Fast, regioselective aminolysis of tetrasubstituted cyclic carbonates and application to recyclable thermoplastics and thermosets

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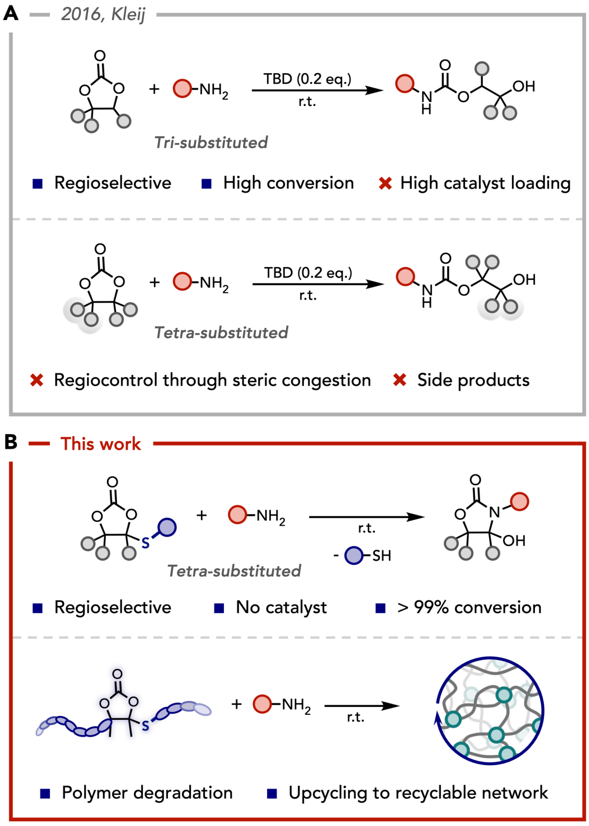
Abstract

Herein is overcome the long-standing challenge of the ring-opening aminolysis of CO$_2$-derived tetrasubstituted cyclic carbonates at room temperature (r.T) under catalyst-free conditions. Molecular design of the cyclic carbonate by substitution of an alkyl group by a thioether unlocks quantitative conversion at r.T and ensures total regioselectivity toward highly substituted oxazolidone scaffolds. An in-depth rationalization of the high reactivity of these cyclic carbonate structures and of the aminolysis reaction mechanism is provided by a computational study supporting experimental observations. The high efficiency of the reaction is then translated to the deconstruction of high-performance thermoplastics containing tetrasubstituted cyclic carbonate linkages to deliver building blocks that are re-used for designing recyclable thermosets bearing dynamic *N,S*-acetal linkages.

Introduction

Over the last decade, carbon dioxide (CO$_2$) has found value as a low cost and renewable resource to produce (commodity) chemicals or for designing complex macromolecular architectures[1–4]. Besides its direct copolymerization with epoxides into polycarbonates[2,5–7], CO$_2$ undergoes catalytic transformations into five-membered cyclic carbonates by coupling with epoxides[8–10] or vicinal alcohols[11–13]. Interestingly, these easily accessible 5-membered scaffolds offer many opportunities of post-modification for fine chemicals[14–16] (e.g. the preparation of carbamates by aminolysis) or serve as monomers in polymers synthesis (e.g. the production of isocyanate-free polyurethanes by copolymerization with polyamines)[17,18]. As most of the cyclic carbonates featured in organic transformations or polymer synthesis predominantly exhibit mono- or di-substitution, their aminolysis delivers two hydroxy-carbamate isomers due to the non-regioselective ring-opening of the cyclic carbonate. Some regioselectivity control is achieved by incorporating electron-withdrawing groups on the cyclic carbonates[19,20]. A full regiocontrol is only observed when introducing fluorine[21] or chlorine[22] atoms, or a neighboring cyclic carbonate with specific stereochemistry[23]. Besides this regioselectivity issue, the cyclic carbonates suffer from a poor reactivity at room temperature (r.T). Their aminolysis is thus accelerated by using catalysts[24,25] or amines of exacerbated reactivity.[26] Another option is to utilize 5-membered cyclic carbonates bearing exovinylene groups that are obtained by coupling CO_2 to propargylic alcohols. This class of highly reactive scaffolds are rapidly ring-opened by various nucleophiles in a regioselective manner, delivering regioregular products at r.T[27–31].

Densely substituted 5-membered cyclic carbonates of high complexity are now made available by various transformation modes of CO_2[32–39]. However, their aminolysis remains a challenge, rarely addressed in the literature. In 2016, Kleij reported the regioselective aminolysis of gem di- and tri-substituted cyclic carbonates at r.T in the presence of a high loading of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as organocatalyst (20 mol%)[40] (Scheme 1A). The steric congestion on one side of the cyclic carbonate was proposed to drive the selective bond scission[14,41]. The strategy was also extended to tetra-substituted cyclic carbonates with limited success, the reaction being extremely slow with the formation of side products. In 2018, some of us attempted the aminolysis of tetra-substituted cyclic carbonate-containing polymers using TBD as catalyst at 80 °C, affording only a low degree of conversion (23 %)[42].



Scheme 1. (A) Prior work on the aminolysis of densely substituted cyclic carbonates[40]. (B) This work: a sulfur substitution strategy for the full, regioselective aminolysis of tetra-substituted cyclic carbonates. The concept was extended to polymer degradation and upcycling into recyclable thermosets.

Herein, we resolve the longstanding challenge of the ring-opening of tetrasubstituted 5-membered cyclic carbonates. Through molecular engineering, we show that replacing an alkyl group of densely substituted ethylene carbonates by a thioether moiety imparts the cyclic compound with unprecedent reactivity, yet enabling their fast and regioselective aminolysis at r.T under catalyst-free conditions (Scheme 1B). This reaction yields a thiol and an oxazolidone, i.e. a five-membered cyclic carbamate template commonly found in bioactive molecules[43–47] and high-performance polyurethanes[48,49]. Then, we showcase the utility of this new chemistry to polymer upcycling. Two thermoplastics embedding tetrasubstituted thioether-containing cyclic carbonate linkages, designed to approach mechanical properties of commodity polyolefins, are deconstructed. In line with the circularity objectives of our modern society, the resulting decomposition products are revalorized into covalent adaptable networks.

We began our investigations by monitoring the aminolysis of a model conventional tetrasubstituted ethylene carbonate **4CC** (see SI Section 2 for synthetic procedures) with an excess of propylamine (3 eq.) at r.T in DMSO without any catalyst (Figure 1A). No reaction was observed after 24 h. Repeating the reaction at 120 °C left the reactants intact, underlying the inert nature of tetra-alkylated 5-membered cyclic carbonates in these conditions (Figures S9-10). Tetrasubstituted sulfur containing cyclic carbonates **4CCS** (Figure 1A) were then prepared to assess the influence of the substitution of an ethyl group by a thioether on the cyclic carbonate aminolysis. Two **4CCS** compounds were synthesized by the DBU-catalyzed addition of a CO_2-sourced α-alkylidene cyclic carbonate (4,4-dimethyl-5-methylene-1,3-dioxolan-2-one) with benzyl mercaptan (**4CCS-a**) or butanethiol (**4CCS-b**)[29] (see SI Section 2 for synthetic procedure). Impressively, both compounds reacted quantitatively with propylamine at r.T in DMSO under catalyst-free conditions, in stark contrast to **4CC**. Kinetic insights of the **4CCS** aminolysis were collected by monitoring the reaction under various operating conditions (i.e. type of solvent, content and nature of the amine) by ^{1}H NMR spectroscopy (see SI Section 4 for details). When **4CCS-a** or **4CCS-b** were simply mixed with 3 eq. of propylamine at r.T, reactions were fast, ending in only 2 h (Figure 1A), showing negligible influence of the thioether substituent on the ring-opening. Remarkably, the reactions were selective with the exclusive formation of a hydroxyoxazolidone **1** and a thiol **2**. The reaction performed well in other solvents such as acetonitrile or THF and were complete in 2 h, however with a slightly lower rate than in DMSO (Figure S15).

The propylamine equivalence was found to affect the kinetics as illustrated for the aminolysis of **4CCS-a** (Figure S18). Decreasing the amine content below 3 eq. readily slowed down the reaction. The reaction using 2 eq. of amine was complete within 24 h, while with 1 eq. it became slow with a moderate **4CCS-a** conversion of 70% after 24 h. This was attributed to the quenching of the amine by the released acidic thiol, forming the amine-thiol salt adduct[50]. With 5 eq. of amine, the reaction was strongly accelerated and complete in only 30 min.

The scope of amines was then extended to bulky benzylamine or cyclohexylamine. As expected, the bulky groups on the amine somehow decreased the reaction rate. The reaction with benzylamine at r.T was complete within 24 h, while the reaction with cyclohexylamine reached a conversion of 96% after

24 h (Figure S19). The reaction of amines with **4CCS** demonstrated pleasing chemoselectivity toward primary amines, with tolerance of challenging functional groups such as secondary amines (Figure S22).

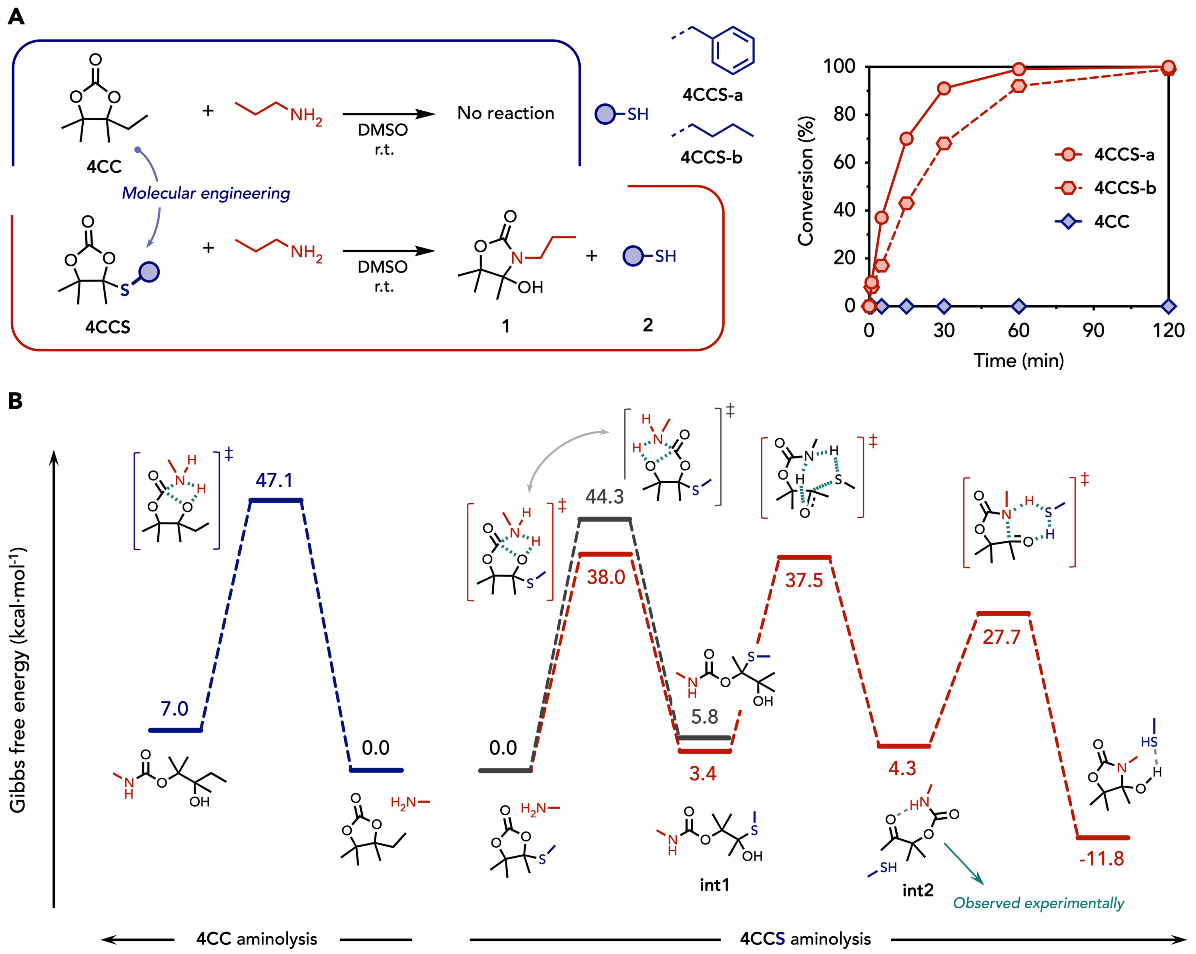


Figure 1. (A) Kinetic study on the aminolysis of **4CC** *vs* **4CCS**. (B) Energetics of the reaction pathways for **4CC** and **4CCS** determined by DFT.

DFT calculations were performed to unveil the increased reactivity of **4CCS** compared to **4CC**. Optimization and comparison of the two cyclic carbonate structures revealed a notable distinction in C-O bond lengths (Figure S23). While both bonds exhibited identical lengths in **4CC** (1.337 Å), the bond length in **4CCS** close to the sulfur atom side exceeded that on the opposite side (1.347 *vs* 1.334 Å). QTAIM and IGM analyses supported this observation, indicating asymmetric bond strength (see SI Section 5.1). Our experimental findings were further complemented by a detailed elucidation of the reaction mechanisms (see SI Sections 5.2-5.3 for details).

The ring-opening of **4CC** by the amine follows a well-established one-step mechanism involving the formation of a carbamate motif and the release of a tertiary alcohol[15,25], although it is thermodynamically disfavored by 7 kcal·mol^{-1} *vs* the reactants (Figure 1B, see Figure S25 for details). A striking difference was observed for **4CCS**, which ring-opening (C-O bond scission near S atom) was characterized by a lower energy barrier of 38.0 kcal·mol^{-1} compared to 47.1 kcal·mol^{-1} for **4CC** (Figure 1B). Interestingly, the ring-opening on the opposite side of the ring in **4CCS** exhibited a high energy barrier of 44.3

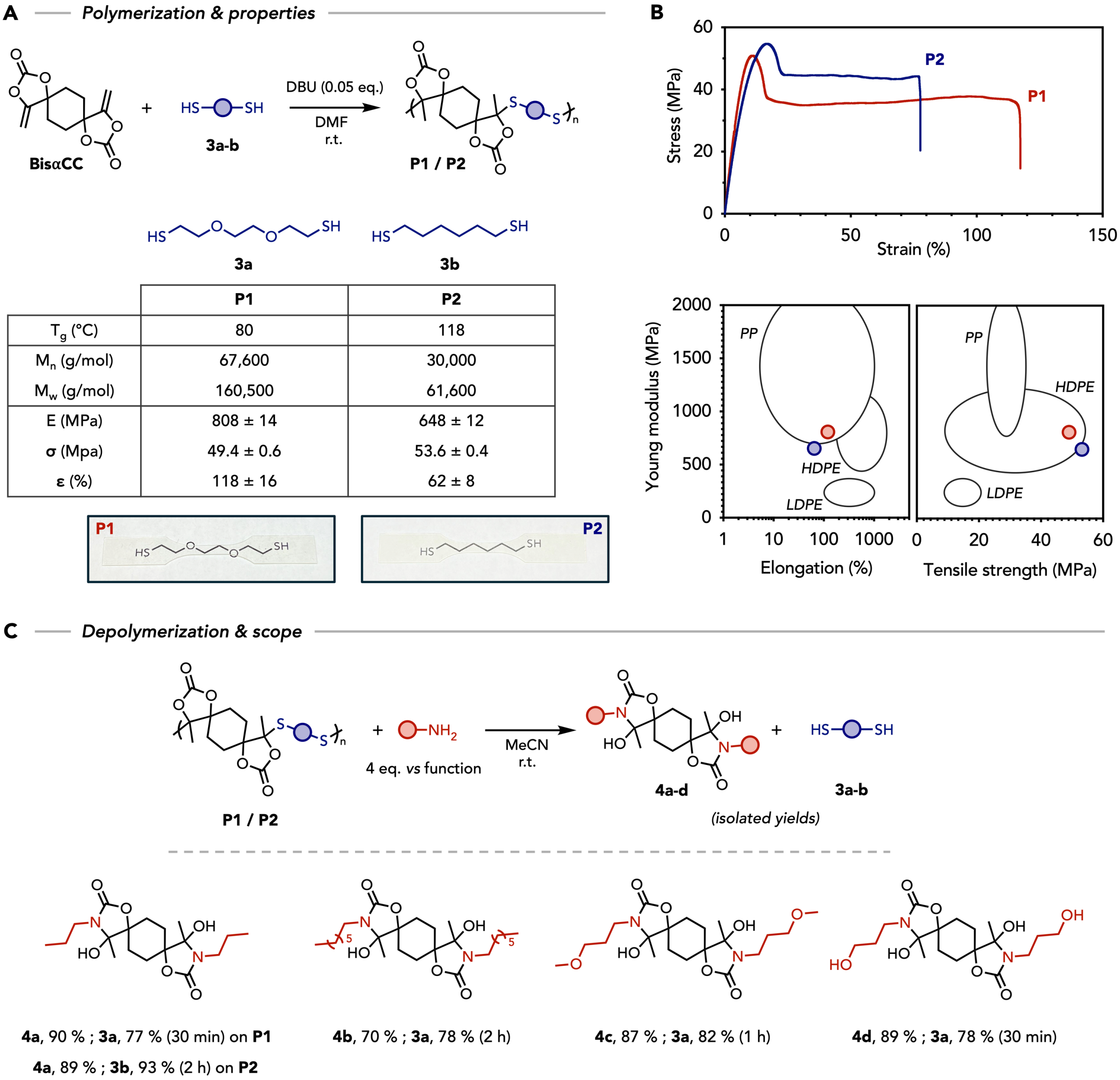
kcal·mol^{-1} and a product destabilization by 5.8 kcal·mol^{-1}, rendering this pathway thermodynamically and kinetically less favorable (Figure S26). This finding strongly supports the regioselective control exerted by the sulfur atom. Unexpectedly, the ring face of attack proved critical, with the amine preferentially approaching near the sulfur atom despite apparent steric hindrance (Figures S27-28). This is likely attributed to stabilizing interactions between the sulfur's lone pair and the H-N bond of the amine (Figures S29-30).

Aminolysis of **4CCS** proceeds through the addition of the amine onto the electrophilic carbonyl group. Two closely competing pathways can then occur depending on the nature of the concomitant proton transfer. The amine proton is (i) directly transferred to the neighboring oxygen atom, providing a hemithioacetal **int1**. The *oxo*-urethane **int2** is subsequently formed by the release of the thiol (Figure 1B). Alternatively, the amine proton is (ii) transferred to the leaving thiolate with concomitant ketone formation, therefore bypassing the second step of the mechanism to directly afford the *oxo*-urethane **int2** (Figure S31, **TS1'**). The final common step involves ring-closure of **int2** into the hydroxyoxazolidone **1** through intramolecular nucleophilic attack of the -NH- group onto the electrophilic ketone. Interestingly, this step is aided by the thiol acting as a proton relay (Figure S27). The low energy barrier for this step corroborates the experimental observations that the *oxo*-urethane **int2** was experimentally barely detectable by NMR during the reaction kinetics (Figures S13, S17).

Modelling the reaction with a second amine showed that all reaction steps barriers were lowered by several kcal·mol^{-1}, suggesting that multiple amine molecules might participate to the mechanism through proton relay effects (see SI Section 5.4). This supports the experiments showing that the rate of **4CCS** aminolysis was significantly increased when raising the amine content.

Overall, both experimental and computational studies demonstrated the profound impact of the sulfur atom on unlocking both reactivity and regioselectivity in densely substituted cyclic carbonates, without requiring any catalyst.

We then exploited these findings for the preparation of high-performance thermoplastics with controlled degradability, aligning with current sustainability objectives in material science.



	P1	P2
T_g (°C)	80	118
M_n (g/mol)	67,600	30,000
M_w (g/mol)	160,500	61,600
E (MPa)	808 ± 14	648 ± 12
σ (Mpa)	49.4 ± 0.6	53.6 ± 0.4
ε (%)	118 ± 16	62 ± 8

4a, 90 % ; **3a**, 77 % (30 min) on **P1**
4a, 89 % ; **3b**, 93 % (2 h) on **P2**

4b, 70 % ; **3a**, 78 % (2 h)

4c, 87 % ; **3a**, 82 % (1 h)

4d, 89 % ; **3a**, 78 % (30 min)

Figure 2. (A) Synthesis of polymers **P1-2** and (B) their mechanical properties as compared to polyethylene (PE) and polypropylene (PP) using Ashby plots[51]. (C) Polymer degradation using a scope of amines to provide **4a-d** and **3a-b**. Isolated yields and reactions time are provided.

Two highly substituted poly(cyclic carbonate-*co*-thioether)s were first synthesized by the r.T, DBU catalyzed step-growth polymerization of a CO_2-sourced spirocyclic bis(exovinylene cyclic carbonate) (**bisαCC**) with dithiols, i.e 2,2′-(Ethylenedioxy)diethanethiol (**3a**) and 1,6-Hexanedithiol (**3b**) (Figure 2a)[27,29,52]. The synthesis protocol was optimized to reach high molecular weight polymers and enhance the mechanical properties through chain entanglement (see SI Section 6 for details). After 24 h, the synthesis from **3a** and **3b** delivered polymer **P1** (M_w = 160,500 g·mol^{-1}) and polymer **P2** (M_w = 61,600 g·mol^{-1}), respectively. Once compression molded as dog bones (120 °C, 6 MT, 15 min for **P1**; 155 °C, 8 MT, 20 min for **P2**), both polymers were amorphous and highly transparent (Figure 2A). Despite their relatively similar chemical structure, they exhibited distinct T_gs, i.e. 80 °C for the more flexible ether-containing **P1** and 118 °C for **P2**. Both polymers were endowed with attractive mechanical properties, somehow lying between those of some grades of commodity HDPE and PP by displaying the low elongation of PP but a typical Young's modulus of HDPE materials (Figure 2B). Their tensile strength was however superior, reaching 53.6 MPa for **P2**. This underlines the potential of **P1** and **P2** to become easily recyclable substitutes to some polyolefins, which are particularly challenging to decompose/revalorize. Indeed, our facile cyclic carbonate aminolysis process was applied with success to the deconstruction of these thermoplastics **P1** and **P2**. For that purpose, **P1** and **P2** underwent total deconstruction at r.T in 30 min to 2 h with an excess of amines (Figure 2C) being either aliphatic (propyl- and heptyl-amine) or functional (3-methoxypropylamine and propanolamine). Bis(hydroxyoxazolidone) **4a-d** and the former dithiols **3a** or **3b** were collected as degradation products and easily isolated in high yields (up to 90% for the oxazolidone **4a-d** and up to 93% for the dithiols). The full characterization of the crude reaction media and the purified products is available in SI (Sections 7-8). It must be noted that the dithiols **3a** and **3b** were successfully recovered by conducting the reaction under inert atmosphere to prevent their oxidation into disulfide.

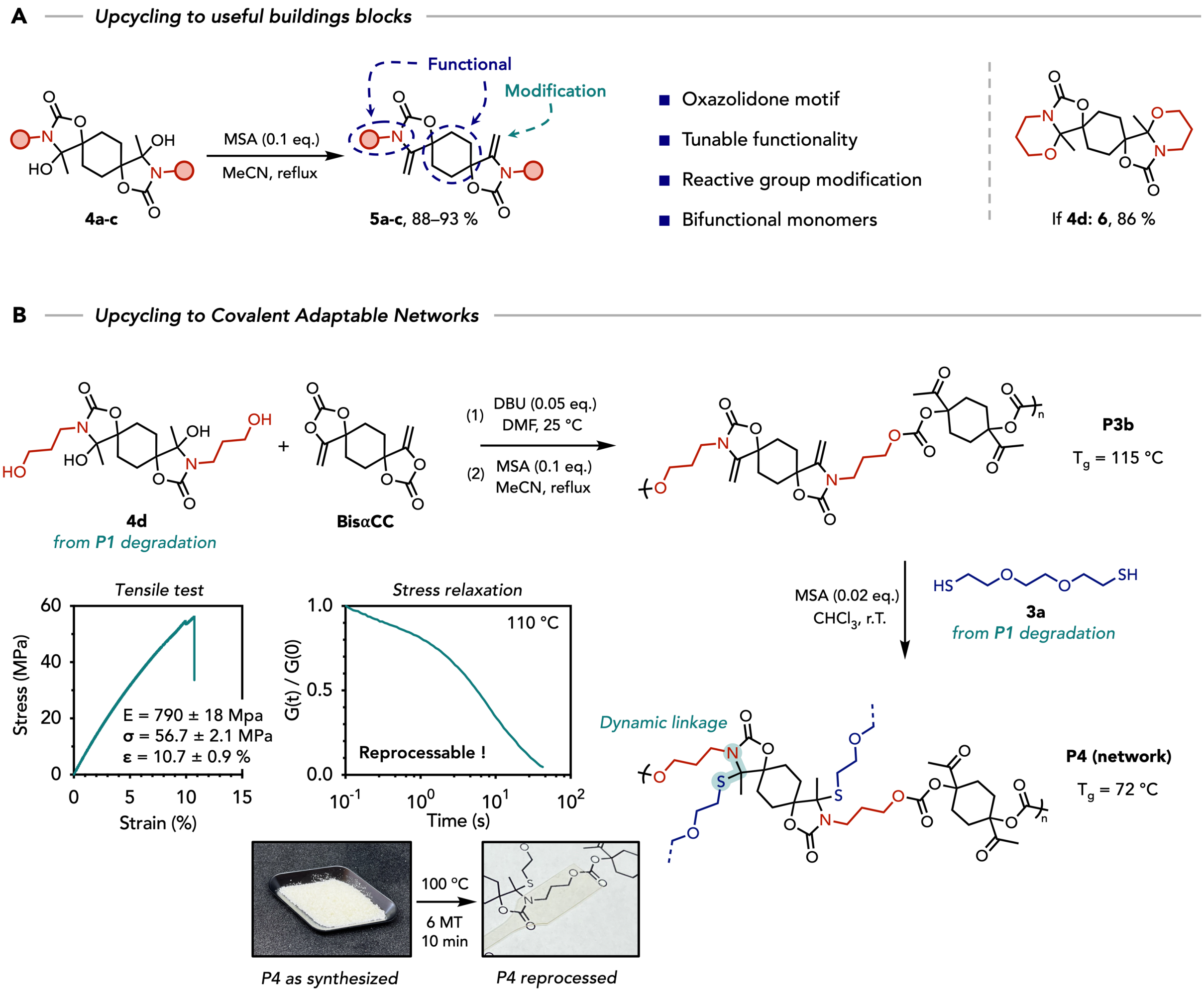


Figure 3 – (A) Dehydration of **4** into useful alkylidene scaffolds **5** and **6** (in the case of **4d**). (B) Upcycling of both **4d** and **3a** into a recyclable thermoset.

On the path to circularity, the revalorization of products **4a-d** and dithiols **3a** and **3b** into new molecules and/or polymeric materials was explored. Previously, we and others established that hydroxy-oxazolidones were easily and quantitatively dehydrated into the corresponding exovinylene oxazolidones[30,49,50]. Following an optimized protocol,[53] products **4a-c** were thus transformed into bis(alkylidene oxazolidone)s **5a-5c** with high isolated yields of 86 to 93% (Figure 3A, Figures S65-70). These compounds **5** are versatile building blocks as they can be finely tuned through the bisαCC structure and the selected amine. They also offer subsequent modification possibilities through the double bond (Figure 3A). The dual functionality of the herein isolated molecules also renders them ideal candidates as monomers. Notably, they can be exploited for the preparation of poly(*N,S*-oxazolidone)s covalent adaptable networks (CANs) by cationic thiol-ene with polythiols.[53] It is important to note that the dehydration of **4d** quantitatively yielded a six-membered cyclic adduct **6** similar to reported five-membered derivatives[54] (Figure 3A, complete characterization in Figures S71-72), likely due to a cascade ring-closure *via* alcohol-ene reaction into a cyclic *N,O*-acetal.

In an effort to repurpose the two post-degradation feedstocks (i.e. the oxazolidone and the thiol), we synthesized a polymer containing alkylidene oxazolidone linkages subsequently cross-linkable by the recovered thiol to obtain a CAN following the strategy described in Figure 3B. The bis(hydroxyoxazolidone) **4d**, containing primary alcohol functions, was reacted with virgin bisαCC to produce poly(hydroxyoxazolidone-*co*-carbonate) **P3a** (M_w = 22,000 g.mol^{-1}; Đ = 1.7) at r.T in the presence of DBU as catalyst (Figures S73-74). The polymer was quantitatively dehydrated into the alkylidene analog **P3b** in a cascade one-pot process by refluxing in acetonitrile with methane sulfonic acid as catalyst (MSA; 0.1 eq.) (see SI Section 10 for details, Figures S75-77). The CAN **P4** featuring dynamic *N,S*-oxazolidone functions was then easily fabricated by the r.T crosslinking of **P3b** with dithiol **3a** via the MSA (2 mol% *vs* oxazolidone functions) catalyzed cationic thiol-ene (see SI Section 11 for the detailed experimental procedure).

Successful thermoset formation was confirmed by ATR-IR analysis (Figure S78), a high gel content of 98.5 % in THF, and a low swelling ratio (2.5 %). The transparent thermoset exhibited the typical temperature response of highly dissociative dynamic networks with a loss of cross-link density above T_g (72 °C, Figure S79) and a flow transition at 129 °C as determined by a temperature sweep experiment (Figure S80)[55–57]. Stress relaxation experiments were also characterized by very short characteristic relaxation times (from around 2 min at 90 °C to few seconds at 125 °C; Figure S81) and were well represented by complex relaxation models (Figures S82-86 and related discussion), aligning with our previous work on *N,S*-oxazolidone CANs[53]. The mechanical properties were typical of highly cross-linked networks with a brittle fracture, and **P4** was characterized by Youngs' modulus and strength that were similar to **P1**/**P2** (Figure 3B and Figure S87). A full characterization of the thermoset and its dynamic behavior is found in SI Section 11.

In summary, we developed a facile, regioselective ring-opening aminolysis of CO_2-sourced tetrasubstituted cyclic carbonates at room temperature under catalyst-free conditions. Substitution of the ring with a sulfur atom not only enhanced the reactivity of the tetrasubstituted ethylene carbonate, but also ensured full regioselectivity in the ring-opening, yielding highly substituted oxazolidones. A thorough modelling study confirmed the significant impact of the sulfur atom on the chemical structure of the tetrasubstituted cyclic carbonate and unveiled the ring-opening mechanisms along with their energetics. This concept was applied to the degradation of thermoplastics embedding tetrasubstituted cyclic carbonate linkages, delivering oxazolidone scaffolds and thiols that were then reused in an open recycling loop for the facile construction of reprocessable covalent adaptable thermosets with dynamic *N,S*-acetal linkages. Besides opening many perspectives for the preparation of new organic synthons of the oxazolidone-type, this novel aminolysis process establishes as a new strategy to open highly substituted scaffolds and reinforces the importance of molecular design in achieving efficient and selective chemical transformations, of particular interest in organic and polymer chemistry.

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Notes

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