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Design of functional isocyanate-free poly(oxazolidone)s under mild conditions

Maliheh Razavi-Esfali[a,b], Thomas Habets[a], Fabiana Siragusa[a], Bruno Grignard[a,c], Haritz Sardon[b] and Christophe Detrembleur[a,d]*

[a] Center for Education and Research on Macromolecules (CERM), CESAM Research Unit, University of Liege, Sart-Tilman B6a, 4000 Liege, Belgium

[b] POLYMAT, University of the Basque Country UPV/EHU, Joxe Mari Korta Center, Avda. Tolosa 7, 20018 Donostia-San Sebastian, Spain

[c] FRITCO2T Platform, University of Liege, Sart-Tilman B6a, 4000 Liege, Belgium

[d] WEL Research Institute, Wavre 1300, Belgium

* Corresponding authors: **E-mail:** christophe.detrembleur@uliege.be

ABSTRACT

Polyoxazolidones, i.e. high performance polymers bearing cyclic carbamate linkages, were recently accessible by a non-isocyanate route under mild conditions. Herein, we report the preparation of polyoxazolidones bearing thioether linkages, which offers multiple opportunities for facile chain functionalization. The process consists in the chemical upcycling of CO_2-based poly(*oxo*-carbonate)s by aminolysis with allylamine. At room temperature, the poly(*oxo*-carbonate) is completely decomposed into an allyl-functionalized bis(oxazolidone) which is then copolymerized with dithiols by UV-initiated thiol-ene polymerization. The allyl-functionalized bis(oxazolidone) monomer is also quantitatively obtained by reacting allyl amine with a CO_2-based bis(alkylidene cyclic carbonate). A library of poly(oxazolidone-*co*-thioether) copolymers is easily accessible by varying the nature of the dithiol and M_w up to 101,000 g/mol is reached. All polymers are quantitatively dehydrated by simple thermal treatment at a temperature ranging from 120 to 140 °C at the solid state, furnishing poly(oxazolidone-*co*-thioether) copolymers bearing exocyclic vinylene moieties and presenting a high thermal stability ($T_{deg10\%}$ up to 360 °C) and various glass transition temperatures. The post-polymerization modifications by thiol oxidation to sulfoxide or sulfone, or through S-alkylation of the thioether linkages, are realized to deliver unprecedented functional polyoxazolidones. Notably, the introduction of sulfonium groups enables to produce the first example of water-soluble polyoxazolidones. This work describes a simple platform to produce a large panel of functional polyoxazolidones that are not accessible by the current isocyanate-based methods, moreover under mild operating conditions by exploiting CO_2-based monomers.

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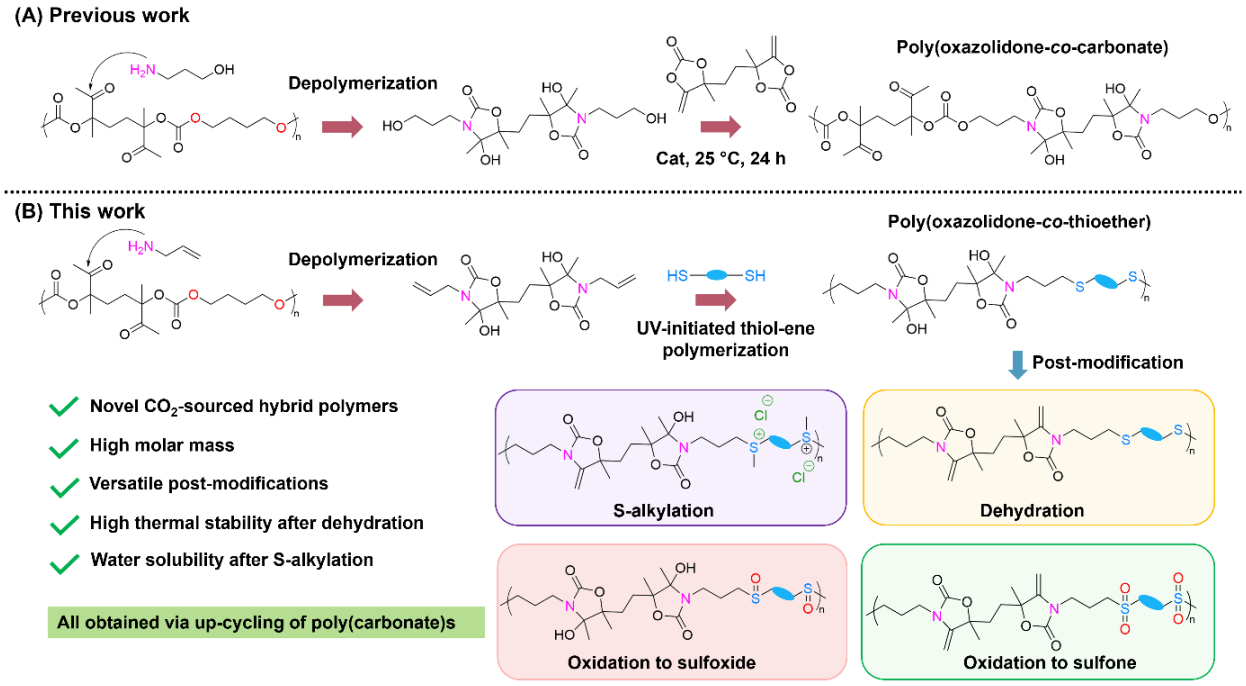
INTRODUCTION

Polyurethanes (PUs), ranking 6th among all polymers, are found in multiple applications such as foams, adhesives, coatings, and elastomers [1-3]. However, most PUs still present a poor resistance to heat which is considered as a serious disadvantage for some high performance applications requiring high thermal stability [4-6]. In response to this challenge, the solution was found in the development of polyoxazolidones (POxa), a specialized class of PUs distinguished by their exceptional thermal stability thanks to the presence of thermally and chemically resistant five-membered cyclic urethane linkages. Their exceptional heat resistance renders them highly promising for industrial applications that demand elevated thermal durability, e.g. in automotive, aerospace, electrical engineering, and electronics sectors [7-12]. POxa are most often produced by copolymerization of diisocyanates with polyepoxides at high temperature (typically 160 °C) in the presence of suitable catalysts [13-15]. Nevertheless, diisocyanates are toxic compounds and numerous epoxides are classified as CMR (carcinogenic, mutagenic and reprotoxic) products, both causing serious harm to the environment and the human body [16, 17]. The high reactivity of the reagents as well as the harsh reaction conditions are also not compatible with the introduction of many functionalities (e.g. ketones and alcohols) in the polymer chains, restricting the possibilities to tune POxa properties. Although POxa are highly appealing for the development of high-performance materials, more versatile, greener, and safer synthetic approaches are searched for their production. To address this challenge, only few works succeeded to find alternative pathways toward these elusive polymers, such as the polycondensation of diurethanes with diepoxides at 90 °C employing a tertiary amine as a catalyst [18], or the copper-catalyzed 4-component reaction of a dialkyne with a diamine, an aldehyde, and carbon dioxide at temperatures ranging from 75 to 80 °C [19, 20]. Some of us pioneered the utilization of novel CO_2-sourced activated cyclic carbonates, i.e. α-alkylidene carbonates (αCC), for preparing isocyanate-free POxa by copolymerization of bifunctional monomers (bisαCC)s with diamines under mild conditions, i.e. at room temperature (RT) and under catalyst-free conditions [21-23]. The scope of POxa was also extended by Schaub's [24] and Lamb's [25] groups by varying the structure of BisαCC. The functional group tolerance of the reaction was proven to be feasible through copolymerization with mixtures of diamines and dithiols, providing elusive poly(oxazolidone-*co*-monothiocarbonate)s [26]. Recently, circular POxa networks embedding dynamic *N,S*-acetal bonds were produced starting from αCC, diamines, and polythiols [27].

BisαCC also served to prepare poly(*oxo*-carbonate)s by organocatalyzed copolymerization with (biorenewable) diols [28-33], some of them having found applications as solid electrolytes for lithium batteries [34]. Interestingly, this class of polycarbonates, also prepared at RT, displayed easy recyclability. By aminolysis with propylamine, the polymer was totally decomposed into the starting diol and an elusive bis(oxazolidone) at RT under catalyst-free conditions. The process has shown to be tolerant to alcohol functional groups and by utilizing aminopropanol, a hydroxyl

functional bis(oxazolidone) was collected at high yield. The building block further served as a comonomer for polymerization with BisαCC to deliver a polymer containing oxazolidone and *oxo*-carbonate linkages (thus, poly(oxazolidone-*co*-carbonate)) [35] (Scheme 1A). The facile depolymerization of poly(*oxo*-carbonate) involved the nucleophilic attack of the primary amine on the pendant ketone groups, leading to an hemiaminal intermediate that could undergo intramolecular cyclization to deliver the five-membered oxazolidone and the leaving alcohol. This approach of polycarbonates upcycling utilizing simple commercially available functional amines thus offered an appealing route to easily produce functional bis(oxazolidone)s re-entering the production of hybrid POxa.

In this work, we exploited this poly(*oxo*-carbonate)s upcycling strategy to deliver an allyl functionalized bis(oxazolidone) by facile aminolysis with allylamine. The monomer was then upcycled into hybrid POxa containing thioether linkages by a radical thiol-ene photopolymerization with various dithiols (Scheme 1B). We showed that various functionalities are easily introduced to the polymer chains, i.e. pendant olefins by dehydration, sulfoxide, or sulfone by partial or total oxidation of the thioethers, or sulfonium by their *S*-alkylation. The successful polymer modifications were demonstrated by NMR and IR spectroscopies, and the thermal properties of the polymers were assessed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). This work enlarged the upcycling possibilities of poly(*oxo*-carbonate)s by utilizing commercially available reagents while giving access to new functional POxa-type polymers of tunable properties. Another alternative route was also proposed to quantitatively deliver the allyl functionalized bis(oxazolidone) needed for the construction of the hybrid POxa by direct aminolysis of a CO_2-based bis(alkylidene cyclic carbonate) with allylamine at RT.



Scheme 1. (A) Depolymerization of PC by aminolysis with propanolamine and its upcycling into a hybrid polyoxazolidone containing carbonate linkages [35]; (B) Depolymerization of PC by aminolysis with allylamine and upcycling into a polyoxazolidone containing thioether bonds via thiol-ene photopolymerization, and further modifications of the polymer.

EXPERIMENTAL

Synthesis of poly(*oxo*-carbonate) (PC)

PC was synthesized according to a procedure described before [28]. **BisαCC** (2 g, 7.86 mmol, 1 equiv), 1,4-butanediol (0.708 g, 7.86 mmol, 1 equiv) and DBU (60 µL, 0.401 mmol, 0.05 equiv) were added to a reaction tube with dry DMSO (10 mL) and the mixture was stirred at 25 °C for 24 h. Then, the polymer was precipitated in diethyl ether followed by centrifugation at 10,000 rpm for 7 min and then dried under vacuum at 25 °C for 8 h. The solid was then solubilized in THF and dialyzed against THF for 24 h, followed by precipitation in diethyl ether and filtration. Finally, the polymer was dried under vacuum at 40 °C for 8 h and characterized by ^{1}H, ^{13}C, and HSQC NMR spectroscopy (Figures S1-S3) and SEC (Figure S4).

Depolymerization of poly(*oxo*-carbonate) (PC) by allylamine into bis(oxazolidone) (1).

PC (400 mg) was added in a reaction tube and dissolved in dry THF (1.2 mL). Then, 1,3,5-trimethoxybenzene (TMB) (25 mg) was added as an internal standard, followed by the addition of allylamine (395 mg, 3 equiv *vs* each ketone functionality of the polymer repeating unit). The mixture was stirred at 25 °C and the depolymerization was monitored by ^{1}H-NMR spectroscopy and SEC by sampling over time. The

bis(oxazolidone) (**1**) was isolated by precipitation of the reaction mixture into diethyl ether followed by filtration. The solid was dried under vacuum at 40 °C for 24 h (isolated yield = 63%, 215 mg). The isolated monomer was characterized by ^{1}H, ^{13}C, COSY, HSQC, and HMBC NMR spectroscopy (Figures S7-S11)

Synthesis of bis(oxazolidone)s (1) by aminolysis of BisαCC

BisαCC (2 g, 7.86 mmol, 1 equiv) was added to an ice bath-cooled glass vial followed by the addition of allylamine (2.24 g, 39.2 mmol, 5 equiv). The reaction was monitored by ^{1}H-NMR. After a 30 min reaction, the monomer was simply purified by removing the solvent under vacuum at 40 °C (isolated yield > 99%). The isolated monomer was characterized by ^{1}H, ^{13}C, COSY, HSQC, and HMBC NMR spectroscopy (see Figures S7-S11).

General procedure for the synthesis of polymers by radical thiol-ene

Bis(oxazolidone) **1** (400 mg, 1.08 mmol, 1 equiv), dithiol **2** (1.08 mmol, 1 equiv) and 2,2-Dimethoxy-2-phenyl acetophenone (DMPA) (13.9 mg, 0.054 mmol, 0.05 equiv) were added in a glass flask, followed by the addition of DMF (600 µL). The reaction mixture was stirred under irradiation of 365 nm UV light (Omnicure series 2000, 200 W) for 24 h. The distance of the light source to the reaction mixture was kept constant at 10 cm for each polymerization reaction. After 24 h, an aliquot of the crude product was sampled for ^{1}H-NMR and SEC characterizations. The polymer was diluted in a minimum amount of THF, precipitated in diethyl ether, and centrifugated at 10,000 rpm for 7 min. After 4 h of vacuum-drying at RT, the solid was solubilized and dialyzed in THF for 24 h, followed by precipitation in diethyl ether and filtration. The pure polymer was dried under vacuum at 40 °C for 24 h and characterized by ^{1}H, ^{13}C, COSY, HSQC, HMBC NMR spectroscopy (see Figure 1, and Figures S26-S50) and SEC (see Table 2).

Representative procedure for the dehydration of polymers

All the dehydration temperatures of polymers were determined by TGA and presented in Table 3. The dehydration of polymers was performed according to a procedure described before [26]. The oven was pre-heated to the dehydration temperature, and then 100 mg of the corresponding polymer was poured onto an aluminum plate and was placed in the oven for 2 h under air. The dehydrated polymers were used for characterizations without any further purification. The dehydrated polymers were characterized by ^{1}H, ^{13}C, COSY, HSQC, HMBC NMR spectroscopy (see Figures S62-S86), and SEC (see Figures S87-91).

Procedures for polymer post-modification

Oxidation of thioether to sulfoxide. Selective oxidation of **P2b** to sulfoxide was performed following modification of a previous procedure [36]. In a glass vial, polymer **P2b** (100 mg, 0.19 mmol) was dissolved in 2 mL DMF. 395 µL of a 30% (w/w) H_2O_2 aqueous solution (10 equiv *vs* thioether function, 3.84 mmol) was added, and the

mixture was stirred for 72 h. The polymer was precipitated in diethyl ether followed by centrifugation at 10,000 rpm for 7 min. The solid was dried under vacuum at 25 °C for 24 h (isolated yield = 90%). The polymer was characterized by ^{1}H, ^{13}C, COSY, HSQC, HMBC NMR spectroscopy (see Figures S115-S120), FTIR (see Figure S121) and SEC (see Figure S122).

Oxidation of thioether to sulfone. Selective oxidation of **P2b** to sulfone was performed following modification of previous procedures [37, 38]. In a glass vial, polymer **P2b** (200 mg, 0.384 mmol) was dissolved in 2 mL DMF. Then, 237 µL (3 equiv *vs* thioether function, 2.3 mmol) of a 30% (w/w) H_2O_2 aqueous solution and 6 mg (0.025 equiv) of diphenyl diselenide (DPDS) were added and the mixture was stirred for 48 h. The polymer was precipitated in diethyl ether followed by centrifugation at 10,000 rpm for 7 min and dried under vacuum at 40 °C for 24 h and then at 60 °C for 16 h (isolated yield = 92%). The polymer was characterized by ^{1}H, ^{13}C, COSY, HSQC, HMBC NMR spectroscopy (see Figures S124-S129), FTIR (Figure S130), and SEC (see Figure S131).

S-Alkylation of thioether. In a glass vial, polymer **P2b** (200 mg, 0.384 mmol) was dissolved in 3 mL DMF. Then, methyl iodide (10 equiv *vs* thioether function, 3.84 mmol) was added, and the reaction mixture was stirred for 48 h. The resulting solution was dialyzed in a solution of NaCl 0.1 M for 2 days to exchange the counterion I^- to Cl^-, and then dialyzed in water for 1 day. The solution was lyophilized to obtain the polymer as a white solid (isolated yield = 70%). The polymer was characterized by ^{1}H, ^{13}C, COSY, HSQC, HMBC NMR spectroscopy (see Figures S133-S138).

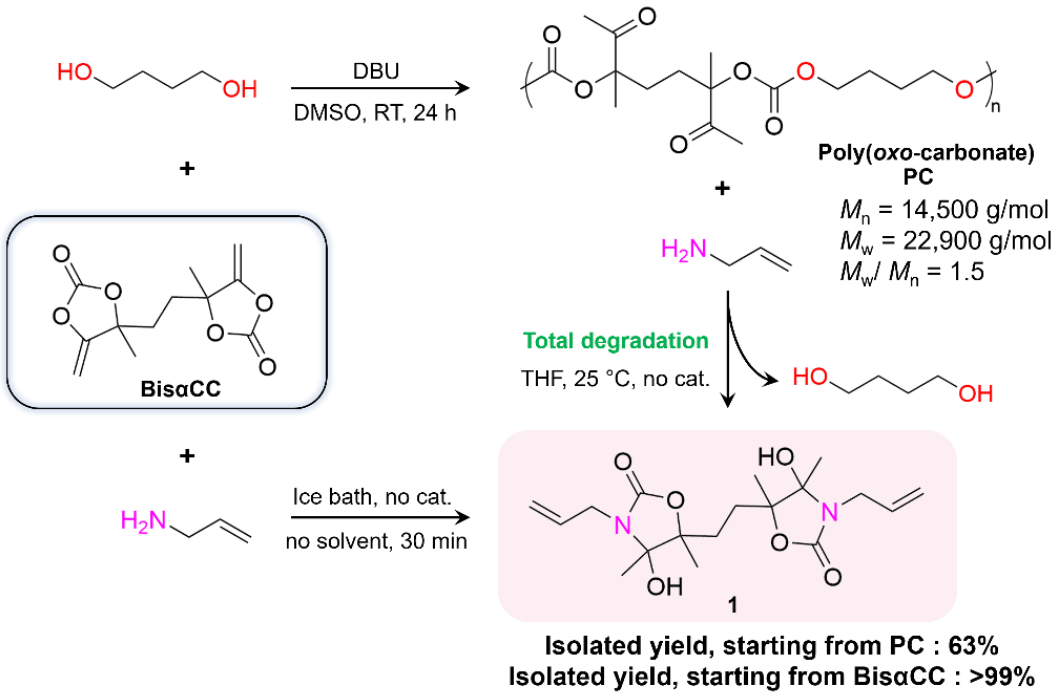
RESULTS AND DISCUSSION

Monomer synthesis

We first studied the aminolysis of a CO_2-sourced poly(*oxo*-carbonate) (**PC**) using allylamine, to provide a new bis(oxazolidone) with allyl functionality. To this aim, **PC** was synthesized via step-growth copolymerization of **BisαCC** with 1,4-butanediol at 25 °C in the presence of DBU as organocatalyst (5 mol % *vs* **BisαCC**), following a previously described procedure [28] (Scheme 2). The microstructure of **PC** was confirmed by ^{1}H, ^{13}C and HSQC NMR spectroscopy (Figures S1-S3) and the molar mass was determined by size exclusion chromatography (SEC; M_w = 22,900 g/mol, Figure S4). The aminolysis of **PC** was conducted at RT in THF using allylamine (3 equiv *vs* each ketone functionality of the polymer repeating unit). The formation of the products and the extent of depolymerization were monitored by ^{1}H-NMR spectroscopy (Figure S4) and SEC (Figure S6). After only 1h, ^{1}H-NMR revealed that the resonance relative to the methyl adjacent to the ketone group of **PC** (δ = 2.10 ppm) drastically decreased (90% of degradation). This was translated in a huge decrease of molar mass as determined by SEC, reaching a low value in M_w of 850 g/mol. The ^{1}H-NMR also revealed characteristic resonances corresponding to the expected products: the released alcohol (HO-$\underline{CH_2}$- at 3.39 ppm), the oxazolidone (N-$\underline{CH_2}$- at 3.76 ppm) and

the imine side-product (N-$\underline{CH_2}$- at 3.95 ppm; see our previous work for the mechanism of formation of this side-product [35]). After 24 h of reaction, the characteristic signals of **PC** totally disappeared, indicating complete polymer degradation (Figure S5). Interestingly, the determined molar composition of the products alcohol/oxazolidone/imine was 0.5/0.4/0.1. The selectivity in oxazolidone product was thus higher compared to the depolymerization performed with propylamine in our previous work (alcohol/oxazolidone/imine was 0.5/0.33/0.17) [35]. The formed bis(oxazolidone) was isolated by precipitation in diethyl ether (isolated yield 63%) (Figures S7-S11).

An alternative route to monomer **1** was the direct aminolysis of **BisαCC** by allylamine (Scheme 2). The reaction was monitored by ^{1}H-NMR using 5 equiv of allylamine as both the reagent and solvent, in an ice bath under catalyst-free conditions (Figure S12). The results evidenced a fast aminolysis, reaching completion within 30 min, with the selective and quantitative production of bis(oxazolidone) **1** (isolated yield of >99%).

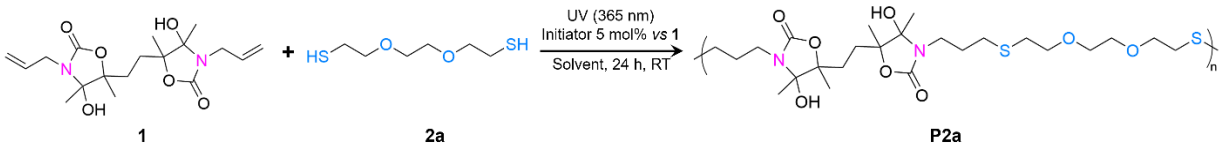


Scheme 2. Aminolysis of PC into **1**, and direct synthesis of **1** by aminolysis of BisαCC

Synthesis of poly(oxazolidone-*co*-thioether)s

The allyl functionalized bis(oxazolidone) **1** was copolymerized with dithiol **2a** by UV-initiated radical thiol-ene in the presence of a photoinitiator (Scheme 3). The experimental setup is shown in Figures S13-14. An equimolar ratio between the two comonomers was used and a series of reaction parameters were explored to

determine the optimal conditions to reach high monomer conversions and molar masses (solvent, concentration, nature of the photoinitiator). All the polymerizations were carried out at RT, using a 365 nm UV lamp for 24 h. Crude reaction mixtures were analyzed by ^{1}H-NMR spectroscopy (to determine the monomer conversion, Figure S15, Eq. S1) and SEC (to determine the relative polymer M_w). The results are summarized in Table 1.



Scheme 3. Reaction scheme for the photoinitiated thiol–ene polymerization of **1** with **2a**

Table 1. Optimization of the reactions conditions for the preparation of poly(oxazolidone-*co*-thioether)s.

Entry	Solvent	Concentration (M)	Initiator [a] (5 mol% *vs* monomer 1)	M_n (g/mol) [b]	M_w (g/mol) [b]	Dispersity [b]	Conv. [c] (%)
1	DMF	0.5	DMPA	4,500	10,000	2.3	90
2	DMF	1.5	DMPA	16,500	74,000	4.5	>99
3	DMF	1.8	DMPA	27,000	116,000	4.2	>99
4	THF	1.8	DMPA	4,500	7,700	1.7	72
5	Acetonitrile	1.8	DMPA	5,000	12,600	2.4	80
6	DMF	1.8	Omnirad 2100	13,000	38,500	2.9	92
7	DMF	1.8	Omnirad 2022	15,000	38,000	2.5	97

[a] The structure of free-radical initiators is shown in Scheme S1 [b] determined by SEC in DMF/LiBr calibrated with PS standards on crude reaction mixture; [c] conversion of monomer **1** calculated by ^{1}H-NMR spectroscopy on crude reaction mixture. Conditions: 365 nm UV light, 24 h, RT.

As shown in Table 1, the monomer conversion and polymer molar mass were strongly dependent on the nature of the solvent. At same concentration (1.8 M) and with the

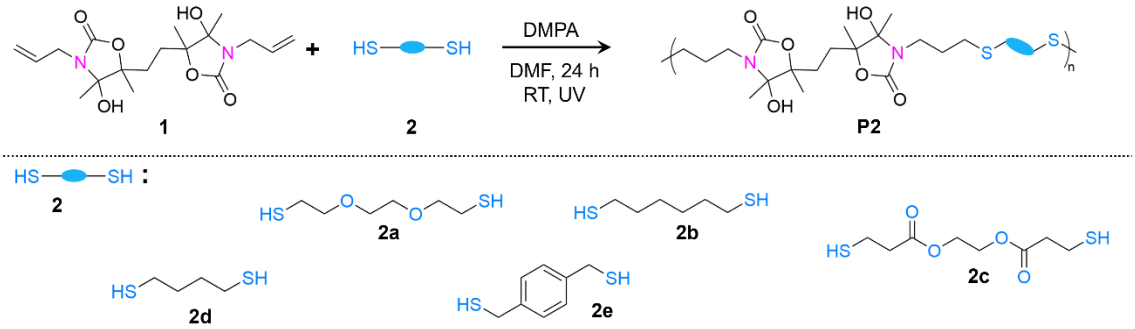
same photoinitiator (2,2-dimethoxy-2-phenyl acetophenone; DMPA), the conversion and polymer M_w were higher in DMF (> 98%; 116,000 g/mol; entry 3) compared to those obtained in THF (72%; 7,700 g/mol; entry 4) or acetonitrile (80%; 12,600 g/mol; entry 5). Hence, DMF proved to be the optimal solvent for this polymerization process. Decreasing the monomer concentration from 1.8 to 1.5 and 0.5 M was detrimental for the reaction (entries 1-3). Replacing DMPA by alternative photoinitiators such as Omnirad 2100 or Omnirad 2022 had adverse effects on both the conversions and the polymer molar mass (entries 6-7). It is worth noting that high monomer conversion resulted in highly viscous reaction mixtures, thereby impeding growing chains diffusion and efficient stirring. This phenomenon led to broad molecular weight distributions with dispersity values growing over the theoretical maximum value of 2.

Having the optimized reaction conditions in hand (DMF as solvent, monomer concentration of 1.8M, DMPA as photoinitiator), the time of UV light exposure required to reach complete monomer conversion was determined by monitoring the photopolymerization process over time using monomer **1** and dithiol **2b** (Figure S16a) by ^{1}H-NMR spectroscopy and SEC. The dithiol **2b** was selected to simplify the ^{1}H-NMR spectrum of the reaction compared to dithiol **2a**. As shown in Figure S16b, the resonance associated to allyl moiety of **1** at δ = 5.06-5.22 ppm was not detectable after 30 min reaction, confirming very high monomer consumption. After 24 h, the viscosity of the reaction medium was high, which prevented any further stirring. The time evolution of the SEC chromatogram, and thus polymer molar mass and dispersity, upon exposure to UV light is shown in Figures S17 and S18. After 5 h of photopolymerization, a moderate M_w of 19,000 g/mol was obtained ($Đ$ = 1.9), and was significantly increased to M_w of 53,000 g/mol ($Đ$ = 2.6) after 24 h of reaction.

Various dithiols **2a-2e** (Scheme 4) were then evaluated for the photopolymerization to illustrate the versatility of the process and to prepare a large scope of polymers (Table 2). All the polymerizations were conducted in the optimized reaction conditions at RT for 24 h. A conversion of more than 98% was obtained for **P2a-d** as determined by ^{1}H-NMR on crude mixtures, evidenced by the almost complete disappearance of the olefinic peak (δ= 5.06-5.22 ppm) of monomer **1** (Figure S19). It is worth noting that a lower conversion of 80% was obtained for polymer **P2e** probably due to the low solubility of dithiol **2e** in DMF. The crude polymers had moderate to high relative M_w, with values ranging from 19,000 (for **P2e**) to 116,000 g/mol (for **P2a**) (Table 2). The molecular characteristics of polymers after purification and their SEC chromatograms are depicted in Table S1 and Figures S20-S25.

The polymers microstructures were fully characterized by NMR spectroscopy, and all ^{1}H- and ^{13}C-NMR spectra are depicted in Figure 1 and Figures S26-S50. ^{1}H-NMR spectra demonstrated the anticipated repeating units consisting of thioether and oxazolidone linkages, with their typical resonances, e.g. S-$\underline{CH_2}$ of thioethers at δ = 2.44-2.50 ppm, and N-$\underline{CH_2}$ of oxazolidones at δ = 3.08-3.19 ppm as well as the resonance of the hydroxyl moiety at δ = 6.01 ppm (Figure 1). The presence of ether linkages in polymer **P2a** was confirmed by the resonance at δ = 3.55 ppm of the methylene group adjacent to ether bond ($\underline{CH_2}$-O). For **P2c** the presence of the ester

linkages was confirmed by the adjacent methylene peak (CH$_2$-COO, δ = 2.61 ppm). The presence of the oxazolidone group was further confirmed by ^{13}C-NMR spectroscopy, with the typical resonance of the carbonyl group at 157 ppm in all synthesized polymers. For **P2c**, in addition to the carbonyl group of oxazolidone, the one of the ester moiety was also present at 171.85 ppm. All the polymers were soluble in DMSO, DMF and THF, and were insoluble in water (Table S2).



Scheme 4. Synthesis of poly(oxazolidone-*co*-thioether)s **P2a-P2e**

Table 2. Scope of the photoinitiated thiol–ene click polymerization of monomer **1** and different dithiols.

Entry	Polymer	Dithiol	M_n (g/mol)[a]	M_w (g/mol)[a]	Dispersity[a]	Conv.[b] (%)
1	P2a	2a	27,000	116,000	4.2	>99
2	P2b	2b	19,000	71,000	3.7	>99
3	P2c	2c	18,000	54,000	2.9	>99
4	P2d	2d	22,000	55,000	2.5	>99
5	P2e	2e	7,000	19,000	2.7	80

Condition: DMF (1.8 M), 2,2-dimethoxy-2-phenyl acetophenone (DMPA) 5 mol% *vs* monomer **1**, 365 nm UV light, 24 h, RT.

[a] determined on crude products by SEC in DMF/LiBr calibrated with PS standards; [b] determined by ^{1}H-NMR spectroscopy on crude reaction mixtures. The calculations were detailed in the supporting information.

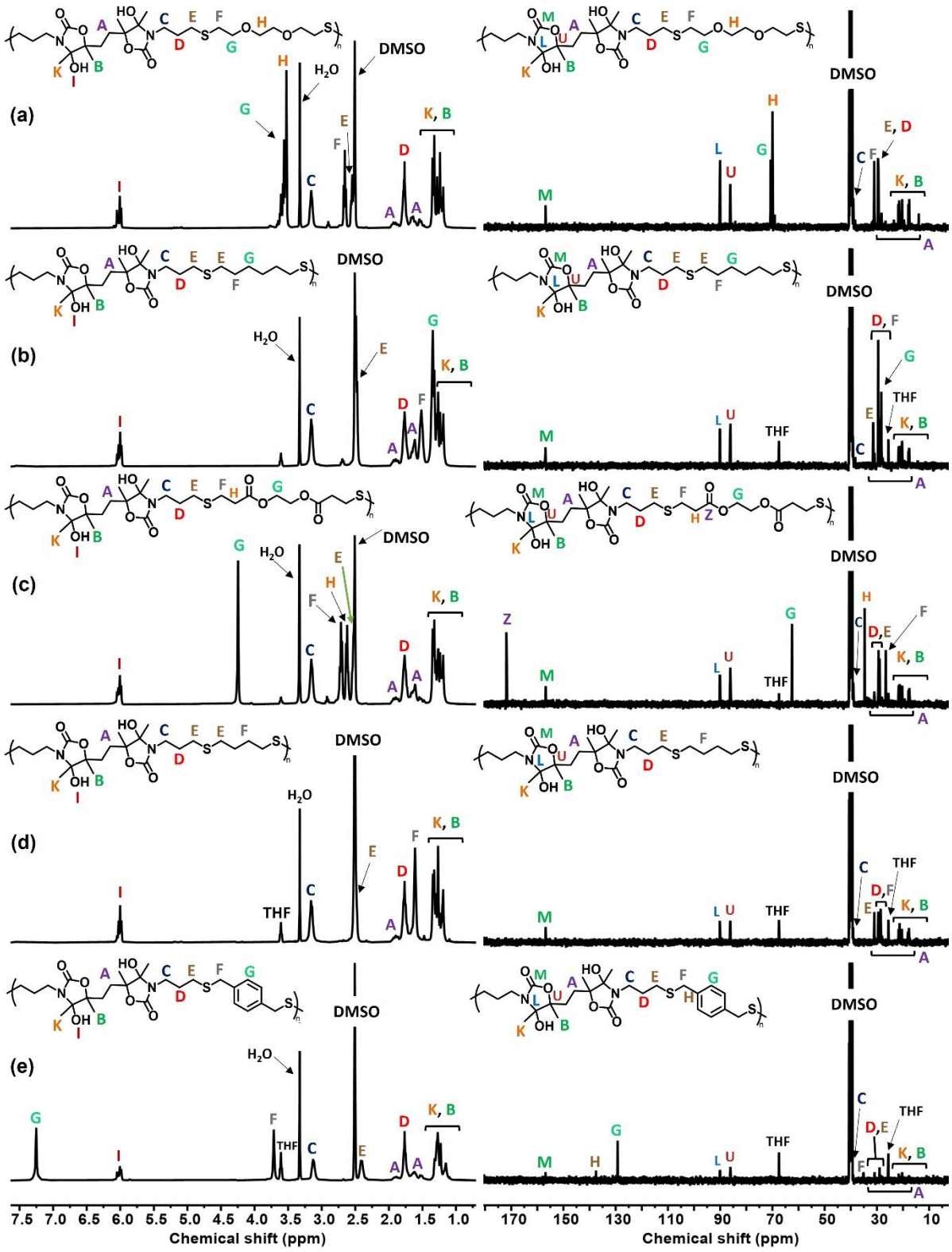


Figure 1. ^{1}H-NMR spectra (left, 400 MHz, DMSO-d_6) and ^{13}C-NMR spectra (right, 100 MHz, DMSO-d_6) of purified polymers (a) **P2a**, (b) **P2b**, (c) **P2c**, (d) **P2d**, (e) **P2e**.

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Polymers dehydration and thermal properties

The thermal stability of all polymers was investigated using thermogravimetric analysis (TGA, Figures S51-S55). A two-step thermal degradation behavior was observed (see Figure 2b, TGA curve of **P2b** as a representative example), a typical feature of poly(hydroxyoxazolidone)s [26]. The first weight loss corresponded to the release of volatile traces and most importantly to the dehydration of hydroxyoxazolidone units in the range of 120 to 140 °C, resulting in the formation of an exocyclic vinylene moiety (Figure 2a). The dehydration temperature (T_{dehy}) was precisely determined by applying a slow heating ramp (2 K/min; Figures S56-S60), as already reported for POxa of the hydroxyoxazolidone-type [26]. The second weight loss was attributed to the degradation of the polymer backbone. The degradation temperature at 10% mass loss ($T_{deg,10\%}$) of the polymers was determined after the dehydration event and was in the range of 320 to 365 °C (Table 3; Figures S51-S55).

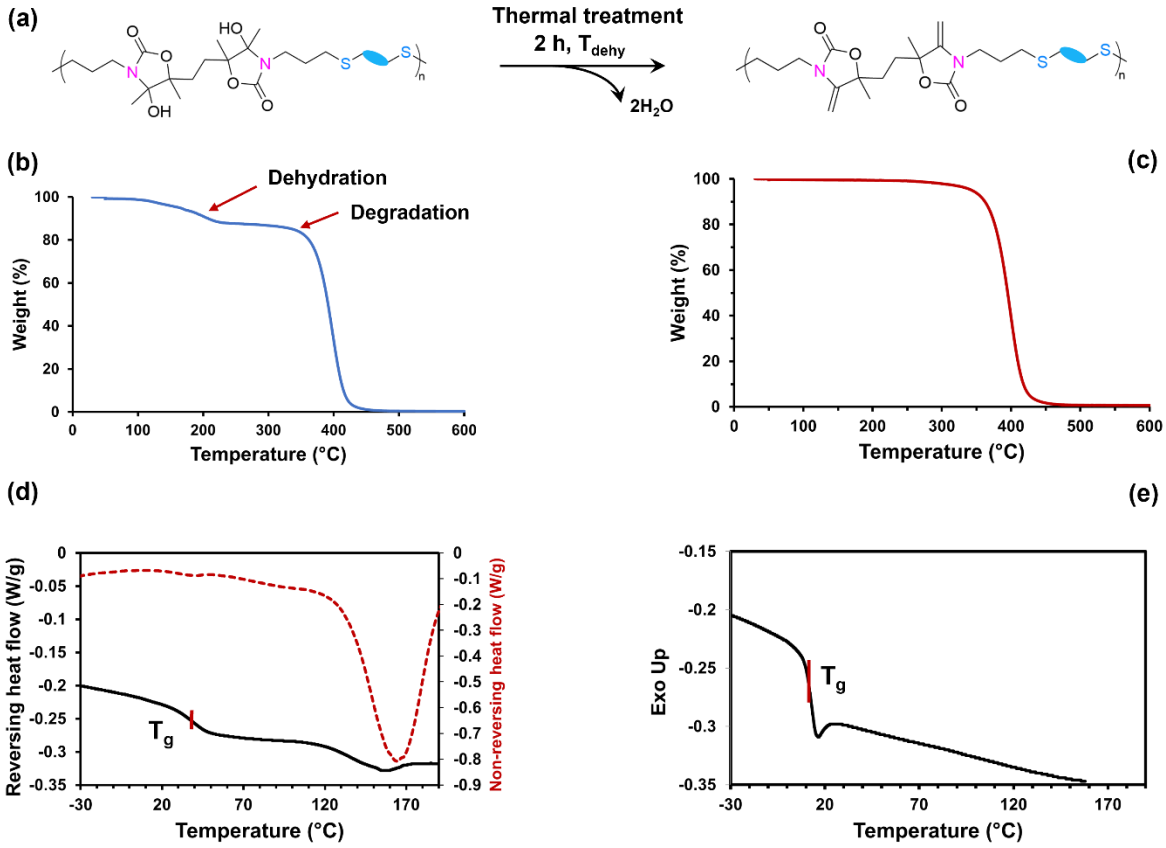

Figure 2. (a) schematic representation of POxa dehydration; (b) TGA pattern of POxa (**P2b**); (c) TGA thermogram of POxa-dehydrated (**P2b-dehydrated**); (d) mDSC thermogram for POxa (**P2b**); (e) DSC thermogram of POxa-dehydrated (**P2b-dehydrated**).

As dehydration affected the polymers functionality, their properties were studied and compared to polymers before dehydration. The quantitative dehydration of POxa was previously reported by treating the polymers with acetic acid [23] or *p*-Toluene sulfonic

acid [25], and more recently by simple neat thermal treatment [26]. Herein, we adopted the thermal treatment methodology as it permitted to quantitatively produce the dehydrated polymers by heating POxa at their T_{dehy} for 2 h under air. As the dehydration process was carried out on neat POxa without requiring any dehydrating agent nor solvent, no purification step was needed after the thermal treatment to provide dehydrated POxa (coined POxa-dehydrated). The complete dehydration was confirmed by NMR spectroscopy (Figure S61-S86). The ^{1}H-NMR spectra of **P2b** and **P2b-dehydrated** are depicted in Figures S61a and S61b as representative examples, which confirmed that the proton signal of tertiary alcohol at δ = 5.95-6.1 ppm completely disappeared, and the characteristic resonance of exocyclic olefinic protons appeared at δ = 4.07-4.36 ppm. The ^{13}C-NMR spectra of **P2b-dehydrated** evidenced the typical olefinic resonance at around δ = 80 ppm and δ = 148 ppm. The SEC chromatograms for dehydrated polymers, displayed in Figures S87-S91, revealed a shift to lower molar mass (Table S3). Although chain scission may have occurred following dehydration, the variation in molecular weight observed before and after dehydration could also be attributed to changes in the hydrodynamic volume of the polymers in the solvent used for SEC analysis.

The TGA analyses of all dehydrated polymers showed a single-step degradation pattern with $T_{deg,10\%}$ in the range of 305 to 361 °C (see Figure 2c, TGA curve of **P2b-dehydrated** as a representative example and Figures S92-S96 for the other polymers). The overlay of TGA thermograms for both hydrated and dehydrated **P2b** copolymers (Figure S97) further confirmed that the first degradation step of hydrated polymers was attributed to their dehydration. Overall, the TGA analyses demonstrated the high thermal stability of the dehydrated hybrid POxa, which is significantly higher than conventional non-isocyanate polyurethanes of the polyhydroxyurethane-type ($T_{deg,\ 10\%}$ around 170-285 °C)[39-43].

POxa polymers were characterized by modulated DSC (mDSC) analyses as the T_g was difficult to detect using conventional DSC analyses (Figures S98-S102). This feature was already observed for other hydroxy-oxazolidone-containing polymers, i.e., poly(hydroxyoxazolidone-*co*-thiocarbonate)s [26] and poly(oxazolidone-*co*-carbonate)s [35], which were characterized by two broad and weak T_gs. For the herein synthesized polymers, no second T_g could be determined due to possible overlapping with early dehydration. As observed in Figure 2d, the reversing contribution of the heat flow allows the determination of the T_g of all polymers, in the range of 7 to 39 °C, and the dehydration event is observed at higher temperature in the non-reversing contribution of the heat flow. For POxa-dehydrated, one strong T_g could be detected by conventional DSC, ranging from 2 to 53 °C depending on the polymer structure (Figures S103-S107). Although a rational trend is not trivial between T_g and the chemical structure in hydrated polymers, the T_g of dehydrated analogs seemed directly related to the rigidity of the dithiol structures, i.e. a low T_g for **P2a** containing ether linkages bringing increased chain flexibility and the highest for **P2e** containing an aromatic moiety.

Table 3. Thermal properties of POxa and POxa-dehydrated.

POxa-hydrated					POxa-dehydrated	
Entry	Polymer	$T_{deg,\ 10\%}$ [a] (°C)	T_{dehy} [a] (°C)	T_g [b] (°C)	$T_{deg,\ 10\%}$ [a] (°C)	T_g [c] (°C)
1	P2a	356	120	7	348	2
2	P2b	364	140	39	361	12
3	P2c	341	130	31	338	7
4	P2d	360	120	37	354	24
5	P2e	324	130	38	305	53

[a] The degradation and dehydration temperatures were determined by TGA. For POxa-hydrated, the $T_{deg,10\%}$ of the polymers was determined after the first weight loss. [b] Glass transition temperatures were determined by modulated DSC (using the reversing heat flow curve). [c] Glass transition temperatures were determined by conventional DSC.

Mechanical properties

Insights into the mechanical properties of poly(oxazolidone)s before and after dehydration were gained through tensile testing. **P2a**, selected for its high molecular weight as determined by SEC, underwent compression molding at 70 °C, a temperature below the dehydration threshold. Testing dogbone-shaped specimens were further obtained via die-cutting (Figure S108). Despite its low T_g (7 °C as determined by DSC), **P2a** exhibited elastic behavior with a Young's modulus value of 398 MPa and a yield strength of 11.4 MPa. The material then underwent plastic deformation until rupture, with a stress at break of 7.6 MPa and a strain at break of 314% (Figure S109). Interestingly, the same experiment conducted on the dehydrated polymer **P2a-dehydrated** revealed flow when exposed to stress, rendering tensile testing impossible. This striking difference between hydrated and dehydrated polymers might be ascribed to intermolecular hydrogen bonding exclusively present in the hydroxyl-containing material.

Chemical stability

The resistance of poly(oxazolidone)s to acidic and basic environments was assessed by immersing **P2a** in sulfuric acid and sodium hydroxide (NaOH) aqueous solutions of varying concentrations (0.1 M, 1 M and 5 M) at room temperature for a period of 48 h (Figure S110). The polymer has shown great stability in acidic conditions, with no apparent chain scission as determined by SEC (Figure S111). However, exposure to acid triggered partial dehydration, with a conversion in hydroxyl groups of 23 % at a concentration of 0.1 M and up to 71 % of conversion accompanied by some Wagner-Meerwein rearrangement of the resulting alkene at a concentration of 5 M (Figure S112) [23]. In contrast, the polymer integrity was affected in basic conditions. In the 0.1 M NaOH aqueous solution, the polymer remained intact as determined by SEC

and NMR (Figure S113 and Figure S114). Unexpectedly, the sample immersed in 1 M NaOH exhibited solubility and subsequent SEC analysis of the solution revealed a shift toward longer elution time, suggesting chain scission events. However, isolation of the product proved to be challenging and would necessitate further investigation on the stability of these polymers in alkaline conditions. Although the same result was expected when the polymer was introduced into the 5 M NaOH solution, SEC analysis didn't reveal any change in elution times and ^{1}H-NMR remained unchanged from the pure polymer. Overall, the poly(oxazolidone)s synthesized herein seemed stable in acidic conditions, although some dehydration of the hydroxyl group is expected with increasing acid content. However, the material integrity showed to be compromised in specific basic environments.

Post-polymerization modifications

All POxa were characterized by the presence of thioether linkages within their backbone, offering multiple possibilities for further modifications, notably by oxidation to sulfoxide or sulfone as well as by alkylation to sulfonium [36, 44]. The polymer **P2b** was selected as a representative polymer for all post-polymerization modifications.

Oxidation. We first explored the oxidation of the thioether linkages into sulfoxide or sulfone. The experiments were conducted at room temperature in DMF as solvent. Aqueous H_2O_2 (10 equiv *vs* thioether repeating unit) was used for the selective and quantitative mono-oxidation of **P2b** to sulfoxide (**P2b-Sulfoxide)**. Reaction completion was confirmed after 72 h by ^{1}H-NMR, where the characteristic resonance of the methylene (CH$_2$-S-) of thioether at δ = 2.43-2.49 ppm totally disappeared. A new peak corresponding to the methylene protons adjacent to the sulfoxide groups (−SO-CH$_2$) at δ= 2.57-2.81 ppm appeared [45, 46] (Figure S115 and Figure 3a-3b). To further confirm the quantitative sulfoxide formation, ^{1}H-NMR was also conducted in DMF-d_7 as typical signals of the thioether function overlapped with the peak attributed to DMSO-d_6 (Figure S120, see ESI for more details). No peak attributed to sulfone groups were observed, confirming that overoxidation did not occur under these experimental conditions. As **P2b-Sulfoxide** was only soluble in DMF and DMSO, complete removal of residual solvent was not possible. The IR spectrum of **P2b-Sulfoxide** also revealed the appearance of sulfoxides (SO) stretching band at ~998 cm^{-1} (Figure S121) [45]. The SEC chromatogram presented the same pattern as **P2b** with only a slight decrease in elution time, suggesting no chain scission events **(**Figure S122).

Tirelli et al. used a diphenyldiselenide (DPDS) catalyst in combination with H_2O_2 for the double oxidation of poly(propylene sulfide) to poly(propylene sulfone) [37]. Herein, we adopted the same methodology to oxidize the thioether linkages into sulfones. This was achieved by using 3 equiv of H_2O_2 per thioether repeating unit and 0.025 equiv of DPDS as the catalyst, in DMF at RT. By monitoring the oxidation over time by ^{1}H-NMR, it appeared that the thioethers were fully oxidized to sulfone after 48 h of

reaction, and that partial dehydration of the hydroxyoxazolidone moieties (10 mol% of functions) was observed (Figure S123).

P2b-Sulfone was purified by precipitation of the reaction mixture in diethyl ether, followed by drying under vacuum at 40 °C for 24 h. As the amount of residual DMF remaining in the polymer was high, the polymer was further dried at 60 °C under vacuum for 16 h. This mild thermal treatment was however enough to fully dehydrate the polymer. Moreover, a Wagner-Meerwein rearrangement was observed following the second thermal treatment resulting in the formation of β-alkylidene oxazolidone linkages (20 mol% of oxazolidone) (Figure S124). For further details and in-depth information regarding this rearrangement, we recommend referring to the article published by our group [23]. The complete oxidation of **P2b** to **P2b-Sulfone** was characterized similarly using NMR and FTIR. ^{1}H-NMR in DMSO-d_6 indicated that the thioether peak at δ= 2.43-2.49 ppm completely disappeared and a new downfield peak attributed to protons adjacent to sulfone at δ= 3.01-3.20 ppm appeared (Figure 3c and S124) [47]. The proton signals corresponding to the tertiary alcohol group, observed at δ = 5.95-6.1 ppm, vanished entirely, while the distinctive resonance of exocyclic olefinic protons emerged within the range of δ = 4.11-4.44 ppm, confirming the complete dehydration of the polymer. The olefinic proton associated to β-alkylidene oxazolidone linkage was observed at δ= 4.59-4.66 ppm, in alignment with the chemical shift observed in analogous structures investigated in a prior study [23]. To corroborate the quantitative formation of sulfone groups, an additional verification was conducted using ^{1}H-NMR in DMF-d_7 as the solvent (Figure S129, see ESI for more details). The two sulfone stretching frequencies could be observed by FTIR as two peaks at ~1200 cm^{-1}, and ~1278 cm^{-1} as shown in Figure S130. No signal correlated to the sulfoxide were observed in ^{1}H-NMR nor FTIR, indicating that double oxidation of the thioether to sulfones was selective. The SEC trace for **P2b-Sulfone** showed a shift to lower molar mass after oxidation (Figure S131). This might be the result of different hydrodynamic volumes of the polymers before and after modification (dehydration and oxidation of the thioether) or some chain scission.

TGA was also employed to assess the thermal stability of the two oxidized polymers, which were both characterized by a multi-step degradation pattern (Figure S132). The initial weight reduction observed between 100 and 200 °C, was attributed to the evaporation of residual DMF and dehydration of the polymer. However, it is obvious that the thermal stability of **P2b-Sulfoxide** is lower than **P2b** as already observed in other sulfoxide-containing polymers [36, 45, 47]. Whereas **P2b** and **P2b-sulfoxide** were completely decomposed at 600 °C, sample **P2b-sulfone** produced 15 wt% of char at that temperature. We did not perform DSC analyses as remaining DMF within the polymers might have a drastic plasticizing effect on chain mobility.

S-Alkylation. As thioethers are reactive towards alkyl halides and form hydrophilic sulfonium salts, we investigated this reaction for introducing sulfonium groups in POxa. We selected iodomethane (10 equiv *vs* **P2b** unit) for the S-alkylation of **P2b** in DMF at RT. After 48 h, the quantitative formation of the sulfonium group was confirmed by ^{1}H-NMR with the characteristic resonance of the methylene (CH_2-S-) of thioether at δ =

2.43-2.49 ppm that disappeared at the benefit of two new resonances at δ = 3.12-3.29 ppm and 3 ppm for the methylene (CH_2-S^+) and the methyl (CH_3-S^+) of the sulfonium group, respectively (Figure 3d, Figure S133). A partial dehydration (50 mol% of hydroxyoxazolidone) was also observed with the characteristic resonance of exocyclic olefinic protons at δ = 4.18-4.48 ppm. To our delight, the polymer has shown to be soluble in water, being the first water-soluble POxa reported so far. Further confirmation of quantitative *S*-alkylation was performed using ^{1}H-NMR characterization in D_2O (Figure S138, see ESI for more details). A multistep degradation pattern for **P2b-Sulfonium** was observed by TGA (Figure S139) that should correspond to dehydration (between 100 and 200 °C) and backbone degradation. However, a comprehensive elucidation of the degradation pathway falls beyond the scope of this study.

DSC characterization (Figure S140) showed a T_g at 35 °C, as well as an endotherm at around 120 °C. The latter might be attributed to the dehydration of the remaining hydroxyoxazolidone moieties that occurred in this temperature range (Table 3).

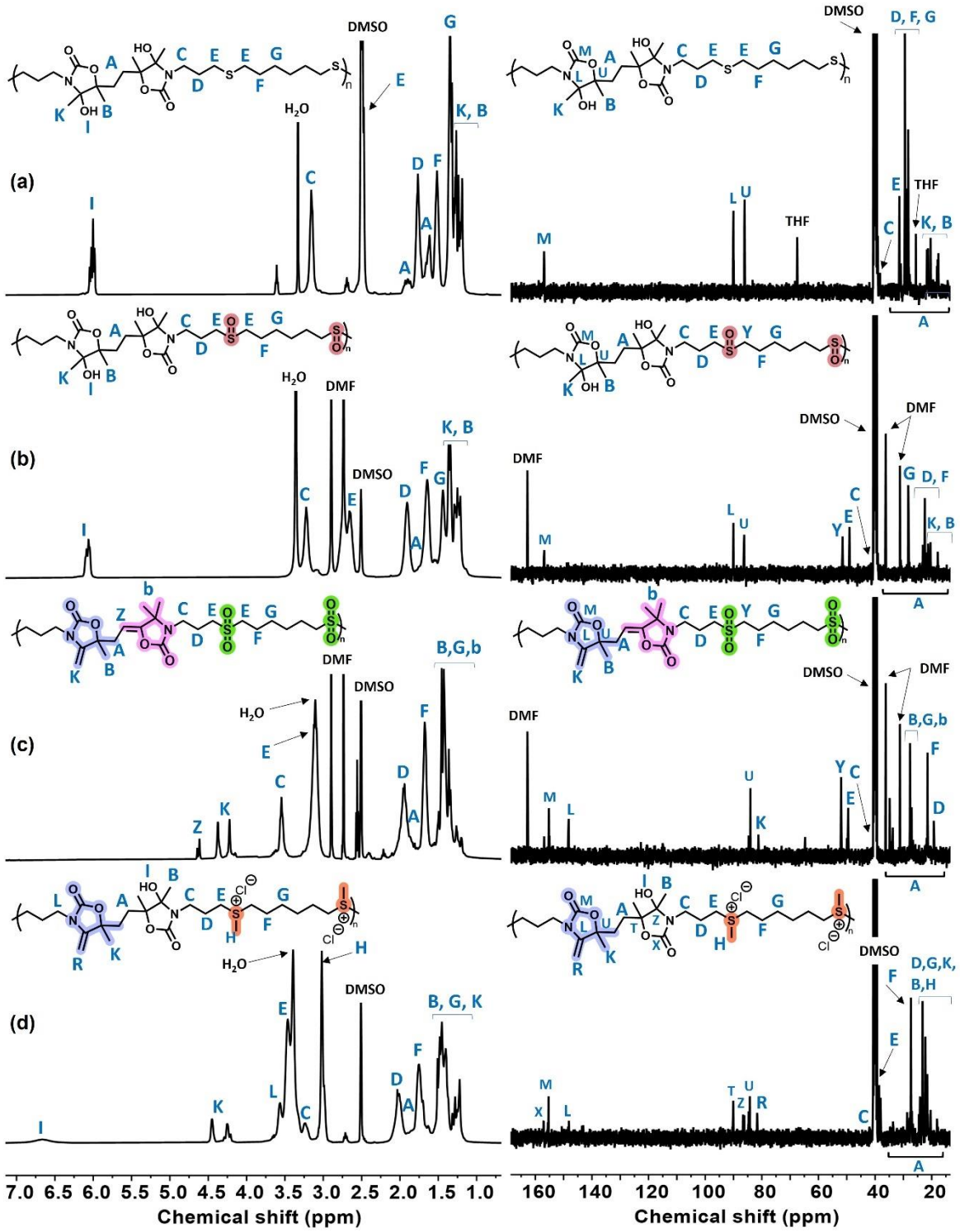

Figure 3. ^{1}H-NMR spectra (left, 400 MHz, DMSO-d_6) and ^{13}C-NMR spectra (right, 100 MHz, DMSO-d_6) of (a) **P2b**, (b) **P2b-Sulfoxide** (c) **P2b-Sulfone** (d) **P2b-Sulfonium**.

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CONCLUSION

In this study, the chemical recycling of CO_2-sourced poly(*oxo*-carbonate)s was achieved under mild condition through aminolysis with allylamine, resulting in the recovery of a new bis(hydroxyoxazolidone) monomer featuring allyl functional groups. This monomer was copolymerized with various commercially available dithiols *via* photoinitiated thiol-ene click reaction at room temperature, delivering elusive poly(oxazolidone)-type polymers containing thioether functions, i.e. poly(oxazolidone-*co*-thioether)s. Optimal reaction conditions were investigated through solvent, initiator, and reaction time adjustments, leading to poly(oxazolidone)-type copolymers with a M_w of up to 101,000 g/mol. All the polymers exhibited an amorphous nature with a T_g spanning from 7 to 39 °C. These polymers displayed a two-step thermal decomposition pattern, with the first step associated with polymer dehydration in the temperature range of 120-140 °C, and the second step attributed to the degradation of the polymer's backbone within the range of 324-364 °C. Following a straightforward thermal treatment at the dehydration temperature for 2 h, the polymers underwent complete dehydration, resulting in the formation of polyoxazolidones enriched with exocyclic olefin moieties. This dehydration occurred at the solid state and did not require any solvent nor dehydrating agent, rendering the process facile and easily upscalable. The dehydrated polymers presented a high degradation temperature (305-361 °C) and a single T_g spanning from 2 to 53 °C. The post-modification of poly(oxazolidone-*co*-thioether)s was further assessed, focusing on the selective single or double oxidation of thioether linkages into sulfoxide or sulfone, as well as the alkylation of thioether to yield sulfonium derivatives. The introduction of sulfonium moieties delivered the first example of a water-soluble poly(oxazolidone). This research exemplifies the strategic utilization of functional monomers derived from the degradation of polycarbonates for the synthesis of a diverse range of novel functional poly(oxazolidone)-type polymers, whose properties have now to be investigated in a forthcoming work. Importantly, the allyl-functional bis(hydroxyoxazolidone) needed for their synthesis can also be quantitatively produced by reacting allylamine with the CO_2-souced bis(alkylidene cyclic carbonate), offering perspective for facile upscaling.

CONFLICTS OF INTEREST

The authors declare no competing financial interest.

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FOOTNOTES

Maliheh Razavi-Esfali[a,b] – E-mail: smrazavi@uliege.be; ORCID: 0000-0002-4637-2390

Thomas Habets[a] – E-mail: thabets@uliege.be ; ORCID: 0000-0001-7619-257X

Fabiana Siragusa[a] – E-mail: fabiana.siragusa@uliege.be ; ORCID: 0000-0001-5744-812X

Bruno Grignard[a,c] – E-mail: bruno.grignard@uliege.be ; ORCID: 0000-0002-6016-3317

Haritz Sardon[b] – E-mail: bruno.grignard@uliege.be ; ORCID: 0000-0002-6268-0916

Christophe Detrembleur[a,d] – E-mail: christophe.detrembleur@uliege.be ; ORCID: 0000-0001-7849-6796

[a] Center for Education and Research on Macromolecules (CERM), CESAM Research Unit, University of Liege, Sart-Tilman B6a, 4000 Liege, Belgium

[b] POLYMAT, University of the Basque Country UPV/EHU, Joxe Mari Korta Center, Avda. Tolosa 7, 20018 Donostia-San Sebastian, Spain

[c] FRITCO2T Platform, University of Liege, Sart-Tilman B6a, 4000 Liege, Belgium

[d] WEL Research Institute, Wavre 1300, Belgium

Electronic supplementary information (ESI) available: Materials and instrumentation, additional information about optimization reactions, solubility tables, NMR spectra, SEC chromatograms, TGA & DSC analyses, FT-IR spectra, setup for the photopolymerization reaction.

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