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# Unprecedented associative exchange in CO<sub>2</sub>-sourced cyclic S,O-acetals based covalent adaptable networks

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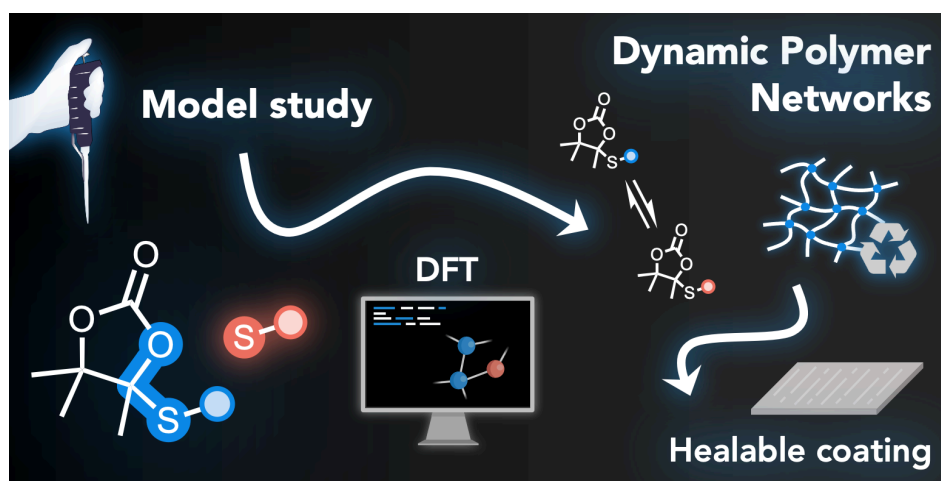
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## Abstract



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New dynamic chemistries are nowadays sought to widen the library of accessible covalent adaptable networks (CANs). Here, we investigate the dynamic nature of CO<sub>2</sub>-sourced cyclic S,O-acetal bonds in unexplored conditions. Model molecule studies were conducted on various compounds and supported by extensive DFT calculations to understand the required conditions for triggering exchange and the underlying reaction mechanisms. This study is the first to report dynamic S,O-acetal bonds with an unprecedented associative exchange mechanism occurring through nucleophilic attack onto a remote function from the exchanged site. Our findings were translated to macromolecular engineering with the successful production of CO<sub>2</sub>-sourced CANs embedding cyclic S,O-acetal bonds from bifunctional alkylidene cyclic carbonates and polythiols. The polymer properties were tuned by the use of structurally-divergent monomers, affording materials with distinct thermal and mechanical properties (e.g. T<sub>g</sub> ranging from 2 to 51°C). Complex relaxation behaviour was recorded by rheology experiments, suggesting concurrent exchange reactions to take place at elevated temperatures. The materials dynamics were leveraged through recycling by compression molding over five cycles. Furthermore, a proof-of-concept coating application was developed, showcasing damage healing at high temperatures.

## Introduction

Regardless the excellent potential of polymer materials, issues regarding environmental pollution have become increasingly prominent in today's society.<sup>1,2</sup> Therefore, research has intensified in the last years with the aim of producing plastics from bio-renewable resources and/or waste (such as CO<sub>2</sub>) while enabling their recycling or upcycling.<sup>3</sup>

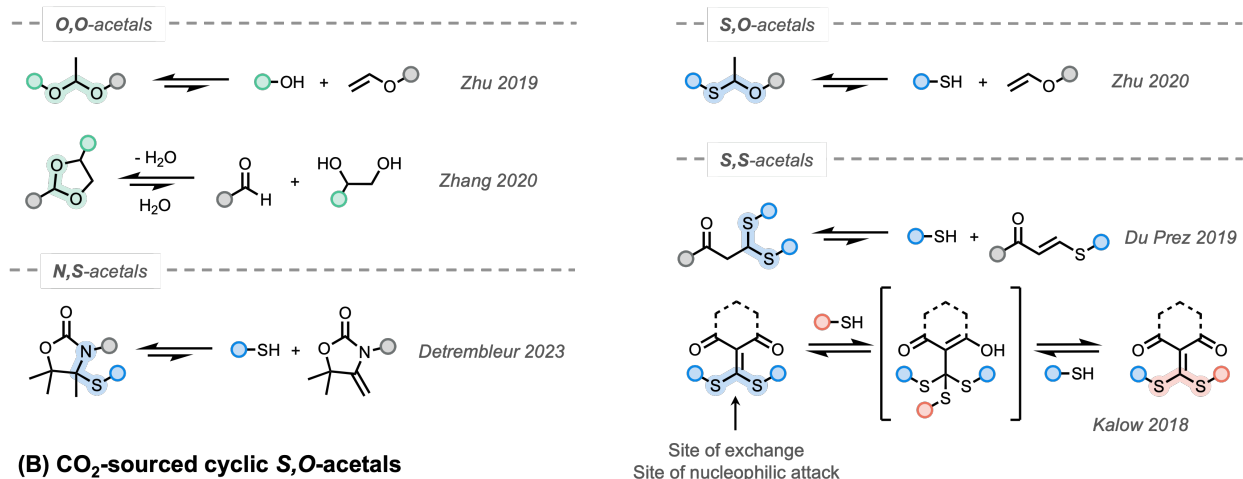
During the last decade, covalent adaptable networks (CANs) have emerged as a new class of polymeric materials that bridge the gap between thermoplastics and thermosets in terms of (re-) processability and mechanical superiority.<sup>4,5</sup> Interestingly, while these materials are effectively cross-linked in standard conditions, an appropriate trigger - most commonly heat - enables the reshuffling of bonds and subsequently allows for recycling of the polymeric networks. CANs are generally divided in two categories depending on their bond exchange mechanism: (i) associative exchange involving new bond creation followed by bond breaking, and (ii) dissociative exchange where bond creation is preceded by bond breaking. Meanwhile, well-established dynamic functionalities have been widely used for the preparation of CANs,<sup>6-8</sup> for example esters,<sup>9-16</sup> carbamates,<sup>17-19</sup> dicarboximides,<sup>20</sup> Diels-Alder adducts,<sup>21,22</sup> or sulfur based chemistries<sup>23</sup> (e.g. disulfides, thioesters, or sulfonium salts)<sup>24-31</sup>. While adjusting architectural features (e.g. cross-link density, backbone stiffness and polarity...) allows for tuning of the dynamic properties of CANs,<sup>32</sup> the discovery of new dynamic chemistry

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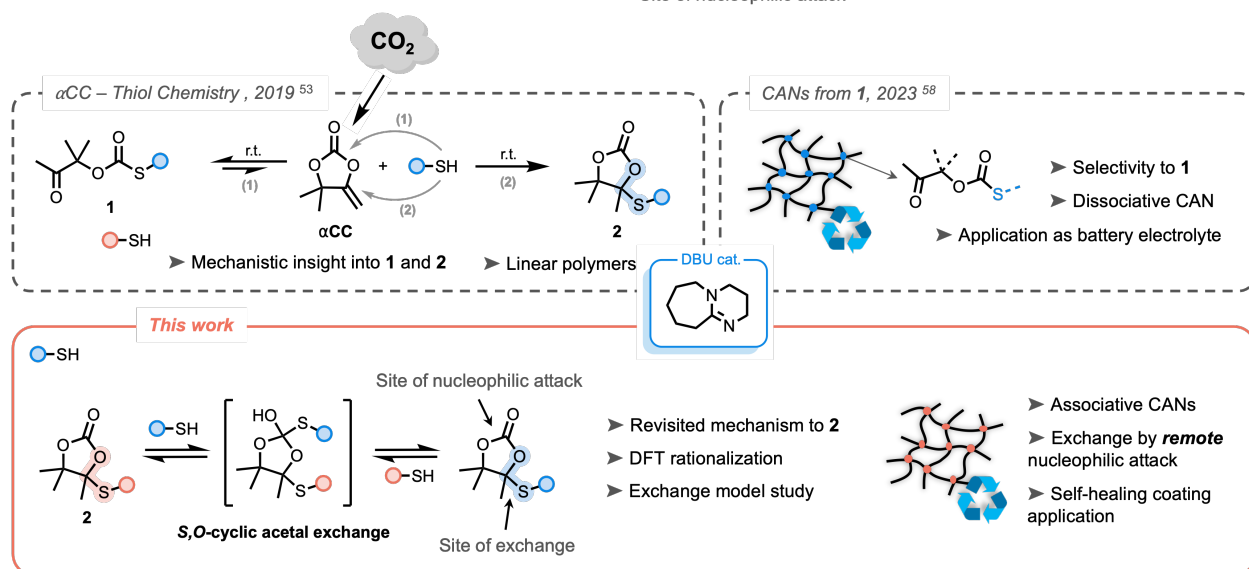
platforms is still encouraged to expand the library of recyclable materials through the CAN strategy with a focus on identifying the most promising candidates.

*X,X*-acetal bonds (*X for heteroatom*) have been at the center of many contributions because of their versatility and many modes of production from various precursors to provide dynamic networks (**Scheme 1A**).<sup>33–37</sup> While the most straightforward acetal system was initially developed by Zhu *et al.*, producing *O,O*-acetal based thermosets from alcohols and vinyl ethers.<sup>33,34,38</sup> The same group reported *S,O*-acetal derivatives by switching the nucleophile to thiols.<sup>39</sup> Well-known as protecting groups in organic synthesis, five- and six-membered cyclic *O,O*-acetal groups were also reported as efficient reversible bonds.<sup>40,41</sup> Although these systems were reported to exchange in catalyst-free conditions, experiments with proton traps confirmed that the reactions were likely activated by residual water providing acidic protons at high temperature. Recently, Detrembleur and coworkers demonstrated that *N,S*-acetal bonds within alkylidene oxazolidone moieties showed reversibility in the presence of an acid catalyst.<sup>42</sup> In 2019, Du Prez and co-workers studied the base-catalyzed exchange of *S,S*-acetal based CANs that were prepared through reversible Michael additions on electron-poor alkenes.<sup>35</sup> It must be noted that all aforementioned *X,X*-acetal bonds were of dissociative nature. Interestingly, in 2018, Kalow's group reported the first example of catalyst-free associative exchangeable *S,S*-acetal bonds using dithioalkylidene cross-linkers.<sup>36,43,44</sup>

**(A) Reported reversible acetal bonds**



**(B) CO<sub>2</sub>-sourced cyclic S,O-acetals**



**Scheme 1.** (A) Reported acetal-derivatives bonds used in covalent adaptable networks. (B) Previous work on  $\alpha$ CC-thiol chemistry and new mechanism proposed in this work for producing **2** toward covalent adaptable networks.

While the design of recyclable polymer networks is an appealing strategy to bypass product disposal at the end of service, the valorization of waste in the manufacturing process is an effective way to produce more sustainable materials. Carbon dioxide (CO<sub>2</sub>) is a prevalent waste product on earth with well-known dramatic consequences for the environment. Its use as a C<sub>1</sub> building block is therefore of high interest in chemistry and polymer science, leading to the design of many CO<sub>2</sub>-sourced polymers.<sup>45–47</sup> Recently, some of us reported the synthesis of  $\alpha$ -alkylidene cyclic carbonates ( $\alpha$ CC)

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from CO<sub>2</sub>. These unconventional cyclic carbonates have shown to benefit from high reactivity through increased ring strain provided by the exocyclic alkene.<sup>48,49</sup> These compounds can thus easily undergo copolymerization by reaction with various nucleophiles under mild (catalytic) conditions, *i.e.* with amines<sup>50,51</sup>, with alcohols<sup>52</sup> and thiols<sup>53</sup>. The scope of the obtained polymers was further expanded by different groups to bring more diversification, tunability, functionality, and emerging applications<sup>54–58</sup> without omitting recyclability<sup>42,59,60</sup>.

The organobase-catalyzed reaction of  $\alpha$ CC with thiols can provide two different products. If a hard base (*e.g.* DBU) is used, the oxo-thiocarbonate **1** is rapidly formed, followed by a rearrangement into a more stable cyclic carbonate embedding a S,O-acetal function **2** (**Scheme 1B**).<sup>53</sup> Using a soft organobase (*e.g.* DBU:acetate), high selectivity toward **1** can be obtained. Interestingly, it was previously determined experimentally and computationally that the formation of **1** was fast and reversible. By taking advantage of the dissociative nature of the bond in the presence of the soft base catalyst, dissociative poly(oxo-thiocarbonate) CANs were produced that could be processed into membranes for solid polymer electrolytes.<sup>58</sup>

Although it was claimed in an earlier work (**Scheme 1B**, top left)<sup>53</sup> that the formation of **2** was irreversible, the dynamic nature of acetal derivatives bonds made us wonder whether the reversibility of these cyclic S,O-acetal bonds could be triggered in previously unexplored conditions.

In this work, we show that the previously claimed irreversible cyclic S,O-acetal linkages within cyclic carbonates **2** can undergo an associative exchange with free thiolates by an unprecedented mechanism that involves a remote nucleophilic attack at a different position than the exchange location of the molecule (**Scheme 1B**, bottom). First, a model study was conducted to demonstrate the associative nature of the exchange reaction and suitable conditions were evaluated by kinetics at elevated temperatures. By means of DFT calculations, a new mechanism rationalizing the formation of **2** was determined to be more favourable than the previously reported one. Next, cross-linked polymer networks embedding cyclic S,O-acetal linkages were prepared from bifunctional CO<sub>2</sub>-sourced  $\alpha$ -alkylidene cyclic carbonates and polythiols. Their dynamics were carefully characterized by rheological measurements and a proof-of-concept applicability was highlighted for their use as healable coatings.

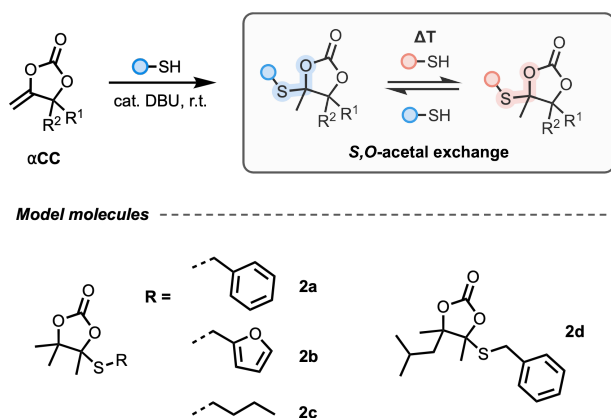
## Results and discussion

While the dissociative behaviour of linear oxo-thiocarbonate **1** motifs was recently discussed for CANs<sup>61</sup>, the potential reversibility of the S,O-acetal bond in **2** remained

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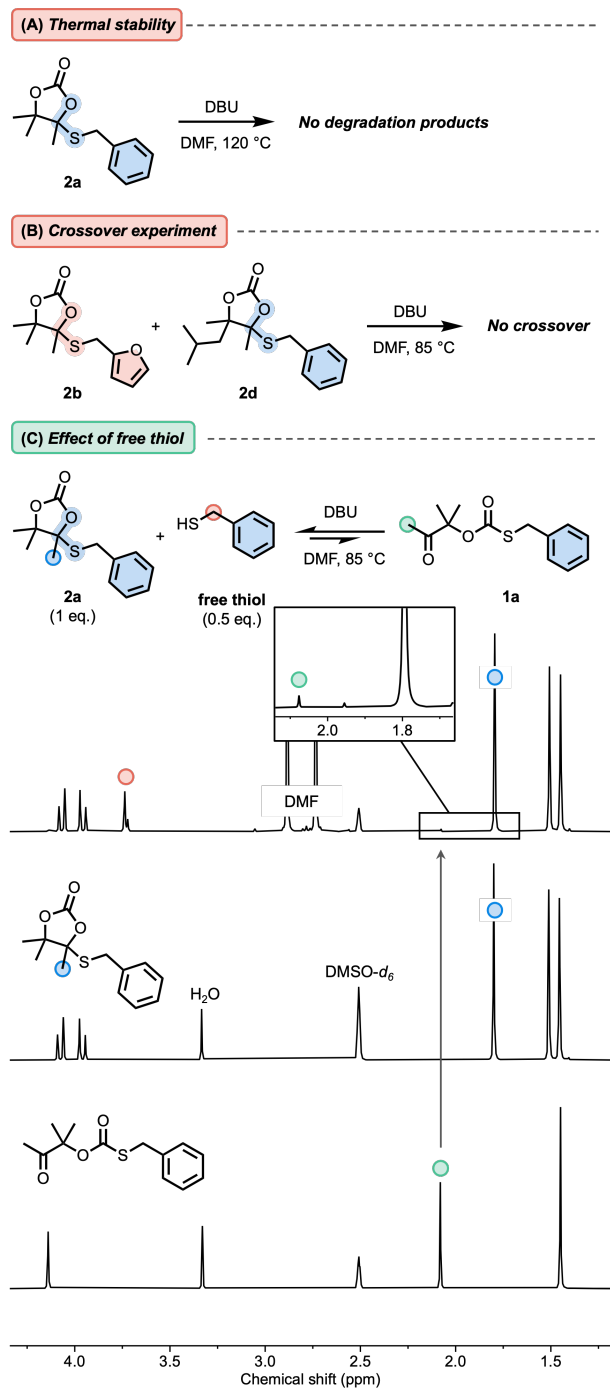
unexplored. Therefore, we first conducted initial model studies to assess the bond stability and reversibility before translating the process to the material level through the synthesis of cyclic *S,O*-acetal containing CANs. Although the formation of **2** was previously claimed to be irreversible at room temperature, we envisaged that heat might trigger reactivity.

## Synthesis of model compounds and evaluation of the exchange mechanism by model studies.



**Figure 1.** Synthesis of **2a-d** from  $\alpha$ CCs and hypothesized exchange reaction.

First, model cyclic carbonates embedding a cyclic *S,O*-acetal bond **2a-d** were prepared in a straightforward fashion from CO<sub>2</sub>-sourced  $\alpha$ CCs and thiols using DBU as catalyst (**Figure 1**, see ESI for details). We initiated our model studies by heating a solution of **2a** in DMF with a catalytic amount of DBU (**Figure 2A**). Analysis by <sup>1</sup>H-NMR spectroscopy of the reaction medium (quenched with formic acid) after 2 hours up to 120 °C did not reveal any significant change in the spectrum, demonstrating the thermal stability of **2a** with no identifiable dissociation occurring at this temperature (**Figure S1**). Furthermore, when equimolar amounts of **2b** and **2d** were combined with DBU in DMF and heated to 85 °C, crossover products were not observed from LC-MS analysis, suggesting that dissociation is not occurring (**Figure 2B** and **Figure S2**) even after prolonged heating. This result confirmed that the *S,O*-acetal bonds in **2** did not present the usual dissociative nature of common acetals reported in CANs.



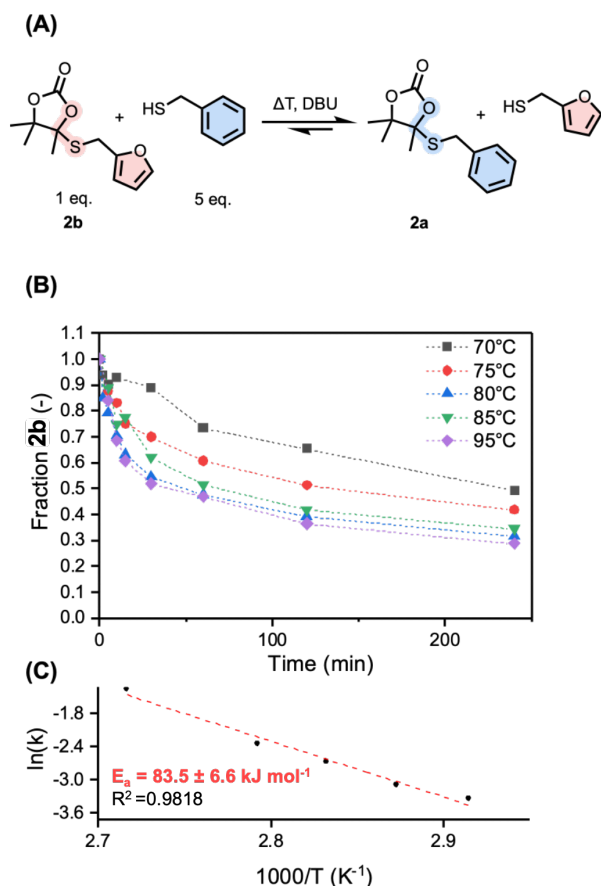
**Figure 2.** (A) Effect of temperature and catalyst (DBU, 0.01 eq.) on the stability of **2a**. (B) Crossover experiment between **2b** and **2d**. (C) Observed reaction between **2a** and 0.5 equivalents of benzyl mercaptan in the presence of DBU (0.01 eq.) at 85 °C as observed by <sup>1</sup>H-NMR spectroscopy (400 MHz, DMSO-*d*<sub>6</sub>). Pure NMR spectra of **2a** and **1a** were stacked to the crude reaction spectrum.

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Interestingly, when 0.5 equivalents of benzyl mercaptan was introduced in the reaction mixture containing **2a** and DBU at 85 °C, the corresponding oxo-thiocarbonate **1a** (1 mol% compared to **2a**) was observed *via* NMR spectroscopy after 1h (**Figure 2C** and **Figure S3**). This indicates that stability of **2** might be altered in the presence of free thiol and DBU.

Motivated by these preliminary results, pointing towards reactivity triggered by the presence of free thiols, we started investigating the DBU-catalyzed exchange reaction kinetics of **2b** with a large excess of free thiol (5 equivalents of benzylmercaptan) to produce **2a** (**Figure 3A**). In these conditions, a pseudo first order reaction law might be used as an approximation to extract reaction rates at different temperatures. Because of inconvenient overlap in NMR, the reaction was followed by means of LC-MS analysis using trimethoxybenzene (TMB) as internal standard in a temperature range from 70 to 95 °C (**Figure 3B** and **Figure S4**). The reaction has shown to be active at 70 °C, with a nearly 10-fold increase in reaction rate when increasing the temperature to 95 °C (0.03 min<sup>-1</sup> at 70 °C and 0.26 min<sup>-1</sup> at 95 °C, **Table S1**). From the related Arrhenius plot (**Figure 3C**), constructed from the extracted reaction rate constants at the respective different temperatures, an activation energy of 83.5 ± 6.6 kJ.mol<sup>-1</sup> was determined. This is slightly higher than previously reported model systems (range of 66.2-76.8 kJ.mol<sup>-1</sup> for *S,S*-acetals and 64.9 kJ.mol<sup>-1</sup> for *N,S*-acetals).<sup>35,42</sup> To ensure that reactivity is not only triggered by the benzyl or furfuryl nature of the substituent in **2a** and **2b**, an additional reaction was carried out from an aliphatic-derived **2c** (from n-butanethiol) at 70 °C with dodecanethiol, showing successful exchange with a similar reaction rate as with **2b** at the same temperature (0.04 min<sup>-1</sup>) (**Figure S5**).



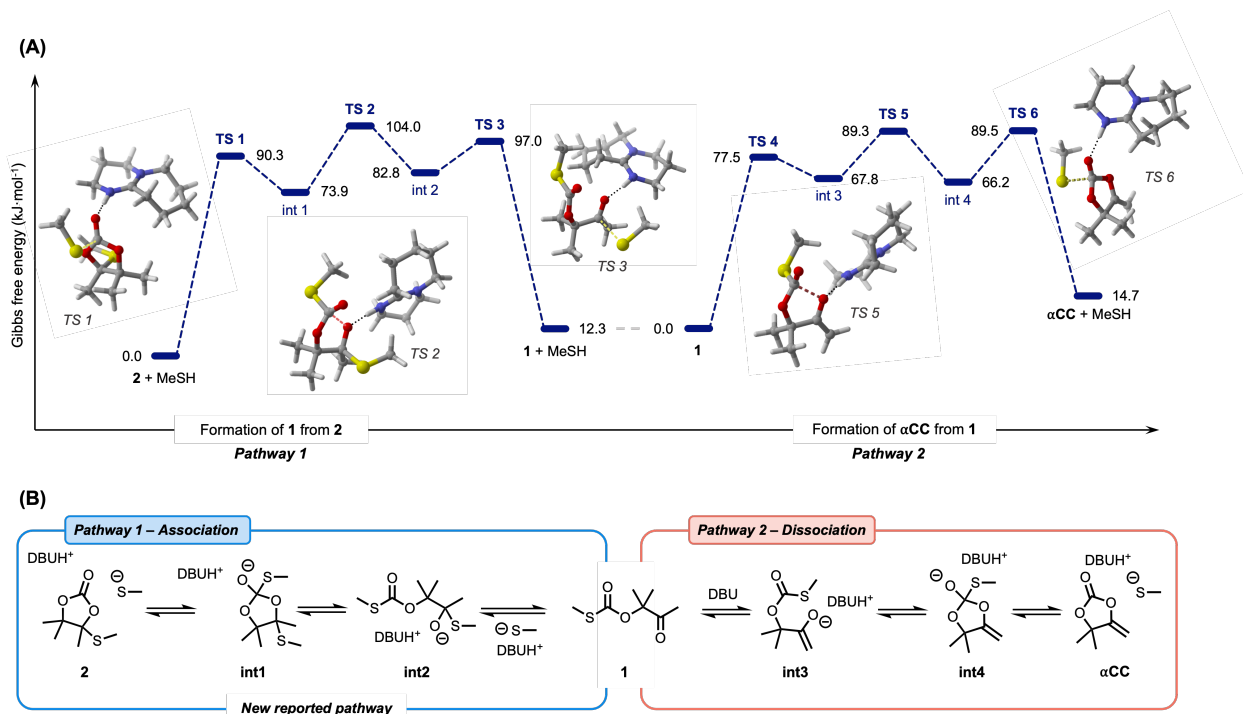


**Figure 3.** (A) Dynamic exchange reaction between **2b** and 5 equivalents benzyl mercaptan at different temperatures catalyzed by DBU. (B) Evolution of the fraction of **2b** over time as followed by LC-MS with 1,3,5-trimethoxybenzene as an internal standard detected at 280 nm. (C) Arrhenius plot fitted to a linear fit (dashed line).

After successfully demonstrating the temperature dependence of the S,O-acetal exchange in **2**, the influence of the concentration of the nucleophile was studied by mixing **2b** with 10 equivalents of benzyl mercaptan (instead of 5 eq.). The reaction was followed over time at 75°C and displayed a significant increase in reaction rate constant (from 0.046 to 0.57 min<sup>-1</sup>) (**Figure S6**). Both the requirement of free thiolates to trigger exchange and the acceleration of reaction rate by the presence of an increased amount of free thiols demonstrate that the exchange mechanism is of associative nature.

## Mechanistic insight into involved reactions

To shed light on this unreported exchange reaction, density functional theory (DFT) calculations were performed at the  $\omega$ B97-XD/6-311++G(d,p) level of theory on model molecules. In a previous work, the mechanism of  $\alpha$ CC thiolation was studied through experimental model reactions and DFT calculations.<sup>53</sup> This study concluded that an oxo-thiocarbonate **1** was first obtained by the reversible DBU-catalyzed attack of the thiolate onto the carbonyl group of  $\alpha$ CC. The formation of **2** was rationalized by two different mechanisms that are rather close in energy, both involving the attack of the thiolate onto the internal carbon of the exocyclic alkene function of  $\alpha$ CC. However, this previous study only provided calculations involving benzyl-derived thiols and some reactions were modelled without including DBU. In the same study, it was however demonstrated that the choice of the DBU catalyst was critical to the selective formation of **2** when other superbases (such as DBN, TBD or MTBD) failed at this task. For a systematic comparison between all herein studied pathways and to eliminate any possible effect of benzyl groups on the energetics of the reactions, our model involves DBU in all steps and methanethiol was selected as a simple aliphatic thiol substrate. All modelled pathways and the relative Gibbs free energies of all studied molecules can be found in ESI (Figures S7-S14) including a more thorough discussion.



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**Figure 4.** (A) Gibbs' free energies in  $\text{kJ mol}^{-1}$  of the studied reaction pathways and representative structures of the transition state geometries (B) Schematic representation of associative and dissociative pathways.

We started our investigation by exploring a new pathway, coined pathway 1, where **2** undergoes thiolation on the electrophilic carbonate function to provide a tetrahedral intermediate **int1** stabilized by DBUH<sup>+</sup> (**Figure 4B**). Subsequently, this intermediate can ring-open to form a hemithioacetal intermediate **int2**. The final step involves the ejection of the thiolate to yield the oxo-thiocarbonate **1**. The rate-determining step of this mechanism involving TS2 is characterized by an energy barrier of  $104.0 \text{ kJ.mol}^{-1}$ . Interestingly, the reverse reaction, from **1** to **2**, exhibits a similar energy barrier of  $91.7 \text{ kJ.mol}^{-1}$ , suggesting reversibility. However, the five-membered cyclic carbonate **2** is thermodynamically slightly favored, with an extra stabilization of  $12.3 \text{ kJ.mol}^{-1}$  compared to the linear thiocarbonate **1**. Apart from the experimental observation that **1** is observed when free thiols are added to pure **2** and DBU (see **Figure 2**), DFT calculations successfully manage to rationalize the stepwise associative exchange through (i) ring-opening of **2** and (ii) ring-closing of **1**.

Compound **1** is a dynamic molecule prone to dissociation into  $\alpha\text{CC}$  and a free thiol (pathway 2). Therefore, the formation of **1** as intermediate opens the door to an additional dissociation process within the system, as this compound is prone to dissociation into  $\alpha\text{CC}$  and a free thiol. In the presence of DBU, the ketone in **1** can rearrange into an enolate intermediate **int3**. This intermediate can undergo ring-closure through attack of the enolate onto the thiocarbonate function to provide a tetrahedral intermediate stabilized by DBUH<sup>+</sup> **int4**. The third step of the reaction involves ejection of the thiolate and re-formation of the carbonate to yield  $\alpha\text{CC}$ . This reaction is characterized by an activation barrier of  $89.5 \text{ kJ.mol}^{-1}$  and a backward reaction barrier of only  $74.8 \text{ kJ.mol}^{-1}$ , suggesting reversibility and fast reaction kinetics from  $\alpha\text{CC}$  to **1**. Furthermore, the formation of **1** is thermodynamically favored by  $14.7 \text{ kJ.mol}^{-1}$ .

Additionally, we reproduced previously reported pathways toward **2** through direct thiol attack onto  $\alpha\text{CC}$  (in a stepwise or concerted fashion), labelled as pathway 3 in our study (see ESI for details). The most favorable stepwise mechanism showed a high energy barrier of  $150.7 \text{ kJ.mol}^{-1}$ , in close agreement with previously determined values ( $155.6 \text{ kJ.mol}^{-1}$ ).<sup>53</sup> Our newly introduced pathway 1, providing **2** from **1** instead of  $\alpha\text{CC}$ , thus exhibited a much lower energy barrier of  $104.0 \text{ kJ.mol}^{-1}$  ( $46.7 \text{ kJ.mol}^{-1}$  less). This huge difference suggests this new path to be much more favorable than the previously reported pathway 3 to explain the formation of **2**. Since the backward reaction barriers are even greater ( $177.7 \text{ kJ.mol}^{-1}$ ), it is unlikely that pathway 3 is the source of

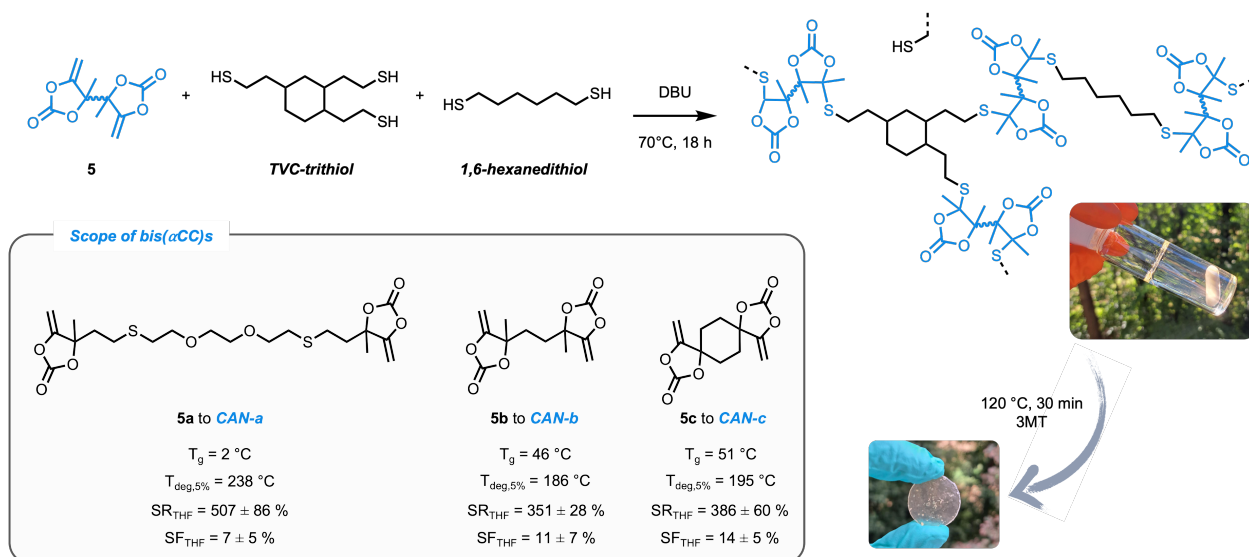
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dissociation from **2** to  $\alpha$ CC and a thiol. This is in line with experiments displaying no dissociation nor crossover of **2** at high temperatures in the absence of free thiols.

Overall, these DFT calculations suggest an unprecedented mechanism of acetal exchange *via* a thiol association onto a remote carbonyl function of **2**, yielding **1** and a free thiol as intermediates. Compound **1** can then undergo thiolation to provide an exchanged cyclic S,O-acetal **2** via a newly proposed mechanism which might be more feasible than the previously reported mechanism starting from  $\alpha$ CC. Once **1** is formed, both association toward **2** or dissociation to  $\alpha$ CC might concurrently occur.

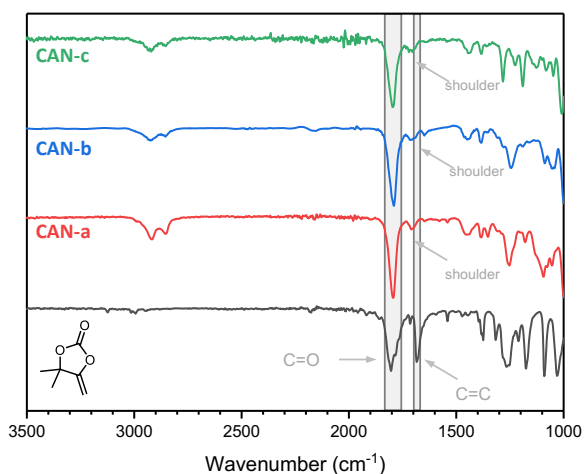
## Preparation and characterization of CANs

After successfully establishing the reaction mechanism, cross-linked materials could be prepared in a straightforward manner from bis( $\alpha$ -alkylidene cyclic carbonate)s (obtained from propargylic alcohols and CO<sub>2</sub>) (**5a-c**, see ESI for full experimental detail and characterisation) and multifunctional thiols (**Figure 5**) to exploit this dynamic exchange at the material level. According to the mechanistic model study, polymeric matrices were produced with an excess of thiol (10 mol% excess of thiol groups with respect to the exocyclic double bonds) to enable associative exchange and, by consequence, reprocessing of the thermoset material.



**Figure 5.** Preparation of covalent adaptable networks starting from bis( $\alpha$ -alkylidene cyclic carbonate)s **5a-c** with multifunctional thiols (TVC-trithiol and 1,6-hexanedithiol) using DBU as catalyst (1 mol% vs thiol functions).  $T_g$  (glass transition temperature) determined by DSC;  $T_{deg,5\%}$  (temperature at 5% of degradation) determined by TGA;  $SR_{THF}$  (swelling ratio) and  $SF_{THF}$  (soluble fraction) after immersion of the networks for 24h in THF.

Initially, a commercially available multifunctional thiol (pentaerythritol tetrakis(3-mercaptopropionate)) was considered. However, this cross-linker could possibly induce issues in the conditions needed for the exchange (high temperature, basic DBU as catalyst) due to *e.g.* transesterification reactions.<sup>35</sup> In order to have the clearest view on the dynamics of the *S,O*-acetals, an aliphatic trithiol (TVC-trithiol) devoid of other functional groups was therefore synthesized and used as cross-linker. Networks (**CANa-c**) were subsequently prepared using compounds **5a-c** together with TVC-trithiol and 1,6-hexanedithiol as chain extender (in a 2.25:1:1 molar ratio) and a catalytic amount of DBU (1 mol% with respect to the thiol functionalities). Conversion of the bis( $\alpha$ CC)s was conveniently monitored using ATR-FTIR spectroscopy as the disappearance of the signal attributed to the exovinylene function at 1675  $\text{cm}^{-1}$  provided evidence of the  $\alpha$ CC monomer consumption (**Figure 6**). A small shoulder at 1718  $\text{cm}^{-1}$  corresponding to the linear thiocarbonate intermediate can be observed. Nevertheless, a strong band at 1797  $\text{cm}^{-1}$ , corresponding to the stretching vibration of the carbonyl from the cyclic carbonate, confirmed the successful preparation of CANs containing cyclic *S,O*-acetal **2** linkages.



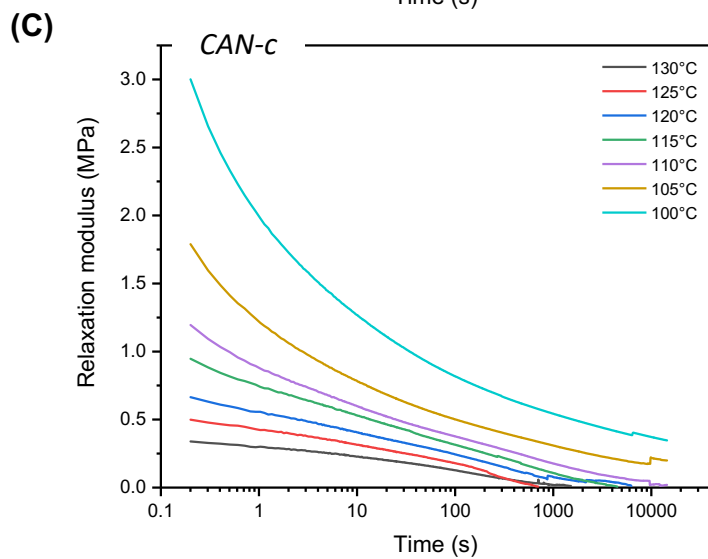
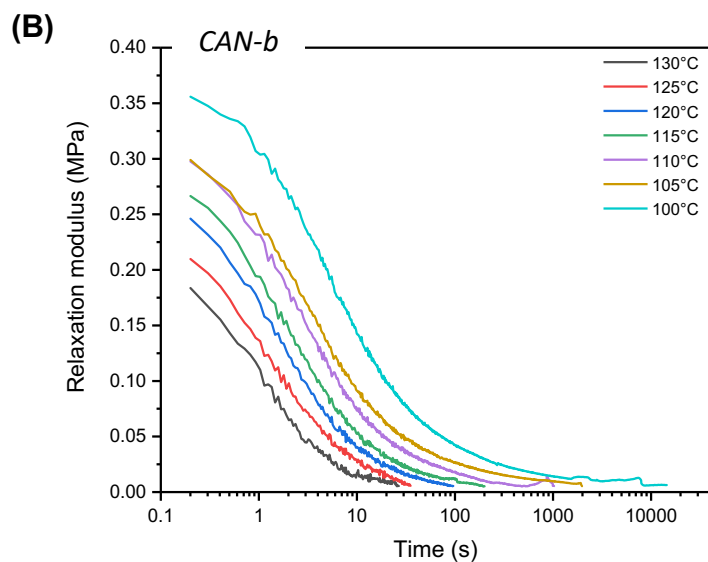
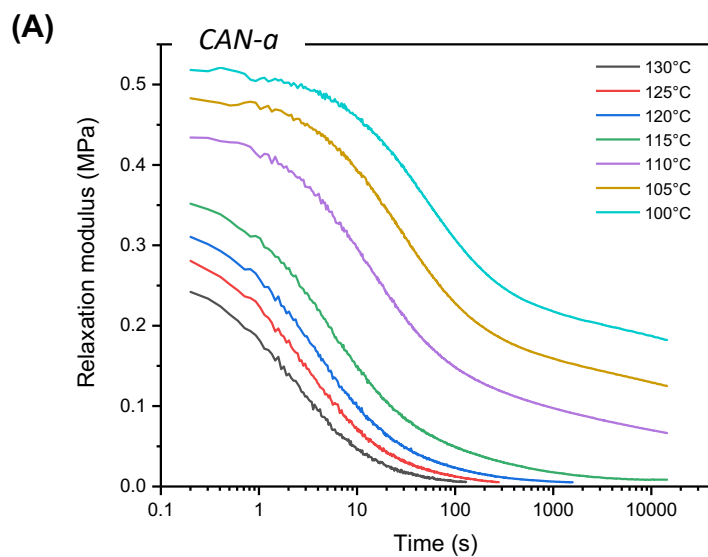
**Figure 6.** FTIR spectra of  $\alpha$ CC and CANa-c.

Homogeneous samples for all CANs were subsequently obtained by compression molding of the pristine material at 120 °C for 30 minutes under 3 tons metric of pressure. By DSC analysis, glass transition temperatures ( $T_g$ ) of 2, 46 and 51 °C were determined for CANs a-c respectively (**Figure S15**). As expected, the lowest  $T_g$  is obtained for **CAN-a** embedding the most flexible bis( $\alpha$ -alkylidene cyclic carbonate) monomer. The thermal stability of the materials was assessed using TGA analysis and degradation temperatures ( $T_{\text{deg}5\%}$ ) around 200 °C were measured for all polymers (**Figure S16**).

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Furthermore, isothermal TGA measurements at 130 °C for 2 hours validated the thermal stability of the materials during processing conditions (**Figure S17**). Finally, adequate network formation was confirmed by acceptable swelling ratios (between 300 and 600%) and soluble fractions of approximately 10 % in THF at room temperature.

In a next step of this study, the rheological behavior of the materials was investigated *via* time sweep experiments. No cross-over of the storage and loss modulus was observed for all materials. However, a rather complex profile is observed (**Figure S18**). The dynamic behaviour of the networks was characterized by stress-relaxation experiments in the viscoelastic region of the materials within a temperature range of 100 to 130 °C (**Figure 7**). Initial experiments were performed on low  $T_g$  material **CAN-a**, displaying full and fast relaxation (less than 100 s) at 130 °C (**Figure 7A**). However, consecutive experiments at lower temperatures showed an unanticipated increase in relaxation modulus. When the temperature was cycled back to 130 °C for a new experiment, a different relaxation pattern was observed with increased storage modulus and relaxation time (**Figure S19a**). To examine the material behavior at high temperature for a prolonged amount of time, a time sweep experiment was performed at 130 °C for 6 hours and showed an increase in  $G'$  over time, likely attributed to additional crosslinking (**Figure S19b**). As this undesired behavior was unique to **CAN-a**, we hypothesized some side reactions to occur from thioether and/or ether functions, however we did not further investigate this phenomenon. We therefore focused our efforts on **CAN-b** and **CAN-c** that are characterized by fully aliphatic chemical structures.





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**Figure 7.** Non-normalized stress-relaxation plots of CAN-a, CAN-b and CAN-c from 130 to 100 °C.

**CAN-b** and **CAN-c** were both able to fully relax in the temperature range of 100 to 130 °C, highlighting the recyclability of the cyclic *S,O*-acetal materials (**Figures 7B** and **7C**). Surprisingly, despite their closely related chemical structures and similar  $T_g$ s, the stress-relaxation profiles of **CAN-b** and **CAN-c** exhibited divergent trends.

It is well-established that - while starting with a single Maxwell approximation to describe relaxation processes is generally a good starting point - reaching more accurate fitting of experimental data generally requires more sophisticated models such as the stretched exponential or the multi-element Maxwell models.<sup>42,63–67</sup> For **CAN-b**, a single element Maxwell model poorly described the rheological data (**Figure S20**) Applying a stretched single Maxwell element already enhanced the fitting quality. However, incorporating more elements (*i.e.* going to a description with two or, even better, three Maxwell elements) improved the fitting quality significantly (**Figure S20**). On the other hand, **CAN-c** presented a very particular relaxation profile, which did not seem to follow a Maxwellian behavior. We were indeed unable to fit to any of the cited models, indicating that far more complex relaxation mechanisms might occur (**Figure S21**). As opposed to **CAN-b**, an abrupt loss in relaxation modulus was observed at low relaxation times and full relaxation was reached at much longer times. Nevertheless, a common feature to both systems was the striking temperature dependence of the relaxation modulus, readily decreasing at higher temperature. Non-normalized stress relaxation profiles indeed showed a decrease of initial modulus with temperature, indicating a decrease in cross-linking density. This behavior might be explained by dissociation events, occurring when the intermediate oxo-thiocarbonate **1** is formed. Once formed, **1** can either react with a free thiol to provide the cyclic *S,O*-acetal **2** or dissociate into  $\alpha$ CC and a free thiol (**Figure 4**). Although our calculations have shown the pathway to be of a much higher energy barrier, a direct dissociation of the *S,O*-cyclic acetal cannot be fully excluded in the high temperature regime. The set of different associative and dissociative reactions, all leading to material relaxation, are thus expected to happen simultaneously and lead to stress relaxation profiles of high complexity.

We hypothesized that the unexpected divergence in stress relaxation profiles between **CAN-b** and **CAN-c** could originate from the complex set of reactions characterized by different kinetics over the temperature range. The incorporation of a spirocyclic cyclohexyl ring in **CAN-c** could indeed potentially influence the global energetics of the different reactions compared to **CAN-b** (containing a simple linear linker). To investigate this hypothesis, we performed again DFT calculations on model molecules and compared all pathways from already studied  $\alpha$ CC (with two methyl groups) to a

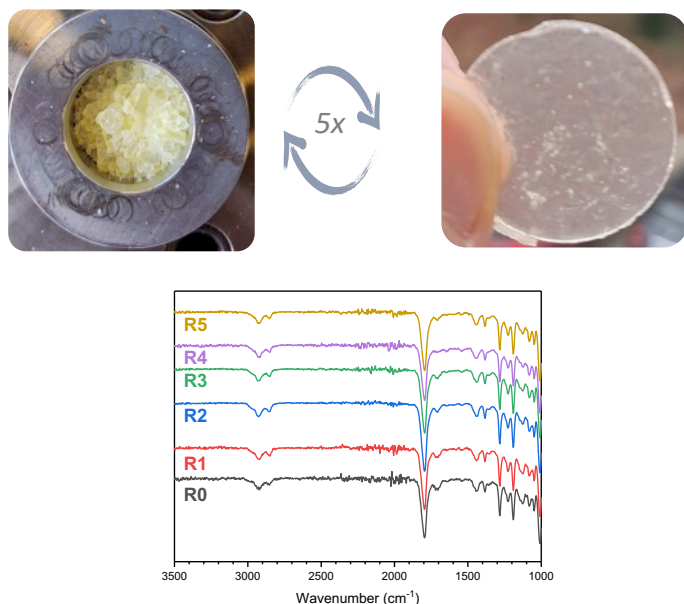


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spirocyclic derivative (with a cyclohexyl group). Although some changes in energetics were observed for elemental steps of both pathway 1 (association reaction) and pathway 2 (dissociation reaction), the change of the substituent did not seem to affect the overall calculated energy barrier in both cases and, consequently, the reaction rates.

## Recycling and proof-of-concept coating application

To demonstrate the recyclability of cyclic S,O-acetal CAN materials, **CAN-c** was subjected to multiple shredding and compression molding cycles at 120 °C for 30 minutes under 3 MT of pressure. While the  $T_g$  over the different reprocessing cycles was varying, the degradation temperatures only slightly altered over the cycles (**Figure S22-23** and **Table S2**). Moreover, the FTIR spectra show no significant change in signals (**Figure 8**).

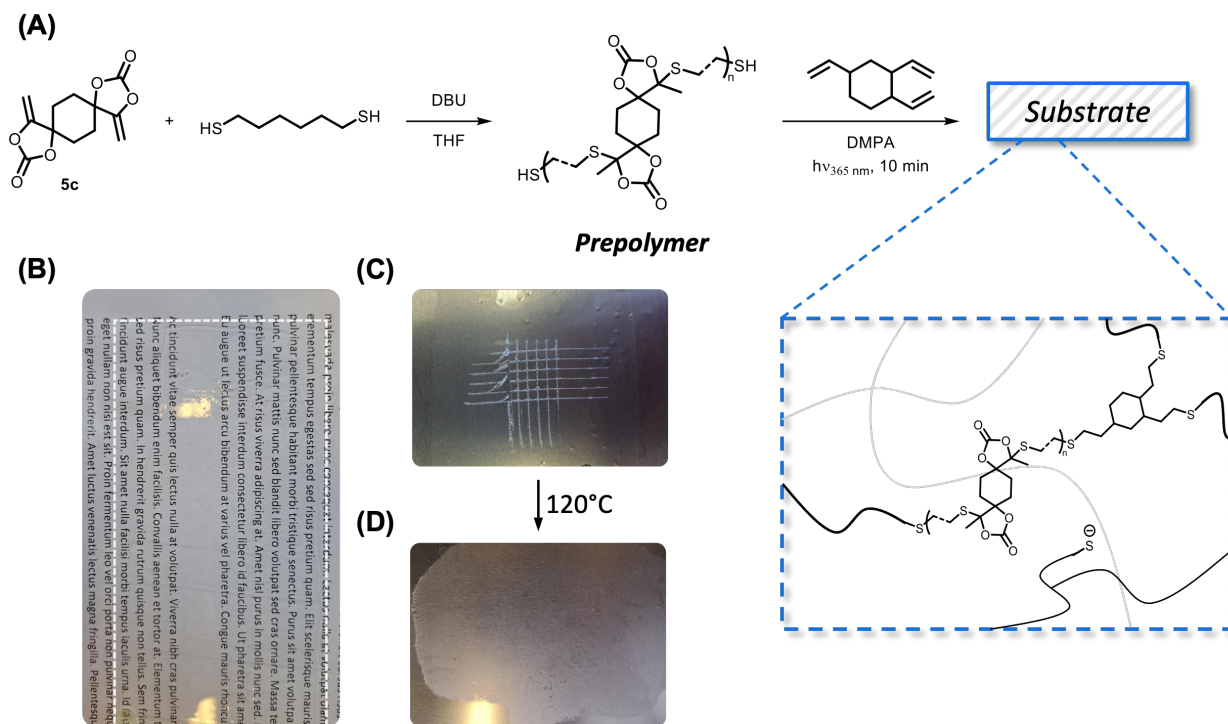


**Figure 8.** FTIR spectra of the recycled CAN-c at 120°C under a pressure of 3 metric ton for 30 minutes.

In a final part of this study, the focus was shifted towards an application involving coatings. The most important function of a coating is to protect a substrate and preferably consists of more resilient thermosetting materials. However, when damage occurs to the coating, its protective capacity is typically compromised, necessitating the application of a new coating. By integrating dynamic bonds in the coating, the inflicted damage could in principle be healed upon applying an appropriate trigger, thereby restoring the protecting capacity.<sup>68</sup> To enable the dynamics in the exchange chemistry of

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S,O-acetals, free thiolates are essential. Interestingly, thiol groups also find utility in photochemical thiol-ene reactions, that are commonly used in coating applications.<sup>69</sup> Moreover, besides the spatio-temporal control, the thiol-ene reaction is rather insensitive to oxygen and because of the mild orthogonal reaction conditions, this reaction can be carried out even with sensitive molecules.<sup>69,70</sup>



**Figure 9.** (A) General scheme for the preparation of S,O-acetal containing coatings starting from a prepolymer that was reacted photochemically in a thiol-ene reaction. (B) Excellent transparency is observed when the coating is applied on a glass substrate. (C) The film exhibits good adhesive properties when scratched on a metal surface and (D) Scratches could be mended after application of heat.

The dynamic S,O-acetal groups were introduced in the coating materials starting from a prepolymer, following a similar approach as previously described for vinylogous urethane coatings.<sup>68</sup> Polymer synthesis using bis $\alpha$ CC was earlier described,<sup>53</sup> however by slightly adjusting the stoichiometry (*i.e.* using a small excess of thiols, see ESI for details), a thiol end-capped prepolymer was obtained and characterized by NMR spectroscopy (**Figure S24-26**). Subsequently, the thiol end-groups were reacted photochemically with TVC using DMPA as photo-initiator (**Figure 9A**).

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Cross-linker **5c** was selected to produce a coating with a desired  $T_g$  value of approximately 50°C and identical FTIR spectrum compared to CAN-c (**Figure S27** and **Figure S28**). The amount of TVC was calculated to ensure the availability of free thiolates in the final material. A transparent layer was obtained when coated on a glass substrate (**Figure 9B**). The adhesive properties were tested on a metal surface, following ASTM D3359-02 standard, which yielded a value of 3B (**Figure 9C**). The scratched surface was thereafter subjected to heat (120°C) for 30 min, which enabled healing of the coating through the dynamic S,O-acetal exchange (**Figure 9D**). While the scratches were visibly healed, the coating also seemed to flow excessively. This preliminary scratch healing test showed that the dynamicity of S,O-acetals is indeed operational in the coatings but more formulations should be investigated to optimize the coating properties, which is beyond the scope of the current study.

## Conclusion

In summary, we have demonstrated an unprecedented associative exchange in CO<sub>2</sub>-sourced cyclic S,O-acetals. The dynamic nature of these cyclic S,O-acetals was investigated through model molecule studies and reaction kinetics at different temperatures. Additionally, DFT calculations were performed to support the findings from the model studies and to elucidate the newly proposed reaction mechanism.

CO<sub>2</sub>-sourced bifunctional alkylidene cyclic carbonates were combined with an excess of polythiols to provide covalent adaptable networks of the associative type. The dynamic nature of these materials was studied by rheology through stress relaxation experiments, revealing complex relaxation profiles that might originate from a set of concurrent exchange mechanisms. Nevertheless, compression molding allowed for the reprocessing of the materials, with good retention of their properties. The potential of these materials was finally assessed in a coating application with excellent transparency, adhesion to the substrates, and healing of scratches at elevated temperature.

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## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENT

S.M. acknowledges Ghent University for funding of his doctoral research (DOCT/009009). The authors of Liege thank FNRS for the financial support in the frame of the CO<sub>2</sub>Switch project under grant T.0075.20. C.D. is a F.R.S.-FNRS Research Director. Computational resources have been provided by the Consortium des Équipements de Calcul Intensif (CÉCI), funded by the Fonds de la Recherche Scientifique de Belgique (F.R.S.-FNRS) under grant no. 2.5020.11 and by the Walloon Region. Computational resources (Stevin Supercomputer Infrastructure) and services used in this work were provided by the VSC (Flemish Supercomputer Center), funded by Ghent University, FWO and the Flemish Government- department EWI. Bernhard De Meyer and Jan Goeman are acknowledged for technical support. Vincent Scholiers is acknowledged for his help during the synthesis of the TVC-trithiol.

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