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A switchable domino process for the construction of novel CO$_2$-sourced sulfur-containing building blocks and polymers

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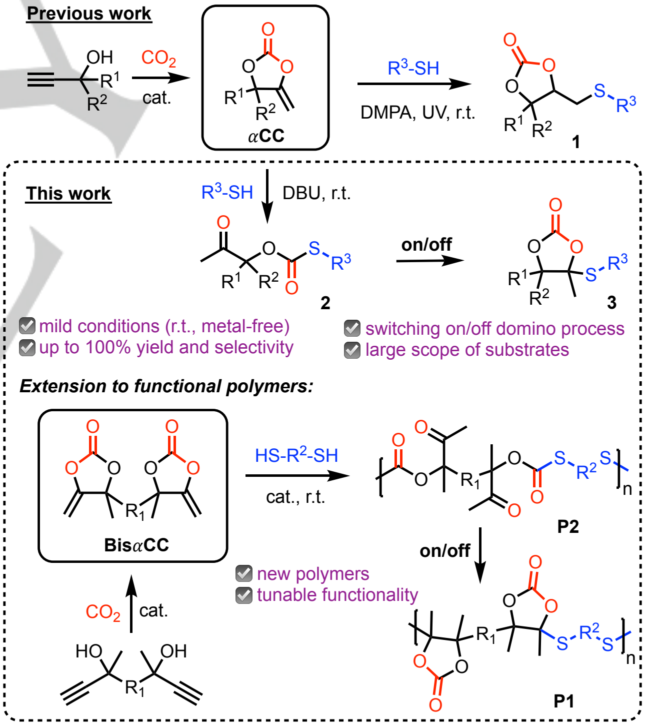
Abstract: α-alkylidene cyclic carbonates (αCCs) recently emerged as attractive CO$_2$-sourced synthons for the construction of complex organic molecules. Herein, we report the transformation of αCCs into novel families of sulfur-containing compounds by organocatalyzed chemoselective addition of thiols, following a domino process that is switched on/off depending on the desired product. The process is extremely fast, 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.

Carbon dioxide (CO$_2$) is an attractive abundant, safe and renewable carbon source for the synthesis of organic cyclic carbonates. Today, these molecules find large 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]

Beside, α-alkylidene cyclic carbonates (αCCs), are 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] Compared to the conventional 5-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 β-oxo-carbamates, β-oxo-carbonates, β-hydroxy-1,3-oxazolidin-2-ones, α-hydroxyketone or 3-dialkylaminooxazolidin-2-one.[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, but 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 DBU catalyzed the quantitative ring-opening of αCCs by various thiols, yielding either the β-oxothiocarbonate **2** or the elusive tetrasubstituted ethylene carbonate **3** at a high yield (Scheme 1). Product **2** was formed extremely rapidly at r.t., whereas **3** resulted from a novel DBU-catalyzed reaction following

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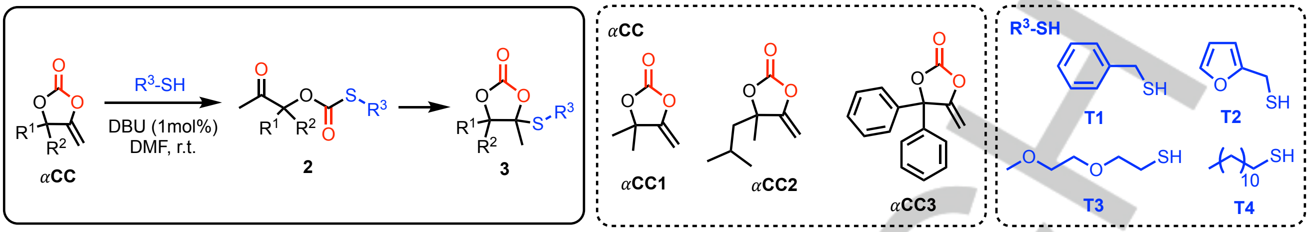
Table 1. Scope of the organocatalyzed addition of thiols to αCCs.



Entry	αCC	Thiol	Time	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			2h	> 99	100	0	100
3	αCC2	T1	1 min	> 99	6.5	93.5	6.5
4			2h	> 99	64	36	64
5			24h	> 99	100	0	100
6	αCC3	T1	1 min	> 99	3	97	3
7			2h	> 99	23	77	23
8			24h	> 99	47	53	47
9	αCC1	T2	1 min	> 99	10.7	89.3	10.7
10			2h	> 99	100	0	100
11	αCC2	T2	1 min	> 99	7.3	92.7	7.3
12			2h	> 99	66.6	33.4	66.6
13			24h	> 99	100	0	100
14	αCC3	T2	1 min	> 99	5.3	94.7	5.3
15			2h	> 99	27	73	27
16			24h	> 99	56	44	56
17	αCC1	T3	1 min	> 99	2	98	2
18			24h	> 99	58	42	58
19			24h[b]	> 99	95	5	95
20	αCC1	T4	1 min	> 99	1	99	1
21			24h	> 99	3	97	3
22			24h[b]	> 99	95	5	95

[a] conversions and yields determined by ^{1}H NMR. 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, r.t.

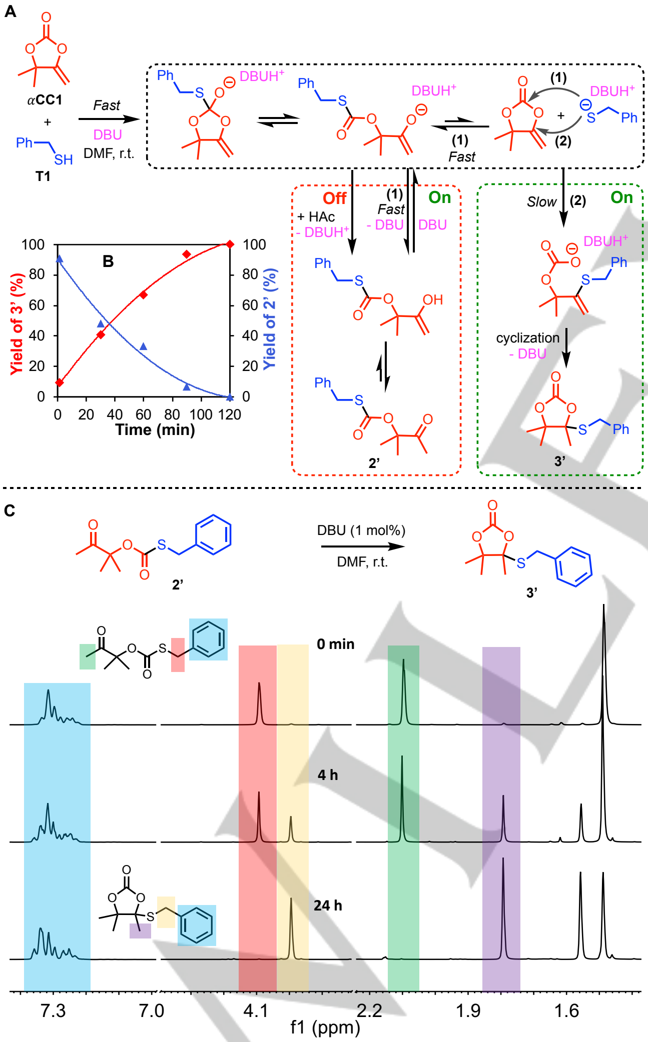
an on/off switchable domino process. Finally, the reactions were implemented for the synthesis of novel families of sulfur containing polymers, including unprecedented polycyclics, with functionalities that were modulated by switching on/off the domino process.

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 CO_2 to 2-methyl-3-butyn-2-ol) with benzylthiol **T1** under stoechiometric conditions at r.t. in DMF without any catalyst. No reaction was observed after 24h.

In order to favor the ring-opening, DBU was added, as it was demonstrated to facilitate the ring-opening 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 β-oxo-carbonates or β-oxo-urethanes, respectively.[8] Substituting **T1** for 2-Furanmethanethiol **T2** gave also the corresponding tetrasubstituted ethylene carbonate (Table 1, entry 10), and not the expected β-oxothiocarbonate **2**. The DBU-catalyzed addition of **T1** to **αCC1** was then followed by ^{1}H- and ^{13}C-NMR spectroscopy to understand the origin of this product (ESI 2.1). After only 1 min, the cyclic carbonate was fully converted into the expected β-oxothiocarbonate **2** as the main product (91%), and the tetrasubstituted cyclic product **3** as the minor one (9%) (Table 1, entry 1). With the reaction time, **2** progressively disappeared in favor of **3**, suggesting that **3** resulted from a rearrangement of **2**. Product **3** was quantitatively recovered after 2h, and its structure was confirmed by ^{1}H- and ^{13}C-NMR spectroscopies, HR-MS, and XRD of the re-crystalized product (Scheme 2C; ESI 4.1, Table S8).

Various CO_2-sourced αCCs (Table 1) were tested to evaluate the influence of the steric hindrance on the 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 ESI 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 2h 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**. By extending the reaction time to 24h, **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 scope of substrate 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 at a high yield (98-99%) after 1 min. Product **3** was formed at 58% yield with **T3** when the reaction time was extended to 24h, whereas trace amount of **3** was detected for **T4**. By carrying out the experiments at 80°C for 24h, 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%) that switched off the domino process.

The course of this domino process can thus be described as illustrated in Scheme 2A for the **αCC1/T1** reaction, and is supported by computational investigations (see ESI 3 for details).



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

Nucleophilic attack of the carbonyl group by the thiolate 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 at 91% yield in 1 min. The process is under equilibrium as suggested by calculations with a backward free energy barrier of only 22.5 kJ.mol^{-1} (ESI 3, Fig. 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 that 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 ESI 3) but at this stage, it is not possible to discriminate the two mechanisms. This addition pathway **(2)** (stepwise or concerted) is however slow (complete in 2h, Scheme 2B) compared to **(1)** as supported by all kinetics of reactions (ESI 2.1-2.6), and in line with higher calculated free energy barriers for pathway **(2)** (ESI 3). In contrast to the formation of **2'** that 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 one. Importantly, when acetic acid was added after 1 min of reaction, the domino process was switched off, as the result of the deactivation of DBU that avoids the reversible reaction to occur, and thus **3'** to be formed; only **2'** is collected. It is important to note that when alcohols were used in the presence of DBU instead of thiols under identical conditions, the domino process was not observed because the formation of the β-oxo-carbonate is irreversible as the result of the poorer leaving group ability of alcoholates compared to 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 ESI 2.7). The transformation of **2'** into **3'** was then monitored at r.t. by ^{1}H-NMR spectroscopy. Scheme 2C shows that the thiocarbonate **2'** was progressively and fully converted into **3'** (ESI 2.7). Also, tiny amount of **αCC1** was detected (<1mol%) when DBU was added to **2'** (Figure S13), supporting the reversibility of the addition mode **(1)** (Scheme 2A). No reaction was observed in the absence of DBU. Importantly, when two thiocarbonates of different structure were mixed in the presence of DBU, four tetrasubstituted ethylene carbonates were collected, attesting again for the reversibility of the addition mode **(1)** (ESI 2.8, Figure S14).

Screening experiments with other bases of different pKa have shown that superbases such as TBD, MTBD and DBN also catalyzed the fast formation of the thiocarbonate **2'** (Table S9, ESI 4.2). The rate of formation of **3'** was however lower compared to the reaction catalyzed by DBU. Weaker bases such as NEt$_3$, DABCO and 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.

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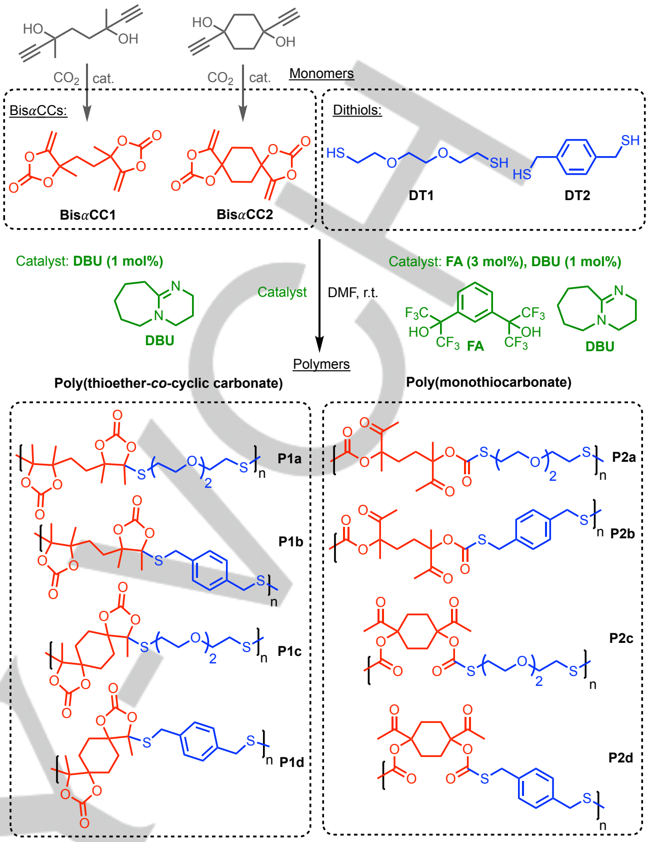
This switchable domino process was then evaluated for the construction of novel regioregular sulfur-containing polymers, by polyaddition of CO_2-sourced bis(α-alkylidene cyclic carbonate) (**bisαCC1** and **bisαCC2**, see ESI 4.3 for their synthesis) with dithiols (**DT1** and **DT2**) (Scheme 3). The 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) **P1a-d** (Scheme 3). All polymerizations were remarkably highly selective for the thioether-*co*-cyclic carbonate linkages (≥ 99%) at r.t. (Figure S41-48), and high conversions were noted after 24h at a low organocatalyst content (1 mol%) (entries 1, 4, 6, 8; Table 2). Moderate to high number average molar masses (M_n) were noted, ranging from 15,700 to 75,300 g/mol. By raising the catalyst content, M_n were also drastically increased from 15,900 to 54,000 g/mol for **bisαCC1**/**DT1** (entry 2; Table 2). For short reaction times (5 min instead of 24h), 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 (entries 2-3; ESI 4.4, Table S10, Figures S36-37).

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 11,800 g/mol (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) that favors the cyclization. These DBU catalyzed polymerizations thus demonstrate that the domino process is impressively fast and efficient, also on macromolecules. Although rapidly quenching the **bisαCC1**/**DT1** polyaddition by acetic acid provided the expected **P2a**, only low M_n was obtained (4,300 g/mol; entry 1, Table S10). In order to increase the M_n, the polymerization period should be extended. However the domino process then occurred, leading to the transformation of the thiocarbonate linkages into thioether-*co*-cyclic carbonate ones (entries 2-3, 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%) added with the fluorinated alcohol **FA** (1,3-bis(2-hydroxyhexafluoroisopropyl) benzene, 3 mol %; Scheme 3, ESI 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 24h (Entries 3, 5, 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**. Despite 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 ring-opening copolymerization that gives access to aliphatic polymers with limited functions.[14]



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

The type and content of polymer linkages has a drastic influence on the glass transition temperature (Tg) of the polymer. As a general trend, Tg significantly increased with the content of thioether-*co*-cyclic carbonate linkages. The most impressive effect on Tg was noted for the polymers prepared with **DT2**, for instance from 61°C to 126°C with 19 and 99% of thioether-*co*-cyclic carbonate linkages, respectively (entries 5 and 4, Table 2). Interestingly, by using **bisαCC2**, unusual hindered polycyclic structures were incorporated within the polymer backbone with an impressive impact on the thermal properties of the polymer. High Tg polymers were formed when **bisαCC2** was polymerized with **DT2** (entries 8-9, Table 2, Figure S49).

In summary, we have developed a novel robust switchable domino process for the construction of important sulfur-containing organic molecules by 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 r.t following a 100% atom economy reaction under stoechiometric 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 switching on/off the domino process offers enormous synthetic possibilities for both organic chemistry and macromolecular engineering.

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	Catalyst content (mol%)	Conv. (%)	M_n (g/mol)[a]	M_w (g/mol)[a]	$Đ$[a]	Polymer linkages[b]	Tg (°C)[c]
1	**BisαCC1**	**DT1**	DBU	1	>99	15900	41000	2.58	**P1a/P2a**: 99/1	45
2			DBU	5	>99	54000	105000	1.94	**P1a/P2a**: 99/1	47
3			FA/DBU	3/1	95	9200	17900	1.94	**P1a/P2a**: 18/82	9
4	**BisαCC1**	**DT2**	DBU	1	>99	22000	39800	1.81	**P1b/P2b**: 99/1	126
5			FA/DBU	3/1	97	21300	45300	2.12	**P1b/P2b**: 19/81	61
6	**BisαCC2**	**DT1**	DBU	1	>99	15700	32800	2.09	**P1c /P2c**: 99/1	76
7			FA/DBU	3/1	98	15300	38000	2.48	**P1c/P2c**: 30/70	32
8	**BisαCC2**	**DT2**	DBU	1	>99	75300	103000	1.37	**P1d/P2d**: 99/1	-[d]
9			FA/DBU	3/1	95	20800	42700	2.05	**P1d/P2d**: 84/16	115

[a]determined by SEC in THF or DMF using PMMA as calibration; [b]determined by ^{1}H-NMR in $CDCl_3$ or DMF-d_7 at rt; [c]determined by dynamic scanning calorimetry (DSC). [d]Tg higher than the degradation temperature of the polymer; Conditions: [bisαCC]/[DT] = 1/1, [bisαCC] = 2 M in DMF, r.t., 24h

Experimental Section

Experimental Details, supplementary characterizations and computational studies are provided in Supporting information

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

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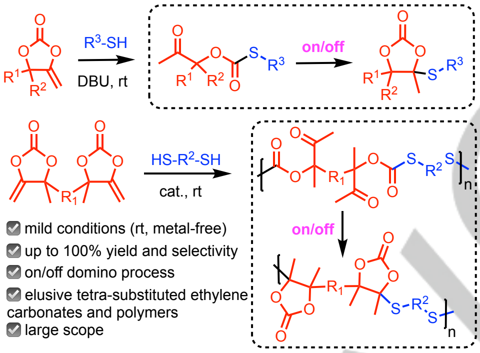
COMMUNICATION

The organocatalyzed chemoselective addition of thiols to α-alkylidene cyclic carbonates is fast and yields linear thiocarbonates or elusive tetrasubstituted ethylene carbonates with high yields by a switchable domino process. This robust synthetic method is also exploited for the facile construction of a large diversity of unprecedented sulfur-containing polymers.



☑ mild conditions (rt, metal-free)
☑ up to 100% yield and selectivity
☑ on/off domino process
☑ elusive tetra-substituted ethylene carbonates and polymers
☑ large scope

*Farid Ouhib, Bruno Grignard, Elias Van Den Broeck, André Luxen, Koen Robeyns, Veronique Van Speybroeck, Christine Jérôme, Christophe Detrembleur**

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A switchable domino process for the construction of novel CO_2-sourced sulfur-containing building blocks and polymers