Chemically Recyclable, High Molar Mass Polyoxazolidinones via Ring-Opening Metathesis Polymerization

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ABSTRACT: The development of robust methods for the synthesis of chemically recyclable polymers with tunable properties is necessary for the design of next-generation materials. Polyoxazolidinones (POxa) – polymers with five-membered urethanes in their backbones – are an attractive target because they are strongly polar and have high thermal stability, but existing step-growth syntheses limit molar masses and methods to chemically recycle POxa to monomer are rare. Herein, we report the synthesis of high molar mass POxa via ring-opening metathesis polymerization of oxazolidinone-fused cyclooctenes. These novel polymers show <5% mass loss up to 382–411 °C and have tunable glass transition temperatures (14–48 °C) controlled by the side chain structure. We demonstrate facile chemical recycling to monomer and re-polymerization despite moderately high monomer ring strain energies, which we hypothesize are facilitated by the conformational restriction introduced by the fused oxazolidinone ring. This method represents the first chain growth synthesis of POxa and provides a versatile platform for the study and application of this emerging subclass of polyurethanes.

Synthetic polymers have revolutionized every aspect of modern life, but current mass polymer production is unsustainable as common materials generate tremendous amounts of waste[1–3] and pollution[4–6] after their intended use. Therefore, next-generation materials require both competitive properties and designed end-of-life strategies to mitigate their environmental impact. Polyoxazolidinones (POxa) are an emerging subclass of polyurethanes with competitive properties for high temperature applications[7,8] due to the five-membered oxazolidinone rings imparting high thermal stability[7,9–13] and glass transition temperatures (T_g).[7,8,11–15] Despite their promise, POxa have been limited to low molar masses ($M_n \leq 32$ kDa[8,13,15,16]) for decades due to the step-growth nature of previous syntheses (Figure 1A) and very little work has been reported on sustainable approaches for their end-of-life.[17] We sought to break this paradigm by using chain growth polymerization to access high molar mass POxa while enabling chemical recycling to monomer via depolymerization.[18–21]

We chose ring-opening metathesis polymerization (ROMP) because (1) it is a powerful chain growth method for strained cycloalkenes[22–24] and (2) ROMP-based polymers obtained from low ring strain monomers (~5.2 kcal/mol) are known to depolymerize at elevated temperatures via ring-closing metathesis (RCM)[25–29] (Figure 1B). This RCM strategy has recently resurfaced in the design of new polymers due to its promising contribution to chemical recycling.[27,28,30–32] Chemical recycling to monomer is ideal for a circular polymer economy because this approach can minimize the net mass loss during recycling[21] compared to other strategies, such as mechanical recycling,[2,33–35] biodegradation,[36,37] and upcycling of commodity plastics to value added products.[38–47] Recently, Wang and co-workers showed that the addition of *trans*-fused cyclobutane or acetonide rings to cyclooctene lowered the monomer ring strain energy (RSE), which they hypothesized was the critical factor that enabled the depolymerization of the resulting polymers.[28,30]

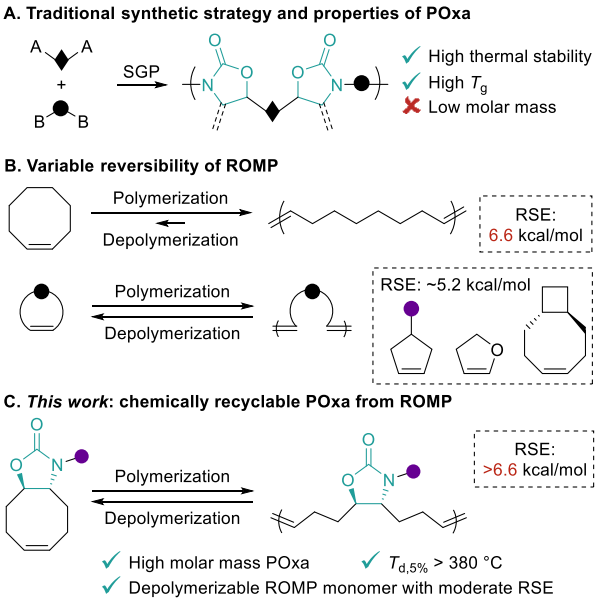
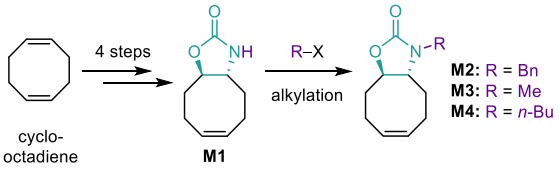


Figure 1.[48] (A) Traditional POxa from step growth polymerization (SGP) (A, B = reactive functionality). (B) Reversibility of ring-opening metathesis for monomers with different ring-strain energies (RSEs). (C) Design of chemically recyclable POxa.

Herein, we utilize ROMP for the first chain growth synthesis of POxa from *trans*-oxazolidinone (Oxa)-fused cyclooctene monomers (Figure 1C). We demonstrate access to POxa with high molar mass, moderate dispersity, and control over molar mass by using a chain transfer agent (CTA). These novel polymers show <5% mass loss up to 382–411 °C and have tunable T_g via side chain alteration and post-polymerization hydrogenation. Furthermore, we show clean depolymerization back to monomer, despite higher RSE than *cis*-cyclooctene (COE) calculated by density functional theory (DFT). This method provides access to POxa with higher molar masses than previous methods, which will enable future structure-property relationship studies and the addition of a broad-spectrum of new Oxa monomers for ROMP and chemical recycling to monomer.

We began our investigation by synthesizing the Oxa-fused COE monomers **M1**–**M4** in 4–5 steps from 1,5-cyclooctadiene (Scheme 1, see Supporting Information Section S3A for full synthetic details). Gratifyingly, **M1** readily polymerized using G2 (see Figure S1 for all catalyst structures) in dichloromethane (DCM) to yield POxa **P1** with a number-average molar mass (M_n) of 23.9 kDa; however, **P1** precipitated out during the polymerization due to poor solubility in DCM and was only soluble in *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), which are incompatible with metathesis catalysts.[49–51] Therefore, we focused on the *N*-alkylated monomers **M2**–**M4** which yielded polymers (**P2**–**P4**) that were soluble in common metathesis solvents (e.g., DCM, $CHCl_3$, and tetrahydrofuran).

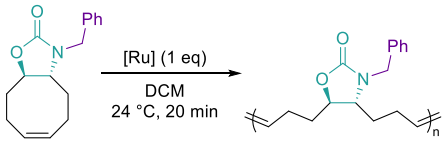
Scheme 1. Oxa-fused COE monomers from cyclooctadiene.



Using **M2** as a model substrate, we optimized the polymerization conditions (Table 1). Except for G1 (entry 1), common metathesis catalysts (i.e., G2, G3, HG2, see Figure S1) all resulted in high conversions and molar masses (M_n = 118–487 kDa, entries 2–4). We selected G2 as the standard catalyst because it resulted in the lowest $Đ$ and is relatively inexpensive. Increasing the initial monomer concentration from 1.0 to 2.0 M decreased conversion in 20 min and resulted in a bimodal distribution with high $Đ$ (entry 5), whereas lowering the concentration to 0.5 and 0.25 M progressively decreased both conversion and molar mass (entries 6 and 7). Therefore, our standard polymerization conditions consisted of 1.0 M monomer in DCM using G2 as the ROMP initiator at 24 °C. **M3** and **M4** were similarly polymerized to access high molar mass POxa (M_n = 112 and 65.3 kDa for **P3** and **P4**, respectively) in 1 h with variable side chains (see Section S3B for synthetic details). Because these Oxa-fused COE monomers are unsymmetrical, we characterized the regioregularity of enchainment for **M2**–**M4** using IR and NMR spectroscopies. While the side chain identity does affect regioregularity to some extent, all polymers had over 88% head-to-tail enchainment (see Section S2E for more details).

As expected for ROMP of COE derivatives,[52–57] we observed evidence of slow initiation: M_n is initially very high and decreases (i.e., approaches $M_{n,theo}$) by extending the reaction time (entry 2 vs. 8–9 and Figure S5) and there was a nonlinear trend between M_n and [M]:[Ru] ratio (Figure 2A). To improve control over M_n, we added *cis*-1,4-diacetoxy-2-butene as a CTA (Figure 2B). CTAs are known to decrease the difference between $M_{n,theo}$ and M_n,[58,59] enable the use of catalytic Ru,[56,60–65] and – for this CTA – result in homotelechelic polymers that can be deprotected to the corresponding diol for further functionalization.[58,59] Despite requiring longer reaction times due to the slower rate of polymerization (78% conv. in 3 h vs. 90% without CTA), M_n had a linear relationship with [M]:([CTA]+[G2]) and was within 1–37 kDa of $M_{n,theo}$ for a wide range of molar masses, demonstrating improved control over POxa molar mass. Secondary cross-metathesis helps dispersity remain relatively constant ($Đ$ ≈ 1.5–1.6) with and without the CTA (when t = 3 h).

Table 1 Optimization of ROMP conditions.



entry	[Ru]	conc. (M)	conv. (%)[a]	M_n (kDa)[b]	$Đ$[b]
1	G1	1.0	9	–	–
2	G2	1.0	82	487	1.20
3	G3	1.0	85	118	1.41
4	HG2	1.0	81	384	1.27
5[c]	G2	2.0	62	203	2.35
6	G2	0.5	69	168	1.40
7	G2	0.25	48	–[d]	–[d]
8[e]	G2	1.0	86	42.7	1.71
9[f]	G2	1.0	86	34.4	1.55

[a]Determined by ^{1}H NMR analysis of the crude reaction mixture. [b]Crude M_n and $Đ$ were determined by size exclusion chromatography with multi-angle light scattering (SEC-MALS) in DMF. [c][**M2**]:[Ru] = 50:1. [d]SEC peak is overlapping with small molecule peaks, but M_n of oligomers is < 1 kDa. [e]Polymerization was run for 1 h. [f]Polymerization was run for 3 h. See Figure S1 for catalyst structures.

Having established the synthesis of POxa via ROMP, we next investigated the thermal properties of **P2**–**P4**. Thermogravimetric analysis (TGA) showed **P2**–**P4** had high decomposition temperatures at 5% mass loss ($T_{d,5\%}$) of 382–411 °C (Figure 3A), as expected for POxa.[7,9–13] Even prolonged heating (1 h) of bulk **P2** at 150 °C did not result in polymer degradation (see Section S2F), as shown by ^{1}H NMR spectroscopy (Figure S30). Some radical-based chain-chain coupling was observed in the SEC, which could be suppressed by the addition of butylated hydroxytoluene (BHT) (see Figure S31). Differential scanning calorimetry (DSC) indicated that the POxa were amorphous with glass transition temperatures (T_g) tuned by the *N*-substituent (Figure 3B). Increasing the substituent length from methyl (**P3**) to *n*-butyl (**P4**)

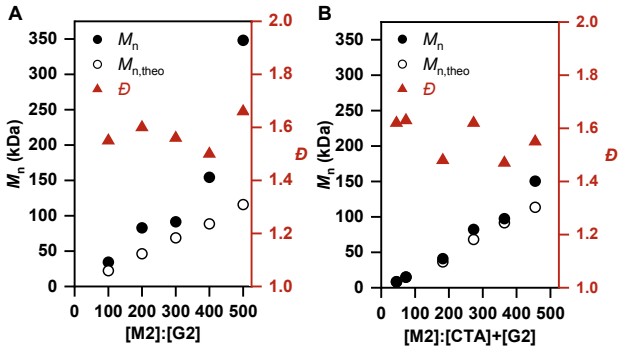


Figure 2. Plots of M_n (black circles), $M_{n,theo}$ (open circles), and $Đ$ (red triangles) as a function of (A) [**M2**]:[G2] and (B) [**M2**]:[CTA]+[G2]. Polymerization time = 3 h.

lowered the T_g from 29 to 14 °C, whereas the benzyl substituent in **P2** increased the T_g to 48 °C. These results indicate that our modular monomer platform can tune POxa T_g while maintaining high $T_{d,5\%}$.

To explore the range of properties accessible via this method, we hydrogenated the backbone olefins of **P2** to form polyethylene-like polymer **[H]P2** that still contains embedded polar Oxa rings (Figure 3C). Such polar-functionalized polyethylene[66] often exhibit excellent ionic conductivity,[67–69] surface hydrophilicity,[70,71] and antimicrobial properties[72,73] while maintaining the mechanical strength of polyethylene. We speculated common olefin hydrogenation catalysts (e.g. Pd/C) would deprotect the benzyl group from the Oxa nitrogen[74] and thus used in situ-generated diimide from *N*-tosyl hydrazide for hydrogenation,[57,75] resulting in 92% conversion of the olefins via ^{1}H NMR spectroscopy after 16 h (see Section S3C). The $T_{d,5\%}$ increased slightly after hydrogenation (436 °C for **[H]P2** vs. 408 °C for **P2**) whereas the T_g decreased from 48 to 42 °C due to increased backbone flexibility,[76–79] indicating that post-polymerization modification provides an additional handle to tune thermal properties. Furthermore, heating **[H]P2** at 150 °C for 1 hour does not result in any chain-chain coupling (Figure S32).

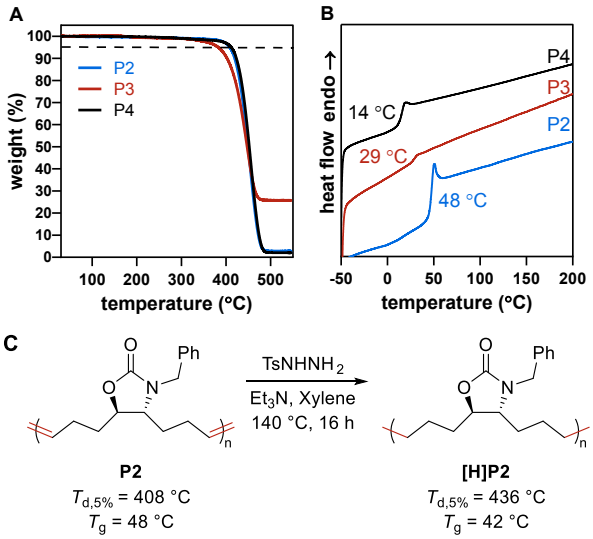


Figure 3. Thermal data – (A) TGA and (B) DSC thermograms – of **P2**–**P4** and (C) hydrogenated **[H]P2**.

Because we are interested in the end-of-life for these materials, we explored the depolymerization of the non-hydrogenated **P2** via RCM. After a brief optimization of the conditions (Table S5) we observed quantitative depolymerization of the polymer to **M2** using G2 in chloroform-*d* (20 mM) at 70 °C for 4 h (Figure 4). No oligomers or side reactions were observed. The recovered monomer (90% by mass) behaved comparably to fresh monomer when re-polymerized using our standard conditions (see Table S6 and Figures S35–S38), demonstrating the facile circular recyclability of these materials. Detrembleur and co-workers recently reported mechanical and chemical recycling of POxa-containing covalent adaptable networks,[17] but this RCM approach is the first example of chemical recycling for linear POxa.

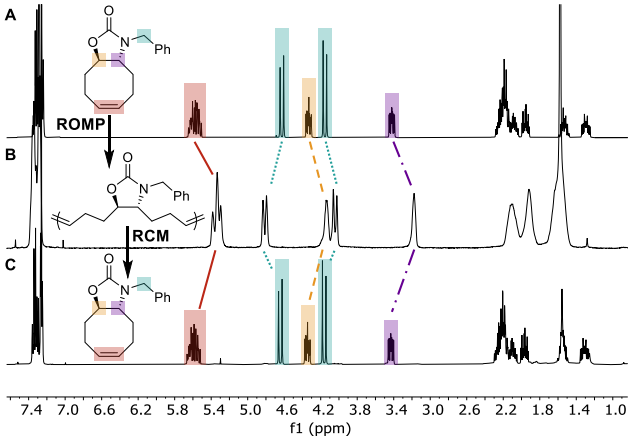


Figure 4. ^{1}H NMR spectra ($CDCl_3$) of (A) **M2**, (B) **P2**, and (C) the crude reaction mixture of **P2** depolymerization. Depolymerization conditions: G2 (1 mol %), $CDCl_3$ (20 mM), 70 °C, 4 h.

Because low monomer RSE (≤5.3 kcal/mol) has been reported as the key factor in the depolymerization of ROMP-based polymers,[28,30] we expected **M1**–**M4** to have lower RSE than COE, which does not readily depolymerize to monomer[24,80] (see Section S4D). However, the calculated RSE values were actually higher for **M1**–**M4** (7.2–8.2 kcal/mol) than COE (6.6 kcal/mol) (Table S7), indicating that RSE is not the most critical factor governing the depolymerization of these polymers. (Note that due to inconsistencies in the reported RSE of COE in the literature,[28,52,81,82] we calculated this value using the same method as **M1**–**M4** at the B3LYP/6-31G (d,p) level of theory.) On the basis of the rich small-molecule literature using RCM to construct medium-sized (5–9 membered) fused rings (RSE >7 kcal/mol),[83–89] we hypothesize the favorable depolymerization to monomer of **P2** is facilitated by the conformational restriction introduced by the fused Oxa ring making the ΔS of polymerization more negative[30,90] and helping bring the adjacent alkenes together (conceptually similar to the Thorpe-Ingold effect[91] that has previously been invoked for polymer depolymerization[30,92]).

In summary, we successfully developed the first chain growth synthesis of POxa. We designed and synthesized novel Oxa-fused COE monomers with easily diversified side chains. **P1** – which contains free N-H groups – was insoluble in common ROMP solvents, but **P2**–**P4** were accessed with high molar masses and moderate dispersities (M_n up to 487 kDa, $Đ \approx 1.5$) via ROMP. We demonstrated that the molar mass could be efficiently controlled using a commercially

available CTA. This method delivers new POxa with $T_{d,5\%}$ > 380 °C and tunable T_g by changing the nitrogen substituent. We showed hydrogenation of the olefin backbone of the polymer to give access to polyethylene-like POxa. We furthermore established the quantitative chemical recyclability to the monomer of **P2** by employing RCM to deliver pure monomer that could be readily repolymerized. Further studies on controlled copolymerization, mechanistic insight, and mechanical properties are underway.

ASSOCIATED CONTENT

The Supporting Information is available free of charge via the internet.

Additional polymer characterization, including SEC chromatograms, TGA and DSC thermograms, tabulated data, experimental details, computational calculation details, methods, reagent sources, synthetic procedures.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Arpan Pal** conceptualization, data curation, formal analysis, investigation, methodology, writing-original draft, writing-review & editing; **Allison R. Wong** data duration, formal analysis, investigation, methodology, writing-review & editing; **Jessica R. Lamb** conceptualization, formal analysis, funding acquisition, project administration, resources, supervision, validation, writing-original draft, writing-review & editing.

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Notes

The authors declare no competing financial interest.

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