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CO_2-sourced α-Alkylidene Cyclic Carbonates: A Step Forward in the Quest for Functional Regioregular Poly(urethane)s and Poly(carbonate)s.

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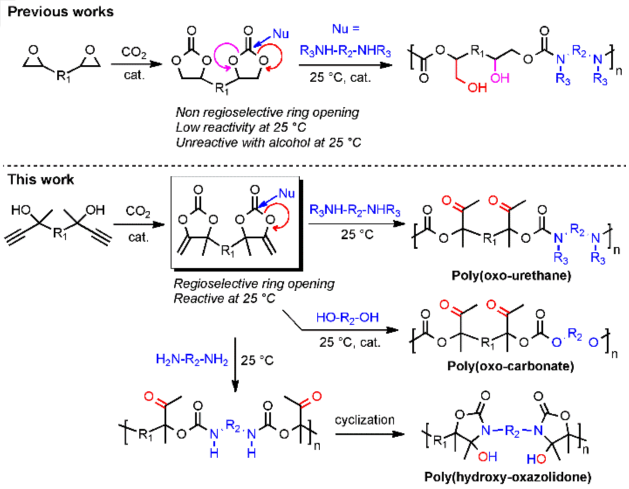
Abstract: We describe a robust platform for the synthesis of a large diversity of novel functional CO_2-sourced polymers by exploiting the regio-controlled and site selective ring-opening of α-alkylidene carbonates by various nucleophiles. The remarkable reactivity of α-alkylidene carbonates is dictated by the exocyclic olefinic group that selectively orients the cyclic carbonate ring-opening with the formation of an enol species. The polyaddition of CO_2-sourced bis-α-alkylidene carbonates (bis-αCCs) with primary and secondary diamines provides novel regioregular functional poly(urethane)s. The reactivity of bis-αCCs is also exploited for producing new poly(β-oxo-carbonate)s by organocatalyzed polyaddition with a diol. All polyadditions were feasible under ambient conditions. This synthesis platform provides new functional variants of world-class leading polymers families (polyurethanes, polycarbonates) and valorises CO_2 as a chemical feedstock.

Making plastics more sustainable by valorizing CO_2 as a cheap, inexhaustible and renewable feedstock imposes itself as a strategic driver for developing future low carbon footprint materials. Beside its direct copolymerization with epoxides or oxetanes that essentially leads to polycarbonates and poly(ether-*co*-carbonate) polyols[1], CO_2 can be converted by transformations into polymerizable building blocks.[2] This second route is highly seducing as it potentially allows broadening the scope of polymers that could be produced from CO_2. To date, five-membered cyclic carbonates (5CCs) prepared by the catalyzed CO_2/epoxide coupling[3] represent some of the most important CO_2-sourced synthons for the production of important polymers, mainly poly(β-hydroxyurethane)s (PHUs) and poly(carbonate)s (PCs). PHUs are synthesized by the polyaddition of bis-cyclic carbonates (bis-5CCs) and diamines.[4] Due to the poor reactivity of the five-membered cyclic carbonate, this aminolysis reaction is however slow, and suffers from the absence of regiocontrol that leads to a mixture of regioisomers with primary and secondary alcohols (Scheme 1).[4d-5] Moreover, side products such as urea, oxazolidones or decarboxylated adducts are most often generated during the polymerization, preventing high monomer conversion and/or high molar mass PHUs to be easily achieved.[6] Lately, intensive research was devoted to explore strategies that facilitate the 5CC aminolysis, notably by introducing some activating substituents[5,7] on the 5CC ring and/or by employing organocatalysts.[8] Although some of them were efficient in accelerating the PHU formation, the two regioisomers were still formed and most of the previous side reactions are still observed. Moreover, the inertness of 5CC towards alcohols avoids the preparation of PCs by polyaddition of bis-5CCs and diols under mild conditions. PCs can only be prepared by ring-opening polymerization of 5CC in the presence of suitable catalysts.[9] Regiocontrol in the ring-opening is of paramount importance because it affects some crucial properties of the final polymer, such as their glass and melting temperatures in polycarbonates and polyesters for instance.[10] Search for CO_2-sourced bis-cyclic carbonates that are able to be copolymerized in a regioselective manner with both diols and diamines under mild conditions remains an important bottleneck for the facile production of advanced CO_2-sourced polymers.

In this paper we engineered a versatile and robust process to access to a large diversity of novel regioregular hydroxyl- or oxo-functional polymers by exploiting easily customizable CO_2-sourced bis-(α-alkylidene cyclic carbonate)s (bis-αCCs). Regio-controlled copolymerizations of these new monomers with diamines or diols are facile and produce novel families of poly(urethane)s or poly(carbonate)s under ambient conditions (25°C, ambient atmosphere) (Scheme 1).



Scheme 1: Conceptual routes for regioregular functional CO_2-sourced poly(urethane)s and poly(carbonate)s.

We have designed two symmetrical CO_2-sourced bis-α-alkylidene cyclic carbonates (bis-αCCs), one with internal exocyclic olefins (C1) and the other one, with external ones (C2) (Scheme 2). C1 was produced by chemo-selective palladium/silver promoted Heck coupling of 1,4-diiodobenzene with CO_2-sourced 4,4-dimethyl-5-methylene-1,3-dioxolan-2-

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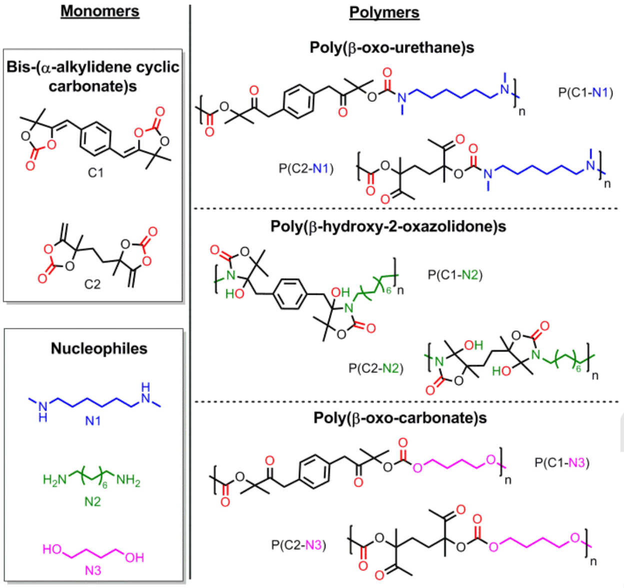
Supporting information for this article is given via a link at the end of the document one (DMACC) according to a previously reported procedure (see ESI1, Scheme S1).[11] The novel compound C2 was synthesized by the carboxylative coupling of bis-alkynol with CO_2 (see ESI2, Scheme S2). The selection of these bis-αCCs was motivated by the presence of exocyclic olefinic groups that enhance the reactivity of cyclic carbonates against various nucleophiles (such as amines and alcohols) with the selective formation of one regioisomer. The driving force for this site-selective and regio-controlled ring-opening of these cyclic carbonates relies on the formation of an enol species that rapidly rearranges into a more stable β-keto tautomer (ESI3, Scheme S3).[12]



Scheme 2: Structures of the monomers and polymers.

These unique characteristics of α-alkylidene carbonates were ascertained by comparative kinetic studies of model reactions between a model α-alkylidene cyclic carbonate, DMACC, or a conventional 5CC, propylene carbonate (PrC), with a primary (1-heptylamine) or secondary amine (*N*-methylbutylamine), or a primary alcohol (butane-1-ol) (Figure 1a). DMACC was formed by the catalyzed coupling of CO_2 with 2-methyl-3-butyn-2-ol according to a reported procedure[13] (ES1, Scheme S1). Figure 1 compares all results of kinetics of reactions carried out in dimethylformamide under ambient conditions. When reacted with 1-heptylamine, DMACC was rapidly converted and selectively produced the corresponding hydroxy-oxazolidone with a conversion of 90% within 45 min. This product results from the ring-opening by the primary amine with the formation of the enol species that rapidly rearranged into the more stable β-keto tautomer (β-oxo-urethane), followed by an intramolecular cyclization (Figure 1b). The structure of the product was confirmed by ^{1}H- and ^{13}C-NMR analyses of the product collected at the end of the reaction (ESI3.1, Fig. S13-S16), and the selectivity of the reaction was demonstrated by the absence of any other side product. Under identical conditions, less than 5% of PrC was reacted, and only 10% of PrC was converted after 2h of reaction into two β-hydroxy-regioisomers with a primary to secondary alcohol selectivity of 66:33 attesting for the absence of regiocontrol (ESI4.1, Fig. S25-S27). The same trend was observed when comparing the reactivity of DMACC and PrC with *N*-methylbutylamine (ESI3.2, Fig. S17-S20 and ESI4.2, Fig. S28-S29, respectively), although the reactions are slower in both cases. The acyclic β-oxo-urethane is selectively formed from DMACC (ESI3.2) whereas only <2mol% PrC are converted into the corresponding hydroxy-urethane regioisomers (ESI4.2). Neither PrC nor DMACC reacted with butane-1-ol at 25°C. However, DMACC was selectively forming the corresponding acyclic β-oxo-carbonate by reaction with butane-1-ol in the presence of 2.5mol% DBU as organocatalyst (reaction complete after 24h), whereas only <2mol% PrC did react under identical conditions (ESI3.3, Fig. S21-S24 and ESI4.3, Fig. S30-S31, respectively).

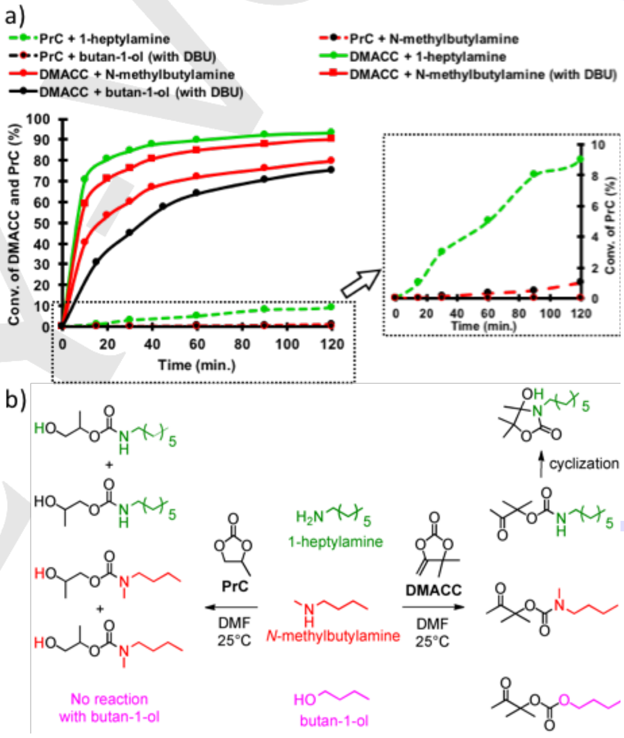


Figure 1: a) Time-conversion curves of 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one (DMACC) or propylene carbonate (PrC) with 1-heptylamine, N-methylbutylamine or butan-1-ol in DMF (1M) under ambient conditions, with or without DBU as catalyst (2.5mol%) (inset: zoom for the reaction profiles for PrC with 1-heptylamine, N-methylbutylamine and butan-1-ol (the latter with DBU); b) Reaction schemes and products formed under ambient conditions in DMF without DBU.

Based on these regioselective reactions on model DMACC, we first considered the polyaddition of bis-αCCs with equimolar amount of a secondary diamine, *N,N'*-dimethyl-1,6-hexanediamine (N1, Scheme 2) in equimolar amount in $CHCl_3$ ([bis-αCCs] and [N1] = 0.5 M) under ambient conditions. Poly(β-oxo-urethane)s with carbonyl groups within the main polymeric backbone are expected to be formed from bis-αCCs bearing internal exocyclic olefin (C1) whereas poly(β-oxo-urethane)s with pendent β-oxo groups should be formed from bis-αCCs bearing external exocyclic olefin (C2) (Scheme 2).

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C1 copolymerized with N1 with the formation of poly(oxo-urethane)s with weight average molar mass (Mw) of 5600 and 9500 g/mol after 3 h and 24 h, respectively (Table 1, entries 1-2). Under similar experimental conditions, no polymer was collected from C2 and N1 after 3h and only oligomers with a molar mass of 4300 g/mol were obtained after 24 h (Table 1, entries 7-8). Importantly, the substitution of $CHCl_3$ for DMF as solvent strongly accelerated the polymerization with a clear increase of the molar mass between 3 and 24 h of reaction (Table 1, entries 3-4, 9-10) and the formation of a high molar mass polymer from C1 (Mw = 40000 g/mol) after 24h. An unprecedented high molar mass polymer (Mw = 87000 g/mol) was collected from C1 after only 3h by adding DBU to boost the reaction (Table 1, entry 5).

Table 1: Poly(ß-oxo-urethane)s, poly(ß-hydroxy-2-oxazolidone)s, and poly(ß-oxo-carbonate)s prepared under ambient conditions: reaction conditions and molecular characteristics.

Poly(ß-oxo-urethane)s

Entry	Polymer	Solvent	Cat.^{d}	t [h]	M_n [g/mol]^a	M_w [g/mol]^a	Conv. CC [%]^b	$Đ^a$
1	P(C1-N1)	$CHCl_3$	-	3	3400	5600	N.d.	1.64
2	P(C1-N1)	$CHCl_3$	-	24	5000	9500	92.6	1.90
3	P(C1-N1)	DMF	-	3	4500	11000	92.0	2.45
4	P(C1-N1)	DMF	-	24	13500	40000	97.2	2.96
5	P(C1-N1)	DMF	DBU	3	20000	87000	97.7	4.35
6	P(C1-N1)	DMF	DBU	24	25000	73000	99.0	2.92
7	P(C2-N1)	$CHCl_3$	-	3	-	-	N.d.	-
8	P(C2-N1)	$CHCl_3$	-	24	2700	4300	91.9	1.59
9	P(C2-N1)	DMF	-	3	2000	3000	85.4	1.50
10	P(C2-N1)	DMF	-	24	5000	7000	95.5	1.40
11	P(C2-N1)	DMF	DBU	3	5000	7500	98.3	1.50
12	P(C2-N1)	DMF	DBU	24	11000	16000	99.0	1.45

Poly(ß-hydroxy-2-oxazolidone)s

	Polymer	Solvent	Cat.	t [h]	M_n [g/mol]	M_w [g/mol]	Conv. CC [%]	Đ
13	P(C1-N2)	DMF	-	3	22000	77000	99.0	3.50
14	P(C1-N2)	DMF	-	24	-	-	-	-
15	P(C2-N2)	DMF	-	3	11000	15000	N.d.	1.37
16	P(C2-N2)	DMF	-	24	21500	31000	97.8	1.44

Poly(ß-oxo-carbonate)s

	Polymer	Solvent	Cat.	t [h]	M_n [g/mol]	M_w [g/mol]	Conv. CC [%]	Đ
17	P(C1-N3)	$CHCl_3$	DBU	24	3000	5500	90.8	1.83
18	P(C1-N3)	DMF	DBU	24	-^{c}	-^{c}	70.0	-
19	P(C2-N3)	$CHCl_3$	DBU	24	13000	17500	96.1	1.35
20	P(C2-N3)	DMF	DBU	24	17000	25000	99.2	1.47

[a] determined by SEC in DMF/LiBr eluent using PMMA standards for calibration. Representative SEC chromatograms are in ESI5 (Fig. S32-S36) [b] conversion in cyclic carbonate determined by ^1H NMR in $CDCl_3$ or DMF-d_7 [c] M_n and M_w values are out of calibration. [d] 5 mol% of DBU. N.d. not determined.

By analogy with the DBU catalyzed aminolysis of 5CC with amines,[8b] DBU is expected to act as an hydrogen bond acceptor that activates the secondary amine and facilitates the ring-opening of bis-αCCs. The same accelerating effect was also noted for C2 but in a lesser extent (Table 1, entries 11-12). It has to be noted that all molar mass determinations by size exclusion chromatography (SEC) analysis were carried out on crude products in order to avoid any fractionation of the polymer during precipitation that would increase further the molar mass. SEC chromatograms of polymers produced in $CHCl_3$, DMF or in DMF with DBU are shown in ESI5, Fig. S32-36. The activation of the polymerization by DMF vs $CHCl_3$, and by DBU was also evidenced on the model reactions (Figure 1) with no noticeable influence on the selectivity of the reactions. All these results also suggest that C1 is more reactive than C2 due to the conjugation of the exocyclic olefin to the aromatic ring that further increases its reactivity.

The structure and regioregularity of the poly(oxo-urethane)s were investigated by ^1H and ^{13}C-NMR spectroscopies on purified products, and all assignments were in agreement with the polymer structures. For the polymer produced from C1, ^1H NMR spectrum (Figure 2b) shows a peak characteristic of a methylene in α position of both an aromatic ring and a ketone group (δ = 3.75 ppm) and ^{13}C NMR spectrum highlights new resonances of the β-oxo group at 207 ppm and the urethane carbonyl group at 155 ppm (ESI5, Fig. S37b). Identical observations pervade for poly(β-oxo-urethane)s synthesized from C2. ^1H-NMR characterizations confirmed the formation of only one type of regioregular chains with pendant oxo groups by the presence of a singlet at 2.11 ppm typical of a methyl group in α position of a ketone (ESI5, Fig. S38b). ^{13}C NMR analysis evidenced resonance of the carbonyl groups of urethane linkage at 154 ppm and oxo group at 207 ppm (ESI5, Fig. S39b). Interestingly, whatever the chemical structure of bis-αCC, no evidence of structural defects such as β-hydroxy urethanes are observed at least within the limit of NMR, in agreement with the selectivity noted on model reactions (ESI3).

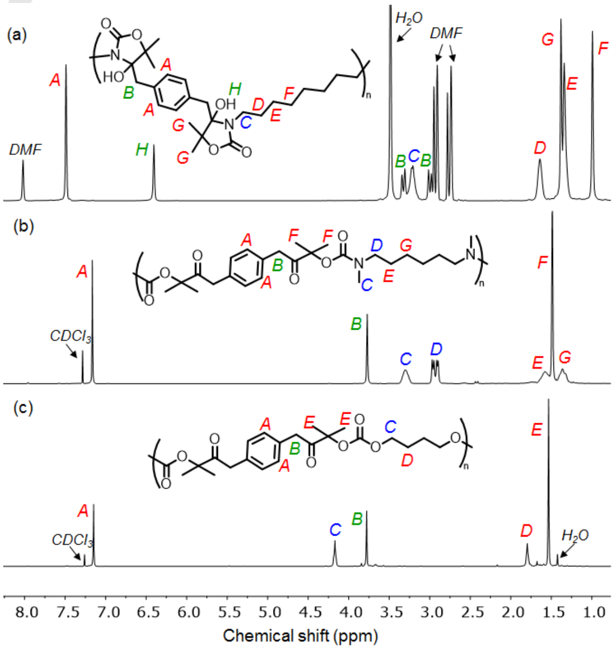

Figure 2. Stacked ^1H NMR spectra of P(C1-N2) (Table 1, entry 13) in DMF-d_7, P(C1-N1) (Table 1, entry 4) in $CDCl_3$ and P(C1-N3) (Table 1, entry 17) in $CDCl_3$ (after purification by precipitation).

Next, the polyaddition of bis-αCCs with a primary diamine, 1,8-octadiamine (N2), was considered in DMF ([bis-αCCs] and [N2] = 0.5 M). Under ambient conditions, C1 rapidly copolymerized with N2 with the formation of a polymer of 77000 g/mol after only 3 h of reaction and did not require the addition of DBU (Table 1, entry 13; ESI5, Fig. S34 for SEC). The primary diamine is more reactive than the secondary one, in line with model reactions (Figure 1a; ESI3.1). A swollen-jelly product was collected after 24h and revealed to be insoluble in most common organic solvents, probably as the result of its high molar mass (Table 1, entry 14). Under identical experimental conditions, the polymer formed from C2 remained soluble after 24h, with a molar mass increase from 15000 to 31000 g/mol after 3h and 24h, respectively (Table 1, entries 15-16; ESI5, Fig. S35 for SEC), in the absence of any catalyst.

As confirmed by ^{1}H-, ^{13}C- and COSY NMR analyses, poly(ß-hydroxy-2-oxazolidone)s were formed (Figure 2a; ESI5, Fig. S37a, S38a, S39a, S43-S44) as the result of the regioselective ring-opening of bis-αCCs with primary amine, followed by an intramolecular cyclization (Scheme S3). Importantly, by working at low temperature (25°C), no dehydration was observed, affording selectively novel regioregular poly(ß-hydroxy-2-oxazolidone)s. This reaction pathway doesn't only enable a facile access to functional polymers but it also provides the first alternative and safer route to conventional poly(oxazolidone)s that are currently produced from nasty di-isocyanates and di- or polyepoxides at high temperature (> 160°C). [14]

Some of the poly(β-oxo-urethane)s (P(C1-N1; Table 1, entries 4-6) and poly(β-hydroxy-oxazolidone)s (P(C1-N2); Table 1, entry 13) were characterized by a high dispersity (*Đ*= 2.9-4.3) that is much higher than the value expected for a polyaddition at full conversion (*Đ*=2).[15] These large dispersities are observed for the polymers of high molar masses, and seem thus to be linked to the high viscosity of the reaction medium.

The enhanced reactivity of bis-αCCs *vs* bis-5CCs was then exploited to produce novel regioregular poly(β-oxo-carbonate)s by reacting C1 or C2 with 1,4-butanediol in $CHCl_3$ ([bis-αCCs] and [N3] = 0.5 M). As primary alcohols are less reactive than amines, copolymerizations were performed using DBU as organocatalyst (5 mol%), no reaction being observed without catalyst, in line with the model reactions. By analogy with the ring-opening polymerization of cyclic esters, the catalytic activity of DBU probably arises from a complex interplay between the alcohol activation via H-bonding and nucleophilic activation of the cyclic carbonate, which facilitates the polyaddition of the diol onto bis-αCCs.[16] After 24h under ambient conditions, a polymer with a molar mass of 17500 g/mol was collected from C2, whereas it was lower from C1 (Table 1, entries 19 and 17). When carried out in DMF, only oligomers of low molar mass (out of SEC calibration) were formed from C1. This result contrasts with polymerizations involving diamines that were faster in DMF. This experiment is however reproducible and further experiments would be required to understand this observation. Importantly, under identical conditions, the polymer collected from C2 showed a molar mass as high as 25000 g/mol (Table 1, entry 20), a value never obtained by polyaddition of di-cyclic carbonates with diols at 25°C. SEC chromatograms for P(C2-N3) produced at 25°C with 5 mol% DBU in $CHCl_3$ or in DMF are shown in Fig. S36.

^{1}H- and ^{13}C-NMR analyses confirmed the structures of the poly(β-oxo-carbonate)s, one bearing keto groups within the main polymer backbone, and the other one with pendant ketone groups (Figure 2c; ESI 5, Fig. S37c, S38C, S39C, S42). The regioselectivity in the ring-opening of the cyclic carbonate is evidenced by the absence of any peak of defects such as β-hydroxyl carbonates or ether links that would result from different αCCs ring-opening pathways. To the best of our knowledge, this synthesis approach provides the first example of the preparation of polycarbonates of high molar mass by polyaddition of 5-membered bis-cyclic carbonates with diols under ambient conditions.

In conclusion, we have demonstrated for the first time that CO_2-sourced bis-α-alkylidene cyclic carbonates (bis-αCCs) are suitable building-blocks for the facile synthesis of a large diversity of unprecedented regioregular CO_2-sourced polymers under mild experimental conditions (25°C, ambient atmosphere, no purification/drying of the co-reagents). The remarkable reactivity of bis-αCCs towards primary/secondary amines and primary alcohols is dictated by the exocyclic olefinic group that selectively orients the cyclic carbonate ring-opening with the formation of an enol species. Novel regioregular poly(β-oxo-urethane)s, poly(ß-hydroxy-2-oxazolidone)s and poly(β-oxo-carbonate)s are therefore accessible by copolymerizing a single bis-αCCs with a secondary diamine, primary diamine or diol, respectively. This robust synthesis platform provides new functional variants of world-class leading polymers families (polyurethanes, polycarbonates) while valorising CO_2 as a chemical feedstock. It gives access to families of functional polymers that are not accessible by any other techniques. These novel conceptual routes will considerably diversify the range of functional polymers via the presence of the hydroxyl- or oxo- groups in the polymer backbone or by their post-modification. Our strategy opens avenues to new applications and novel research perspectives in the field of CO_2 transformation. The protocols for the synthesis of bis-αCCs have now to be optimized in order to facilitate the synthesis of the regioregular polymers at a large scale and at a competitive cost.

Experimental Section

Materials, experimental protocols and additional characterizations (SEC, ^{1}H-NMR, ^{13}C-NMR, COSY, HRMS) and schemes.

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Keywords: polymerization • regioselectivity • carbon dioxide • polyurethane • polycarbonate

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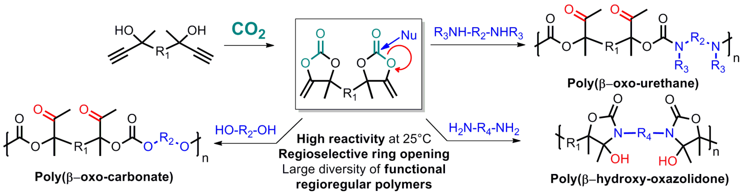
COMMUNICATION

The regio-selective ring-opening and high reactivity of bis(α-alkylidene carbonate)s with diamines and diols is exploited to provide a broad scope of functional regioregular polymers under ambient conditions. This robust synthesis platform provides new functional variants of world-class leading polymers families (polyurethanes and polycarbonates) and valorizes CO_2 as a chemical feedstock.



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CO_2-sourced α-alkylidene cyclic carbonates: a step forward in the quest for functional regioregular poly(urethane)s and poly(carbonate)s