSQC (¹H–¹³C) NMRs in Figure 2c–f provided comprehensive information on the structural alterations between the unmodified lignin and prepared cyclic carbonate monomer. In Figure 2c,d, the signals from the hydroxyl group in the α , β , and γ positions of the unmodified lignin appeared at $\delta_{\text{H}}/\delta_{\text{C}}$: 3.2–4.5 ppm/58–80 ppm, where the signals were assigned following the earlier literature.^[59–61] The methoxy group signal displayed at $\delta_{\text{H}}/\delta_{\text{C}}$: 3.78 ppm/56 ppm.^[62] In general, the HSQC NMR spectrum of unmodified natural lignin (Figure 2c; Figure S3, Supporting In-

formation) demonstrates the distinctive lignin chemical structure with a high concentration of hydroxyl groups. After the carbonation, the peaks from α and γ hydroxyl groups were disappeared in the HSQC NMR spectrum of the cyclic carbonate monomer (Figure 2d; Figure S4, Supporting Information). However, there were some unreacted hydroxyl groups that are still observable in the HSQC NMR even after the completion of reaction. These signals correspond to the hydroxyl groups at the γ -positions of the phenylcoumaran (D- γ) and cinnamyl (C- γ) units.^[59,60,63] Distinct chemical shifts manifested as two small signals at $\delta_{\text{H}}/\delta_{\text{C}}$: 3.4 ppm/60 ppm and $\delta_{\text{H}}/\delta_{\text{C}}$: 4.1 ppm/68 ppm as depicted in Figure 2d,f (cyclic carbonate monomer).^[54,55,58] These remaining hydroxyl groups played an important role as initiators

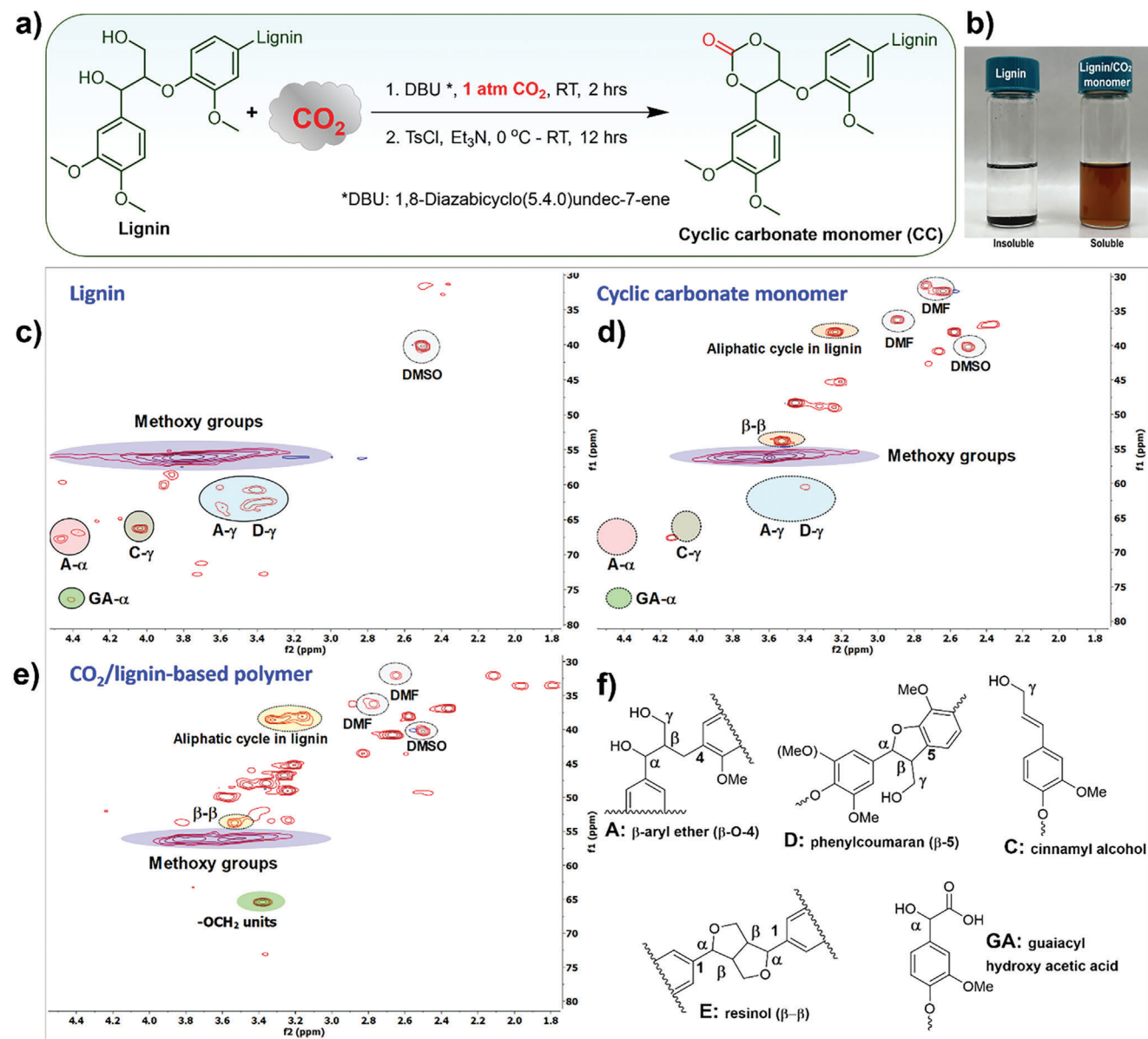


Figure 2. a) Synthesis of monomer from CO₂ and lignin possessing a cyclic carbonate. The reaction performed under atmospheric pressure at room temperature; 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), triethylamine (Et₃N), p-toluenesulfonyl chloride (TsCl). b) Solubility difference between CO₂/lignin-based cyclic carbonate monomer (CC) and raw lignin in dichloromethane (DCM). Raw lignin is insoluble in DCM, while the CC monomer exhibits full solubility in DCM. c) 2D HSQC (¹H–¹³C) NMR spectrum of raw lignin. d) 2D HSQC (¹H–¹³C) NMR spectrum of CO₂ and lignin-based cyclic carbonate monomer. e) 2D HSQC NMR spectrum of the polymer. f) Main chemical structural units of lignins.

of ring opening polymerization (ROP) during the following polymerization process. Overall, the consumption of the α and γ hydroxyl groups of β -O-4 units in unmodified lignin demonstrated the successful carbonation reaction of lignin with CO₂.

We also examined the chemical structure in detail using non-2D ¹³C and ¹H NMR, as depicted in Figure 3 and Figures S5 and S6 (Supporting Information). The distinct signal at 146.5 ppm from carbonyl carbon of the cyclic carbonate group in the ¹³C NMR spectrum indicated the successful incorporation of the carbonyl unit into the cyclic carbonate monomer (Figure 3c; Figure S5, Supporting Information).^[57] The aliphatic oxygenated (ether

linkage) and nonoxygenated (non-ether linkages) connections among the different structural units in lignin were responsible for the signals seen in the range of 86–50 ppm (Figure 3c, cyclic carbonate monomer). Specifically, the peaks seen in the range of 18–38, 44–54, 55–56, and 67–89 ppm (Figure 3c, cyclic carbonate monomer), could be identified as the carbon signals from the aliphatic carbons (–CH₃ and –CH₂), β -carbons (β - β and β -5), methoxy groups (–OCH₃) and α , β , γ -carbons of β -aryl ether units, respectively (Figure 3c, cyclic carbonate monomer).^[59,63] The ¹H NMR spectrum of CO₂ and lignin-based cyclic carbonate monomer is displayed in Figure 3b and Figure S6 (Supporting

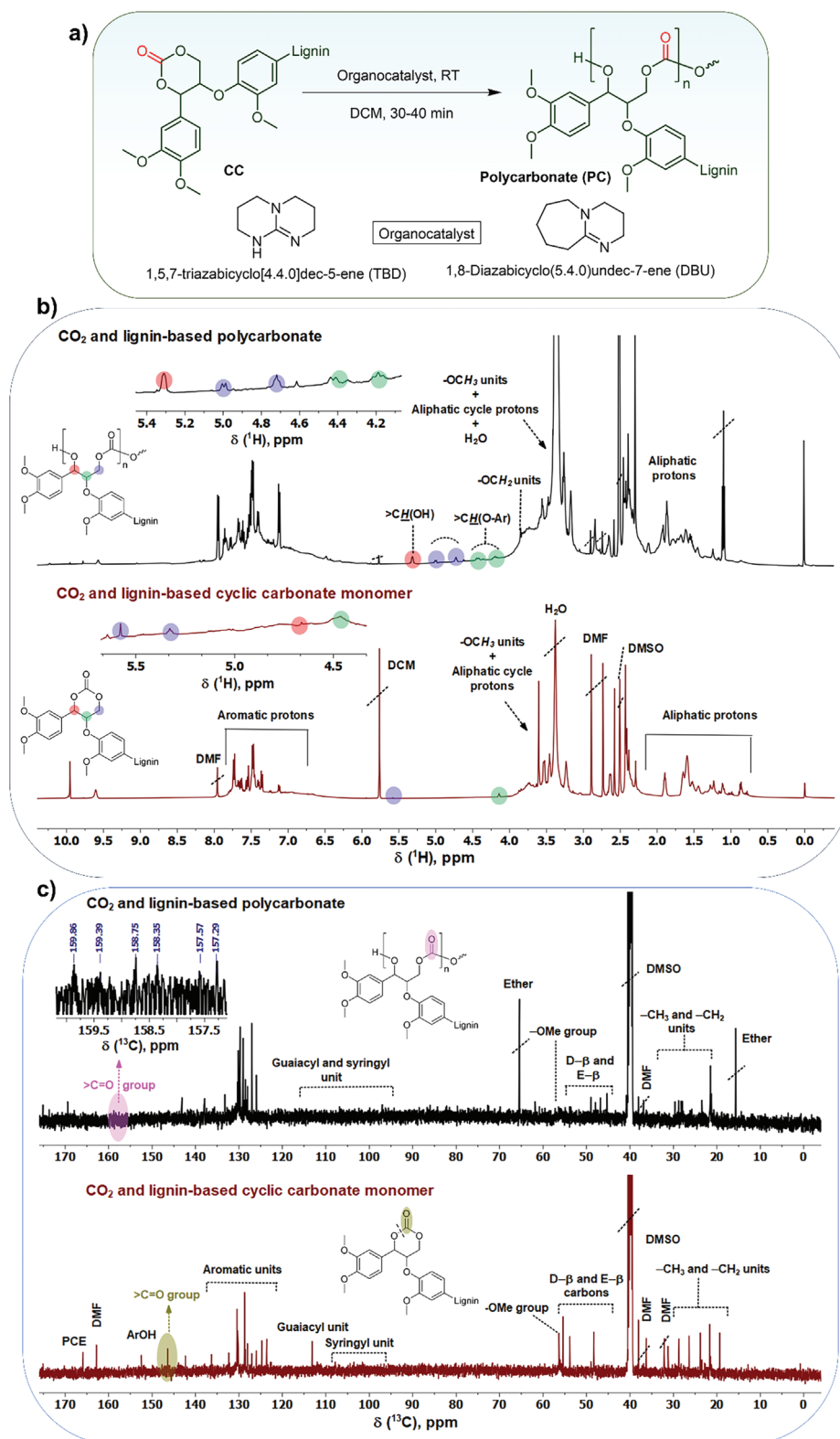


Figure 3. a) Ring-opening polymerization (ROP) of CO₂ and lignin-based cyclic carbonate monomer, where 1, 8-diazabicyclo (5.4.0) undec-7-ene (DBU), and 1, 5, 7-triazabicyclo [4.4.0] dec-5-ene (TBD) were used as organocatalytic bases for the polymerization. b) ¹H NMR and c) ¹³C NMR spectra of monomer and polymer (P-4 polymer, where catalyst: TBD; monomer: catalyst = 100:1, reaction time: 30 min).

Table 1. Organocatalytic scope in the ring-opening polymerization of CO₂ and lignin-based cyclic carbonate monomer and properties of the synthesized polycarbonates.

Polymer	Catalyst	[M]:[C] ^{a)}	Time [Min]	Yield [%]	M _n ^{b)} [kDa]	M _w ^{c)} [kDa]	Đ ^{d)}	T _{d5%} ^{e)} [°C]	T _g ^{f)} [°C]
P-1	TBD	100:1	2	90	123.2	190.5	1.55	244	45
P-2	TBD	100:1	5	93	125.8	201.2	1.60	257	47
P-3	TBD	100:1	10	98	144.8	189.5	1.31	259	50
P-4	TBD	100:1	30	>99	154.6	229.3	1.48	277	52
P-5	TBD	100:2	30	97	141.0	211.2	1.50	253	46
P-6	TBD	100:5	30	94	129.9	205.1	1.58	255	43
P-7	TBD	200:1	30	99	139.5	223.0	1.60	260	48
P-8	DBU	100:1	40	92	128.9	191.4	1.49	265	47
P-9	DBU	100:2	40	77	122.9	182.4	1.48	263	40
P-10	DBU	100:5	40	64	120.3	229.2	1.90	253	33

^{a)} monomer: catalyst ratio; ^{b)} number-average molecular weight; ^{c)} weight-average molecular weight; ^{d)} polydispersity index; ^{e)} 5% decomposition temperature in TGA; ^{f)} glass transition temperature from DSC.

Information). While we have not conducted the quantitative ³¹P NMR ourselves, as we have supplied ample data for chemical structure determination, it is common technique for monitoring hydroxyl groups in lignin. In this method, the hydroxyl groups in lignin react with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane and subsequent NMR spectroscopy is employed to detect and analyze the ³¹P signals within the lignin.^[61,64] We employed HSQC (Figure 2c) to accurately determine hydroxyl groups in lignin without the necessity of performing additional organic reactions to introduce phosphorous compound. Therefore, our utilization of HSQC characterization offers advantages compared to the conventional ³¹P NMR characterization of lignin. A characteristic carbonyl peak at 1747 cm⁻¹ in the FT-IR spectrum (Figure S7a, Supporting Information) provided further evidence for the efficient synthesis of carbonate monomers.^[47]

2.2. Synthesis of Biomass Lignin and CO₂-Based Polymer via Ring-Opening Polymerization

The polymerization of the cyclic carbonate monomer was performed at room temperature via organocatalyzed ROP as presented in Figure 3a. The ROP occurs through activation of the cyclic carbonate monomer which is cleavage of acyl-oxygen bond and subsequent propagation of polymeric chains. In the initial stage of the ROP, the organocatalyst activates the cyclic carbonate groups through the nucleophilic attack. Following this, a tetrahedral intermediate on carbonyl carbon forms in presence of alcohol initiator. Subsequently, rearrangement and proton shifting of the tetrahedral intermediate occurs. Lastly, regioselective cleavage of the acyl-oxygen bond takes place, leading to polymer chain propagation in a head-tail fashion.^[53] The γ -hydroxyl groups (i.e., alcohols) of the phenylcoumaran and cinnamyl units, as observed in the HSQC NMR spectrum of the monomer, was served as initiator of the ROP (Figure 2c). Therefore, ROP of the synthesized cyclic carbonate monomer proceeded without the need for the addition of external alcohol, which is commonly necessary in classic ROP for other cases. The organocatalytic bases, TBD and DBU, were utilized for the ROP of the cyclic carbonate monomer.^[48,53]

In our experiments, organocatalytic ROP reactions were carried out without the presence of an external alcohol initiator. As discussed earlier, -OH groups of the monomer play a role as an initiator. To perform comparative studies (P-1 to P-10, Table 1), the reaction conditions of the ROP reactions were adjusted by varying the type of catalysts (DBU and TBD), catalyst loading (0.5–5.0%) and reaction time (2–40 min). The synthesized polymers were thoroughly characterized by FT-IR, ¹H NMR, ¹³C NMR, 2D HSQC NMR, and GPC (Figures 2 and 3; Figures S8–S42, Supporting Information). Among all the synthesized polymers, P-4, with a feed ratio of cyclic carbonate: TBD ratio at 100:1 and a reaction time of 30 min, exhibited the highest efficiency in achieving the best yield (Table 1). Here, the spectroscopic changes of P-4 are elaborated as an example in Figures 2c and 3b,c and Figure S21 (Supporting Information). Initially, the presence of carbonyl groups was assured from the strong absorption band at 1755 cm⁻¹ in the FT-IR spectra (Figure S21, Supporting Information). The ¹H NMR spectrum of the synthesized polymer was compared with that of the monomer in Figure 3b. The downfield shift of >C H(OH) in the ¹H NMR spectrum (red, Figure 3b, polycarbonate) to 5.30 ppm was the most obvious indication of ring opening. Additional compelling evidence of the ROP of the cyclic carbonate monomer is shown in Figure S8 (Supporting Information) with kinetic studies using NMR. A noticeable gradual increase in the intensity of the peak, corresponding to >C H(OH) located within the red circle in the chemical structure at Figure 3b in the polycarbonate spectrum, was observed at 5.30 ppm over the reaction time.

The ¹³C NMR in Figure 3c shows the obvious disappearance of the monomer's cyclic carbonyl at 146.5 ppm, whereas new peaks originating from the linear carbonyl in the synthesized polymer appear in the range of 157–160 ppm. Likewise, the carbonyl carbon resonance's distinctive downfield shift was seen in the ¹³C NMR spectra as a result of the successful ROP (Figure 3c, polycarbonate).^[57] Multiple peaks were detected between 157 and 160 ppm due to the diverse chemical structures around the carbonate in the polycarbonates that is originated from a natural lignin. The spitting was typically distributed in three areas, which were ascribed to head-to-tail (HT), tail-to-tail (TT), and

head-to-head (HH) carbonate linkages.^[48] According to the earlier literature, it can be stated that this HT, TT, and HH could be nonselective during the chain propagation due to non-controllable acyl-oxygen bond ($-\text{C}(=\text{O})-\text{O}-$) cleavage at either side of the carbonate carbonyl to produce regio-random polymers.^[48,49,57] The opening locations of the ring [acyl-oxygen bond ($-\text{C}(=\text{O})-\text{O}-$) cleavage] are indicated with broken lines in the monomer's chemical structure in Figure 3c. The dominant ring opening occurred to form secondary alcohol-substituted polymers (resulting from the cleavage of the left bond of the carbonyl group in the monomer's chemical structure, as shown in Figure 3c). This is supported by the intense signal observed at 5.30 ppm in the ¹H NMR spectrum of the polymer, as shown at red circled proton in the chemical structure of Figure 3b polycarbonate.

Additionally, 2D HSQC (¹H-¹³C) NMR experiments were performed to determine the synthesized polymer's structure (Figure 2c; Figure S9, Supporting Information). The disappearance of the aforementioned residual γ -hydroxyl groups of the carbonate monomer in the region of $\delta_{\text{H}}/\delta_{\text{C}}$: 3.2-4.5 ppm/58-80 ppm affirmed our hypothesis on the effective ROP without the addition of any initiator (Figure 2c). The HSQC NMR also possessed the signal of the oxymethylene units ($-\text{OCH}_2-$) at 3.4 ppm/64 ppm, which came from the polycarbonate structure. Overall, all spectroscopic analyses confirmed the successful synthesis of polycarbonates from biomass lignin and CO₂ through ROP.

GPC was employed to evaluate the molecular weights and molecular weight distributions (polydispersity index, PDI) of the developed polymer. Various polymerization conditions were comparatively studied to determine the key parameters for governing molecular weights of the newly synthesized polymers.^[57,65,66] The narrow and unimodal GPC traces were observed for all polymers, indicating narrow molecular weight distributions and the formation of a single type of polymer (Figures S12, S15, S17, S22, S25, S28, S31, S36, S39, and S42, Supporting Information). A refractive index increment value (dn/dc) of 0.1512 mL g⁻¹ from recent literature was utilized to determine the molecular weights of the polymers.^[67] The lignin, serving as the starting material, exhibits a molecular weight of 24 kDa, as documented in previous literature.^[17,61] Furthermore, the molecular weight of the cyclic carbonate monomer was found to be 25 kDa (Figure S7b, Supporting Information). The molecular weights of the polymers were greatly dependent on the reaction time, type of catalyst, and feed ratio as presented in Table 1. A surge in molecular weights was noticed with the increase of reaction time compared to the lignin. Considering the heterogeneous nature of lignin, it is reasonable to anticipate that a polymerization reaction would lead to crosslinking, attributed to the abundance of hydroxyl groups in lignin. Nevertheless, it is noteworthy that the observed good solubility indicates the absence of any crosslinking process. The overall trend of molecular weight variation with catalyst amount suggested an increase in polymer molecular weight with decreasing catalyst loading. The linear reduction trend in molecular weight was observed from 1% to 5% catalyst loading. This drop in molecular weight could be attributed to backbiting reactions between the alcohols in polymer and the carbonyl units of the carbonate, potentially causing a change in the molecular weight of the polymer (P-4: 155 kDa,

1% TBD → P-6: 130 kDa, 5% TBD).^[53] However, it is important to note that the trend is not strictly linear in all the time. For instance, P-7, with a catalyst loading of 0.5%, exhibited a lower polymer molecular weight compared to P-4 with 1% catalyst loading (P-4: 155 kDa, 1.0% TBD; and P-7: 139 kDa, 0.5% TBD). TBD functioned as a more effective organocatalyst in ROP compared to DBU (P-5: 141 kDa, 2% TBD → P-9: 123 kDa, 2% DBU). Although all the polycarbonates exhibited high molecular weights, P-4 polymer demonstrated the highest molecular weight of 155 kDa among all synthesized polymers.

2.3. Structure-Property Relationships of New Polymers

The thermal properties of the polymers were evaluated from the TGA and DSC. All polymers from P-1 to P-10 showed step-wise degradations in TGA according to the 5% decomposition temperature ($T_{d5\%}$: 5% weight loss temperature point). Table 1 summarizes the $T_{d5\%}$ of all tested polymers (Figure 4a; Figures S43-S47, Supporting Information). Note that all solvents were completely removed through prior thermal evaporation in order to avoid any influence on $T_{d5\%}$ measurement. The $T_{d5\%}$ values of the polymers enhanced with the extended reaction time and decreased with the catalyst loading percentage (Figure 4a and Table 1). The P-4 and P-8 displayed high thermal stability, with $T_{d5\%}$ values of 277 and 265 °C, respectively (Figure 4a and Table 1; Figures S43-S47, Supporting Information). The polymers did not experience complete degradation due to its characteristic chemical structures which only consisted of C, H, and O. On the other hand, the DSC analysis of P-1 to P-10 polymers revealed consistent single glass-transition temperatures (T_g) ranging from 33 to 52 °C (Figure 4b; Figures S48 and S49, Supporting Information). All these polymers were found to be amorphous since they exhibited no melting transition temperature (T_m). Increases in molecular weight of polycarbonate led to higher T_g values for polymers (Table 1).^[68] P-4 (monomer: TBD = 100:1, reaction time: 30 min) demonstrated the highest T_g of 52 °C, which was higher compared to some of recently reported sustainable polycarbonates that is prepared from cyclic carbonate monomers.^[68] The higher T_g values arose from the inclusion of rigid lignin units into the polymer, which inhibited the chain rotellations.^[69] Therefore, the controllable thermal behavior exhibited by the CO₂ and lignin-based polycarbonate enhances its high feasibility as a candidate for the development of novel, high-performance sustainable materials.

The mechanical properties of the CO₂ and lignin-based polycarbonate were evaluated under compression mode. P-4 polymer (catalyst: 1% TBD, reaction time: 30 min) was selected for the mechanical testing, as it exhibited the best thermal properties and highest molecular weight among all the polymers. The data provided were average values together with standard deviations derived from four distinct measurements as shown in Figure 4c,d. The polymer had a modulus of 418.52 ± 66.33 kPa and a stress at 10% strain of 47.09 ± 7.54 kPa (Figure 4d; Table S1, Supporting Information). It is important to mention that the polymer exhibited greater modulus (153% enhancement) and stress at 10% strain values compared to some earlier reported lignin-based polymers.^[70,71] This was primarily attributed to the increased content of lignin unit in the polymer. The substantial quantity of

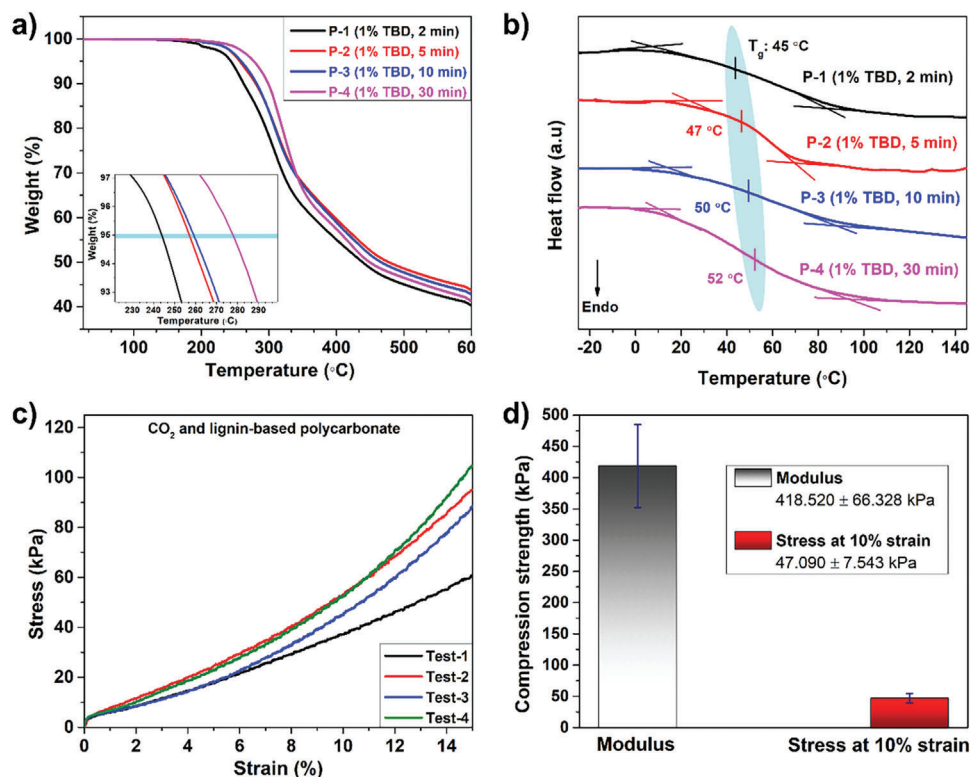


Figure 4. a) Thermogravimetric analysis (TGA) and b) differential scanning calorimetry (DSC) of P-1 to P-4 polymers under a constant argon atmosphere. The 5% decomposition temperatures ($T_{d5\%}$) were obtained from the inset plot in TGA, whereas the glass-transition temperatures (T_g) were attained from the DSC thermograms. The representative polymerization conditions for each sample are indicated in parenthesis next to the respective sample name. c) Stress–strain plot of the CO₂ and lignin-based polycarbonate (P-4) under compression mode. Four distinct tests were performed to check the consistency of the results. d) Summary of the mechanical characteristics of P-4. The data provided were average values together with standard deviations derived from four distinct measurements. All values were shown in Table S1 (Supporting Information).

aromatic structures was present in lignin and served as reinforcing hard segments within the polymer. Thus, the enhancement of mechanical qualities in the CO₂ and lignin-based polycarbonate demonstrates that chemical structure modification techniques of biomass can improve the common properties of any polymers, which can be useful in various practical applications.

2.4. Chemical Recycling (Polymer ↔ Monomer)

Innovative polymer designs that enable low-cost and straightforward chemical recycling, allowing the transformation of polymers back to their original monomers without compromising chemical structures and properties, are essential for promoting the growth of a circular economy for polymers. It is significant to note that the ROP of a six-membered cyclic carbonate monomer displays a much more facilitated thermodynamic equilibrium than cyclic ester analogs.^[72–74] This crucial feature can be directly utilized in the chemical recycling of our newly synthesized polycarbonate. The ceiling temperature (T_c) of a polymerization system is defined as the temperature at which the rates of polymerization and depolymerization are equal, and the Gibbs free energy of polymerization becomes zero.^[74,75] Therefore, T_c can be regarded as the lower temperature limit for chemical recycling to monomer by the ring-

closing depolymerization in a closed system. When the temperature is lower than T_c , polymerization is preferred, while depolymerization is favored when the temperature is higher than T_c . Besides, T_c is system-dependent and affected by concentration, solvent, ring size, and chemical environments.^[73] Moreover, the equilibrium between depolymerization and thermal stability is an essential consideration for a polymer system that is chemically recyclable. Additionally, recent studies suggested that the chemically recyclable lignin-based polymers could be a viable option toward the development of a sustainable circular economy.^[63,76,77]

Taking notes from the prior literature, the concept of chemical recycling was hypothesized to determine if the new polycarbonate can be depolymerized back to its original cyclic carbonate monomer. Acetonitrile was used as a solvent in the depolymerization reaction. Due to the comparable dielectric constant values of cyclic carbonates and acetonitrile (64 and 37.5 respectively), acetonitrile exhibits a higher favorability for depolymerization (from polycarbonate to a 6-membered ring cyclic carbonate monomer) compared to other non-polar solvents such as toluene (dielectric constant: 2.4).^[73] Olsén et al. specified that the ceiling temperature of the six-member cyclic carbonate system in 0.5 M acetonitrile was 82 °C.^[73] We employed the similar experimental condition which is the acetonitrile concentration 0.5 M at 90 °C of reaction temperature (Figure 5a).

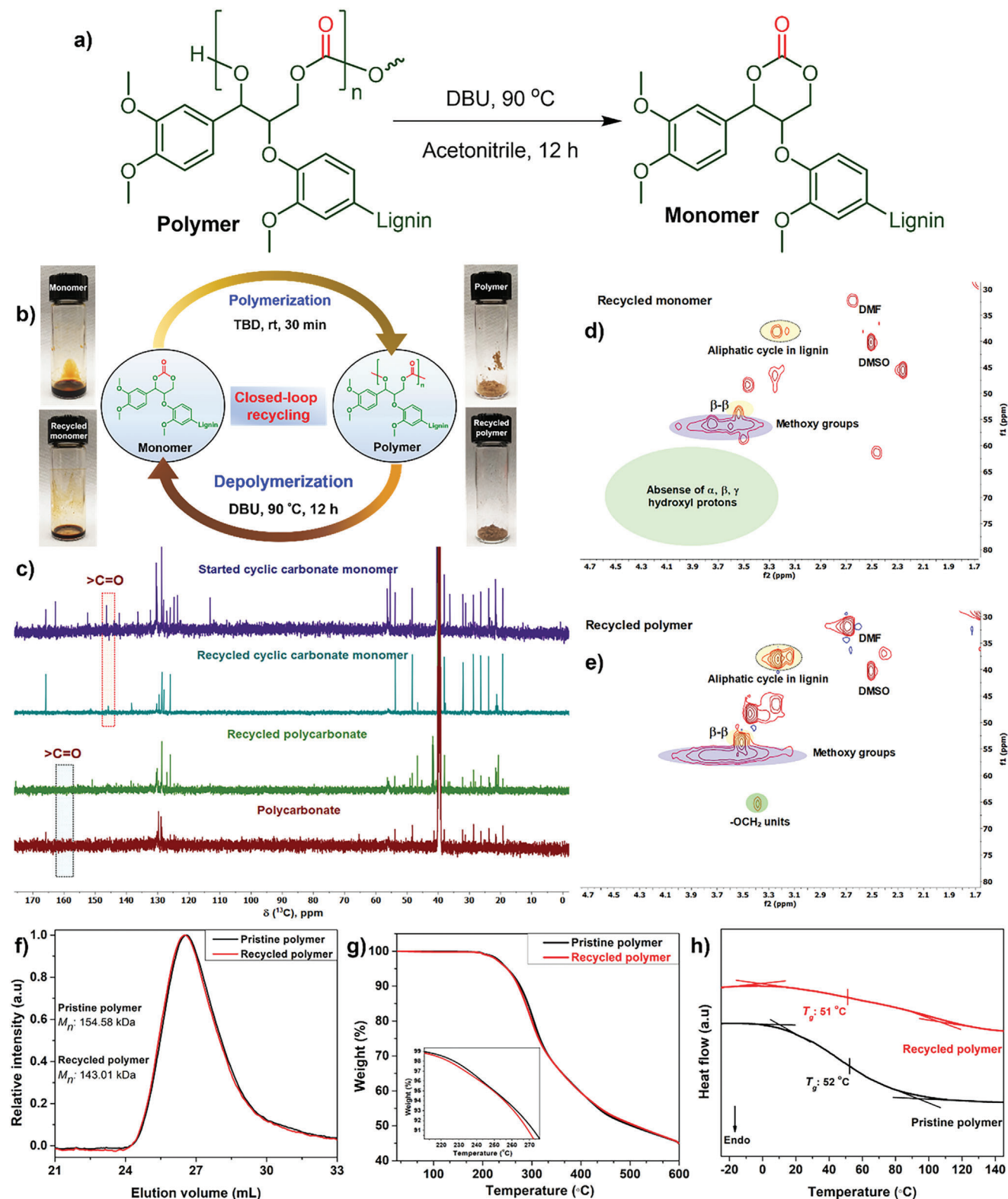


Figure 5. a) Chemical depolymerization of CO₂ and lignin-based polymer to cyclic carbonate monomer. b) Graphical representation of closed-loop chemical recycling of polymer ↔ monomer. The second-generation polymer was obtained from the repolymerization of the recycled monomer. c) Stacked ¹³C NMR spectra of original monomer, synthesized polycarbonate, recycled monomer, and recycled polycarbonates. d) 2D HSQC (¹H–¹³C) NMR of recycled monomer. e) 2D HSQC (¹H–¹³C) NMR of polymer that is synthesized from the recycled monomer. f) GPC trace profiles of pristine polymer and recycled polymer. g) Comparative thermogravimetric analysis (TGA) between pristine polymer and recycled polymer. h) Differential scanning calorimetry (DSC) graphs of initial polymer and recycled polymer.

After the depolymerization, the recycled cyclic carbonated monomer was successfully obtained. The resulting monomer was a viscous liquid, while polycarbonate was a dry solid powder (Figure 5b). Note that the original lignin-based cyclic carbonate monomer was viscous liquid. ^{13}C NMR spectroscopic data revealed a consistent result as visual observation. The distinct peak at 146 ppm from the cyclic carbonate (carbon on carbonyl group) in ^{13}C NMR confirmed the formation of monomer via the ring closing depolymerization (Figure 5c). After polymerization, this carbonyl peak on 146 ppm disappeared and switched to 158 ppm which is from carbonyl on polycarbonate. After depolymerization in Figure 5c, the disappeared peak on 146 ppm (carbonyl from monomer) was revived. The 2D HSQC (^1H - ^{13}C) NMR spectra in Figure 5d also supported the successful synthesis of the monomer. Subsequently, to assess our close-loop recycling concept, the recycled monomer had been utilized in repolymerization with the organocatalyst, TBD. Excitingly, the recycled monomer was repolymerized and the chemical structure was spectroscopically confirmed (Figure 5b,c,e). As we successfully obtained the identical chemical structure of the original monomer, the resulting polymer after polymerization showed the same chemical structure as the initial polymer. Moreover, GPC, TGA, and DSC studies were conducted to confirm the repeatability and efficiency of the recycling process (pristine polymer \rightarrow recycled monomer \rightarrow recycled polymer), comparing the initial and recycled polymers. Significantly, the recycled polymer exhibited similar GPC traces in Figure 5f, analogous thermal degradations in TGA as showed in Figure 5g, and comparable glass transition temperatures (pristine polymer: 52 °C and recycled polymer: 51 °C) from DSC in Figure 5h to the pristine polymer. These findings emphasized the potential of recycling methods in maintaining the key properties of the polymer. Therefore, this work offered a promising route toward the closed-loop recycling of “polymer \rightarrow depolymerization \rightarrow monomer formation \rightarrow polymer synthesis” for a complete circular sustainable economy.

3. Conclusion

This study presents an innovative, safe, and cost-effective methodology developed for synthesizing cyclic carbonate monomers derived from biomass lignin and CO_2 , and subsequently producing recyclable polycarbonates. Most notably, this work demonstrated the synthesis of CO_2 and lignin-based cyclic carbonate monomer for the first time. The monomer synthesis involves the direct integration of lignin with CO_2 under safe and moderate conditions, including atmospheric pressure and eliminating the need for hazardous phosgene derivatives used in traditional polycarbonate synthesis. Utilizing the new monomer, systematic synthesis of CO_2 and lignin-based polycarbonates was achieved by organocatalyzed ROPs in the presence of TBD and DBU. The polymerization's feasibility was investigated by varying catalysts, catalyst loading, and reaction times. The ROP reaction, utilizing a feed ratio of cyclic carbonate to TBD at 100:1 and a reaction duration of 30 min at room temperature, exhibited the highest efficiency. The chemical structures of CO_2 and lignin-based monomer and polymers were determined using FT-IR, ^1H NMR, ^{13}C NMR, and 2D HSQC (^1H - ^{13}C) NMR. The results from the GPC studies indicated the formation of high molecular weight polymers, which could be precisely programable with

the reaction conditions. Besides, the $T_{d5\%}$ and T_g values of the optimal polymer sample were 277 and 77 °C, respectively. The superior thermal characteristics broadened the suitability of the polymers for multiple applications in complex environments. Furthermore, depolymerization and repolymerization reactions were performed to evaluate the closed-loop recycling of the developed polymer. Fascinatingly, the CO_2 and the lignin-based polymer was completely cyclable for the circular economy via fully controlled depolymerization in presence of DBU by heating at 90 °C for 12 h. The chemical recycling of polymer to monomer is further validated by the ^{13}C and 2D HSQC NMR results. It is significant to note that the synthesized polycarbonate can be depolymerized to the recycled monomer, which can undergo another polymerization. Therefore, the successful development of CO_2 and lignin-based polymers, along with their chemical recycling (polymer \leftrightarrow monomer), introduces novel avenues for creating stable, robust, and sustainable polymers from naturally abundant lignin and CO_2 .

4. Experimental Section

Synthesis of CO_2 and Lignin-Based Cyclic Carbonate Monomer: Three grams of lignin was placed into a dry three-neck round bottom flask furnished with two dropping funnels, and a magnetic stirrer. The anhydrous DMF (0.1 mol L^{-1} , 135 mL) was added to the sealed flask and stirred until it formed a homogeneous dark brown solution. The system was purged of air by continuous argon gas flow to create a closed inert atmosphere. Then, a carbon dioxide (CO_2) gas-filled balloon was inserted into the system to replace the argon gas with CO_2 . The reaction mixture was saturated with CO_2 for 10 min and 2.02 mL of DBU (13.5 mmol) was added dropwise into the CO_2 -infused saturated solution of lignin in DMF. The reaction mixture became viscous after the addition. After being stirred for 2 h at room temperature, the flask was placed in an ice bath to cool down the temperature to 0 °C. Subsequently, CO_2 -saturated 1.88 mL TEA (13.5 mmol) was added gradually to the solution followed by the slow addition of CO_2 -saturated TsCl (2.57 g, 13.5 mmol) solution in DMF. Both the TEA and TsCl solutions were added in a dropwise manner using the attached dropping funnels. Afterward, the reaction mixture was allowed to come to room temperature and stirred for additional 24 h. The crude product was washed several times with deionized water, DCM, and brine solution. The organic layer was collected and passed through the anhydrous MgSO_4 to eliminate the trapped water. Lastly, a dark brown sticky product was obtained after evaporating the organic layer using a rotary evaporator. The total yield was 1.92 g (64 wt%).

Synthesis of CO_2 and Lignin-Based Polycarbonates via Ring-Opening Polymerization Using TBD: The different sets of CO_2 and lignin-based polycarbonates (P-1 to P-7, Table 1) were synthesized using TBD as an organocatalytic base. Here, the polymerization process for P-4 polymer (Table 1) is described in more detail (Table 1). The cyclic carbonate monomer (410 mg, OH content: 4.5 mmol g^{-1} , 1 equivalent) was taken in a pressure relief cap-containing 20 mL vial with a magnetic stirrer. 1.8 mL (1 mol L^{-1}) of anhydrous DCM was added in the vial and continuously flushed with argon gas. A solution of TBD (2.57 mg, 0.018 mmol, 0.01 equivalent) was prepared in anhydrous DCM with a concentration of 1 mol L^{-1} . Then, 18 μL of TBD solution was added in the monomer solution under argon atmosphere. The reaction mixture was stirred at room temperature. The samples were collected in aliquots to track the polymer formation by ^1H NMR spectroscopy and GPC. In the case of P-4, the reaction mixture was stirred for 30 min. Subsequently, the collected reaction solutions were quenched with benzoic acid. After removing the solvent under reduced pressure, the crude product was dissolved in the least quantity of DCM and precipitated from diethyl ether. Multiple washes with diethyl ether yielded a light yellowish product. The reaction time (2, 5, 10, and 30 min) and amount of TBD (0.5, 1.0, 2.0, and 5.0%) varied in different

polymerization reactions (Table 1). Polycarbonate synthesis with DBU is described in the Supporting Information.

Chemical Recycling (Polymer \leftrightarrow Monomer): The P-4 polymer was preferred for the chemical recycling procedure due to its superior performance compared to the other synthesized polymers. The chemical recycling process of P-4 to the cyclic monomer was elaborated as follows. P-4 (250 mg, OH content: 4.5 mmol g⁻¹, 1 equivalent), DBU (8.56 mg, 0.05 equivalent), and 2.2 mL of acetonitrile (0.5 mol L⁻¹) were taken in a 4 mL vial charged with a magnetic stirrer. After attaining a homogeneous brown solution, the reaction mixture was placed in an oil bath at 90 °C and stirred for 24 h. Afterward, the temperature cooled down to room temperature. Rotary evaporation was used to concentrate the crude solution. Subsequently, the product was washed several times with DCM and water. Finally, a dark brown sticky substance was obtained after concentrating the filtered organic layer. The total yield was 190 mg (76 wt %).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

biomass, carbon dioxide, degradable and recyclable polymer, lignin, sustainable polymer synthesis

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