

Sustainable and Recyclable Polymers from CO₂ and Lignin: Enabling Waste to Wealth Transformation

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Abstract

The fast expansion of the plastics industry has intensified the global crisis of plastic waste pollution, ecological imbalance, and greenhouse gas emissions. 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 CO₂ and lignin-based cyclic carbonate monomer has been synthesized using a cost-effective, non-phosgene-based and greener approach under atmospheric pressure and room temperature. The fully controllable synthesis of CO₂ and lignin-based polymers is accomplished via ring opening polymerization (ROP) by varying the catalyst [1, 8-diazabicyclo (5.4.0) undec-7-ene (DBU), and 1, 5, 7-triazabicyclo [4.4.0] dec-5-ene (TBD)], catalyst loading (0.5–5.0%) and reaction time (2–40 min). Among the polymers, the best polymer obtained in 1% TBD with a reaction time of 30 minutes. The structural elucidations of the synthesized cyclic carbonate monomer and polymer are established using various spectroscopic analyses including ¹H, ¹³C, and 2D HSQC NMR, FT-IR, and GPC. The high molecular weights (M_n: 120.34–154.58 kDa) and excellent thermal stabilities (T_{d5%}: 244–277 °C from TGA and T_g: 33–52 °C from DSC) of the polymers are 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 hours in presence of DBU. This process yields original structure of monomers that can be used for another polymerization without unwanted change of chemical structures, making it a sustainable solution. Therefore, this work illustrates an innovative hybrid approach of both the synthesis of 100% biomass-based polymer and infinite closed-loop recycling of polymer-monomer using abundant renewable resources, that further leads to a sustainable circular plastic economy alternative to the linear petroleum-based polymers.

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 within this century 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} Development of efficient procedures to produce polymers from renewable resources (carbon dioxide; CO₂) and biomass has thus gained considerable interest. In contrast to conventional polymers derived from petroleum, bio-based polymers are gaining momentum in the category sustainable materials due to their plentiful 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 sources of the bio-based monomers are debatable as the majority of monomers are derived from food-based resources (for example, maize starch → glucose → lactic acid → poly(lactic acid), sugar → glucose →

polycarbonate).^{2,11} As significant food resources, these types of bio-based monomers compete with the utilization as a feedstock for generating polymers. Thus, monomers derived from non-food resources are considered a viable option for the developing sustainable polymers. Furthermore, the chemical recycling of the polymer offers the potential of turning waste into treasure by converting polymers back into the fundamental building blocks that may re-enter the value stream for plastic manufacture.

Lignin is a sustainable raw resource and the second-most abundant plant-based biopolymer after cellulose.^{12,13} Lignin is a crucial structural element of plants and accounts for around one-third of the mass of trees because of its high aromatic content, which improves mechanical qualities.¹⁴ As an unwanted by-product primarily from the paper industry that yields more than 50 billion tons of material annually.¹⁵ Lignin is advantageous for its many appealing features, including biodegradability, antioxidant activity, high carbon content, high thermal stability, and rigidity, in addition to its availability and affordable supply.^{16,17} Lignin is a great substitute for other components used to make biodegradable polymers, such as maize, soy, sugar, and gelatin, which also have industrial, food, and agricultural applications.^{14,15,18,19} In particular, lignin's mass production cost was between \$250 and \$500 per ton, whereas the cost of other food-grade biomass-based monomers is much higher. For instance, the market price for lactic acid is \$1,600 to \$1,900 per ton.^{20–22} The lignin which is an important raw resource of polymers can be covalently linked to CO₂ that is removed from the atmosphere.

CO₂ is the primary component of greenhouse effect gases, and the concentration of CO₂ in the atmosphere is rising annually owing to the expansion of the economy. Consequently, the temperature has progressively risen by more than 1 K since the year of 1900, resulting in a variety of difficulties such as inconsistent weather, ecological disturbance, desertification, an increase in seawater temperature and sea level, and food shortages.^{23,24} Therefore, the reduction of CO₂ emissions is of supreme importance, and the development of efficient systems for CO₂ management is very much required to make the transition to a reliable, and low-carbon economy toward combating climate change.^{25,26} The transformation of CO₂ into useful compounds is ideal from the perspective of a circular and low-carbon economy, but the high chemical stability of CO₂ makes this process more challenging.²⁷ CO₂ is a sustainable, renewable, non-toxic, and non-flammable C1 feedstock that might be utilized for a range of chemical conversions.

Investigations have been conducted on the use of CO₂ as a raw material in the synthesis of ureas,²⁸ organic carbonates,²⁹ carbamates,³⁰ and polycarbonates.^{31–33} To synthesize aliphatic polycarbonates from CO₂, four well-developed synthetic routes have been developed, including polycondensation of aliphatic diols with phosgene derivatives or dialkyl carbonates,³¹ copolymerizations of CO₂ with epoxides,^{34–36} direct polymerization of CO₂,^{33,37–39} and ring-opening polymerization of cyclic carbonate monomers.^{31,32,40} Conventionally, hazardous phosgene has been used as a raw material in industrial processes to prepare polycarbonates, which produce a lot of salt waste.³⁷ Although copolymerization of epoxides or oxetanes with CO₂ has been investigated, 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.⁴¹ Nevertheless, a number of issues still need to be resolved, including the high CO₂ pressure, a special type of reactor (autoclave), regeneration of the dehydrating agents, and side reactions from the dehydrating agents. In this state, researchers have accomplished the direct ring-opening polymerization of cyclic carbonate monomers in order to synthesize aliphatic polycarbonates,^{32, 42–45} where the cyclic carbonate monomer can be prepared in mild reaction conditions using CO₂ as a raw resource at room temperature and atmospheric pressure.^{46–48}

The conceptual outline of this work is to synthesize recyclable polymer from biomass and CO₂ under atmospheric pressure for the circular plastic economy towards sustainable development (Fig. 1). Taking notes from the earlier literature, it has been found that the polymers were prepared either from biomass or CO₂.^{40,42,43,47,49} It is also important to mention that the majority of the CO₂-based polymers have been synthesized under high atmospheric pressure.^{32,33,35,37,50} So far very few studies have showcased polymer synthesis under atmospheric pressure.^{48,51} Therefore, there is a significant opportunity to develop a variety of polymers based on biomass lignin by utilizing CO₂ under atmospheric pressure as sustainable alternatives to replace polymers derived from traditional petroleum in order to address environmental concerns.

In this current work, 100% biomass-based recyclable polymers have been developed using CO₂ and lignin (biomass). The synthesized cyclic carbonate monomer and polymer are structurally elucidated using the spectroscopic techniques [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 polymerization have been further explored by synthesizing different polycarbonate through the manipulation of the reaction conditions. The thermal properties of the polymers have assessed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) thoroughly to understand the structure-property relationships and their potential applications. Subsequently, the prepared polycarbonate is systematically depolymerized to the original monomer which can synthesize polymers again. Therefore, this synthetic methodology is leading towards a complete circular economy (biomass / CO₂ → monomer → polymer → upcycle to original monomer → polymer production) without generating plastic / chemical wastes.

Results

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 (Figs. 1 and S1). The synthesis process consisted of two steps (Fig. 2a). Initially, the addition of DBU lead the generation of an ionic salt intermediate by capturing the CO₂ in the less sterically hindered primary hydroxyl groups of lignin.^{52,53} 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 had been performed in highly diluted condition (0.1 mol / L) and at low temperature to accomplish the targeted unimolecular cyclization over competing dimerization processes.⁵² Finally, a deep brown viscous liquid product (cyclic carbonate monomer) was obtained (**Figure S2, Supporting Information**). Notably, in contrast to unmodified lignin, which is insoluble in dichloromethane (DCM), the synthesized cyclic carbonate monomer demonstrated excellent solubility in DCM (Fig. 2b).

As the main hypothesis of this work was the synthesis of CO₂ and lignin-based cyclic carbonate monomer, the chemical structure of the monomer was structurally elucidated by various spectroscopic analyses. The 2D HSQC (¹H – ¹³C) NMR provided comprehensive information on the structural alterations between the unmodified lignin and cyclic carbonate monomer. In Fig. 2c, the signals from the hydroxyl group in the α, β, and γ positions of the unmodified lignin appeared at δ_H / δ_C: 3.2–4.5 ppm / 58–80 ppm, where the signals were assigned following the earlier literature.^{54–56} The methoxy group signal displayed at δ_H / δ_C: 3.78 ppm / 56 ppm.⁵⁷ In general, the HSQC NMR spectrum of unmodified natural lignin (Figs. 2c and S3) demonstrates the distinctive lignin chemical structure with a high concentration of hydroxyl groups. After the carbonylation, the peaks from α and γ hydroxyl groups were disappeared in the HSQC NMR spectrum of the cyclic carbonate monomer (Figs. 2c and S4). However, there are some unreacted hydroxyl groups that are still observable in the HSQC NMR even after the reaction. These signals correspond to the hydroxyl groups at the γ-positions of the phenylcoumaran (D-γ) and cinnamyl (C-γ) units.^{55,56,58} Specific chemical shifts are two small signals at δ_H / δ_C: 3.4 ppm / 60 ppm and δ_H / δ_C: 4.1 ppm / 68 ppm as shown in Fig. 2c (cyclic carbonate monomer).^{55,56,58} These remaining hydroxyl groups play an important role as initiators of ROP during the following polymerization process. Overall, the consumption of the α and γ hydroxyl groups of β-O-4 units in unmodified lignin manifested the successful carbonylation reaction of lignin with CO₂.

Additionally, the ¹³C and ¹H NMR studies were investigated for detailed information of the chemical structure (Figs. 3 and S5-6, **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 (Figs. 3c and S5).⁵² 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 (Fig. 3c, cyclic carbonate monomer). For instance, the peaks seen in the range of 18–38, 44–54, 55–56, and 67–89 ppm (Fig. 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 (Fig. 3c, cyclic carbonate monomer).^{55,58} The ¹H spectrum of CO₂ and lignin-based cyclic carbonate monomer is displayed in Figs. 3b and S6. A characteristic carbonyl peak at 1747 cm^{–1} in the FT-IR spectrum (**Figure S7, Supporting Information**) provided further evidence for the efficient synthesis of carbonate monomers.⁴²

Synthesis of biomass lignin and CO₂-based polymer via ring-opening polymerization

The polymerization of the cyclic carbonate monomer had been performed at room temperature via organocatalyzed ROP as presented in Fig. 3a. The ROP consists of activation of the cyclic carbonate monomer, cleavage of acyl-oxygen bond and propagation of polymeric chains. Initially, the organocatalyst activated the cyclic carbonate groups via the nucleophilic attack. Then, a tetrahedral intermediate had been formed in presence of alcohol initiator. Afterward, the partial ring opening occurred through the proton transfer. Lastly, the regioselective cleavage of acyl-oxygen bond took place and the polymer chains were propagated with the head-tail linkages.⁴⁸ The γ -hydroxyl groups of the phenylcoumaran and cinnamyl units, as observed in the HSQC NMR spectrum of the monomer, was served as initiator of the ROP (Fig. 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.^{43,48}

In our experiments, organocatalytic ROP reactions were carried out in the absence of 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). Among all the polymers, P-4, with a feed ratio of cyclic carbonate : TBD ratio at 100:1 and a reaction time of 30 minutes, exhibited the highest efficiency in achieving the best yield (Table 1). The synthesized polymers were thoroughly characterized by FT-IR, ¹H NMR, ¹³C NMR, and 2D HSQC NMR. Those characterizations were employed to inspect the structural elucidations, and the GPC analysis was used to ascertain the molecular weight and molecular weight distribution (polydispersity index, PDI) (Figs. 2–3 and S8-42, **Supporting Information**). Here, the spectroscopic changes of P-4 are elaborated as an example in Figs. 2c, 3b-c and S21. Initially, the attendance of carbonyl groups was assured from the strong absorption band at 1755 cm⁻¹ in the FT-IR spectra (**Figure S21**). The ¹H NMR spectrum of the synthesized product was compared with that of the monomer in Fig. 3b. The downfield shift of -CH(OH) in the ¹H NMR spectrum (red, Fig. 3b **polycarbonate**) to 5.30 ppm was the most obvious sign of ring opening. Additional compelling evidence of the ROP of the cyclic carbonate monomer is shown in Figure S8 with kinetic studies using NMR. The gradual increment of the peak intensity at 5.30 ppm was clearly observed over reaction time.

The ¹³C NMR in Fig. 3c shows the obvious disappearance of the monomer's carbonyl at 146.5 ppm and new peaks appeared in the range of 157–160 ppm. The carbonyl carbon resonance's distinctive downfield shift was seen in the ¹³C NMR spectra as a result of the successful ROP (Fig. 3c, **polycarbonate**).⁵² Multiple peaks had been detected between 157 to 160 ppm due to the diverse chemical structures around the carbonate in the polycarbonates that contain 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.⁴³ According to the earlier literature it can be stated that this HT, TT, and HH can be nonselective during the chain propagation due to non-controllable acyl-oxygen bond ($-C(=O)-O-$) cleavage at either side of the carbonate carbonyl to produce regio-random polymers.^{43,44,52} The opening locations of the ring [acyl-oxygen bond ($-C(=O)-O-$) cleavage] are indicated with broken lines in the monomer's chemical structure in Fig. 3c. The dominant ring opening will occur to form secondary substituted polymers (resulting from the cleavage of the left bond of the carbonyl group in the monomer's chemical structure, as shown in Fig. 3c). This is supported by the intense signal observed at 5.30 ppm in the ^1H NMR spectrum of the polymer, as shown in Fig. 3b polycarbonate.

Furthermore, 2D HSQC ($^1H - ^{13}C$) NMR experiments had been performed to support the expected polymeric structure (Figs. 2c and S9). The disappearance of the aforementioned residual γ -hydroxyl groups of the monomer in the region of δ_H / δ_C : 3.2–4.5 ppm / 58–80 ppm affirmed our hypothesis on the effective ROP without the addition of any initiator (Fig. 2c). The HSQC NMR also possessed the signal of the oxymethylene units ($-OCH_2-$) at 3.4 ppm/ 64 ppm, which came from the polycarbonate structure. Overall, all spectroscopic analyses confirmed the successful synthesis of sustainable polycarbonates from biomass lignin and CO_2 through ROP.

GPC was employed to evaluate the molecular weights and molecular weight distributions of the developed polymer. Various polymerization conditions were comparatively studied to determine the key parameters for controlling molecular weights of the newly synthesized polymers.^{52,59,60} 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, 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.⁶¹ The molecular weights of the polymers were greatly dependent on the reaction time, type of catalyst, and feed ratio (Table 1). A surge in molecular weights was noticed with the increase of reaction time. Besides, the increment of catalyst loading (from 0.5 % to 5%) resulted in a decrease in molecular weight. This drop could be attributed to the dominant increase in backbiting between the alcohol polymer end groups and carbonyl units of carbonate, potentially causing this effect (P-7: 139 kDa, 0.5% TBD $\rightarrow$ P-6: 130 kDa, 5% TBD).⁴⁸ TBD functioned as a more effective organocatalyst in ROP compared to DBU (P-5: 141 kDa, 2 % TBD $\rightarrow$ P-9: 123 kDa, 2% DBU). Although all the polycarbonates exhibited high molecular weights, P-4 polymer demonstrated the highest molecular weight of 154.58 kDa among the polymers.

Table 1
Organocatalytic scope in the ring-opening polymerization of CO₂ and lignin-based cyclic carbonate monomer and properties of the synthesized 100% biomass-based polycarbonates.

Polymer	Catalyst	[M]:[C] ^a	Time (Min)	M _n ^b (kDa)	M _w ^c (kDa)	T _{d5%} ^e (°C)	T _g ^f (°C)	
P-1	TBD	100:1	123.22	190.47	1.55	244	45	
P-2	TBD	100:1	5	125.78	201.17	1.60	257	47
P-3	TBD	100:1	144.78	189.46	1.31	259	50	
P-4	TBD	100:1	30	154.58	229.34	1.48	277	52
P-5	TBD	100:2	30	141.04	211.20	1.50	253	46
P-6	TBD	100:5	30	129.88	205.06	1.58	255	43
P-7	TBD	200:1	30	139.50	223.01	1.60	260	48
P-8	DBU	100:1	40	128.87	191.44	1.49	265	47
P-9	DBU	100:2	40	122.93	182.38	1.48	263	40
P-10	DBU	100:5	40	120.34	229.22	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.

Structure-property relationships of new polymers

The thermal properties of the polymers were evaluated from the TGA and DSC. P-1 to P-10 polymers showed step-wise degradations in TGA and Table 1 summarizes the decomposition temperature (T_{d5%}) at which 5% weight loss was observed for the polymers (Figs. 4a and S43-47, **Supporting Information**). Note that all solvents were removed through prior thermal evaporation. The T_{d5%} values of the polymers enhanced with the reaction time and decreased with the catalyst loading percentage. The polymers' T_{d5%} values improved as the reaction time increased and dropped with the rise in catalyst loading percentage (Table 1 and Fig. 4a). The P-4 and P-8 displayed reasonably high thermal stability, with T_{d5%} values of 277 and 265°C, respectively (Table 1, and Figs. 4a and S43-47). On the other hand, single glass-transition temperatures (T_g) from 33 to 52°C were seen in the DSC of P-1 to P-10 polymers (Figs. 4b and S48-49, **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).⁶² P-4 (monomer: TBD = 100:1, reaction time: 30 minutes) 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.⁶² The higher T_g values arose from the inclusion of rigid lignin

units into the polymer, which inhibited the chain rotations. Hence, the controllable thermal behavior of the CO₂ and lignin-based polycarbonate enhanced its feasibility as a candidate for the development of novel, high-performance sustainable materials.

Chemical recycling (monomer ↔ polymer)

Innovative polymer designs that enable low-cost and straightforward chemical recycling of polymers back to their original monomers, without compromising the chemical structures and properties, are crucial for fostering 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 thermodynamic equilibrium behavior that can be directly utilized in the chemical recycling of polymers.^{63–65} The ceiling temperature (T_c) of a polymerization system is the temperature at which the polymerization and depolymerization rates are equal and the Gibbs free energy of polymerization is zero.⁶⁵ 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.⁶⁴ Moreover, the equilibrium between depolymerization and thermal stability is an essential consideration for a polymer system that is chemically recyclable.

Taking notes from the prior literature, the concept of chemical recycling had been 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 similar order of dielectric constant values of cyclic carbonates and acetonitrile (64 and 37.5 respectively), acetonitrile is highly favourable on depolymerization (polycarbonate ↔ 6-membered ring cyclic carbonate monomer) than other non-polar solvents (e.g., toluene, dielectric constant: 2.4).⁶⁴ Olsén et al. specified that the ceiling temperature of the six-member cyclic carbonate system in 0.5 M acetonitrile was 82°C.⁶⁴ We have employed the similar experimental condition which is the acetonitrile concentration 0.5 M at 90°C of reaction temperature (Fig. 5a).

After the depolymerization, the recycled cyclic carbonated monomer had been successfully obtained. The resulting monomer was a viscous liquid, while polycarbonate was a dry solid powder (Fig. 5b). Note that the original lignin-based cyclic carbonate monomer was viscous liquid. ¹³C NMR spectroscopic data revealed a consistent result as visual observation. The distinct peak at 146 ppm from the cyclic carbonate group in ¹³C NMR confirmed the formation of monomer via the ring closing depolymerization (Fig. 5c). After polymerization, this carbonyl peak on 146 ppm disappeared and switched to 158 ppm which is from carbonyl on polycarbonate. After depolymerization in Fig. 5c, the disappeared peak on 146 ppm (carbonyl from monomer) was revived. The 2D HSQC (¹H – ¹³C) NMR spectra in Fig. 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. Excitingly,

the recycled monomer was repolymerized and the chemical structure was spectroscopically confirmed (Fig. 5b, c, e). Therefore, this work offered a promising route towards the closed-loop recycling of “polymer → depolymerization → monomer formation → polymer synthesis” for a complete circular sustainable economy.

Discussions

This study presents an innovative, safe, and cost-effective methodology developed for synthesizing cyclic carbonate monomers derived from biomass lignin and CO₂, and subsequently producing recyclable polycarbonates using these monomers.

Most notably, this work demonstrated the pioneering synthesis of CO₂ and lignin-based cyclic carbonate monomer for the first time by the direct integration of readily available cost-effective biomass lignin with the greenhouse gas CO₂ under atmospheric pressure, eliminating the need for hazardous phosgene derivatives commonly employed in traditional polycarbonate synthesis methods.

The CO₂ and lignin-based polycarbonates were synthesized in controlled manners via organocatalyzed ROPs in presence of TBD and DBU. The polymerization's controllability was systematically investigated by varying catalysts, catalyst loading amounts, and reaction times. The ROP reaction, utilizing a feed ratio of cyclic carbonate to TBD at 100:1 and a reaction duration of 30 minutes at room temperature, exhibited the highest efficiency in achieving the highest yield. Hence, this methodology has emerged as the most viable approach for utilizing biomass lignin and CO₂ in sustainable polymer synthesis.

The chemical structures of CO₂ and lignin-based monomer and polymers were determined using FT-IR, ¹H NMR, ¹³C NMR, and 2D HSQC (¹H – ¹³C) 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 are 277°C 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 CO₂ and the lignin-based polymer is completely cyclable for the circular economy via fully controlled depolymerization in presence of DBU by heating at 90 °C for 12 hours. The synthesized polycarbonate can be depolymerized to the recycled monomer which can undergo another polymerization.

Therefore, the successful development of CO₂ and lignin-based polymers, along with their chemical recycling (monomer ↔ polymer), introduces novel avenues for creating stable, robust, and sustainable polymers from naturally abundant biomass and renewable resources. In the future, this alternative approach is expected to replace non-sustainable petroleum-based polymers.

Methods

Synthesis of CO₂ 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 (CO₂) gas-filled balloon was inserted into the system to replace the argon gas with CO₂. The reaction mixture was saturated with CO₂ for 10 minutes and 2.02 mL of DBU (13.5 mmol) was added dropwise into the CO₂-infused saturated solution of lignin in DMF. The reaction mixture became viscous after the addition. After being stirred for 2 hours at room temperature, the flask was placed in an ice bath to cool down the temperature to 0°C. Subsequently, CO₂-saturated 1.88 mL TEA (13.5 mmol) was added gradually to the solution followed by the slow addition of CO₂-saturated TsCl (2.57g, 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 hours. The crude product was washed several times with deionized water, DCM, and brine solution. The organic layer was collected and passed through the anhydrous MgSO₄ 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 and lignin-based polycarbonates via ring-opening polymerization using TBD

The different sets of CO₂ and lignin-based polycarbonates (P-1 to P-7, Table 1) had been 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 minutes. 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).

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 hours. 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 %).

Declarations

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Figures

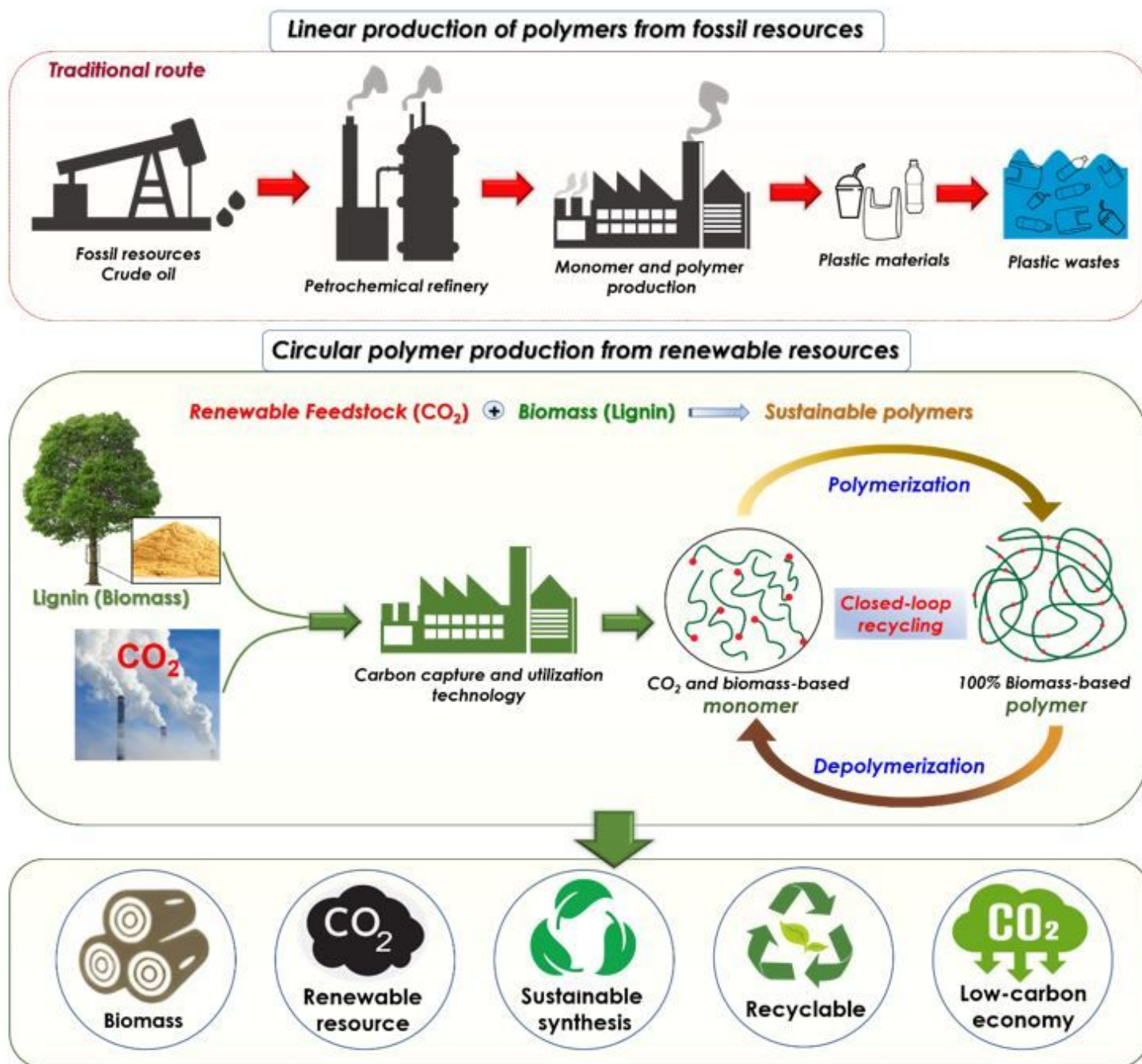


Figure 1

Conceptual outline of the synthesis of polymers (bottom) from CO₂ (renewable resource) and lignin (biomass) via carbon capture and utilization (CCU) as an alternative to the present fossil-based polymer production (top).

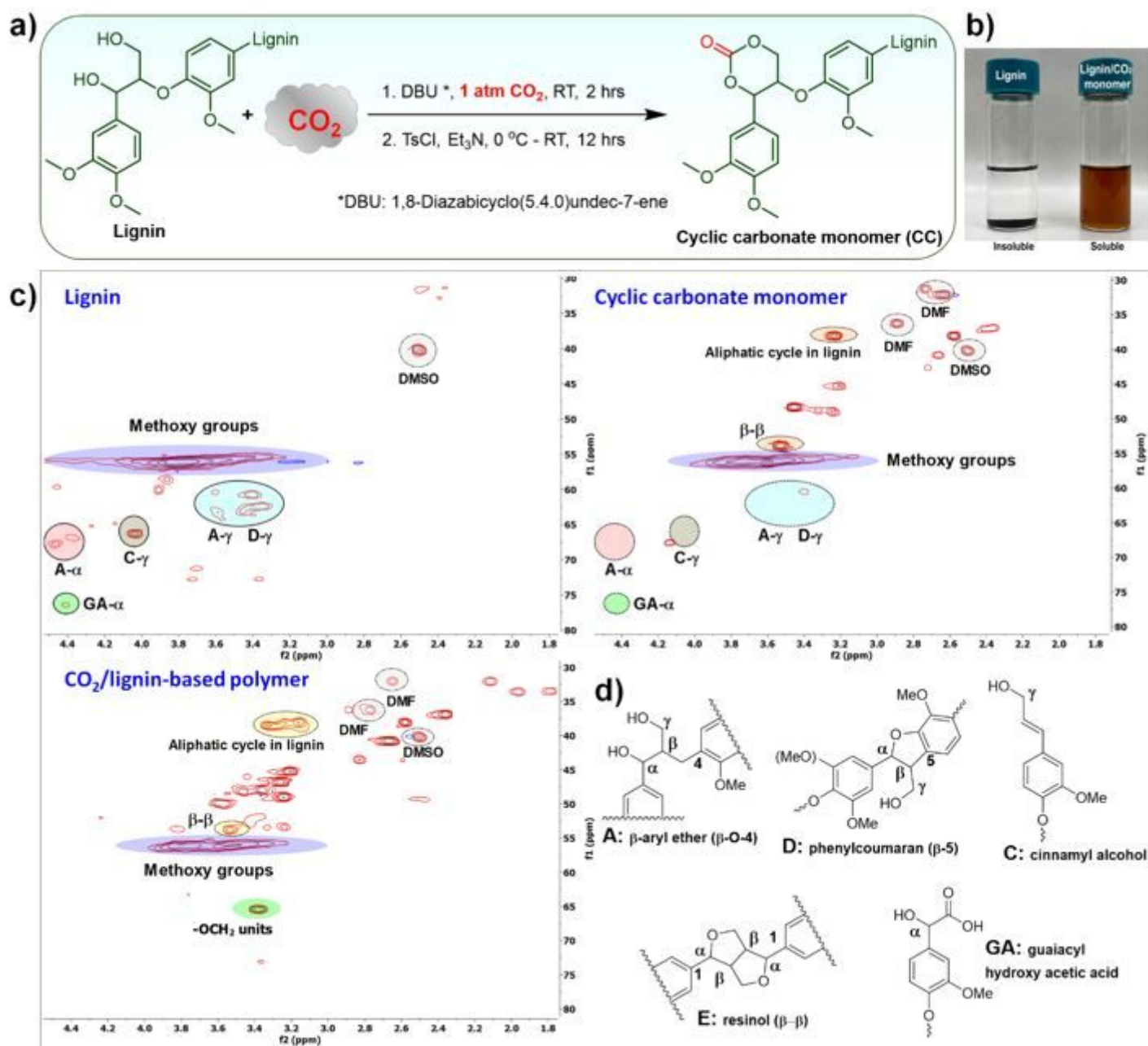


Figure 2

(a) Monomer synthesis from CO₂ and lignin. The monomer possesses 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)** The solubility difference of cyclic CO₂/lignin-based cyclic carbonate monomer (CC) and raw lignin in dichloromethane (DCM). Lignin is insoluble in DCM, whereas after the cyclization the CC monomer is fully soluble in DCM. **(c)** 2D HSQC (¹H – ¹³C) NMR of lignin, CO₂ and lignin-based cyclic carbonate monomer, and polymer. **(d)** Main chemical structural units of lignins.

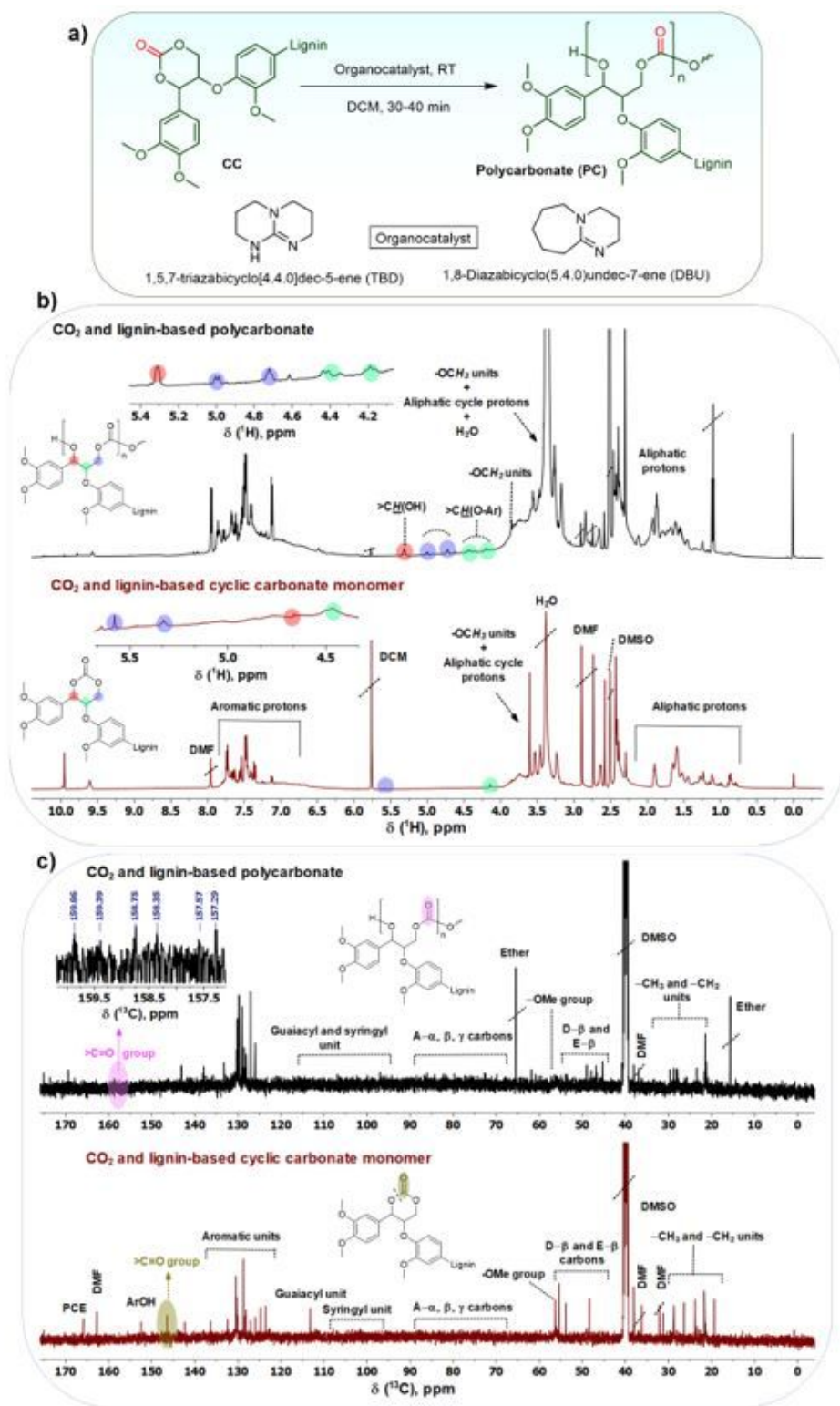


Figure 3

(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).

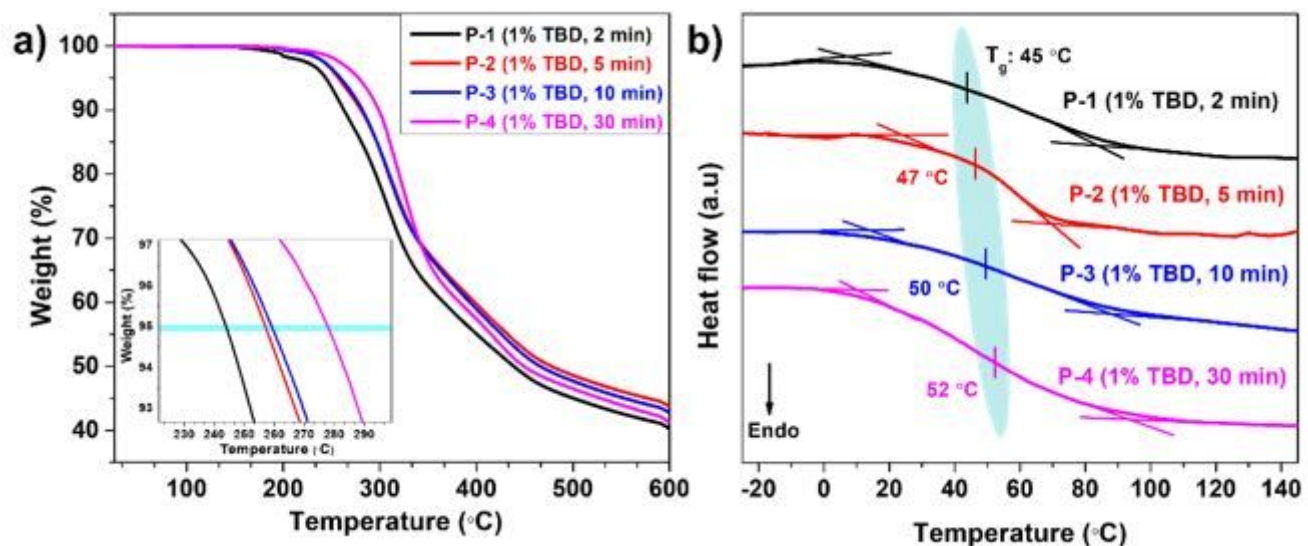


Figure 4

(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.

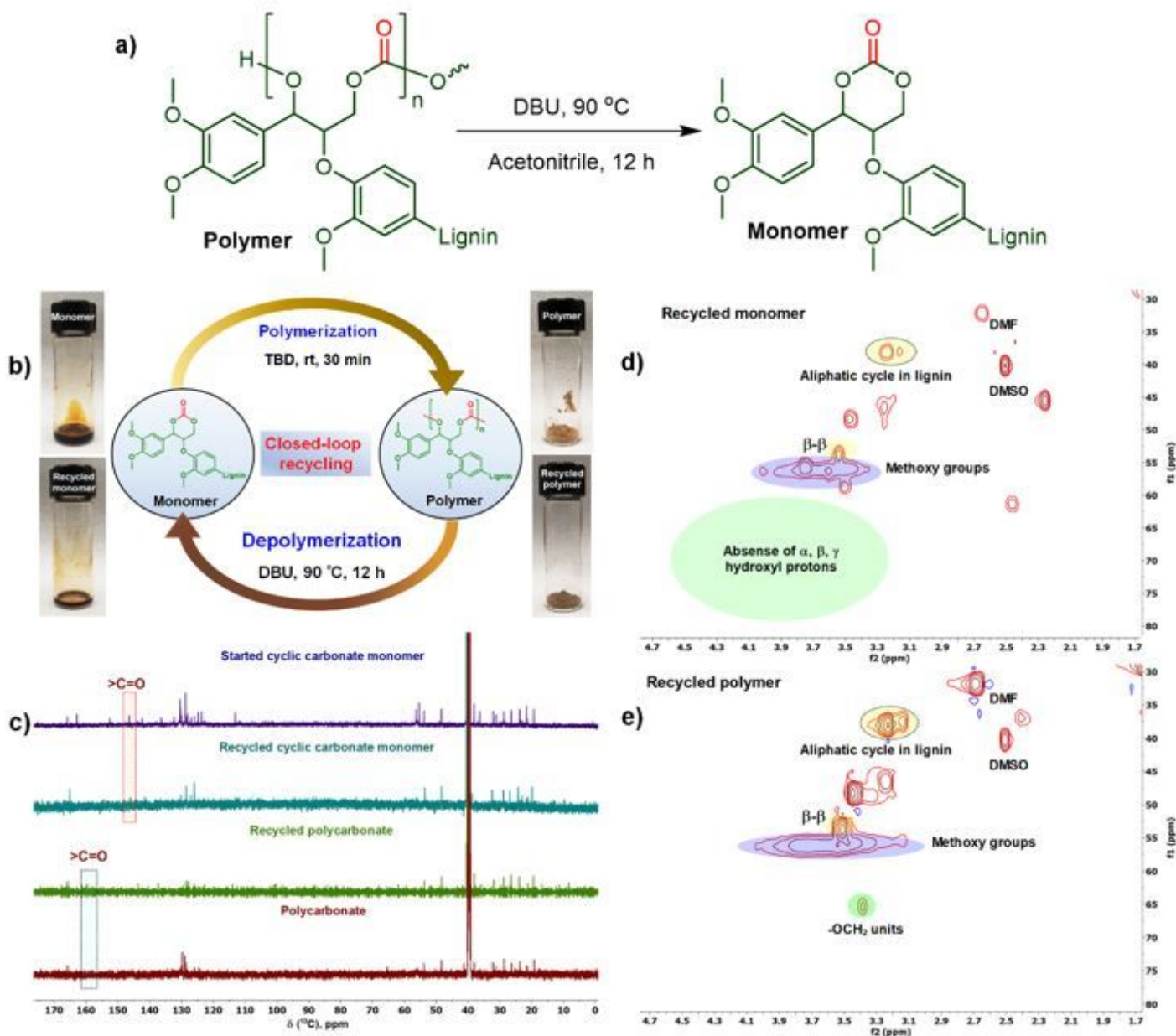


Figure 5

(a) Chemical depolymerization of CO_2 and lignin-based polymer to cyclic carbonate monomer. **(b)** Graphical representation of closed-loop chemical recycling of monomer ↔ polymer. The second-generation polymer was obtained from the repolymerization of the recycled monomer. **(c)** Stacked ^{13}C NMR spectra of original monomer, synthesized polycarbonate, recycled monomer, and recycled polycarbonates. **(d)** 2D HSQC (^1H – ^{13}C) NMR of recycled monomer. **(e)** 2D HSQC (^1H – ^{13}C) NMR of polymer that is synthesized from the recycled monomer.

Supplementary Files

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