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Letter

Rapid Synthesis of Chemically Recyclable Polycarbonates from Renewable Feedstocks

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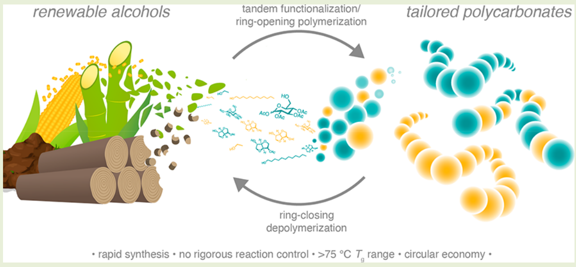
ABSTRACT: We report the rapid, one-pot synthesis of functional polycarbonates derived from renewable alcohols (i.e., glucose tetraacetate, acetyl isosorbide, lauryl alcohol, and ethanol) and a cyclic carbonate bearing an imidazolecarboxylate. This tandem functionalization/ring-opening polymerization strategy can be performed on multigram scale and eliminates the need for rigorous purification and specialized equipment. A wide range of glass transition temperatures (T_g) was accessible from these renewable pendant groups (>75 °C T_g window). We also synthesized several statistical copolycarbonates to show the thermal properties can be tailored with this tandem method. Additionally, we demonstrate a circular polymer economy via chemical recycling to a cyclic carbonate precursor. This work may facilitate development of sustainable polycarbonates with tailored properties that work toward eliminating plastic waste streams.



Developing a circular economy for plastics has become critically important in recent years.[1] Challenges regarding the degradation and recycling of commercial plastics have unlocked new opportunities to design degradable and chemically recyclable polymers derived from renewable resources.[2−6] Aliphatic polycarbonates (APCs) are a useful class of materials because of their excellent thermal and mechanical properties, as well as better resistance to hydrolytic degradation than polyesters,[7−9] enabling high-performance applications to be targeted while still allowing for end-of-life considerations.[7−11] Ring-opening polymerization (ROP) has become a convenient strategy for synthesizing APCs from cyclic carbonates derived from 1,3-diols[7−13] as well as alternating copolymerization of epoxides and CO_2.[14−16] Consequently, this has stimulated efforts to develop novel polycarbonates from renewable feedstocks, including sugars and their derivatives.[7,8,11,17−23]

Two building blocks that have been used extensively in the polymer industry—2,2-bis(hydroxymethyl)propionic acid (bis-MPA) and 1,1,1-tris(hydroxymethyl)propane (TMP)—have emerged as versatile, low-cost cyclic carbonate precursors and have inspired a library of monomers and polymers. Organocatalytic ROP of the functional cyclic carbonates is facile, proceeding in a controlled manner.[7−10] Recently reported monomer syntheses involve the use of a reactive carbonyl source (e.g., 1,1′-carbonyldiimidazole or pentafluorophenyl carbonate) to simultaneously form the cyclic carbonate and install a reactive pendant group.[24,25] The pendant group has been substituted with a wide variety of functionalities prior to polymerization,[7−10] which ultimately dictate the thermomechanical properties of the polymers.[26,27] Moreover, post-polymerization modification has been performed when the side-chain substituents have orthogonal reactivity to ROP (e.g., allyl, propargyl).[7−10] However, previous reports demonstrate the need to isolate the carbonate monomer and subsequently subject to ROP conditions under strict control of conditions (with the exception of one report of water-initiated ROP of a bis-MPA carbonate[28]). This has often posed synthetic and purification challenges (e.g., low-to-moderate yields, oligomeric byproducts) as well as necessitating specialized equipment (e.g., Schlenk techniques, glovebox) that hinder widespread exploration of these materials.

With the ever-growing emphasis on polymer end-of-life, chemical recyclability via ring-closing depolymerization (RCDP) is highly attractive.[6] Polycarbonates with trimethylolalkane backbones like TMP have exhibited this behavior.[29−31] RCDP can be triggered by base and heat under vacuum or dilute conditions to drive the equilibrium back to cyclized monomer.[29−33] Additionally, depolymerization of commodity polycarbonates has been employed to synthesize cyclic carbonates of this nature, effectively upcycling previous generation polycarbonates from waste streams to value-added monomers.[34,35] While TMP-based polycarbonate derivatives show great promise, there have been limited studies of renewable materials designed for a circular economy.

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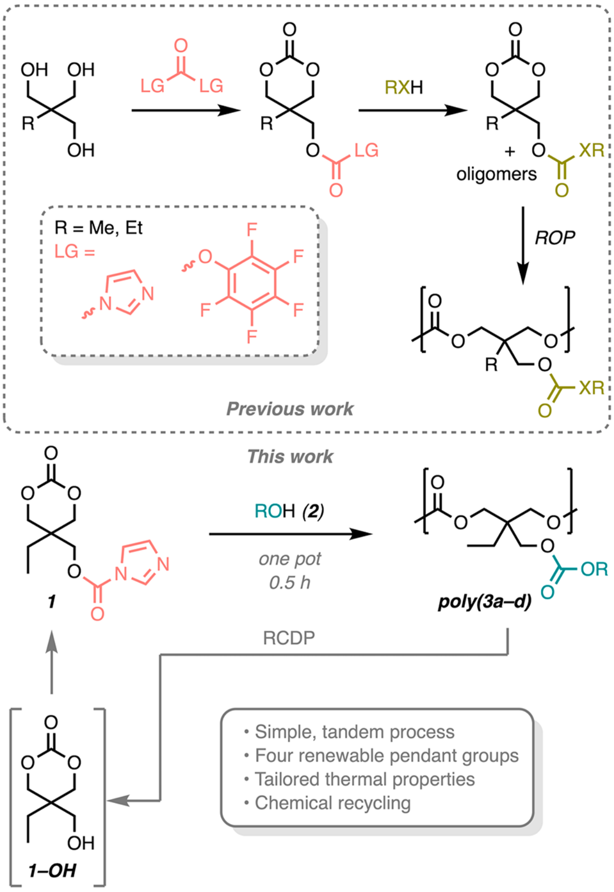
Many renewably sourced alcohols—namely glucose, isosorbide, lauryl alcohol, and ethanol—have reached industrial production and have thus garnered attention in the area of sustainable polymers. For example, glucose-derived polycarbonates[20,23] and polyacrylates[36,37] have exhibited high glass transition temperatures and strong mechanical properties. Isosorbide is a rigid bicyclic diol derived from glucose that has been used as a greener alternative in several commercial step-growth polymers over the past decade.[38] Although there have been improvements in step-growth polymerization strategies,[38−42] recent advances have seen isosorbide incorporated as a vinyl and (meth)acrylic pendant group[37,43−46] as well as derivatives amenable to cationic polymerization.[47,48] Lauryl alcohol and ethanol derived pendant groups—which can be produced from vegetable oils and agricultural waste—have been shown to exhibit softer polymer properties (e.g., acrylic thermoplastic elastomers[49−51]). Unfortunately, most of these materials do not have a sustainable end-of-life process available. Thus, a method for construction of sustainable polycarbonates from low-cost, commercially available building blocks that combines (*i*) the chemical recyclability of a TMP-derived carbonate backbone and (*ii*) the variable properties of these renewable alcohols as pendant groups is highly attractive.

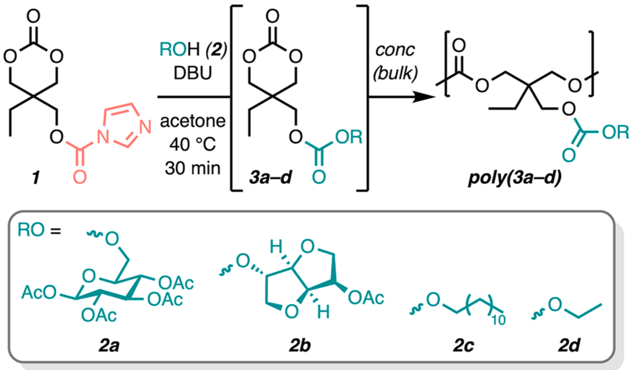
Herein, we report the tandem functionalization/ROP of a cyclic carbonate bearing an imidazolecarboxylate (**1**) to afford polycarbonates with pendant functional groups derived from renewable feedstocks in one step [**poly(3a−d)**, Scheme 1]. Tandem functionalization/ROP with renewably sourced alcohols—including glucose tetraacetate (**2a**), acetylated isosorbide (**2b**), lauryl alcohol (**2c**), and ethanol (**2d**)—was achieved in the presence of an organocatalyst without the need for rigorous purification, drying, or inert atmosphere control. We hypothesized we could access a wide range of thermal properties from these pendant groups and tailor the properties via statistical copolymerization. Finally, the polycarbonates could be chemically recycled to recover a cyclic carbonate with a free hydroxyl group (**1−OH**), which can be refunctionalized with an imidazolecarboxylate to afford **1**, establishing a circular polymer economy.

Scheme 1. Circular Economy of Polycarbonates Derived from Renewable Alcohols



Reactive monomer **1** was synthesized as previously reported and could be isolated on large scale (>20 g).[24] Characterization by NMR spectroscopy and high-resolution mass spectrometry agreed well with the literature (see Supporting Information). To achieve one-pot functionalization and polymerization, the alcohol of choice (**2a−d**) was reacted with **1** in the presence of DBU (5 mol %) at 40 °C and an initial monomer concentration ($[M]_0$) of 0.7 mol L^{-1} (Scheme 2). After dissolution of the functionalized monomer (5−10 min), the solvent was removed under constant N_2 flow, resulting in bulk polymerization. After 30 min, the polymerization was quenched with excess acetic acid and an aliquot was removed to analyze conversion (^{1}H NMR). Each polymer was purified and characterized by ^{1}H NMR spectroscopy, size-exclusion chromatography with multiangle light scattering (SEC-MALS), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC).

Scheme 2. DBU-Catalyzed Tandem Functionalization/Ring-Opening Polymerization of Imidazolecarboxylate 1 with Renewable Alcohols 2a−2d



A slight excess of alcohol was used in order to control the amount of initiator present upon full substitution of the imidazolecarboxylate. For example, to target a monomer-to-initiator ratio (M/I) of 50, 1.02 equiv of alcohol was used (Table 1). Modifying the stoichiometry of **1**:**2a−2d** also allowed for different molar masses to be targeted. For example, a ratio of 1:1.01 (M/I = 100) afforded polymers with higher molar mass. The observed number-average molar masses (M_n) are generally in agreement with the theoretical values while maintaining dispersity ($Đ$) values below 2.0, even without rigorous drying and inert atmosphere control (i.e., noncontrolled polymerization conditions). Thus, molar masses can still reasonably be targeted without substantially sacrificing dispersity. Notably, **poly(3b)** exhibited higher M_n than expected at M/I = 100, which we attribute to the lower reactivity of the secondary alcohol initiating species **2b** when

Table 1. Synthesis of Homo- and Co-Polycarbonates via Tandem Functionalization/Ring-Opening Polymerization

ROH	M/I	conv[b] (%)	$M_{n,theor}$[c] (kDa)	$M_{n,SEC}$[d] (kDa)	$M_{w,SEC}$[d] (kDa)	$Đ$[d]
2a	50	72	19.4	1.7	1.8	1.06
2a	100	69	36.9	1.8	6.1	3.43
2b	50	81	10.0	9.6	16.7	1.74
2b	100	83	23.9	57.4	98.4	1.72
2c	50	91	16.9	2.3	4.2	1.80
2c	100	95	44.2	39.4	43.6	1.12
2d	50	78	8.7	6.9	11.9	1.72
2d	100	88	22.7	15.6	19.4	1.25
2a/2c[e]	100	70	30.7	6.6	26.0	3.96
2b/2c[e]	100	92	34.3	218	401	1.84

[a] Polymerization conditions: $[\mathbf{1}]_0 = 0.7$ mol L^{-1}, DBU (5 mol %), 40 °C, 30 min, constant N_2 flow (concentrated for bulk polymerization). [b] Determined by ^{1}H NMR spectroscopy. [c] Based on measured monomer conversion. [d] Determined by SEC-MALS (THF). [e] $f_{a/b}/f_c$ = 50/50 (**2c** used in slight excess as initiating alcohol); F_a/F_c = 41/59; F_b/F_c = 38/62.

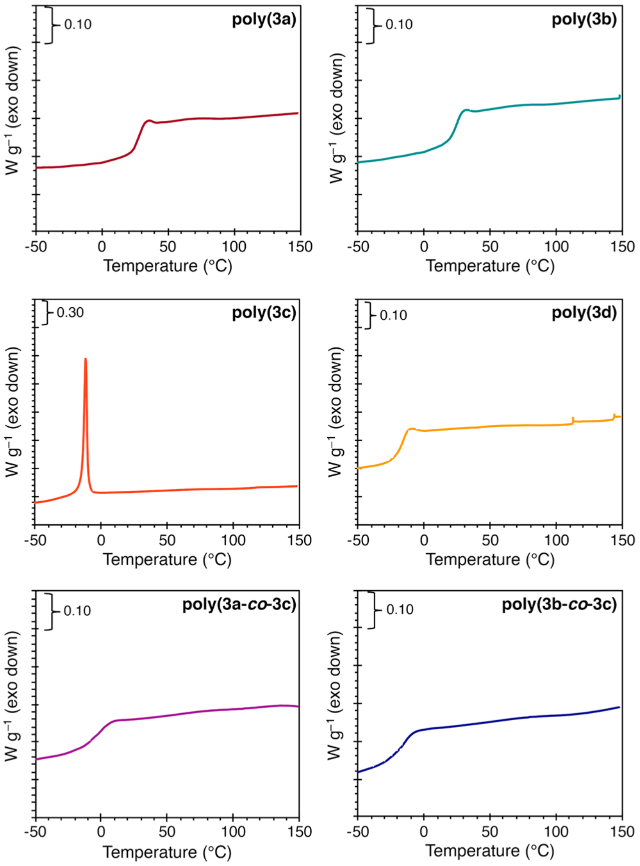
compared with primary alcohols **2a**, **2c**, and **2d**. This is evidenced by unreacted **2b** in the crude aliquot taken after polymerization (^{1}H NMR). Conversely, the molar mass of **poly(3a)** was lower than the theoretical value in both cases; moreover, a high molar mass shoulder was observed by SEC-MALS for the M/I = 100 sample. We hypothesize that propagation of **3a** is hindered because of steric accessibility and chain mobility, especially after the polymerization is concentrated.

The conversion from functionalized monomers **3a–d** to **poly(3a–d)** was generally high (69–95%). Regardless of initiating alcohol, we observed full consumption of the imidazolecarboxylate in all cases. We also identified a terminal hydroxyl group via acetylation of **poly(3a–d)** (^{1}H NMR). The polymerization can easily be performed on multigram scale [2.5 g, **poly(3c)**, M/I = 50]; additionally, the imidazole byproduct and catalytic DBU can be removed with an acidic resin (see SI), reducing the need for wasteful purification techniques. This strategy enables expeditious polycarbonate synthesis, especially since isolation of functionalized monomers is unnecessary.[24,25]

In order to better understand the tandem process, we monitored the reaction of **1** with **2d** at lower concentration (0.2 mol L^{-1}) and temperature (rt) (^{1}H NMR), which revealed the formation of **3d** *in situ* followed by polymerization (Figure S1). We observed evidence of oligomer formation before full consumption of **1**, which is likely due to the establishment of the monomer–polymer equilibrium [i.e., **3d** ⇌ **poly(3d)**].[33] Oligomer formation was also observed at 0 °C within 1 h, though to a lesser degree than at room temperature (16% at 0 °C vs 29% at rt) (Figure S2).

We then synthesized several statistical copolymers, demonstrating polymers with tailored properties may be designed with this tandem method. A total M/I of 100 and a feed ratio of 50/50 was targeted for copolymers of **2a**/**2c** and **2b**/**2c** (Table 1). The incorporation of each pendant group agreed well with the feed ratio (F_a/F_c = 41/59; F_b/F_c = 38/62). The molar mass and dispersity also followed what was observed during homopolymerization of the sugar-derived monomers. For example, the glucose-containing copolymer exhibited a lower molar mass than the theoretical M_n, with a broad distribution due to a high molar mass shoulder. The high conversion and incorporation of **3a** ($F_{3a}/f_{3a} \times 100 = 82\%$) further supports our hypothesis that steric bulk and chain mobility hamper homopropagation of **3a**. The isosorbide-containing copolymer exhibited a molar mass much higher than the theoretical value, again due to a portion of unreacted **2b** that resulted in a higher effective M/I ratio.

The thermal properties of the (co)polycarbonates were probed by TGA and DSC. Each of the homopolymers demonstrated thermal stability up to ~200 °C (see SI), which is in accordance with other APCs.[10] We observed glass transition temperature (T_g) values for **poly(3a)** and **poly(3b)** of 27 and 24 °C, respectively (Figure 1). No T_g was observed for **poly(3c)** down to −50 °C and **poly(3d)** showed a T_g of −18 °C; however, **poly(3c)** exhibited a T_m of −12 °C, likely as result of side chain crystallization.[51] The thermal properties of **poly(3c)** and **poly(3d)** are comparable to the analogous acrylic polymers reported in the literature.[51,52] Conversely, the observed T_g values for sugar-derived **poly(3a)** and **poly(3b)** were much lower than their analogous polyacrylates,[36,37,45] likely as a result of greater chain flexibility of the TMP-derived



	T_g (°C)	T_m (°C)
poly(3a)	27	–
poly(3c)	n.o.	−12
poly(3a-co-3c)	−1	–

	T_g (°C)	T_m (°C)
poly(3b)	24	–
poly(3d)	−18	–
poly(3b-co-3c)	−14	–

Figure 1. DSC thermograms of **poly(3a–d)**, **poly(3a-*co*-3c)**, and **poly(3b-*co*-3c)**. Samples were annealed, cooled to −50 °C, and heated to 150 °C at a rate of 10 °C min^{-1}.

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polycarbonate backbone. The statistical copolymers exhibited intermediary T_g values, demonstrating that tailored thermal properties can be achieved with this synthetic strategy [**poly(3a-*co*-3c)** = −1 °C, **poly(3b-*co*-3c)** = −14 °C].

Lastly, the chemical recyclability of **poly(3a−d)** was examined. Each homopolymer was diluted to 0.2 mol L^{-1} in acetonitrile and heated to 90 °C in the presence of DBU (5 mol %) for 24 h. Quantitative RCDP yielded cyclic carbonate **1−OH** and alcohols **2a−2d** (Figure 2). Previous studies report isolation of the functionalized cyclic carbonate upon depolymerization of the TMP-derived polycarbonates; however, those pendant groups were linked with less labile bonds (e.g., ether, carbon−carbon).[29−33]

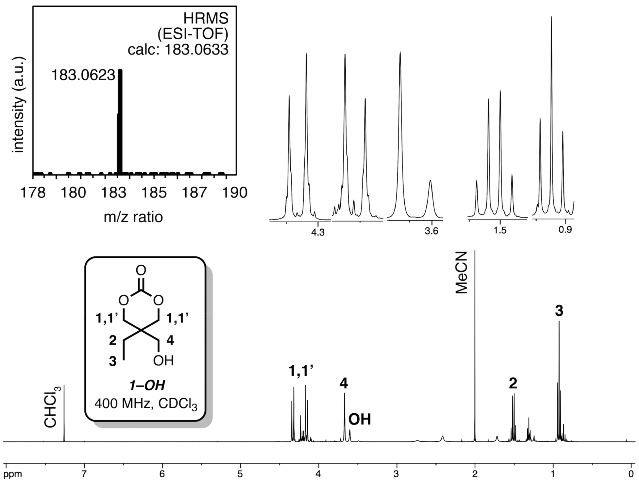
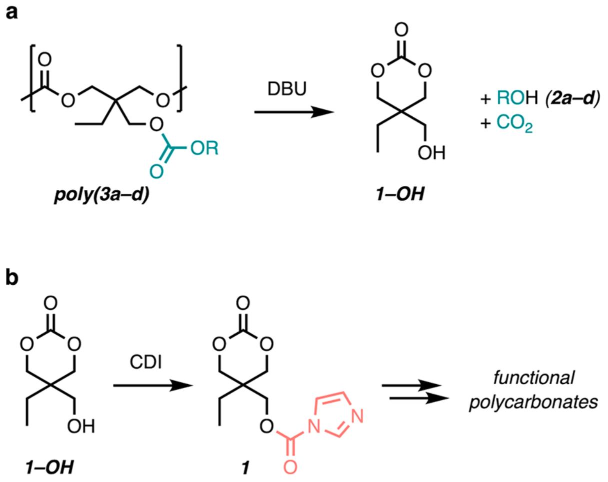


Figure 2. ^1H NMR spectrum (400 MHz, $CDCl_3$) and HRMS (ESI-TOF) (*inset*) of chemically recycled **1−OH**.

Decarboxylation of the pendant group is presumed to undergo a hydrolytic mechanism because of adventitious water (Scheme 3a), comparable to DBU-catalyzed alcoholysis of waste polycarbonates.[53] We explored several other amine bases (imidazole, triethylamine, tetramethylpiperidine) as well as lower temperature (40−60 °C) to keep the pendant groups intact, but incomplete depolymerization was observed (<30%) and decarboxylation was still evident. Thus, we proceeded with DBU at higher temperature since the fully depolymerized mixture could be separated for reuse via installation of the imidazolecarboxylate on **1−OH** to afford **1** with quantitative conversion, enabling further tandem functionalization/ROP (Scheme 3b). We are currently probing alternate chemical recycling methods in order to retain the pendant group upon RCDP, removing additional input of CDI, and creating a more ideal circular economy.

Scheme 3. Chemical Recycling of Poly(3a−3d) and Refunctionalization of 1−OH



In summary, we have presented a rapid, one-pot synthesis of functional polycarbonates derived from renewable alcohols. This simple tandem strategy eliminates the need for rigorous purification and specialized equipment. Moreover, statistical copolymers can be accessed via this tandem polymerization strategy, and the (co)polycarbonates exhibit a wide range of thermal properties. We demonstrated a circular polymer economy via chemical recycling to a cyclic monomer precursor and subsequent functionalization to the reactive monomer. Ongoing efforts are aimed at expanding the scope of renewable pendant groups, studying the thermomechanical properties of the materials, and investigating alternate depolymerization methods. We believe this work may stimulate development of sustainable APCs with a circular polymer economy aimed at eliminating plastic waste streams.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.0c00747.

> General experimental protocols; preparation and characterization of small molecules and polymers (^1H and ^{13}C NMR, HRMS, SEC-MALS); polymer thermal characterization (TGA, DSC); chemical recycling procedure and characterization (^1H NMR, HRMS); SI references; copies of NMR spectra (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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