

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

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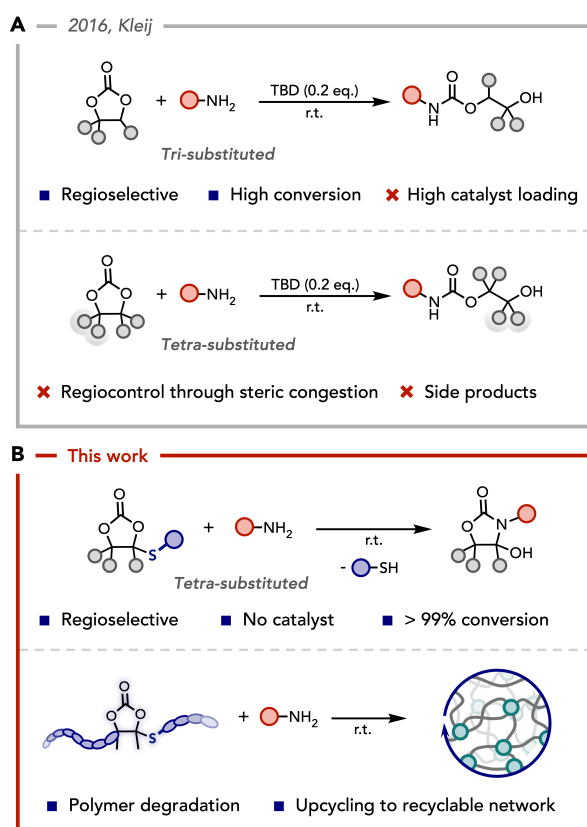
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Herein is overcome the long-standing challenge of the ring-opening aminolysis of CO₂-derived tetrasubstituted cyclic carbonates at room temperature (r.T) under catalyst-free conditions. Molecular design of the cyclic carbonate by substitution of an 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.

Over the last decade, carbon dioxide (CO₂) has found value as a low cost and renewable resource to produce (commodity) chemicals or for designing complex macromolecular architectures¹⁻⁴. Besides its direct copolymerization with epoxides into polycarbonates^{2,5-7}, CO₂ undergoes catalytic transformations into five-membered cyclic carbonates by coupling with epoxides⁸⁻¹⁰ or vicinal alcohols¹¹⁻¹³. Interestingly, these easily accessible 5-membered scaffolds offer many opportunities of post-modification for fine chemicals¹⁴⁻¹⁶ (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 fluorine²¹ or chlorine²² atoms, or a neighboring cyclic carbonate with specific stereochemistry²³. 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 CO₂ to propargylic alcohols. This class of highly reactive scaffolds are rapidly ring-opened by various nucleophiles in a regioselective manner, delivering regioregular (macro)molecules at r.T^{27–31}.

Densely substituted 5-membered cyclic carbonates of high complexity are now made available by various transformation modes of CO₂^{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 carbonates⁴⁰. (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 unprecedented 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 CO₂-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 ¹H 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 adduct⁵⁰. 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).

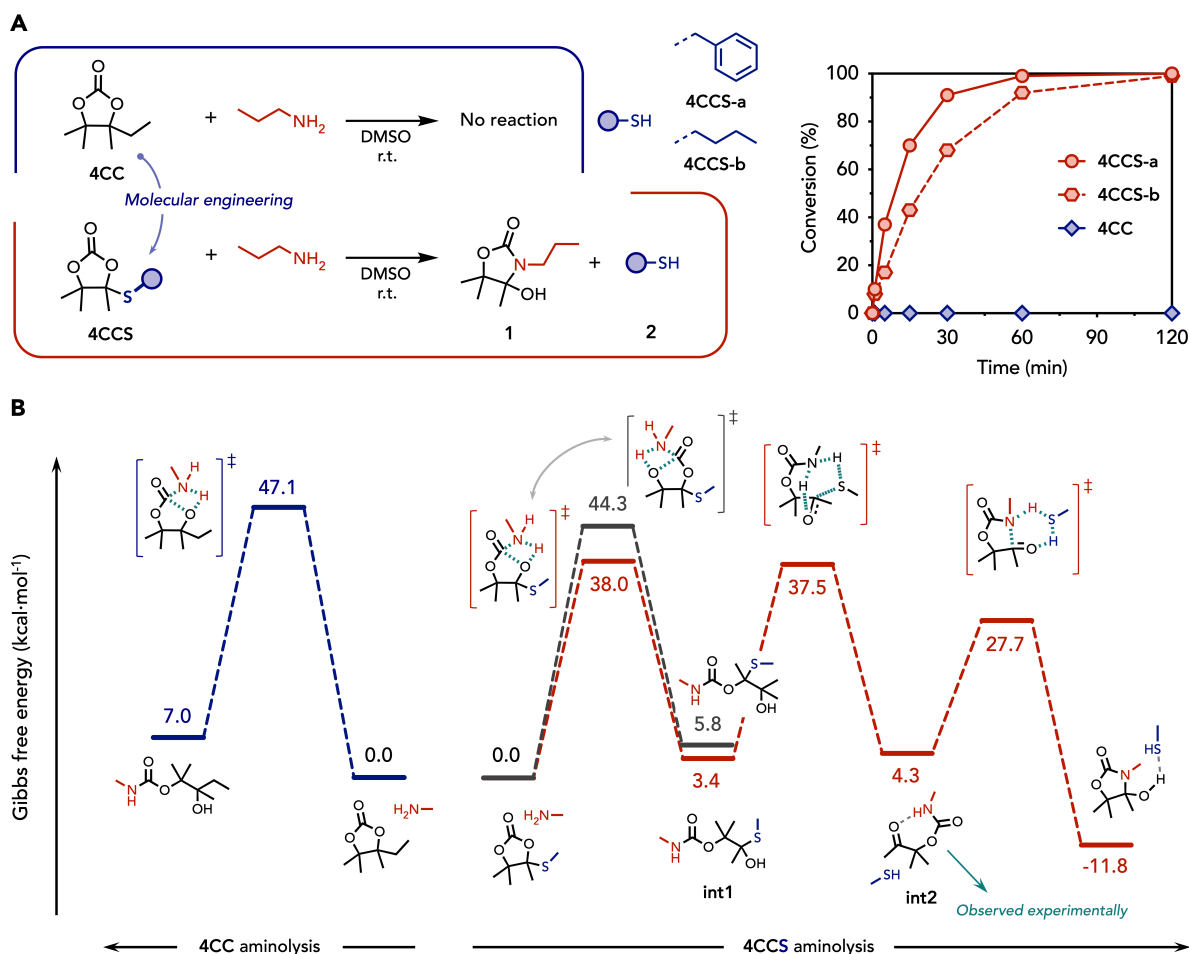


Figure 1. (A) Kinetic study on the aminolysis of **4CC** vs **4CCS**. (B) Energetics of the reaction pathways for **4CC** and **4CCS** determined by DFT.

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), indicating that this bond was weaker and more facile to break by reaction with amines. 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.

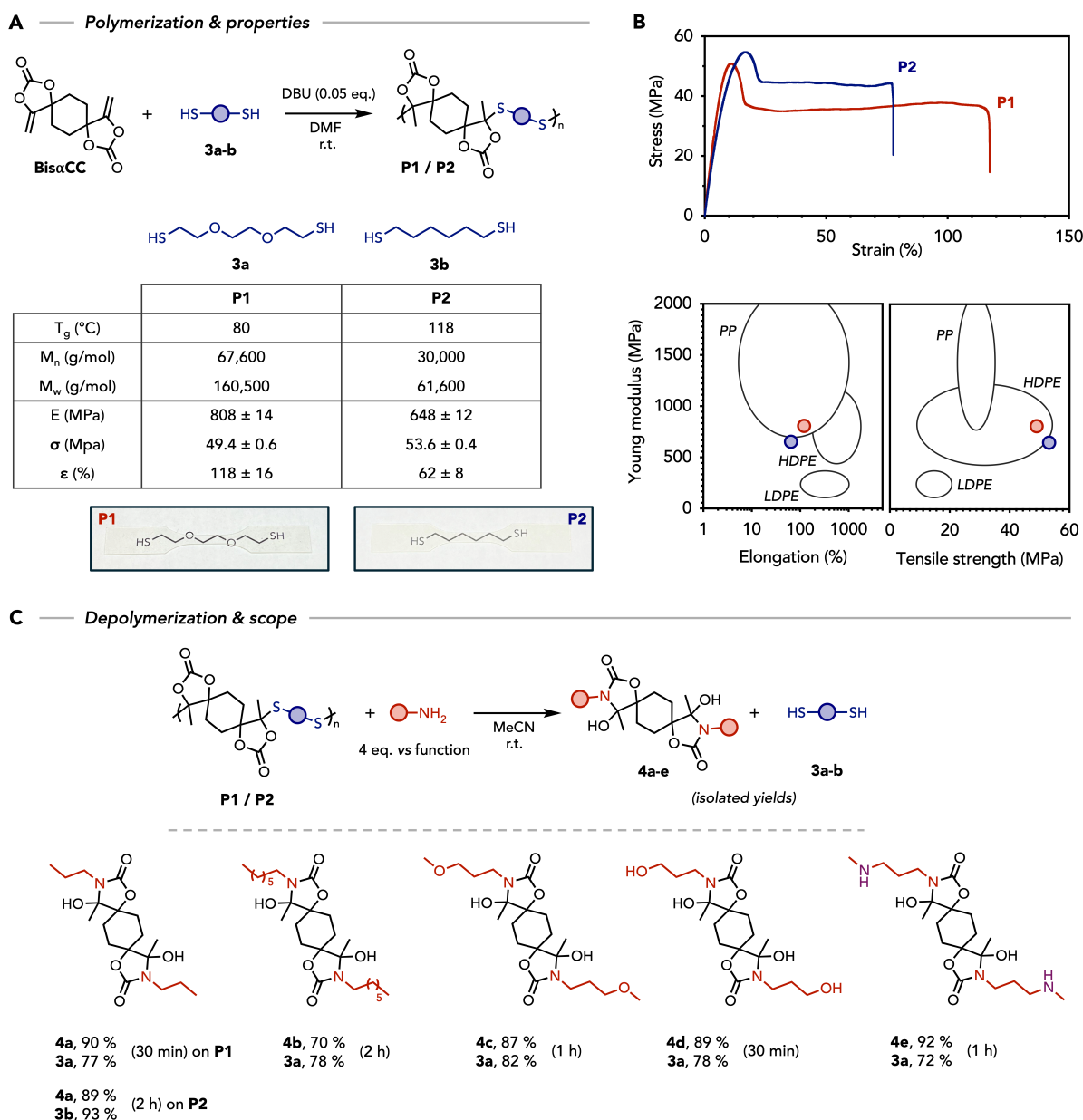
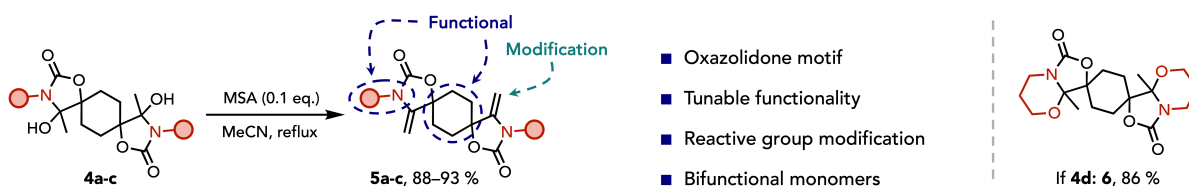


Figure 2. (A) Synthesis of polymers **P1-2** and (B) their mechanical properties as compared to polyethylene (PE) and polypropylene (PP) using Ashby plots⁵¹. (C) Polymer degradation using a scope of amines to provide **4a-e** and **3a-b**. Isolated yields and reactions time are provided.

Two highly substituted poly(cyclic carbonate-co-thioether)s were first synthesized by the r.T, DBU catalyzed step-growth polymerization of a CO₂-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** ($M_w = 160,500 \text{ g} \cdot \text{mol}^{-1}$) and polymer **P2** ($M_w = 61,600 \text{ g} \cdot \text{mol}^{-1}$), 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_g s, 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, propanolamine, and n-methyl-1,3-diaminopropane). Bis(hydroxyoxazolidone) **4a-e** and the former dithiols **3a** or **3b** were collected as degradation products and easily isolated in high yields (up to 92% for the oxazolidone **4a-e** 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.

A — Upcycling to useful buildings blocks



B — Upcycling to Covalent Adaptable Networks

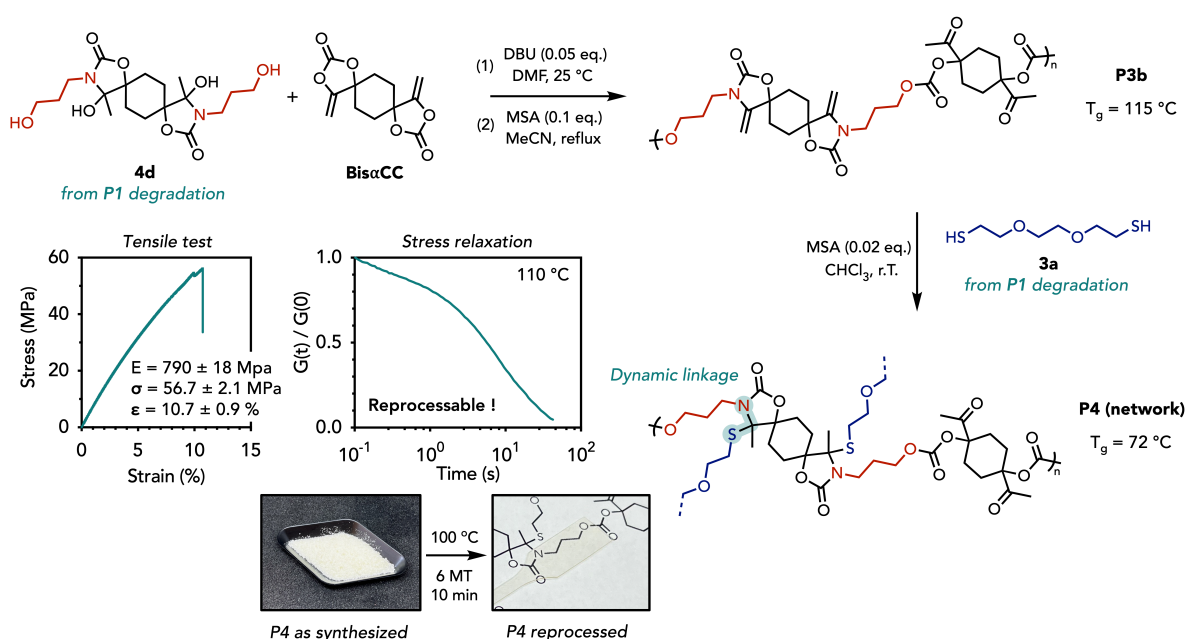


Figure 3 – (A) Dehydration of **4** into useful alkylidene scaffolds **5** and **6** (in the case of **4d**). (B) Upcycling of both **4d** and **3a** into a recyclable thermoset.

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 S69-74). These compounds **5** are versatile building blocks as they can be finely tuned through the bis α CC 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 derivatives⁵⁴ (Figure 3A, complete characterization in Figures S75-76), 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 bis α CC to produce poly(hydroxyoxazolidone-*co*-carbonate) **P3a** ($M_w = 22,000 \text{ g.mol}^{-1}$; $D = 1.7$) at r.T in the presence of DBU as catalyst (Figures S77-78). 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 S79-81). 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 S82), 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 S83) and a flow transition at 129 °C as determined by a temperature sweep experiment (Figure S84)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 S85) and were well represented by complex relaxation models (Figures S86-90 and related discussion), aligning with our previous work on *N,S*-oxazolidone CANs⁵³. 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 S91). 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 CO₂-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.

ASSOCIATED CONTENT

Supporting information available: Materials and methods; synthetic procedures; ¹H and ¹³C NMR spectra of kinetic studies, isolated molecules, and polymers; DFT protocols, thorough discussion, and coordinates; SEC chromatograms; TGA and DSC thermograms; rheological study of the covalent adaptable network.

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Notes

The authors declare no competing financial interest.

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References

- (1) Liu, Q.; Wu, L.; Jackstell, R.; Beller, M. Using Carbon Dioxide as a Building Block in Organic Synthesis. *Nat Commun* **2015**, *6* (1), 5933. <https://doi.org/10.1038/ncomms6933>.
- (2) Grignard, B.; Gennen, S.; Jérôme, C.; Kleij, A. W.; Detrembleur, C. Advances in the Use of CO₂ as a Renewable Feedstock for the Synthesis of Polymers. *Chem. Soc. Rev.* **2019**, *48* (16), 4466–4514. <https://doi.org/10.1039/C9CS00047J>.
- (3) Dabral, S.; Schaub, T. The Use of Carbon Dioxide (CO₂) as a Building Block in Organic Synthesis from an Industrial Perspective. *Adv Synth Catal* **2019**, *361* (2), 223–246. <https://doi.org/10.1002/adsc.201801215>.
- (4) Vidal, F.; Van Der Marel, E. R.; Kerr, R. W. F.; McElroy, C.; Schroeder, N.; Mitchell, C.; Rosetto, G.; Chen, T. T. D.; Bailey, R. M.; Hepburn, C.; Redgwell, C.; Williams, C. K. Designing a Circular Carbon and Plastics Economy for a Sustainable Future. *Nature* **2024**, *626* (7997), 45–57. <https://doi.org/10.1038/s41586-023-06939-z>.
- (5) Siragusa, F.; Detrembleur, C.; Grignard, B. The Advent of Recyclable CO₂-Based Polycarbonates. *Polym. Chem.* **2023**, *14* (11), 1164–1183. <https://doi.org/10.1039/D2PY01258H>.
- (6) Rosetto, G.; Vidal, F.; McGuire, T. M.; Kerr, R. W. F.; Williams, C. K. High Molar Mass Polycarbonates as Closed-Loop Recyclable Thermoplastics. *J. Am. Chem. Soc.* **2024**, *146* (12), 8381–8393. <https://doi.org/10.1021/jacs.3c14170>.
- (7) Bhat, G. A.; Darensbourg, D. J. Progress in the Catalytic Reactions of CO₂ and Epoxides to Selectively Provide Cyclic or Polymeric Carbonates. *Green Chem.* **2022**, *24* (13), 5007–5034. <https://doi.org/10.1039/D2GC01422J>.
- (8) Cokoja, M.; Wilhelm, M. E.; Anthofer, M. H.; Herrmann, W. A.; Kühn, F. E. Synthesis of Cyclic Carbonates from Epoxides and Carbon Dioxide by Using Organocatalysts. *ChemSusChem* **2015**, *8* (15), 2436–2454. <https://doi.org/10.1002/cssc.201500161>.
- (9) Guo, L.; Lamb, K. J.; North, M. Recent Developments in Organocatalysed Transformations of Epoxides and Carbon Dioxide into Cyclic Carbonates. *Green Chem.* **2021**, *23* (1), 77–118. <https://doi.org/10.1039/D0GC03465G>.
- (10) Martín, C.; Fiorani, G.; Kleij, A. W. Recent Advances in the Catalytic Preparation of Cyclic Organic Carbonates. *ACS Catal.* **2015**, *5* (2), 1353–1370. <https://doi.org/10.1021/cs5018997>.
- (11) Tamura, M.; Honda, M.; Nakagawa, Y.; Tomishige, K. Direct Conversion of CO₂ with Diols, Aminoalcohols and Diamines to Cyclic Carbonates, Cyclic Carbamates and Cyclic Ureas Using Heterogeneous Catalysts. *J of Chemical Tech & Biotech* **2014**, *89* (1), 19–33. <https://doi.org/10.1002/jctb.4209>.
- (12) Honda, M.; Tamura, M.; Nakao, K.; Suzuki, K.; Nakagawa, Y.; Tomishige, K. Direct Cyclic Carbonate Synthesis from CO₂ and Diol over Carboxylation/Hydration Cascade Catalyst of CeO₂ with 2-Cyanopyridine. *ACS Catal.* **2014**, *4* (6), 1893–1896. <https://doi.org/10.1021/cs500301d>.
- (13) Kindermann, N.; Jose, T.; Kleij, A. W. Synthesis of Carbonates from Alcohols and CO₂. *Top Curr Chem (Z)* **2017**, *375* (1), 15. <https://doi.org/10.1007/s41061-016-0101-8>.
- (14) Guo, W.; Gómez, J. E.; Cristòfol, À.; Xie, J.; Kleij, A. W. Catalytic Transformations of Functionalized Cyclic Organic Carbonates. *Angew Chem Int Ed* **2018**, *57* (42), 13735–13747. <https://doi.org/10.1002/anie.201805009>.
- (15) Guo, W.; González-Fabra, J.; Bandeira, N. A. G.; Bo, C.; Kleij, A. W. A Metal-Free Synthesis of N-Aryl Carbamates under Ambient Conditions. *Angew Chem Int Ed* **2015**, *54* (40), 11686–11690. <https://doi.org/10.1002/anie.201504956>.

- (16) Ni, J.; Lanzi, M.; Kleij, A. W. Unusual DBU-Catalyzed Decarboxylative Formation of Allylic Thioethers from Vinyl Cyclic Carbonates and Thiols. *Org. Chem. Front.* **2022**, *9* (24), 6780–6785. <https://doi.org/10.1039/D2QO01511K>.
- (17) Lanzi, M.; Kleij, A. W. Recent Advances in the Synthesis and Polymerization of New CO₂-BASED Cyclic [†]. *Chin. J. Chem.* **2024**, *42* (4), 430–443. <https://doi.org/10.1002/cjoc.202300502>.
- (18) Maisonneuve, L.; Lamarzelle, O.; Rix, E.; Grau, E.; Cramail, H. Isocyanate-Free Routes to Polyurethanes and Poly(Hydroxy Urethane)s. *Chem. Rev.* **2015**, *115* (22), 12407–12439. <https://doi.org/10.1021/acs.chemrev.5b00355>.
- (19) Lamarzelle, O.; Hibert, G.; Lecommandoux, S.; Grau, E.; Cramail, H. A Thioglycerol Route to Bio-Based Bis-Cyclic Carbonates: Poly(Hydroxyurethane) Preparation and Post-Functionalization. *Polym. Chem.* **2017**, *8* (22), 3438–3447. <https://doi.org/10.1039/C7PY00556C>.
- (20) Cornille, A.; Blain, M.; Auvergne, R.; Andrioletti, B.; Boutevin, B.; Caillol, S. A Study of Cyclic Carbonate Aminolysis at Room Temperature: Effect of Cyclic Carbonate Structures and Solvents on Polyhydroxyurethane Synthesis. *Polym. Chem.* **2017**, *8* (3), 592–604. <https://doi.org/10.1039/C6PY01854H>.
- (21) Tomita, H.; Sanda, F.; Endo, T. Model Reaction for the Synthesis of Polyhydroxyurethanes from Cyclic Carbonates with Amines: Substituent Effect on the Reactivity and Selectivity of Ring-opening Direction in the Reaction of Five-membered Cyclic Carbonates with Amine. *J. Polym. Sci. A Polym. Chem.* **2001**, *39* (21), 3678–3685. <https://doi.org/10.1002/pola.10009>.
- (22) Ochiai, B.; Koda, K.; Endo, T. Branched Cationic Polyurethane Prepared by Polyaddition of Chloromethylated Five-membered Cyclic Carbonate and Diethylenetriamine in Molten Salts. *J. Polym. Sci. A Polym. Chem.* **2012**, *50* (1), 47–51. <https://doi.org/10.1002/pola.24969>.
- (23) Salvado, V.; Dolatkhani, M.; Grau, É.; Vidil, T.; Cramail, H. Sequence-Controlled Polyhydroxyurethanes with Tunable Regioregularity Obtained from Sugar-Based Vicinal Bis-Cyclic Carbonates. *Macromolecules* **2022**, *55* (16), 7249–7264. <https://doi.org/10.1021/acs.macromol.2c01112>.
- (24) Blain, M.; Jean-Gérard, L.; Auvergne, R.; Benazet, D.; Caillol, S.; Andrioletti, B. Rational Investigations in the Ring Opening of Cyclic Carbonates by Amines. *Green Chem.* **2014**, *16* (9), 4286–4291. <https://doi.org/10.1039/C4GC01032A>.
- (25) Alves, M.; Méreau, R.; Grignard, B.; Detrembleur, C.; Jérôme, C.; Tassaing, T. DFT Investigation of the Reaction Mechanism for the Guanidine Catalysed Ring-Opening of Cyclic Carbonates by Aromatic and Alkyl-Amines. *RSC Adv.* **2017**, *7* (31), 18993–19001. <https://doi.org/10.1039/C7RA00220C>.
- (26) Quienne, B.; Poli, R.; Pinaud, J.; Caillol, S. Enhanced Aminolysis of Cyclic Carbonates by β-Hydroxylamines for the Production of Fully Biobased Polyhydroxyurethanes. *Green Chem.* **2021**, *23* (4), 1678–1690. <https://doi.org/10.1039/D0GC04120C>.
- (27) Ngassam Tounzoua, C.; Grignard, B.; Detrembleur, C. Exovinylene Cyclic Carbonates: Multifaceted CO₂-Based Building Blocks for Modern Chemistry and Polymer Science. *Angew Chem Int Ed* **2022**, *61* (22), e202116066. <https://doi.org/10.1002/anie.202116066>.
- (28) Gennen, S.; Grignard, B.; Tassaing, T.; Jérôme, C.; Detrembleur, C. CO₂-Sourced α-Alkylidene Cyclic Carbonates: A Step Forward in the Quest for Functional Regioregular Poly(Urethane)s and Poly(Carbonate)s. *Angew. Chem. Int. Ed.* **2017**, *56* (35), 10394–10398. <https://doi.org/10.1002/anie.201704467>.
- (29) Ouhib, F.; Grignard, B.; Van Den Broeck, E.; Luxen, A.; Robeyns, K.; Van

- Speybroeck, V.; Jerome, C.; Detrembleur, C. A Switchable Domino Process for the Construction of Novel CO₂-Sourced Sulfur-Containing Building Blocks and Polymers. *Angew. Chem. Int. Ed.* **2019**, *58* (34), 11768–11773. <https://doi.org/10.1002/anie.201905969>.
- (30) Wong, A. R.; Barrera, M.; Pal, A.; Lamb, J. R. Improved Characterization of Polyoxazolidinones by Incorporating Solubilizing Side Chains. *Macromolecules* **2022**, *55* (24), 11006–11012. <https://doi.org/10.1021/acs.macromol.2c02104>.
- (31) Dabral, S.; Licht, U.; Rudolf, P.; Bollmann, G.; Hashmi, A. S. K.; Schaub, T. Synthesis and Polymerisation of α -Alkylidene Cyclic Carbonates from Carbon Dioxide, Epoxides and the Primary Propargylic Alcohol 1,4-Butynediol. *Green Chem.* **2020**, *22* (5), 1553–1558. <https://doi.org/10.1039/C9GC04320A>.
- (32) Li, X.; Villar-Yanez, A.; Ngassam Tounzoua, C.; Benet-Buchholz, J.; Grignard, B.; Bo, C.; Detrembleur, C.; Kleij, A. W. Cascade Transformation of Carbon Dioxide and Alkyne-1, *n* -Diols into Densely Substituted Cyclic Carbonates. *ACS Catal.* **2022**, *12* (5), 2854–2860. <https://doi.org/10.1021/acscatal.1c05773>.
- (33) Laserna, V.; Martin, E.; Escudero-Adán, E. C.; Kleij, A. W. Substrate-Triggered Stereoselective Preparation of Highly Substituted Organic Carbonates. *ACS Catal.* **2017**, *7* (8), 5478–5482. <https://doi.org/10.1021/acscatal.7b01748>.
- (34) Sopeña, S.; Cozzolino, M.; Maquilón, C.; Escudero-Adán, E. C.; Martínez Belmonte, M.; Kleij, A. W. Organocatalyzed Domino [3+2] Cycloaddition/Payne-Type Rearrangement Using Carbon Dioxide and Epoxy Alcohols. *Angew Chem Int Ed* **2018**, *57* (35), 11203–11207. <https://doi.org/10.1002/anie.201803967>.
- (35) Longwitz, L.; Steinbauer, J.; Spannenberg, A.; Werner, T. Calcium-Based Catalytic System for the Synthesis of Bio-Derived Cyclic Carbonates under Mild Conditions. *ACS Catal.* **2018**, *8* (1), 665–672. <https://doi.org/10.1021/acscatal.7b03367>.
- (36) Martínez, J.; Fernández-Baeza, J.; Sánchez-Barba, L. F.; Castro-Osma, J. A.; Lara-Sánchez, A.; Otero, A. An Efficient and Versatile Lanthanum Heteroscorpionate Catalyst for Carbon Dioxide Fixation into Cyclic Carbonates. *ChemSusChem* **2017**, *10* (14), 2886–2890. <https://doi.org/10.1002/cssc.201700898>.
- (37) Fiorani, G.; Stuck, M.; Martín, C.; Belmonte, M. M.; Martin, E.; Escudero-Adán, E. C.; Kleij, A. W. Catalytic Coupling of Carbon Dioxide with Terpene Scaffolds: Access to Challenging Bio-Based Organic Carbonates. *ChemSusChem* **2016**, *9* (11), 1304–1311. <https://doi.org/10.1002/cssc.201600238>.
- (38) Rintjema, J.; Epping, R.; Fiorani, G.; Martín, E.; Escudero-Adán, E. C.; Kleij, A. W. Substrate-Controlled Product Divergence: Conversion of CO₂ into Heterocyclic Products. *Angew Chem Int Ed* **2016**, *55* (12), 3972–3976. <https://doi.org/10.1002/anie.201511521>.
- (39) Maeda, C.; Shimonishi, J.; Miyazaki, R.; Hasegawa, J.; Ema, T. Highly Active and Robust Metalloporphyrin Catalysts for the Synthesis of Cyclic Carbonates from a Broad Range of Epoxides and Carbon Dioxide. *Chemistry A European J* **2016**, *22* (19), 6556–6563. <https://doi.org/10.1002/chem.201600164>.
- (40) Sopeña, S.; Laserna, V.; Guo, W.; Martin, E.; Escudero-Adán, E. C.; Kleij, A. W. Regioselective Organocatalytic Formation of Carbamates from Substituted Cyclic Carbonates. *Adv Synth Catal* **2016**, *358* (13), 2172–2178. <https://doi.org/10.1002/adsc.201600290>.
- (41) De La Cruz-Martínez, F.; Francés-Poveda, E.; North, M.; Castro-Osma, J. A.; Lara-Sánchez, A. Base-Catalyzed Highly Regioselective Synthesis of Bio-Based Hydroxyurethanes. *Eur J Org Chem* **2024**, e202400275. <https://doi.org/10.1002/ejoc.202400275>.
- (42) Scholten, P. B. V.; Demartean, J.; Gennen, S.; De Winter, J.; Grignard, B.; Debuigne, A.; Meier, M. A. R.; Detrembleur, C. Merging CO₂-Based Building Blocks with Cobalt-Mediated Radical Polymerization for the Synthesis of Functional Poly(Vinyl Alcohol)s. *Macromolecules* **2018**, *51* (9), 3379–3393. <https://doi.org/10.1021/acs.macromol.8b00492>.

- (43) Chiu, S.-K.; Keifer, L.; Timberlake, J. W. Synthesis of Imidazolidinediones and Oxazolidinediones from Cyclization of Propargylureas and Propargyl Carbamates. *J. Med. Chem.* **1979**, *22* (6), 746–748. <https://doi.org/10.1021/jm00192a026>.
- (44) Jo, Y. W.; Im, W. B.; Rhee, J. K.; Shim, M. J.; Kim, W. B.; Choi, E. C. Synthesis and Antibacterial Activity of Oxazolidinones Containing Pyridine Substituted with Heteroaromatic Ring. *Bioorganic & Medicinal Chemistry* **2004**, *12* (22), 5909–5915. <https://doi.org/10.1016/j.bmc.2004.08.025>.
- (45) Fernandes, G. F. S.; Scarim, C. B.; Kim, S.-H.; Wu, J.; Castagnolo, D. Oxazolidinones as Versatile Scaffolds in Medicinal Chemistry. *RSC Med. Chem.* **2023**, *14* (5), 823–847. <https://doi.org/10.1039/D2MD00415A>.
- (46) Armentano, B.; Curcio, R.; Brindisi, M.; Mancuso, R.; Rago, V.; Ziccarelli, I.; Frattaruolo, L.; Fiorillo, M.; Dolce, V.; Gabriele, B.; Cappello, A. R. 5-(Carbamoylmethylene)-Oxazolidin-2-Ones as a Promising Class of Heterocycles Inducing Apoptosis Triggered by Increased ROS Levels and Mitochondrial Dysfunction in Breast and Cervical Cancer. *Biomedicines* **2020**, *8* (2), 35. <https://doi.org/10.3390/biomedicines8020035>.
- (47) Pathania, S.; Petrova-Szczasiuk, K.; Pentikäinen, O.; Singh, P. K. Oxazolidinones: Are They Only Good for the Discovery of Antibiotics? A Worm's Eye View. *Journal of Molecular Structure* **2023**, *1286*, 135630. <https://doi.org/10.1016/j.molstruc.2023.135630>.
- (48) Altmann, H. J.; Clauss, M.; König, S.; Frick-Delaittre, E.; Koopmans, C.; Wolf, A.; Guertler, C.; Naumann, S.; Buchmeiser, M. R. Synthesis of Linear Poly(Oxazolidin-2-One)s by Cooperative Catalysis Based on *N*-Heterocyclic Carbenes and Simple Lewis Acids. *Macromolecules* **2019**, *52* (2), 487–494. <https://doi.org/10.1021/acs.macromol.8b02403>.
- (49) Habets, T.; Siragusa, F.; Grignard, B.; Detrembleur, C. Advancing the Synthesis of Isocyanate-Free Poly(Oxazolidones)s: Scope and Limitations. *Macromolecules* **2020**, *53* (15), 6396–6408. <https://doi.org/10.1021/acs.macromol.0c01231>.
- (50) Habets, T.; Siragusa, F.; Müller, A. J.; Grossman, Q.; Ruffoni, D.; Grignard, B.; Detrembleur, C. Facile Construction of Functional Poly(Monothiocarbonate) Copolymers under Mild Operating Conditions. *Polym. Chem.* **2022**, *13* (21), 3076–3090. <https://doi.org/10.1039/D2PY00307D>.
- (51) Lin, S.-K. Handbook of Polymers. By George Wypych, ChemTec Publishing, 2012; 680 Pages. Price \$395.00, ISBN 978-1-895198-47-8. *Polymers* **2013**, *5* (1), 225–233. <https://doi.org/10.3390/polym5010225>.
- (52) Ouhib, F.; Meabe, L.; Mahmoud, A.; Grignard, B.; Thomassin, J.-M.; Boschini, F.; Zhu, H.; Forsyth, M.; Mecerreyes, D.; Detrembleur, C. Influence of the Cyclic versus Linear Carbonate Segments in the Properties and Performance of CO₂-Sourced Polymer Electrolytes for Lithium Batteries. *ACS Appl. Polym. Mater.* **2020**, *2* (2), 922–931. <https://doi.org/10.1021/acsapm.9b01130>.
- (53) Habets, T.; Seychal, G.; Caliori, M.; Raquez, J.-M.; Sardon, H.; Grignard, B.; Detrembleur, C. Covalent Adaptable Networks through Dynamic *N*, *S*-Acetal Chemistry: Toward Recyclable CO₂-Based Thermosets. *J. Am. Chem. Soc.* **2023**, *145* (46), 25450–25462. <https://doi.org/10.1021/jacs.3c10080>.
- (54) Song, Q.-W.; Yu, B.; Li, X.-D.; Ma, R.; Diao, Z.-F.; Li, R.-G.; Li, W.; He, L.-N. Efficient Chemical Fixation of CO₂ Promoted by a Bifunctional Ag₂WO₄/Ph₃P System. *Green Chem.* **2014**, *16* (3), 1633. <https://doi.org/10.1039/c3gc42406e>.
- (55) Elling, B. R.; Dichtel, W. R. Reprocessable Cross-Linked Polymer Networks: Are Associative Exchange Mechanisms Desirable? *ACS Cent. Sci.* **2020**, *6* (9), 1488–1496. <https://doi.org/10.1021/acscentsci.0c00567>.
- (56) Scheutz, G. M.; Lessard, J. J.; Sims, M. B.; Sumerlin, B. S. Adaptable Crosslinks in Polymeric Materials: Resolving the Intersection of Thermoplastics and Thermosets. *J. Am. Chem. Soc.* **2019**, *141* (41), 16181–16196. <https://doi.org/10.1021/jacs.9b07922>.

(57) Denissen, W.; Winne, J. M.; Du Prez, F. E. Vitrimers: Permanent Organic Networks with Glass-like Fluidity. *Chem. Sci.* **2016**, 7 (1), 30–38. <https://doi.org/10.1039/C5SC02223A>.