Published in : ACS Macro Lett. (2024), vol. 13, pp. 644–650
DOI: 10.1021/acsmacrolett.4c00203
Status : Postprint (Author's version)

Continuous Flow Synthesis of Functional Isocyanate-Free Poly(oxazolidone)s by Step-Growth Polymerization

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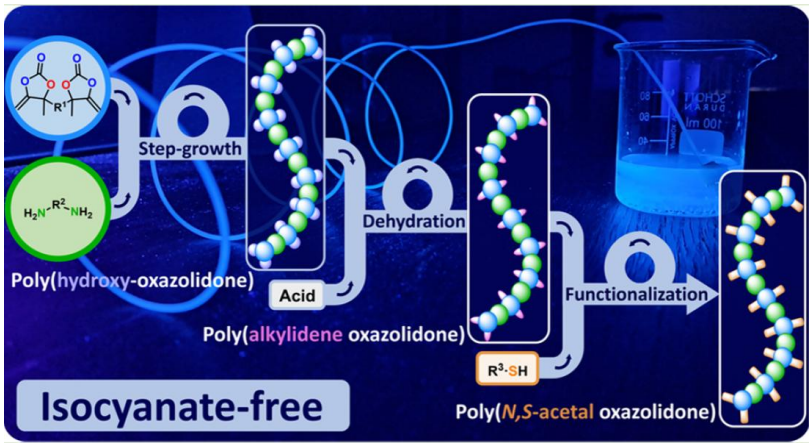
Abstract

Flow chemistry presents many advantages over batch processes for the fast and continuous production of polymers under more robust, safer, and easily scalable conditions. Although largely exploited for chain-growth polymerizations, it has rarely been applied to step-growth polymerizations (SGP) due to their inherent limitations. Here, we report the facile and fast preparation of an emerging class of nonisocyanate polyurethanes, i.e., CO2based poly(oxazolidone)s, by SGP in continuous flow reactors. Importantly, we also demonstrate that functional poly(oxazolidone)s are easily prepared by telescoping a flow module where SGP occurs with reagents able to simultaneously promote two polymer derivatizations in a second module, i.e., dehydration followed by cationic thiol−ene to yield poly(N,S-acetal oxazolidone)s. The functional polymer is produced at a high rate and functionalization degree, without requiring the isolation of any intermediates. This work demonstrates the enormous potential of flow technology for the facile and fast continuous production of functional polymers by SGP.



Polyurethanes (PUs) are commodity polymers entering in the fabrication of multiple everyday life consumer goods and industrial products such as coatings and adhesives, foams, sealants, elastomers, artificial leathers, etc.(1)-(6)Among them, poly(oxazolidone)s (POxa) belong to an emerging subclass of PUs with unique properties.(6)-(10)Their particular microstructure embedding cyclic urethane moieties within their skeleton endows POxa with remarkable chemical inertness, high thermal stability, and high glass transition temperature; all these attributes render them highly valuable as high performance engineering plastics.(10) The main route to POxa relies on the step-growth polymerization of bis-epoxides with diisocyanates at high temperature (T > 150 °C).(11)−(14)These harsh conditions are responsible for the formation of isocyanurate and ether

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defects, some cross-linking nodes, and 4- and 5-substituted oxazolidinone rings formed in response to the nonselective ring-forming step. To address these issues and avoid the use of toxic isocyanates, the step-growth polymerization of CO2-based bis-exovinylene cyclic carbonates (bisαCC) with diamines to produce POxa under mild conditions was introduced by our group.[(15)] The presence of the exocyclic double bond facilitated their rapid and regioselectivity ring-opening by primary amines to deliver poly(hydroxy-oxazolidone)s at room temperature.(15)[(15)−(17)] Moreover, upon adequate thermal or acidic treatment, the polymers were easily dehydrated into the corresponding poly(alkylidene oxazolidone)s,[(16)],[(18)],[(19)] opening the doors to novel functional materials via olefin postmodification by thiol−ene click chemistry.[(19)],[(20)] However, the high reactivity of bisαCC toward the amines imparts significant exotherms during the early stage of the polymerization and hampers the easy scaling up of the production of POxa. In this context, the assets of continuous flow set-ups (i.e., precise control on reagent addition and enhanced heat transfer that avoids temperature overshoots) are expected to offer better reproducibility and the facile production of the polymers in a continuous way and thus their scaling-up. In addition, the continuous flow strategy would enable the concatenation of the POxa synthesis with their direct postpolymerization modification without intermediate purification steps.

While chain-growth techniques, such as ionic, (controlled) radical, or ring-opening polymerizations, have been largely deployed in flow reactors,[(21)−(36)] examples of step-growth polymerizations conducted in these reactors are rather limited.[(37)−(42)] This owns to the intrinsic complications and challenges associated with this class of polymerization, such as (a) the long reaction times required to achieve high monomer conversion, (b) the presence of side reactions that prevents achieving decent molar masses, and (c) the concentration issue leading to either high viscosity when too concentrated causing the clogging of the reactor or dramatic slowdown of the polymerization when too diluted. When PUs are considered, to the best of our knowledge, only one recent report described the step-growth polymerization in flow of isocyanate-based PUs (M_n = up to 13000 g/mol) within a short time (3−20 min) at room temperature by copolymerizing 4,4′-methylene diphenyl diisocyanate (MDI) with 1,6-hexanediol and/or PEG macrodiol with a tin catalyst.[43]

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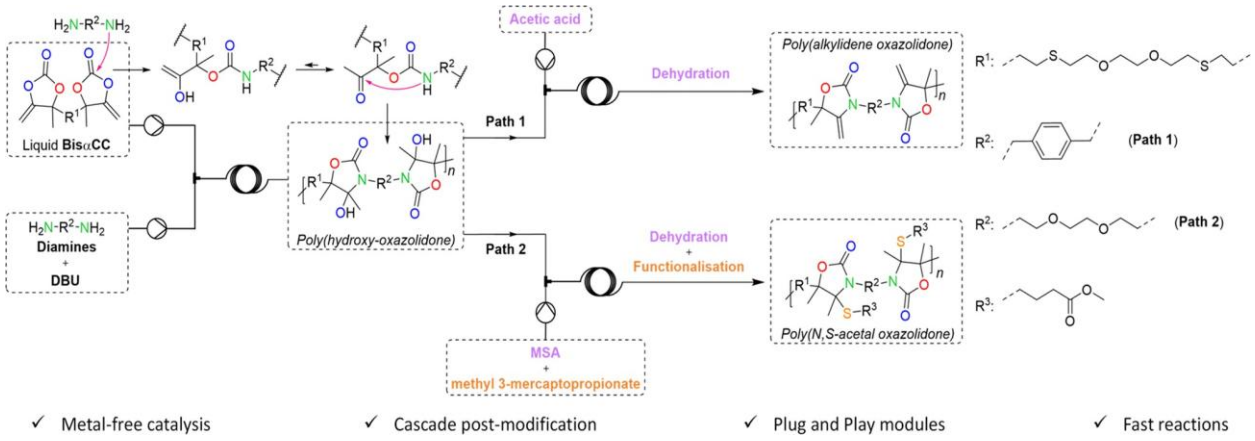
Scheme 1. *Continuous-Flow Synthesis of Functional Isocyanate-Free Poly(oxazolidone)s by Step-Growth Copolymerization: Path 1, Poly(alkylidene oxazolidone) with the Reaction Mechanism for the Formation of Oxazolidone Linkages; Path 2, Poly(N,S-acetal oxazolidone)*



Herein we report the fast preparation of poly(oxazolidone)s by step-growth polymerization in flow devices by exploiting the intrinsic high reactivity features of bisαCC chemistry (Scheme 1). For the first time, we show that "plug-and-play" microfluidic modules can be concatenated to prepare functional poly(oxazolidone)s following two derivatizations, i.e., dehydration to provide pending alkylidene groups and cationic thiol−ene to yield *N*,*S*-acetal moieties.[19,20] All steps are realized at high yield and rate in a single setup. This work opens groundbreaking perspectives for the fast preparation of functional POxa in a continuous way without the need to isolate intermediates.

The synthesis of poly(hydroxy-oxazolidone)s by polyaddition of aliphatic or spirocyclic CO_2-sourced bisαCC and primary diamines in batch reactors was previously optimized.[15,16,19] Like conventional thermoplastic PUs, poly(hydroxy-oxazolidone)s were only soluble in polar solvents such as DMF or DMSO. The toxicity of DMF encouraged us to select DMSO as the solvent for the flow process. Our recently reported liquid bisαCCs monomer (LBisαCC, Scheme 1), highly soluble in classical organic solvents, was used for this study to ensure better solubility of resulting POxas and avoid clogging.[44]

To estimate the polymerization features and the polymer microstructure prior proceeding to flow conditions, we first investigated the polyaddition of LBisαCC with 3,3'-diaminoN-methyldipropylamine A1 in a traditional batch reactor with magnetic stirring. Experiments were carried out in DMSO using DBU catalyst (5 mol % vs LBisαCC) with a polymerization time of 12 and 24 min to mimic typical residence times in flow set-ups. After optimization of the reaction conditions, we worked at a concentration of 0.69 M that enabled maintaining the viscosity of the reaction medium low enough to permit continuous stirring during the entire polymerization. When carried out at 25 °C, the poly(hydroxyoxazolidone) Mn reached 4400 and 4900 g/mol after 12 and 24 min, respectively (Table S1, entries 1A and 1B; Figure S1a). Although increasing the temperature to 40 °C did not bring significant improvement in terms of Mn (Table S1, entries 2A and 2B; Figures S1b), performing the

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reaction at 60 °C increased Mn up to 6000 and 7400 g/mol after 12 and 24 min, respectively (Table S1, entries 3A and 3B; Figure S1c). Mn was further increased to 8100 and 12000 g/mol at 80 °C after the same reaction times (Table S1, Figure S1d). As confirmed by 1H NMR spectroscopy, regardless of reaction time or temperature, all polymers displayed the microstructure of a pure poly(hydroxy-oxazolidone) (Figure S2).

We thus selected an initial concentration of each monomer of 1.38 M in DMSO and a residence time of 23.5 min as standard conditions to translate the polymerizations from batch to continuous flow reactors. To respect this residence time, both monomer solutions were injected through a Tmixer junction in the tubular reactor (internal diameter of 0.762 mm) at a flow rate of 0.021 mL/min for each monomer leading to a final flow of 0.042 mL/min and a concentration of 0.69 M. Conducting the polymerization at 25 °C delivered a low molar mass polymer of 3000 g/mol, further increased to M_n of 3600 and 4200 g/mol at 40 and 60 °C, respectively (Table S2, entries 1, 2A and 3A, Figure S3). However, these molar masses remained lower than those obtained in batch. This observation was in agreement with Sardon's work on the isocyanate-based PU synthesis in continuous flow reactors.[43] This was explained by a combination of a more efficient heat transfer in the tubular reactor reducing the exotherm-induced rate acceleration and poor mixing under laminar flow limiting encounters between oligomers.

Therefore, to provide effective mixing of the medium in the flow process, we repeated experiments at 40 and 60 °C using intense active mixing under ultrasonic (US) irradiation (i.e., the flow reactor was immersed in an ultrasonic bath). At both temperatures, M_n remarkably increased after 23.5 min, reaching 6700 g/mol and 11000 g/mol at 40 and 60 °C, respectively (Table S2, entries 2B and 3B). For the sake of comparison, the same experiments were performed under ultrasound treatment in batch (no mechanical stirring, Table S2, entries 2C and 3C, Figure S4) and the M_ns were found to be very similar. Note that the experiments were not carried out at 80 °C as our ultrasound setup was limited to 60 °C.

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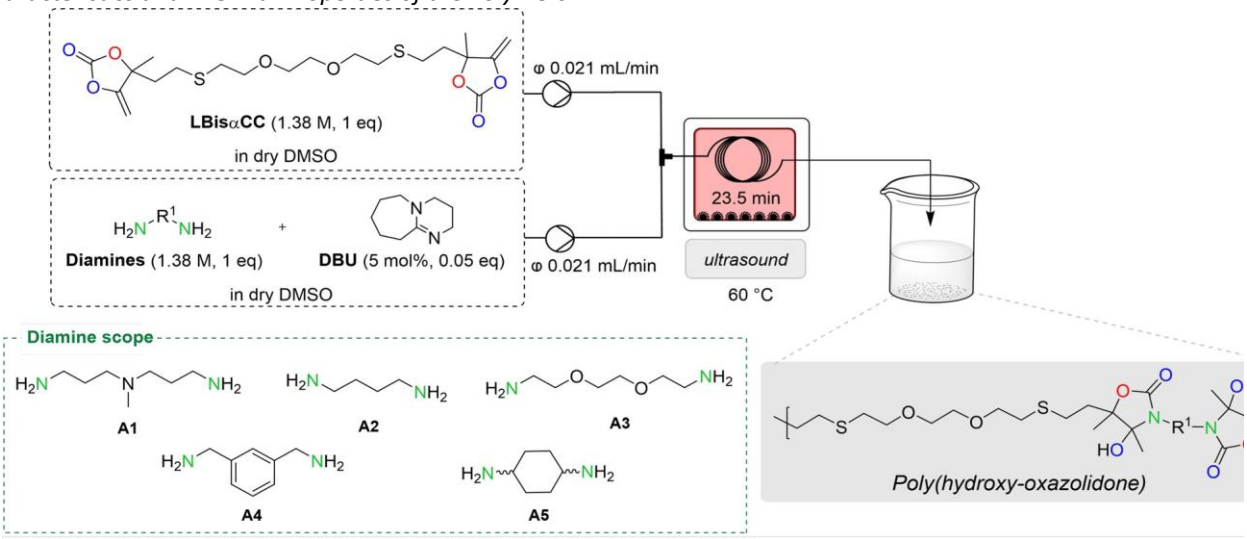
Table 1. *Poly(hydroxy-oxazolidone)s Synthesis by Continuous Flow Step-Growth Copolymerization of LBisαCC with Different Primary Diamines: Structure of the Reagents and Products, Flow Device and Conditions, Molecular Characteristics and Thermal Properties of the Polymers*[a]



polymer	diamine	M_n[b] (g/mol)	M_w[b] (g/mol)	$Đ$[b]	T_{dehyd}[c] (°C)	$T_{deg10\%}$[d] (°C)	$T_{g,1}$[e] (°C)	$T_{g,2}$[e] (°C)
P1	A1	12400	21000	1.70	158	339	13	[f]
P2	A2	8600	18100	2.10	128	357	−9	90
P3	A3	7700	15500	2.26	151	358	−7	[f]
P4	A4	5400	9500	1.76	126	356	25	[f]
P5	A5	4000	5900	1.48	141	279	24	[f]

[a]Reaction conditions: LBisαCC (1.38 M in DMSO) with 0.021 mL/min, diamine (1.38 M in DMSO) + DBU (5 mol %) with 0.021 mL/min, 60 °C, Tr = 23.5 min. [b]Determined on purified products by SEC in DMF/LiBr, PS calibration. [c]Determined by TGA at slow heating (2 K min^{-1} and its derivative (DTG). The dehydration temperature T_{dehyd} is determined at the start of the mass loss peak DTG. [d]Determined by TGA (10% of weight loss) at heating rate of 20 K/min. [e]Determined by modulated DSC. [f]$T_{g,2}$ could not be determined due to overlapping with dehydration event.

To demonstrate the versatility of the flow process, the scope of poly(hydroxy-oxazolidone)s was extended by replacing A1 with various primary diamines including 1,4-butanediamine A2, 1,2-bis(2-aminoethoxy)ethane A3, *m*-xylenediamine A4, and 1,4-cyclohexanediamine A5 (Table 1). LBisαCC was copolymerized with the primary diamines (A2−A5) at 60 °C under ultrasonic irradiation using DBU as the catalyst. After a residence time of 23.5 min (outlet flow rate = 0.042 mL/min), the polymers (P2−P5) flowing out of the tubular reactor were purified by direct precipitation in water slightly acidified by acetic acid (to deactivate and remove DBU). They were then characterized by SEC, ^{1}H and ^{13}C NMR, TGA, and DSC analyses (Table 1 and Figures S5−S34). After purification, the polymer obtained by copolymerization of LBisαCC and the reference diamine A1, displayed a M_n of 12400 g/mol and a dispersity of 1.70 (Figure S5). Lower molar mass polymers were obtained with the aliphatic monomers A2 and A3, which displayed similar M_n between 7700 and 8600 g/mol (Figures S6 and S7). Promoting a

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polymerization with less nucleophile and sterically congested diamines, A4 and A5, led to lower M_n of 5400 and 4000 g/mol, respectively (Figures S8 and S9). The P2–P4 microstructures, elucidated by ^{1}H and ^{13}C NMR spectroscopies (Figures S10–S19), displayed exclusively hydroxy-oxazolidone-type linkage, while P5 was constituted by 58% of hydroxy-oxazolidone linkages and 42% of *oxo*urethane defects (Figures S18 and S19). This was in line with our seminal work in batch showing that sterically congested diamines such as A5 delivered chains sharing both hydroxyoxazolidone and *oxo*-urethane linkages, the ring closure being hampered.[16] The polymer chain-ends consisted of alkylidene cyclic carbonate and amine moieties, along with some hydroxyketone coming from the hydrolysis of αCC (Figure S2).

The thermogravimetric analysis (TGA) of the poly(hydroxyoxazolidone)s evidenced a multistep degradation pattern (Figures S20–S24). The first mass loss corresponded to the well-known dehydration phenomena, yielding poly(alkylideneoxazolidone), as reported in our previous work.[16] The dehydration temperatures, T_{dehyd}, in the range 126–158 °C (Table 1), were determined as the start of the mass loss peak of the derivative thermogravimetry (DTG) plots (Figures S25–S29). The degradation of the polymeric backbone was then observed at the second mass loss. The temperature at 10% of degradation ($T_{deg10\%}$) was determined after the dehydration step and estimated between 279 and 358 °C. P1–P4 containing exclusively oxazolidone linkages presented a high $T_{deg10\%}$ (339–358 °C). P5, that displayed oxazolidone and *oxo*-urethane linkages in a 58/42 molar ratio, presented a lower thermal stability $T_{deg10\%}$ = 279 °C; the linear urethane linkages being less thermally stable than the cyclic ones.[45,46]

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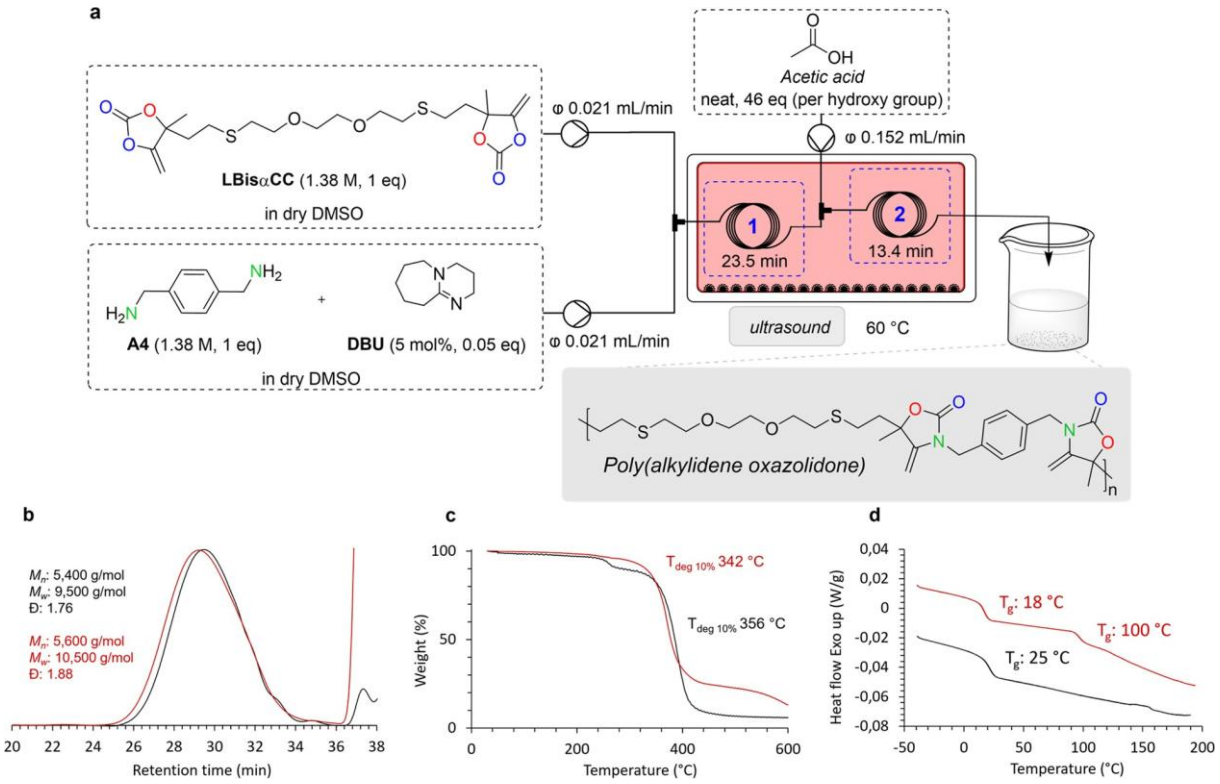
Modulated differential scanning calorimetry (mDSC) evidenced a glass-transition temperature (T_g) for the polymers, with a T_g of −7 to 13 °C for the less rigid polymers P3 and P1, and values of 24 to 25 °C for P5 and P4 derived from the more sterically hindered diamines A5 and A4 (Table 1, Figures S30–S34). Similar to previous observations,[16,47] P2 was characterized by two glass-transition temperatures at −9 and 90 °C (Figure S31). The second T_g for P1, P3, P4, and P5 could not be observed due to overlapping with the dehydration event at this temperature range (Figures S30, S32, S33, and S34).

Figure 1. *P4 (black) and dehydrated P4 (P4D) (red) characterizations: (a) scheme of the direct synthesis of poly(alkylidene oxazolidone) from LBisαCC and A4 via concatenation of two continuous flow setups; (b) SEC chromatogram of the purified polymers; (c) TGA plot at heating rate of 20 K/min; (d) reversing heat flow plot of modulated DSC analysis.*



We previously demonstrated that poly(hydroxyoxazolidone)s can be quantitatively dehydrated by refluxing them in acetic acid for 2 h, delivering the corresponding poly(alkylidene oxazolidone).[16] We thus evaluated the preparation of these unsaturated poly(oxazolidone)s in a single flow device containing two microfluidic modules connected in series. Poly(hydroxy-oxazolidone) was first prepared by the copolymerization of LBisαCC with a diamine in the first module, prior to telescoping with acetic acid in the second one (Figure 1a). For the proof of concept, we selected P4 as a model polymer for ease of characterization by ^{1}HNMR spectroscopy. The overall process was carried out at 60 °C using ultrasound treatment. The first module was dedicated to the synthesis of the poly(hydroxy-oxazolidone) P4 following our optimized operative conditions (outlet flow rate = 0.042 mL/min,

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residence time of 23.5 min). The second module was plugged via a T-Mixer junction, by which excess acetic acid (i.e., 0.152 mL/min, 46 equiv/hydroxy function) was injected to promote the polymer dehydration. After a residence time of 13.4 min, the dehydrated P4 was collected, purified by precipitation, and analyzed by NMR and SEC. Importantly, after this short period of time and rather low temperature (60 °C), the polymer was characterized by a M_n of 5600 g/mol (Figure 1b) and 85% of the hydroxy-oxazolidone linkages of P4 were converted into the alkylidene oxazolidone ones, as demonstrated by NMR spectroscopy (Figures S35 and S36, see SI for details).

The dehydrated polymer P4 displayed a single mass loss at a $T_{deg10\%}$ of 342 °C (Figure 1c) and two glass transition temperatures at $T_{g,1}$ = 18 °C and $T_{g,2}$ = 100 °C (Figures 1d and S37). The presence of the two T_gs was an uncommon feature already observed for other oxazolidone-containing polymers.[19,44] They are assumed to originate from two amorphous glassy phases with the hydroxyoxazolidone linkages that are responsible for the high-T_g due to increased backbone rigidity and hydrogen bonding.

The dehydration of poly(hydroxy-oxazolidone)s gives access to poly(alkylidene oxazolidone)s with olefin groups that in turn allow postpolymerization modifications. Indeed, as studied in a previous work, their modification by cationic thiol−ene reaction produced poly(*N*,*S*-acetal oxazolidone)s, and occurred at room temperature within 24 h, with a catalytic amount of methanesulfonic acid (MSA).[19,20] Coupling the step-growth polymerization of LBisαCC with a diamine to the cascade reaction (i.e., the polymer dehydration followed by the cationic thiol−ene) into a telescopic continuous flow device was thus expected to provide functional poly(oxazolidone)s. To do so, acetic acid was replaced by MSA to support both the dehydration of the poly(hydroxy-oxazolidone) and the catalysis of the cationic thiol−ene reaction on the poly(alkylidene oxazolidone). The dehydration was optimized with MSA (see SI, section 6, Table S3, Figure S38), notably by replacing DMSO with DMF for solubility issue, and A3 was preferred to A4 for the same reason.

Practically, in the first module, the poly(hydroxy-oxazolidone) was synthesized in a 23.5 min residence time reactor at 60 °C in DMF (outlet flow rate = 0.042 mL/min; Figure 2a). The outlet was telescoped in a second module with a T-mixer where 5.5 equiv of MSA (vs hydroxy functions) were injected, followed shortly by an additional T-mixer delivering 3.3 equiv of methyl 3-mercaptopropionate (per alkylidene function). The resulting mixture reacted in the second module with a residence time of 11.2 min at 60 °C under ultrasound (Figure 2a).

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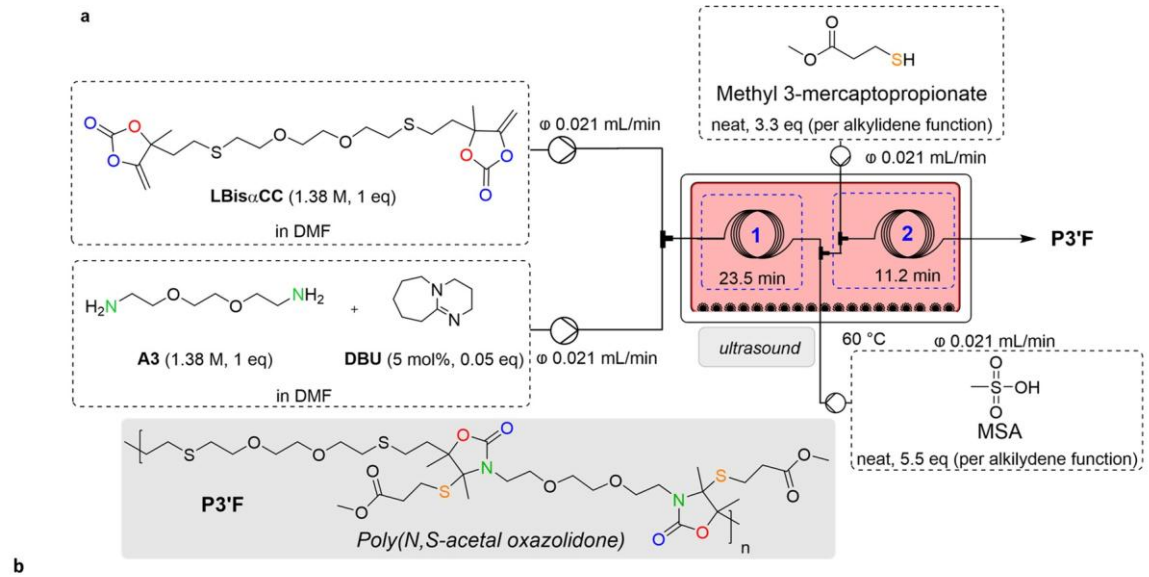

Polymer	Hydroxy-oxazolidone (%)[a]	Alkylidene oxazolidone (%)[a]	*N,S*-acetal oxazolidone (%)[a]	M_n (g/mol)[b]	M_w (g/mol)[b]	Đ[b]	T_g (°C)[c]	Isolated yield (%)
P3'	100	0	0	12,100	28,500	2.35	4	96
P3'D	9	91	0	13,700	35,100	2.55	2	92
P3'F	7	20	73	8,800	19,100	2.17	-8	95

***Figure 2**. (a) Direct synthesis of poly(N,S-acetal oxazolidone) P3′F from LBisαCC and A3 via a single uninterrupted reactor, and simplified structure of P3′F; (b) macromolecular characteristics, T_g values, and isolated yields for P3′, dehydrated (P3′D) and functionalized P3' (P3′F). Complete NMR characterizations of P3′, P3′D, and P3′F are provided in SI (Figures S40 and S42−S53). [a]Determined by ^{1}H NMR (see ESI for details). [b]Determined on purified products by SEC in DMF/LiBr, PS calibration. [c]Determined by modulated DSC.*

We showed the successful polymerization of A3 with LBisαCC in DMF by sampling directly at the end of the first module, with the formation of poly(hydroxy-oxazolidone) P3′ with a M_n of 12100 g/mol (96% isolated yield, 24.4 g/d). When telescoped with the second module, it was only fed with MSA (flow rate of 0.021 mL/min, Tr of 14.9 min, Figure S39), the dehydrated polymer P3′D was obtained with a conversion of hydroxy functions of 91%, a M_n of 13700 g/mol and an isolated yield of 92% with an output of 22.2 g per day (Figures 2b and S40). Eventually, the functionalization was carried out simultaneously with the dehydration by turning on the feeding of methyl 3-mercaptopropionate (flow rate of 0.021 mL/min, Tr of 11.2 min), affording the corresponding poly(*N*,*S*-acetal oxazolidone) P3′F. The latter was obtained with 95% isolated yield within a total residence time of 34.7 min at 60 °C, the output is about 29.8 g per day, and a space-time yield of 1.15 kg $h^{-1}L^{-1}$ (see SI). The polymer was then characterized by SEC (M_n 8800 g/mol) and NMR spectroscopies (Figures S40 and S41). P3′F was composed of 73% of *N*,*S*-acetal oxazolidone, 20% alkylidene oxazolidone, and 7% hydroxyoxazolidone functions (Figure 2b). The successful functionalization was highlighted using NMR (Figures S40 and S42– S53) by the appearance of two signals at 1.60 and 1.37 ppm for methyl group a′′ (Figure S40), and the decrease of the signals of the methyl group close to the alcohol function of poly(hydroxy-

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oxazolidone) b at 1.42 (Figure S40). The remaining alkylidene functions were present at 4.13 and 4.30 ppm (see SI for the calculation mode of the functionalization degree). The functionalized polymer P3'F displayed a single mass loss at $T_{deg10\%}$ of 198 °C and a T_g of −8 °C (Figure S41). Note that, though the apparent M_n decreased from P3' to P3'F (Figure 2b), we do not think that this is due to degradation but rather to a change of the polymer hydrodynamic volume. This is in line with our last work that showed the great stability of polyoxazolidones under strong acidic conditions, with no chain scission.[48]

In summary, we have developed the first continuous flow synthesis of an emerging class of CO_2-based nonisocyanate polyurethanes, i.e. poly(hydroxy-oxazolidone)s, by step-growth polymerization. The advantage of flow conditions over batch was empowered by the facile and fast preparation of poly(oxazolidone)s and their functionalization by a telescoping polymerization module with reagents able to dehydrate the polymer in situ and, if desired, simultaneously promote the polymer functionalization by a cationic thiol−ene reaction in the second module. This process provided the functional polymer with a high functionalization degree (73%) within a short total residence time of 34.7 min at 60 °C, without the need to isolate any intermediates. While further enhancement of the polymers' molar masses remains, this research underscores the feasibility and simplicity of step-growth polymerization and polymer derivatizations under flow conditions. This work establishes new avenues for bringing this crucial SGP process to larger scales through the assets of flow (i.e., process intensification with increased reaction output and seamless scalability toward higher productivity capabilities).

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CRediT: Fabiana Siragusa formal analysis, investigation, methodology, writing-review & editing; Lionel Crane formal analysis, investigation, resources, writing-original draft; Pierre Stiernet formal analysis, investigation, methodology, writingreview & editing; Thomas Habets conceptualization, formal analysis, methodology, validation; Bruno Grignard conceptualization, methodology; Jean-Christophe M Monbaliu conceptualization, methodology, resources, supervision, validation, writing-review & editing; Christophe Detrembleur conceptualization, funding acquisition, project administration, supervision, writing-review & editing.

Notes : The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research program was funded by the University of Liège and the French Community of Belgium through Concerted Research Action CO2FLUIDICS 21/25-04 (PI: C.D., co-PI: J.-C.M.M.). C.D. is F.R.S.-FNRS Research Director and thanks

FNRS for funding the CO2Switch project underGrantT.0075.20.

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Published in : ACS Macro Lett. (2024), vol. 13, pp. 644–650
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