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A SWITCHABLE DOMINO PROCESS FOR THE CONSTRUCTION OF NOVEL CO2-SOURCED SULFUR-CONTAINING BUILDING BLOCKS AND POLYMERS

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Abstract: α-Alkylidene cyclic carbonates (αCCs) recently emerged as attractive CO_2-sourced synthons for the construction of complex organic molecules. Herein, we report the transformation of αCCs into novel families of sulfur-containing compounds by organocatalyzed chemoselective addition of thiols, following a domino process that is switched on/off depending on the desired

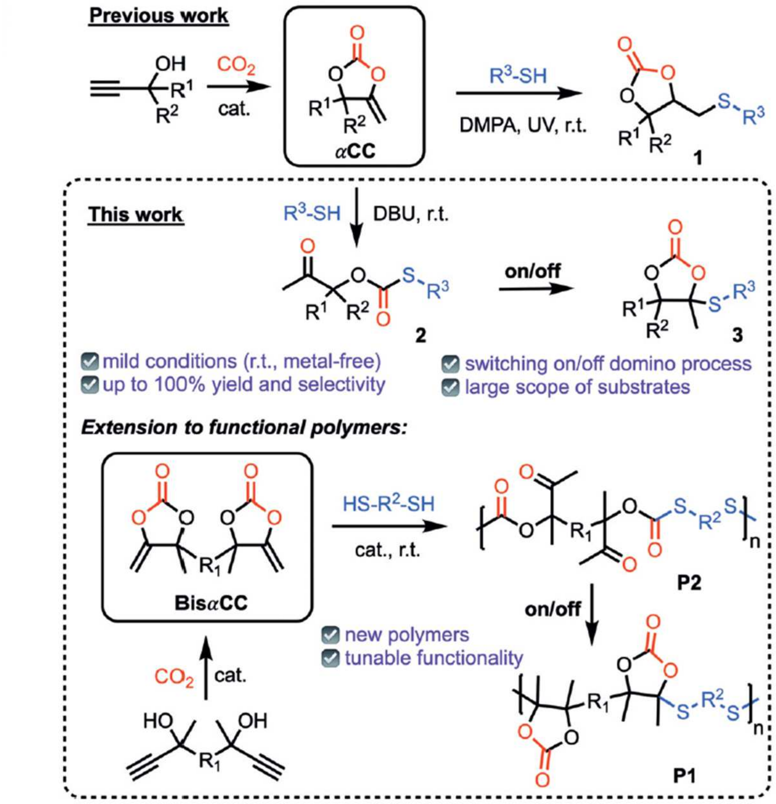
product. The process is extremely fast and versatile in substrate scope, provides selectively linear thiocarbonates or elusive tetrasubstituted ethylene carbonates with high yields following a 100% atom economy reaction, and valorizes CO_2 as a renewable feedstock. It is also exploited to produce a large diversity of unprecedented functional polymers. It constitutes a robust platform for the design of new sulfur-containing organic synthons and important families of polymers.

Keywords: carbon dioxide · domino process · organocatalysis · polymerization · synthetic methods

Carbon dioxide (CO_2) is an attractive abundant, safe, and renewable carbon source for the synthesis of organic cyclic carbonates. Today, these molecules find many and diverse applications as intermediates for fine chemical synthesis, electrolytes in Li-ion batteries, polar aprotic solvents, and monomers for the preparation of world-relevant polymers such as polycarbonates and polyurethanes.[1] The [3+2] cycloaddition of CO_2 to epoxides is the most popular and straightforward approach to five-membered cyclic carbonates[2] and, with the recent breakthroughs in their catalyzed transformations,[3] new CO_2-based organic molecules with a high degree of complexity are now accessible.[4]

α-Alkylidene cyclic carbonates (αCCs) are also rapidly emerging as another important class of industrially relevant CO_2-sourced cyclic carbonates.[5] They are produced by catalytic carboxylative coupling of propargylic alcohols with CO_2.[6] In contrast to the conventional five-membered cyclic carbonates, the presence of an exocyclic vinylic group facilitates the regioselective ring-opening of the cyclic carbonate by various nucleophiles, leading to new potentials in modern organic chemistry for the selective construction of novel molecules. The potential of αCCs for the preparation of new building blocks is enormous, but examples are still limited to ß-oxocarbamates, ß-oxocarbonates, ß-hydroxy-1,3oxazolidin-2-ones, α-hydroxyketones, and 3-dialkylaminooxazolidin-2-ones.[7,8] Recently, some of us demonstrated their utility for the synthesis of functional polyurethanes and polycarbonates, opening new perspectives for the design of advanced materials.[8]

The ring-opening of αCCs by thiols is potentially attractive to drastically enlarge the scope of these CO_2-based synthons but is surprisingly unexplored. It is expected to provide new relevant sulfur-containing products for both synthetic organic (e.g. thiocarbonates) and polymer chemistries (e.g. poly(monothiocarbonates)). Thiocarbonates are notably important synthetic intermediates in organic chemistry[9] and are used as protecting groups for thiols.[10] Poly(monothiocarbonate)s are attractive polymers for optic applications due to their high refractive index,[11] but also for water purification due to the strong binding ability of sulfur atom to metals.[12] Only one article reports the reaction of thiols with αCCs, and this only by UV-activated thiol–ene addition to yield the trisubstituted ethylene carbonate **1** (Scheme 1, previous work).[13]

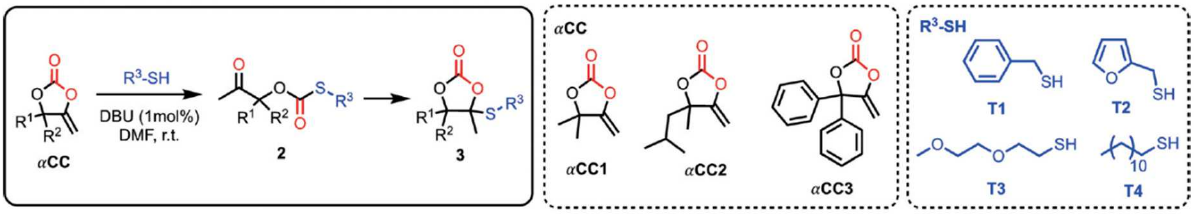


Scheme 1. Organocatalyzed addition of thiols to CO$_2$-sourced α-alkylidene cyclic carbonates and extension to functional polymers.

In this work, we investigated the organocatalyzed thiolation of αCCs as an unprecedented source of a large palette of novel sulfur-containing organic scaffolds and polymers. We discovered that 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) catalyzed the quantitative ring-opening of αCCs by various thiols, yielding either the ß-oxothiocarbonate **2** or the elusive tetrasubstituted ethylene carbonate **3** in high yield (Scheme 1). Product **2** was formed extremely rapidly at room temperature, whereas **3** resulted from a novel DBU-catalyzed reaction following an on/off switchable domino process. Finally, the reactions were implemented for the synthesis of novel families of sulfur-containing polymers, including unprecedented polycyclics, with functionalities that were modulated by switching on/off the domino process.

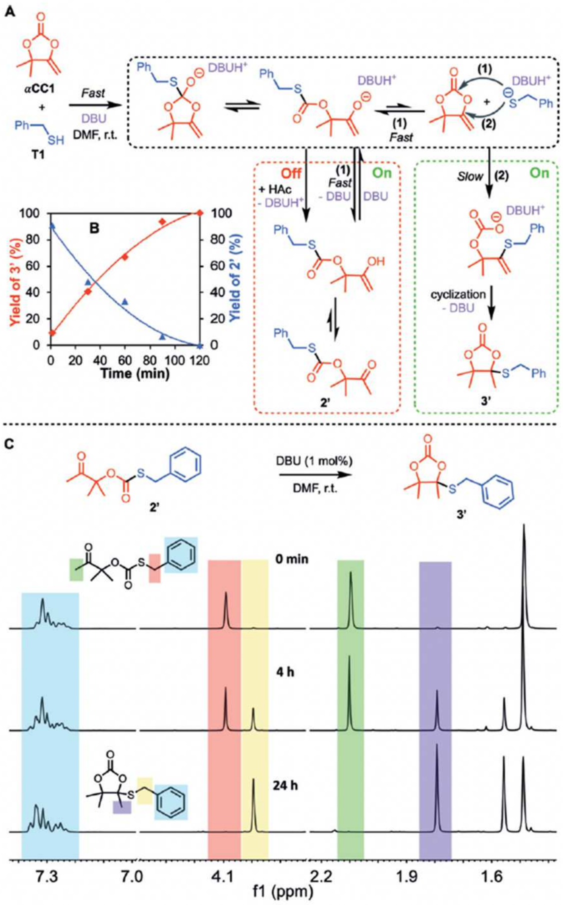
First, we tested the reaction of 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one (**αCC1**, Table 1, prepared by the catalyzed carboxylative coupling of CO2 to 2-methyl-3-butyn-2-ol) with benzylthiol **T1** under stoichiometric conditions at room temperature in DMF without any catalyst. No reaction was observed after 24 h. In order to favor the ring-opening, DBU was added, as it had been demonstrated to facilitate the ringopening of αCCs with alcohols.[8] Surprisingly, the unexpected tetrasubstituted ethylene carbonate **3** was quantitatively formed after only 2 h at low DBU loading (1 mol%) (Table 1, entry 2). This observation is in sharp contrast to the selective DBU-catalyzed ring-opening of αCCs by alcohols or secondary diamines that yielded ß-oxocarbonates or ß-oxourethanes, respectively.[8] Replacing **T1** with 2furanmethanethiol **T2** also resulted in the corresponding tetrasubstituted ethylene carbonate (Table 1, entry 10) and not the expected ß-oxothiocarbonate **2**. The DBU-catalyzed addition of **T1** to ***α*CC1** was then followed by ^{1}H and ^{13}C NMR spectroscopy to understand the origin of this product (Supporting Information (SI), Section 2.1). After only 1 min, the cyclic carbonate was fully converted into the expected ß-oxothiocarbonate **2** as the main product (91%), and the tetrasubstituted cyclic product **3** as the minor one (9%) (Table 1, entry 1). With increasing reaction time, **2** progressively disappeared in favor of **3**, suggesting that **3** resulted from a rearrangement of **2**. Product **3** was quantitatively recovered after 2 h, and its structure was confirmed by ^{1}H and ^{13}C NMR spectroscopy, HR-MS, and XRD of the recrystallized product (Scheme 2C; SI Section 4.1, Table S8).

Table 1: Scope of the organocatalyzed addition of thiols to αCCs.



Entry	αCC	Thiol	*t*	Conv$_{\alpha CC}$ [%][a]	Conv$_2$ [%][a]	Yield **2** [%][a]	Yield **3** [%][a]
1	**αCC1**	**T1**	1 min	>99	9.1	90.9	9.1
2			2 h	>99	100	0	100
3	**αCC2**	**T1**	1 min	>99	6.5	93.5	6.5
4			2 h	>99	64	36	64
5			24 h	>99	100	0	100
6	**αCC3**	**T1**	1 min	>99	3	97	3
7			2 h	>99	23	77	23
8			24 h	>99	47	53	47
9	**αCC1**	**T2**	1 min	>99	10.7	89.3	10.7
10			2 h	>99	100	0	100
11	**αCC2**	**T2**	1 min	>99	7.3	92.7	7.3
12			2 h	>99	66.6	33.4	66.6
13			24 h	>99	100	0	100
14	**αCC3**	**T2**	1 min	>99	5.3	94.7	5.3
15			2 h	>99	27	73	27
16			24 h	>99	56	44	56
17	**αCC1**	**T3**	1 min	>99	2	98	2
18			24 h	>99	58	42	58
19			24h[b]	>99	95	5	95
20	**αCC1**	**T4**	1 min	>99	1	99	1
21			24 h	>99	3	97	3
22			24 h[b]	>99	95	5	95

[a] Conversions and yields determined by ^{1}H NMR analysis. Conv$_{\alpha CC}$ = conversion of αCC; Conv$_2$ = conversion of **2**. [b] Reaction at 80 °C. Conditions: [αCC]/[thiol] = 1/1, αCC = 4 mmol, V_{DMF} = 1 mL, room temperature.



Scheme 2. A) Switchable domino process for the **αCC1**/**T1** reaction and B) plot of the yields of **2′** and **3′** vs. time; C) ^1H NMR study of the DBU-catalyzed rearrangement of **2′** into **3′**.

Various CO_2-sourced αCCs (Table 1) were tested to evaluate the influence of the steric hindrance selectivity of the reactions after both 1 min and 2 h of reaction. All αCCs were fully converted after only 1 min of reaction, demonstrating the impressively fast ring-opening of the cyclic carbonate (see SI Sections 2.1–2.6 for kinetics of reactions). The selectivity in **2** after 1 min slightly increased with the steric hindrance, from 91% for **αCC1**, to 93.5% for **αCC2**, and to 97% for the bulkier **αCC3** (entries 1, 3, and 6, Table 1). In parallel, the selectivity in **3** after 2 h drastically decreased with the steric hindrance from 100% for **αCC1**, to 64% for **αCC2**, and 23% for **αCC3** (entries 2, 4 and 7, Table 1). Bulky groups on αCCs therefore strongly slowed down the rearrangement of **2** into **3**. When the reaction time was extended to 24 h, **2** was fully converted into **3** for **αCC2**, compared to only 47% for the bulkiest **αCC3** (entries 5 and 8, Table 1). The same trend was noted for 2-furanmethanethiol **T2** (entries 9–16). The substrate scope was further extended by screening the reaction of **αCC1** with thiols **T3** and **T4** (entries 17–22, Table 1). The corresponding products **2** were produced in high yield (98–99%) after 1 min. Product **3** was formed in 58% yield with **T3** when the reaction time was extended to 24 h, whereas a trace amount of **3** was detected for **T4**. When the experiments were carried out at 80°C for 24 h, product **3** was almost quantitatively formed in both cases. For all experiments, the products **2** were collected at high yields provided that the reactions were quenched after 1 min by the addition of acetic acid (10–20 mol%) which switched off the domino process.

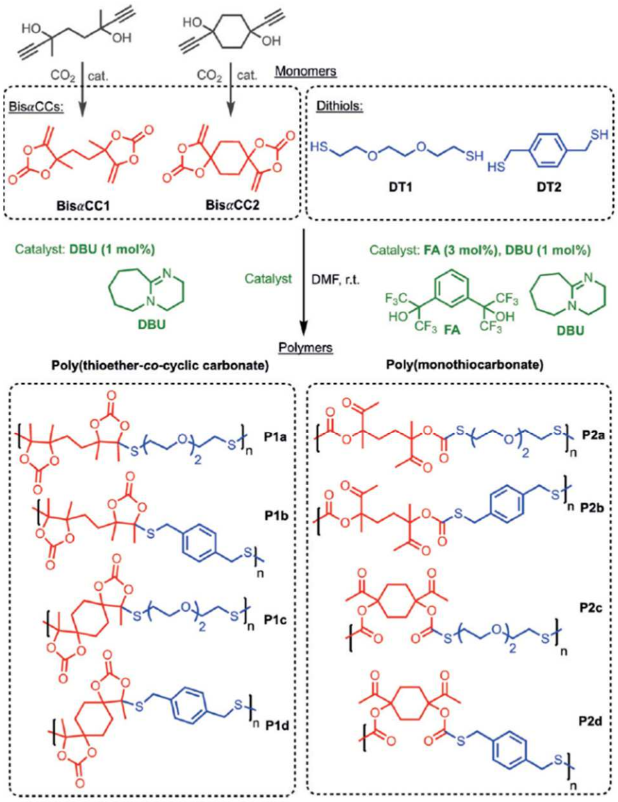
The course of this domino process, illustrated in Scheme 2A for the **αCC1/T1** reaction, is supported by computational investigations (see SI Section 3 for details). Nucleophilic attack of the thiolate on the carbonyl group provides the metastable five-membered intermediate that ring-opens into the thiocarbonate. Proton transfer from DBUH$^+$ gives the corresponding enol that tautomerizes into the thiocarbonate **2'**. This addition mode is very fast, as **2'** is formed in 91% yield in 1 min. The process is under equilibrium, as suggested by calculations that give a free energy barrier for the back reaction of only 22.5 kJmol^{-1} (SI Section 3, Figure S15).

Importantly, the thiolate is also able to add to the carbon of the C=C bond (addition pathway (2)). Computational investigations suggest that this addition mode provides the corresponding carbonate anion adduct, which follows an irreversible intramolecular cyclization, aided by DBUH$^+$, to provide the tetrasubstituted ethylene carbonate **3'** and the release of the catalyst. A concerted mechanism might also be involved (see SI Section 3) but at this stage, it is not possible to discriminate the two mechanisms. Addition pathway (2) (stepwise or concerted) is, however, slow (complete in 2 h, Scheme 2B) compared to pathway (1) as supported by the complete kinetic analysis of the reactions (SI Sections 2.1– 2.6), and in line with higher calculated free energy barriers for pathway (2) (SI Section 3). In contrast to the formation of **2'** which is reversible, the reaction pathway to **3'** is assumed to be irreversible. Therefore **2'** is progressively fully converted into **3'** in the presence of DBU, and this irreversible reaction is the main driving force for the cyclization. The formation of **2'** is therefore under kinetic control, whereas the formation of **3'** is under thermodynamic control. Importantly, when acetic acid was added after 1 min of reaction, the domino process was switched off. Since DBU is deactivated in this way, the reversible reaction does not occur and thus **3'** is not formed; only **2'** is collected. It is important to note that when alcohols were used instead of thiols in the presence of DBU under identical conditions, the domino process was not observed because the formation of the ß-oxocarbonate is irreversible since alcoholates are poorer leaving groups than thiolates. The same conclusion prevails for the reaction with amines.

To further support this proposed mechanism, the thiocarbonate **2'** was synthesized according to conditions established in Table 1, entry 1. The purified compound was then dissolved in DMF to which 1 mol% of DBU was added (see SI Section 2.7). The transformation of **2'** into **3'** was then monitored at room temperature by ^{1}H NMR spectroscopy. Scheme 2C shows that the thiocarbonate **2'** was progressively and fully converted into **3'** (SI Section 2.7). Also, a tiny amount of **αCC1** was detected (<1 mol%) when DBU was added to **2'** (Figure S13), supporting the reversibility of addition mode (1) (Scheme 2A). No reaction was observed in the absence of DBU. Importantly, when two different thiocarbonates were mixed in the presence of DBU, four tetrasubstituted ethylene carbonates were collected, attesting again for the reversibility of addition mode (1) (SI Section 2.8, Figure S14).

Screening experiments with other bases of different pK$_a$ have shown that superbases such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), and 1,5-diazabicyclo[4.3.0]non-5ene (DBN) also catalyzed the fast formation of the thiocarbonate **2'** (Table S9, SI Section 4.2). The rate of formation of **3'** was, however, slower than the reaction catalyzed by DBU. Weaker bases such as triethylamine (NEt3,), 1,4-diazabicyclo[2.2.2]octane (DABCO), and 4-dimethylaminopyridine (DMAP) presented poor catalytic activity for the formation **2'** and did not catalyze the synthesis of **3'**. Mechanistic studies are ongoing in our laboratories in order to explain this difference of behavior.

This switchable domino process was then evaluated for the construction of novel regioregular sulfur-containing polymers, by polyaddition of CO$_2$-sourced bis(α-alkylidene cyclic carbonate) (**BisαCC1** and **BisαCC2**, see SI Section 4.3 for their synthesis) with dithiols (**DT1** and **DT2**) (Scheme 3). The conversions, linkage selectivity, and molecular characteristics of the polymers are collected in Table 2. The DBU-catalyzed polyadditions provided a novel family of polymers, poly(thioether-*co*-cyclic carbonate)s **P1a–d** (Scheme 3). All polymerizations were remarkably highly selective for the thioether-*co*-cyclic carbonate linkages (≥ 99%) at room temperature (Figures S41–48), and high conversions were noted after 24 h at a low organocatalyst content (1 mol%) (entries 1, 4, 6, and 8, Table 2). Moderate to high number average molar masses (M_n) were noted, ranging from 15700 to 75300 gmol^{-1}. When the catalyst loading was increased, M_n also drastically increased from 15900 to 54000 gmol^{-1} for **BisαCC1/DT1** (entry 2, Table 2). For short reaction times (5 min instead of 24 h), the polymer obtained by polymerizing the **BisαCC1/DT1** mixture was the poly(monothiocarbonate) **P2a** (90% thiocarbonate linkages) (entry 1, Table S10). These linkages were progressively fully converted into thioether-*co*-cyclic carbonate moieties, providing **P1a**, after few hours (SI Section 4.4; entries 2 and 3, Table S10; Figures S36 and S37).



Scheme 3. Polyadditions of dithiols with bis(α-alkylidene cyclic carbonate)s.

Importantly, for the **BisαCC2/DT2** mixture, the polymerization was extremely fast with a conversion of 95% after only 1 min, and the selective formation of **P1d** (thioether-*co*-cyclic carbonate linkage of 95%) with a M$_n$ of 11800 gmol^{-1} (entry 1, Table S11). The rapid formation of this linkage is assumed to be the result of the high leaving group ability of the thiolate of **DT2** (Scheme 2A), which favors the cyclization. These DBU-catalyzed polymerizations thus demonstrate that the domino process is impressively fast and efficient, also for macromolecules. Although rapidly quenching the **BisαCC1/DT1** polyaddition with acetic acid provided the expected **P2a**, only low M$_n$ was obtained (4300 gmol@^{1}; entry 1, Table S10). In order to increase the M$_n$, the polymerization period was extended. However the domino process then occurred, leading to the transformation of the thiocarbonate linkages into thioether-*co*-cyclic carbonate ones (entries 2 and 3, Table S10).

With the objective to prepare polymers rich in thiocarbonate linkages and of reasonable M$_n$, we carried out the polymerizations in the presence of DBU (1 mol%) along with the fluorinated alcohol 1,3-bis(2-hydroxyhexafluoroisopropyl)benzene (**FA**, 3 mol%; Scheme 3, SI Section 4.6). Under these conditions, the series of poly(monothiocarbonate)s **P2a–c** with a selectivity in thiocarbonate linkages of 70– 82% were prepared after 24 h (entries 3, 5, and 7, Table 2). Interestingly, by tuning the **FA** content, we have access to polymers with intermediate linkages content and functionality (Table S12, Figure S41). No polymerization was observed in the absence of DBU, even with 3 mol% **FA**. Although further mechanistic investigations are required to understand the action mode of **FA**, this novel strategy towards regioregular poly(monothiocarbonate)s with a potentially large scope of structures (aliphatic and aromatic) is an attractive alternative to the conventional epoxide/COS ringopening copolymerization that gives access to aliphatic polymers with limited functions.[14]

Table 2: Scope of the step-growth polyaddition of CO$_2$-sourced bis(α-alkylidene cyclic carbonate)s with dithiols (see Scheme 3 for chemical structures).

Entry	BisαCC	Thiol	Catalyst	Cat. content [mol %]	Conv. [%]	M$_n$ [g mol^{-1}][a]	M$_w$ [g mol^{-1}][a]	$Đ$[a]	Polymer linkages[b]	T_g [°C][c]
1	**BisαCC1**	**DT1**	DBU	1	> 99	15 900	41 000	2.58	**P1a/P2a**: 99/1	45
2			DBU	5	> 99	54 000	105 000	1.94	**P1a/P2a**: 99/1	47
3			FA/DBU	3/1	95	9200	17 900	1.94	**P1a/P2a**: 18/82	9
4	**BisαCC1**	**DT2**	DBU	1	> 99	22 000	39 800	1.81	**P1b/P2b**: 99/1	126
5			FA/DBU	3/1	97	21 300	45 300	2.12	**P1b/P2b**: 19/81	61
6	**BisαCC2**	**DT1**	DBU	1	> 99	15 700	32 800	2.09	**P1c/P2c**: 99/1	76
7			FA/DBU	3/1	98	15 300	38 000	2.48	**P1c/P2c**: 30/70	32
8	**BisαCC2**	**DT2**	DBU	1	> 99	75 300	103 000	1.37	**P1d/P2d**: 99/1	–[d]
9			FA/DBU	3/1	95	20 800	42 700	2.05	**P1d/P2d**: 84/16	115

[a] Determined by size exclusion chromatography (SEC) in THF or DMF using PMMA for calibration. [b] Determined by ^{1}H NMR analysis in CDCl$_3$ or [D$_7$]DMF at room temperature. [c] Determined by dynamic scanning calorimetry (DSC). [d] T_g higher than the degradation temperature of the polymer; conditions: [BisαCC]/[DT] = 1/1, [BisαCC] = 2 M in DMF, room temperature, 24 h.

The type and content of polymer linkages has a drastic influence on the glass transition temperature (T_g) of the polymer. As a general trend, T_g significantly increased with the content of thioether-*co*-cyclic carbonate linkages. The most impressive effect on T_g was noted for the polymers prepared with **DT2**, for instance a change in T_g from 61°C to 126°C with 19 and 99% of thioether-*co*-cyclic carbonate linkages, respectively (entries 5 and 4, Table 2). Interestingly, when **BisαCC2** was used, unusual hindered polycyclic structures were incorporated within the polymer backbone with an impressive impact on the thermal properties of the polymer. High-T_g polymers were formed when **BisαCC2** was polymerized with **DT2** (entries 8 and 9, Table 2, Figure S49).

In summary, we have developed a novel robust switchable domino process for the construction of important sulfurcontaining organic molecules by the organocatalyzed chemoselective addition of thiols to CO_2-sourced α-alkylidene cyclic carbonates. Thiocarbonates but also challenging tetrasubstituted ethylene carbonates were selectively produced at high yield and at room temperature following a 100% atom economy reaction under stoichiometric conditions. This process was also exploited to prepare unprecedented regioregular sulfur-containing polymers. The "on-demand" modulation of the structure and functionality of the final product by the switching on/off of the domino process offers enormous synthetic possibilities for both organic chemistry and macromolecular engineering.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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