

A scalable and continuous access to pure cyclic polymers enabled by “quarantined” heterogeneous catalysts

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Cyclic polymers are topologically interesting and envisioned as a lubricant material. However, scalable synthesis of pure cyclic polymers remains elusive. The most straightforward way is to recycle a used catalyst for the synthesis of cyclic polymers. Unfortunately, it is demanding because of the catalyst’s vulnerability and inseparability from polymers, which depreciates the practicality of the process. Here, we develop a continuous process streamlined in a circular way that polymerization, polymer separation, and catalyst recovery happen in situ, to dispense a pure cyclic polymer after bulk ring-expansion metathesis polymerization of cyclopentene. It is enabled by introducing silica-supported ruthenium catalysts and a newly-designed glassware. Also, different depolymerization kinetics of the cyclic polymer from its linear analogue is discussed. This process minimizes manual labor, maximizes security of vulnerable

1 *catalysts, and guarantees purity of cyclic polymers, thereby showcasing a prototype of a scalable*
2 *access to cyclic polymers with increased reusability of precious catalysts ($\geq 415,000$ turnovers).*

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4 The economy of lubrication is encumbered by a high replacement cost of lubricants in
5 many applications^{1,2}. One of its countermeasures is to increase the lifespan of lubricants, thereby
6 decreasing the replacement frequency. The most common synthetic lubricant by far is
7 polyalphaolefin³⁻⁵, which gradually loses its viscosity due to permanent chain scissions over time⁶.
8 Cyclic hydrocarbon polymers similar to polyalphaolefins or mineral oils (e.g. polyethylene,
9 polypropylene, polybutadiene, etc.)^{7,8} are tribologically interesting because the initial chain
10 scission of cyclic topology increases its viscosity by producing an opened linear topology with a
11 higher chain volume⁹⁻¹¹. This feature of cyclic polymers is envisioned as a viscosity modifier to
12 prolong the lubricant lifetime. Since our discovery of the ring expansion route to cyclic polymers
13 in 2002¹¹, we¹²⁻¹⁶ and other groups¹⁷⁻²⁶ have done exciting research on more functionalized and
14 purer cyclic polymers.

15 One of the most important needs is the development of a practical synthetic process to
16 produce pure cyclic polymers on a larger scale for testing in many applications. To date, all the
17 reported synthetic protocols were operated on a milligram scale in solution by homogeneous
18 catalysis, which was accompanied by rigorous *ex situ* processes for polymer purification without
19 actual catalyst recovery (Fig. 1a)²⁴⁻²⁷. Nonetheless, the residual metal catalysts remained at a few
20 hundred ppm level¹²; in this conventional process, it is difficult not only to obtain an
21 uncontaminated white polymer but also to recycle the precious metal catalysts.

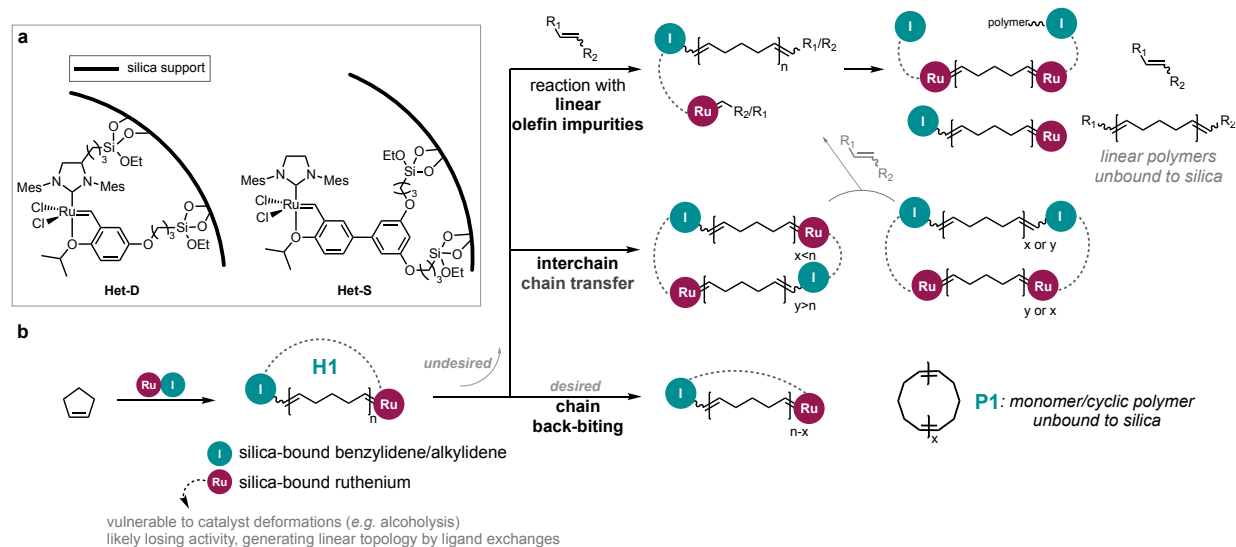
polymerization with a concomitant separation of cyclic polymers from the heterogeneous catalysts. A thimble containing the catalysts that is mounted as a cartridge on the dispenser is situated in the original place throughout the process. This *in situ* continuous process minimizes manual labor, quarantines the vulnerable catalytic species secured from any deactivating events that can occur otherwise upon *ex situ* purifications, and guarantees purity of cyclic polymers. Serendipitously, it is also found that the resulting cyclic polymer depolymerizes noticeably faster than its linear analogue. Overall, this report demonstrates a prototype of a scalable and practical access to a chemically-recyclable cyclic polymer with enlarged reusability of precious catalysts.

Results and Discussion

REMP catalyst design for simple polymer separation: from homogeneity to heterogeneity.

Previous REMP studies have adhered to a typical purification method conducted after ring-opening metathesis polymerization (ROMP), which is multiple polymer precipitation or crystallization in cold polar protic solvents²⁴⁻²⁷. The rigorous purification was inevitable because polarity and crystallinity of cyclic polymers were not sufficiently distinct from undesired polymeric metal complexes (*e.g.* **P1** vs **H1** in Fig. 2b). While this purification is still suitable for the removal of metal which is already deactivated with a quencher in ROMP, it is in fact inappropriate from the aspect of catalyst *recovery* in REMP in which the regenerated catalyst is active upon the release of cyclic polymers. Furthermore, all the polymeric ruthenium species generated *via* the side pathways are *de facto* active catalysts for REMP (Fig. 2b). Thus, the demanding post-synthetic purification likely decomposes the metal catalysts by oxygen, moisture, or purification solvents²⁸, potentially followed by release of unwanted linear polymers or polymeric metal

1 complexes, which are difficult to separate from the desired cyclic polymers, once generated (Fig.
 2 1a).



3
 4 **Fig. 2 REMP of CP with the immobilized ruthenium catalysts.** **a**, The silica-supported ruthenium catalysts
 5 used in this study. **b**, Possible olefin metathesis pathways of cyclopentene ring opening.

6 Previous ruthenium-based catalysts for REMP shared a common structure of metallacycle
 7 where the N-heterocyclic carbene (NHC) and alkylidenes¹¹⁻¹³/benzylidenes¹⁷ were tethered by
 8 organic linkers in the cyclic form (Fig. 1c). By replacing the organic linker with the silica gel support,
 9 we envisioned a simpler and more guaranteed separation of the desired cyclic polymer from the
 10 rest by filtration — the cyclic polymer is the only product chemically unbound from the silica
 11 support unless linear chain-transfer agents are present in the system (Fig. 2b). The envisioned
 12 catalyst, **Het-D** (a silica-containing metallacycle), was synthesized with the longest linear steps of
 13 ten (Fig. 2a, See Supplementary Information for the synthetic details). In addition, acyclic **Het-S**
 14 was prepared in fewer steps for comparison and found as effective (*vide infra*). These REMP
 15 catalysts consist of the chelating benzylidene structure, which are more stable in the air than the
 16 previous REMP catalysts. The amount of the ruthenium catalyst anchored onto silica support was

determined from the Ru to Si ratio (4.0 $\mu\text{mol Ru/g silica}$ for **Het-D**, 2.8 $\mu\text{mol Ru/g silica}$ for **Het-S**) obtained by the inductively coupled plasma mass spectrometry (ICP-MS) (Table S1). The degree of heterogeneity of the catalysts was confirmed with the hot filtration test^{29,30} (Table S2).

Monomer selection and purification: “garbage in, garbage out”. Although known as a low-strain monomer that is challenging for exergonic ROMP/REMP³¹⁻³³, cyclopentene (CP) was selected as the monomer for initial studies. Given a typical molar mass range of polyalphaolefins used for lubrication (<50 kDa)³, it is unnecessary to design higher-molar-mass cyclic polyCP/polyethylene for viscosity modifier purposes. In this respect, limited monomer conversion, even in bulk polymerization (*e.g.* 84% at r.t.³¹), which was considered a problem in previous studies aiming to synthesize linear polyCP with higher molar masses (>100 kDa)^{32,34,35}, is no longer a drawback since the low boiling-point cyclopentene can play the dual role of monomer and solvent with no need of additional solvent. Furthermore, residual CP can be easily separated from polyCP by simple distillation or evaporation under ambient conditions (bp= 45 °C). Moreover, the resulting polyCP itself is interesting, as it is a chemically recyclable natural rubber analog, as well as a pre-hydrogenated polymer of unique polyethylene featuring odd-numbered CH₂ periodicity, which is otherwise hard to access³².

Unfortunately, commercially available CP contained detectable amounts of acyclic olefin impurities (~2000 ppm)³⁵. These impurities acting as chain transfer agents can not only decrease the molar mass of polyCP³⁵⁻³⁷ but also deteriorate the purity of cyclic topology in the REMP process¹⁶ (Fig. 3b). Previously, fractional distillation equipped with 28-inch Hempel column and ceramic Berl saddles was exploited to separate these impurities from CP because of the proximal

boiling points between them³⁵. We envisaged that this strict distillation method could be replaced with a simpler method, provided that a chemical treatment distinguishing acyclic olefins from CP would be found. We selected the cobalt-catalyzed olefin isomerization—selective hydroboration of terminal olefins developed by Chirik’s group³⁸; with only 0.001 mol% of the cobalt catalyst based on CP, the acyclic olefin impurities were transformed into much heavier hydroborated products *via* isomerized terminal olefins. On the other hand, CP remained intact because the isomerization of CP never generates a terminal olefin (Fig. 3a) so that light CP could be separated by simple distillation (Fig. 3b and S1).

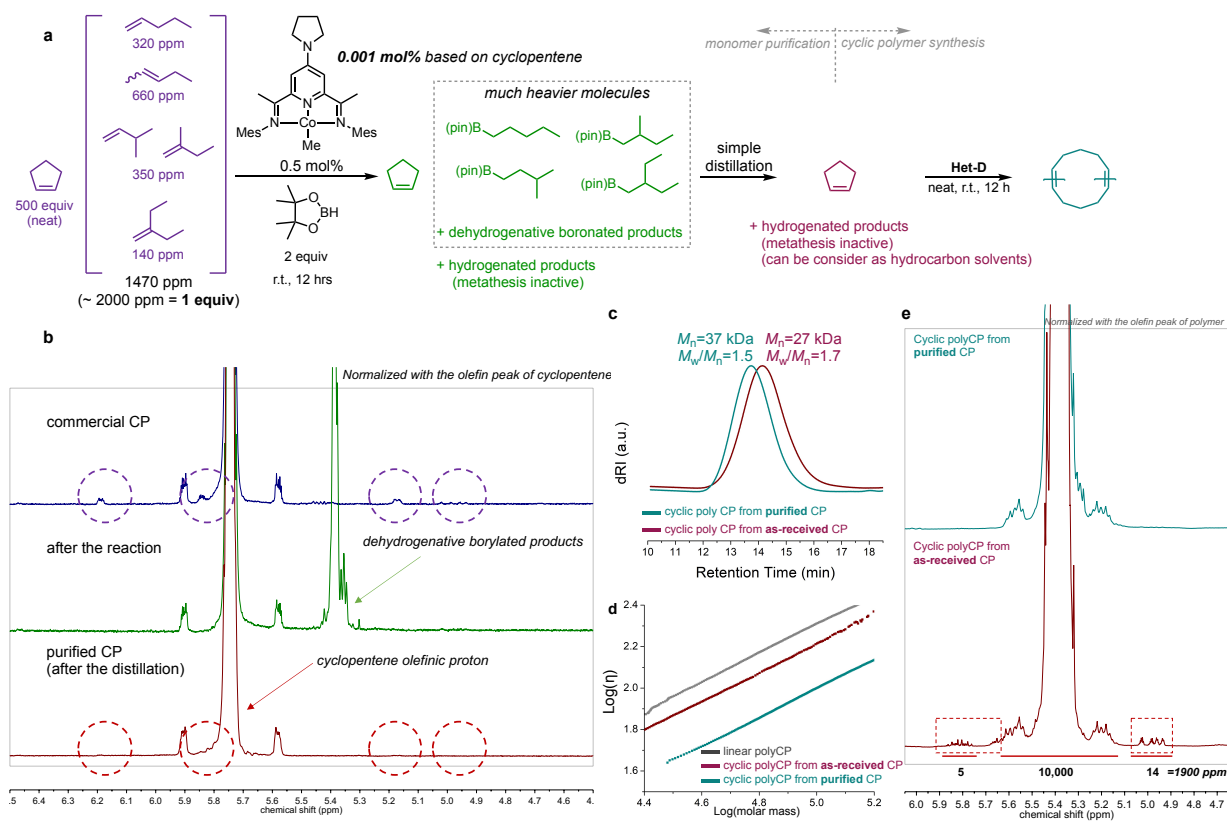


Fig. 3. Importance of monomer purity for REMP. **a**, A chemical treatment to differentiate CP from linear olefin impurities. **b**, ¹H NMR spectra of olefinic regions before and after the hydroboration, as well as after simple distillation. comparison of cyclic polyCP made of the purified CP ($M_n=37$ kDa, $M_w/M_n=1.5$) vs cyclic polyCP made of commercial CP as received ($M_n=27$ kDa, $M_w/M_n=1.5$). **c**, SEC traces. **d**, Mark–Houwink–Sakurada plots **e**, ¹H NMR spectra.

We conducted bulk REMP of purified CP (vs commercial one) with 1.0 mL of CP (11.3 mmol) and 20 mg of **Het-D** (0.08 μ mol) at room temperature in a 20-mL vial under an argon atmosphere. After filtration, the molar mass of the polymer made of commercial CP was found to be lower than that of the polymer from purified CP (Fig. 3c, see Fig. S2 for the similar result of the corresponding ROMP). Also, the cyclic topology was clearly deteriorated when commercial CP was used. The intrinsic viscosities (η) of the two polyCPs over a range of molar masses, measured by size-exclusion chromatography (SEC) equipped with a differential viscometer, showed that the cyclic polyCP from purified CP ($\langle\eta\rangle_{\text{cyclic}}/\langle\eta\rangle_{\text{linear}}=0.44$) had a lower intrinsic viscosity than the one from commercial CP over the whole range ($\langle\eta\rangle_{\text{cyclic}}/\langle\eta\rangle_{\text{linear}}=0.81$), which indicated linear contaminants in the polymer from commercial CP (Fig. 3e, S3 and Table S3). The ^1H NMR spectrum of polyCP made of commercial CP shows minor olefinic proton signals around the major signal of polyCP, which were undetected from the cyclic polyCP made of purified CP (Fig. 3e). The integration of the minor signals was calculated to 1900 ppm, which is close to the amount of linear olefin impurities in commercial CP stock, implying the undesired chain transfer by the impurities. This negative effect on topology was also corroborated by DEPT 135 ^{13}C NMR spectroscopy, where ill-defined side signals were detected in the case of REMP of commercial CP (Fig. S3). These results highlighted that the use of a purer monomer is critical in REMP, where small changes of monomer purity make a big difference of topological purity.

A cyclic polymer dispenser: “monomer in, polymer out”. Despite the simplified separation, there remain practical challenges to catalyst recovery. Although the initiating catalyst is stabilized with the chelating benzylidene structure, catalysts regenerated after release of cyclic polyCP can result in vulnerable alkylidene structures³⁹; in the presence of such catalysts, the post-synthetic

1 filtration requires anhydrous degassed washing solvents under inert conditions for the catalyst
2 recovery. In addition, the required amount of solvent increases as the amount or molar-mass of
3 polymer increases. This *ex situ* filtration endangers the catalysts and ultimately depreciates the
4 practicality of the process.

5 Just as many synthetic chemists such as Dean, Stark, Schlenk and Soxhlet did in the past,
6 we anticipated that a well-designed glassware would be a game changer, which streamlines the
7 process. Our initial attempt was to use a commercial solid-liquid extractor, known as the Soxhlet
8 extractor, where **Het-D** was placed with a cellulose thimble as a cartridge in the extraction
9 chamber, and then CP was refluxed in neat under an argon atmosphere. While CP was
10 polymerized as a monomer inside of the thimble, unreacted CP as a solvent washed the released
11 cyclic polyCP off the thimble, brought the filtered polymer to a collection flask, and was then
12 freshly distilled back to the thimble. Since all the active catalytic species always remained in the
13 thimble under the inert atmosphere, this *in situ* separation system provided the possible
14 maximum level of the catalyst security.

15 Nevertheless, two drawbacks were realized. One was that the reaction temperature was
16 dictated by boiling points of refluxing monomer/solvent. This is a problem since in the REMP of
17 CP, the ceiling temperature is low ($[M]_{eq}=1.17$ at $30\text{ }^{\circ}\text{C}^{40}$). Indeed, the REMP of neat CP (bp=45
18 $^{\circ}\text{C}$) in a Soxhlet extractor afforded cyclic polyCP not exceeding the molar mass of 20 kDa. The
19 other drawback was that the collection flask always contained a mixture of cyclic polyCP and CP,
20 which required an additional step for CP recovery.

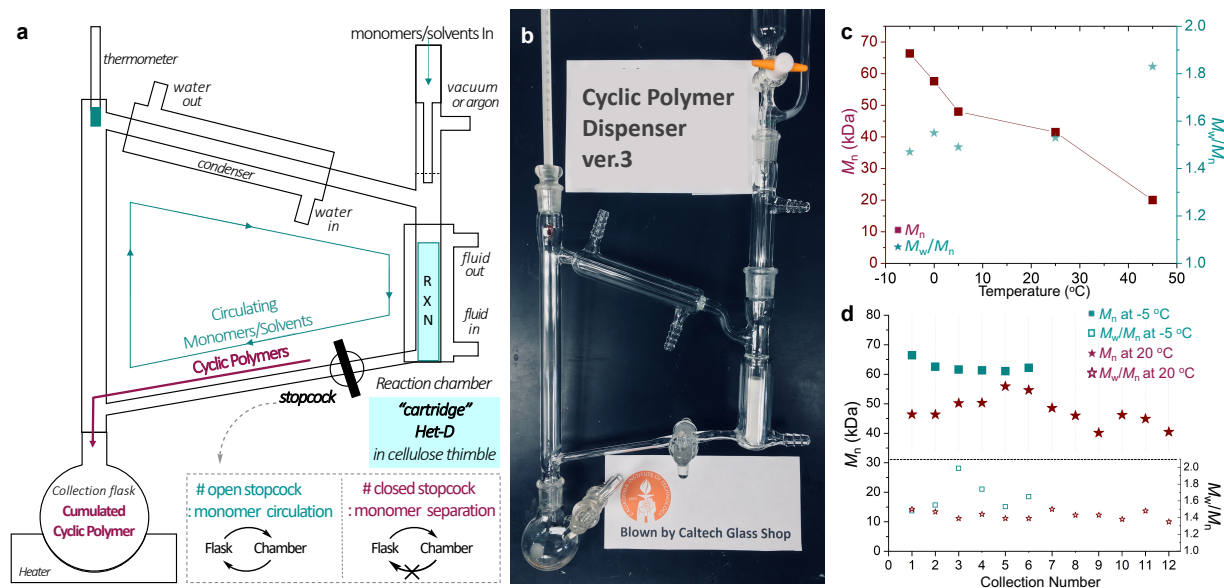


Fig. 4. "Monomer in, Polymer out". **a**, Schematic illustration of the cyclic polymer extractor mechanism. **b**, Photo of the extractor. **c**, Temperature dependence of REMP of CP **d**, Multiple collection of duplicate cyclic polyCPs *via* the dispenser.

Accordingly, an apparatus that is a hybrid of the distillation apparatus and the Soxhlet extractor was customized with two intended features (Fig. 4b, see Fig. S4 for our initial drawing and preliminary versions). The custom glassware, namely a cyclic polymer dispenser, consists of a fluid jacket surrounding the reaction chamber so that the reaction temperature can be controlled by a recirculating chiller/heater (Fig. 4a). By decreasing the reaction temperature, increased molar masses of cyclic polyCP up to $M_n = 66.4$ kDa were observed, showing that the molar mass is thermodynamically controllable (Fig. 4c)³³. Another feature is to segregate the monomer and the polymer in the collection flask by closing a stopcock installed on the pathway between the reaction chamber and the collection flask (Fig. 4a). When the stopcock is closed, CP distilled from the flask into the reaction chamber cannot return to the flask, which leaves cyclic polyCP in the flask. Once the thermometer temperature drops (indicating the end of CP distillation), the flask filled with cyclic polyCP is rapidly switched to an empty flask under an

1 increased argon pressure, and then the stopcock is reopened, which resumes CP circulation (and
2 additional CP is added to maintain monomer levels).

3 After mounting a cartridge on the cyclic polymer dispenser — *i.e.* a cellulose thimble
4 containing 100-mg **Het-D** (400 nmol Ru) — we began to operate the process by adding CP. The
5 stopcock was closed whenever cyclic polyCP needed to be collected, and then reopened. After
6 collecting cyclic polyCPs 12 times that were dispensed to collection flasks, we obtained 11.3
7 grams of combined cyclic polyCP in overall 73% yield based on recovered CP (415,000 catalytic
8 turnovers). The amount of residual CP in the flasks, which was insufficient to be recovered by
9 distillation, caused the yield loss upon sample drying. Each collection offered a cyclic polyCP with
10 similar molar masses (Fig. 4d). High purity of cyclic topology of each round was confirmed with
11 SEC-viscometry and DEPT 135 ¹³C NMR analysis (Fig. S5). The polymers were white with negligible
12 sign of metal residue (< 10 ppb) (Table S1).

13 It is noted that the catalyst was kept on duty, “quarantined” safely in the cellulose
14 cartridge under an argon atmosphere throughout the whole process. In many cases, regenerated
15 catalysts are too vulnerable to recycle in a conventional way which includes an *ex situ step of off-*
16 *duty* catalyst recovery. The use of the cyclic polymer dispenser showcases a new approach to
17 preserve the reusability of precious REMP catalysts by quarantining them *in situ*, as
18 demonstrated by constant activity over multiple collections with high total turnover number. In
19 addition, it can be extended for the synthesis of cyclic polymers with higher molar masses by
20 switching CP to higher ring-strain monomers such as cyclooctadiene (Fig. S6).

“Social distancing” Effect of the immobilized catalyst. We came to realize a noncyclic catalyst in which only the benzylidene moiety is tethered to the silica (**Het-S** in Fig. 2a) can be as effective as **Het-D**, since only cyclic polymers can be released from the support by backbiting. If the ruthenium loading on silica gel is sufficiently low, “socially distancing” ruthenium centers may exclusively allow the desired backbiting pathway, physically disallowing the undesired interchain interaction pathway that would release linear polymeric ruthenium complexes unless the silica support holds both the NHC and benzylidene parts (Fig. 5a). On the other hand, if densely populated, the propagating ruthenium could undergo this undesired pathway to release linear defects because of chain proximity.

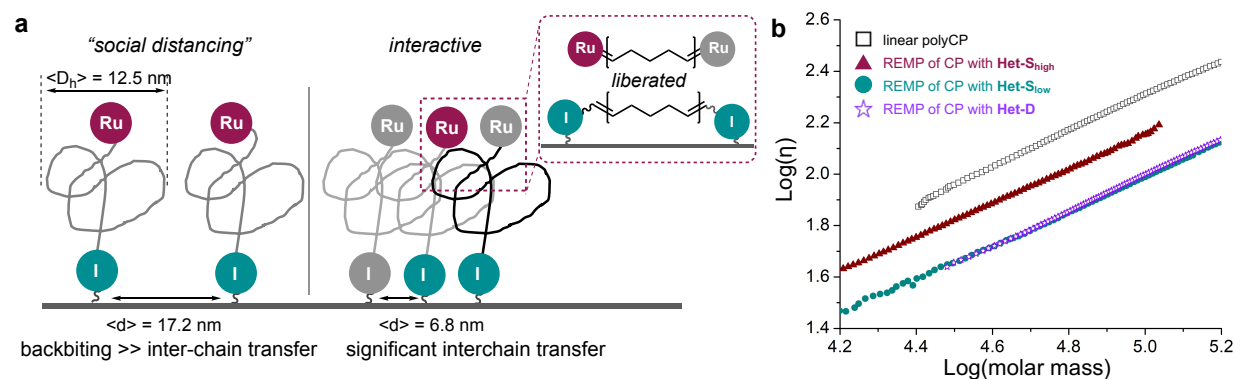


Fig. 5. “Social distancing” effect. **a**, Schematic illustration of the propensity for the interchain interaction affected by ruthenium density on silica gel. **b**, Mark–Houwink–Sakurada plots of cyclic polyCP made with **Het-D**, **Het-S_{low}** and **Het-S_{high}**.

To demonstrate the “social distancing” effect, densely populated **Het-S** (**Het-S_{high}**, 18 $\mu\text{mol Ru}/1$ g silica) and a low populated catalyst (**Het-S_{low}**, 2.8 $\mu\text{mol Ru}/1$ g silica) were prepared. Based on surface area of silica gel, the average ruthenium distance of **Het-S_{low}** was estimated to be 17.2 nm, which is larger than the hydrodynamic diameter ($12.5 \text{ nm} \pm 0.6$) of the isolated cyclic

polyCP measured in CP at 22 °C by dynamic light scattering, whereas the ruthenium distance of **Het-S_{high}** was 6.8 nm, indicating more congested environment (Table S5).

All characterization data of two cyclic polyCPs obtained with **Het-D** and **Het-S_{low}** — molar masses, the Mark–Houwink–Sakurada plots, the conformation plots, ¹H NMR and DEPT 135 ¹³C NMR spectra — were nearly identical (Fig. 5b&S7). In contrast, **Het-S_{high}** afforded polyCP with a higher intrinsic viscosity than **Het-S_{low}**, which implied more interchain transfer events. DEPT 135 ¹³C NMR spectrum also manifested ill-defined side signals. ICP-MS detected 2000 times higher ruthenium content in the polymer made with **Het-S_{high}** (30,000 ppb vs 15 ppb) than one made with **Het-S_{low}** (Table S1). Each characterization consistently led us to a conclusion that **Het-S_{low}** provided cyclic polyCP with as pure topology as does **Het-D**, while “REMP” of CP with **Het-S_{high}** suffered from the undesired side pathways. The discovery of the “social distancing” effect paves the way for potential manipulation of catalytic activity/selectivity of the catalysts by modifying the NHC⁴¹. In addition, noncyclic silica-supported catalysts are easier to prepare, which increases the practicality of the system.

Hydrogenation of cyclic polyCP to cyclic polyethylene. The isolated cyclic polyCP was hydrogenated to cyclic polyethylenes using the tosylhydrazine decomposition method¹¹. The full conversion was confirmed by solid-state ¹³C NMR analysis (Fig. S8). The cyclic polyethylene had a slightly lower melting point (T_m= 131 °C) and crystallization point (T_c=113 °C) when compared with its linear analog (T_m= 133°C, T_c= 115°C) (Fig. S9), which is an opposite trend to our previous observation with higher-molar mass cyclic polyethylenes (T_m= 132 °C, T_c= 115°C vs for the cyclic

one vs. $T_m = 130\text{ }^{\circ}\text{C}$, $T_c = 113\text{ }^{\circ}\text{C}$ for the linear one)¹¹. This discrepancy as well as other properties of cyclic polyethylene are currently under thorough investigation.

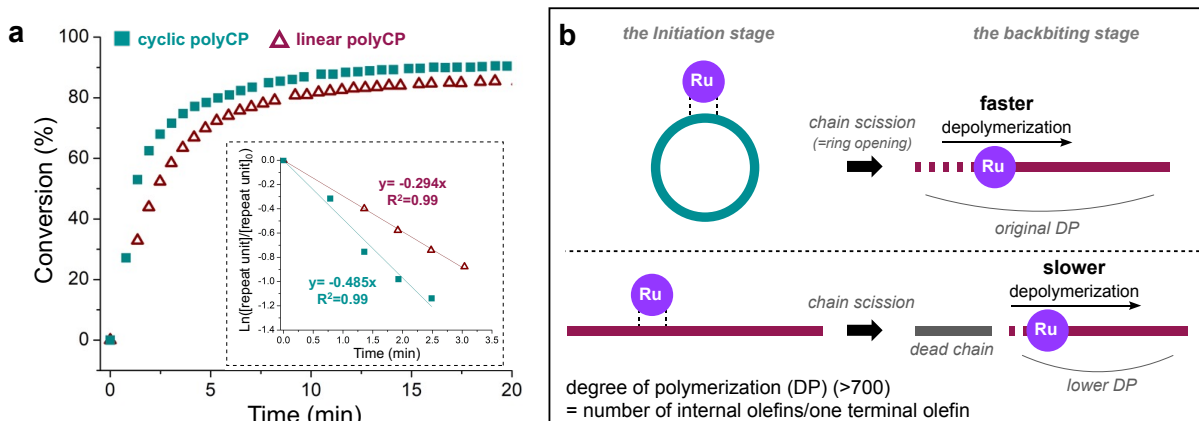


Fig. 6. Topology dependence of depolymerization. **a**, Depolymerization conversions of cyclic polyCP ($M_n=56.8\text{ kDa}$, $M_w/M_n=1.37$) and linear polyCP ($M_n=52.8\text{ kDa}$, $M_w/M_n=1.66$). conditions: ^1H NMR, CDCl_3 (25 mM based on the repeat unit), 0.5 mol% Grubbs 1st generation catalyst, room temperature. **b**, A proposed rationale of the expedited depolymerization rate of cyclic polyCP.

Depolymerization kinetics: cyclic polyCP vs linear polyCP. One of the merits of polyCP is its chemical recyclability to monomer in the presence of an olefin metathesis catalyst, which permits a circular polymer economy⁴². When cyclic and linear polyCPs with similar molar masses were treated respectively with the 1st generation Grubbs catalyst in chloroform, the cyclic polyCP was found to depolymerize 1.6 times faster than its linear analogue ($k_{\text{depolymerization}} = -0.485\text{ min}^{-1}$ for cyclic polyCP vs -0.294 min^{-1} for linear polyCP in Fig. 6a&S10). Considering that the initiation process occurs dominantly by random chain cleavages of abundant internal olefins over terminal olefins (degree of polymerization (DP) >700), we tentatively believe that after the first metathesis turnover, the linear polyCP was bisected into two shorter linear polyCPs, one with an active

1 ruthenium carbene and the other without it (Fig. 6b)^{43,44}. On the other hand, cyclic polyCP would
2 be always opened to active linear polyCP with the original DP without dead fragments¹⁰, and this
3 expedited depolymerization. Research on the detailed topology effect depending on other
4 variables (molar mass, temperature, solvent, *etc.*) is ongoing.

6 Conclusion

7 We have developed a convenient synthetic approach for the synthesis of cyclic
8 polycyclopentenamer by leveraging heterogeneity of the catalysts with the help of the newly-
9 designed glassware. Once the heterogeneous catalyst was placed in the thimble and
10 cyclopentene was added to the reaction apparatus, the circular loop of polymerization, polymer
11 separation, and catalyst recovery operated on its own, and then dispensed cyclic
12 polycyclopentenamer into the collection flask. This vending-machine-like process not only
13 minimized manual labor but also maximized security and reusability of vulnerable REMP catalysts,
14 purity of cyclic topology, as well as scalability of polymer. In addition, the first example that a
15 cyclic polymer depolymerizes faster than its linear analogue was discussed, with which we hope
16 to give an intriguing insight to promote the circular polymer economy. Currently, preliminary
17 tests of cyclic polymers as a lubricant material are ongoing in our laboratories.

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1 **Methods**

2 Experimental details are provided in the Supplementary Information.

3

4 **Procedure for the synthesis of cyclic polyCP.** All glasses were dried in a 165 °C oven prior to use.

5 The cyclic polymer dispenser was connected to a 25-mL Schlenk flask, a thermometer, and a

6 dropping funnel with the help of suitable joints. The upper cooling jacket was equipped with a

7 water circulator, and the lower jacket was equipped with a circulating chiller or heater,

8 depending on the required reaction temperature. The detailed glassware setup is described with

9 photos in the Supplementary Information. The heterogeneous catalyst (**Het-D** or **Het-S**) was

10 weighed in air and placed in a commercial cellulose thimble. The thimble containing the catalyst

11 was transferred in the reaction chamber of the cyclic polymer dispenser. The whole glass system

12 was charged with argon by repetitive vacuum and argon backfilling. Afterwards, the purified CP

13 was added to the reaction chamber via the dropping funnel. The distillation column part was

14 wrapped with cotton and foils for heat insulation. The heater was set to 70 °C. For convenience,

15 a heating block was used instead of an oil bath. Once the circulation of CP began, the

16 thermometer turned to 45 °C. After 3–6 hours when the polymer needed to be collected, the

17 stopcock of the dispenser was closed. When the thermometer temperature dropped to room

18 temperature, the argon pressure was increased, and then the filled 25-mL flask was replaced with

19 a new 25-mL Schlenk flask. On the switching process, the air contaminant was vented out of the

20 system by briefly opening the valve of the Schlenk flask. The argon pressure was reduced back to

21 normal, and the stopcock was reopened, and then the CP circulation resumed. The stopcock was

22 closed for the next collection and the procedure was reiterated.

Data availability

All data supporting the findings of this study are available within the Article and its Supplementary Information.

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Author contributions

R.H.G. and K.-Y.Y. conceived and designed the project. R.H.G. and T.-L.C. directed the project and provided valuable input. K.-Y.Y., Q.G. and J.P.E synthesized the catalysts. K.-Y.Y. designed the glassware. K.-Y.Y., J.N. and Q.G. characterized the polymers. J.N. performed depolymerization experiments. R.T. demonstrated the first heterogeneous cyclic polymer process. All authors analyzed the data and discussed the results. K.-Y.Y prepared the initial manuscript and then all authors reviewed and commented on the manuscript. K.-Y.Y., J.N. and Q.G. contributed the project equally.

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2 **Competing interests**

3 The authors declare no competing interests.

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