

Allylic Epoxides Increase the Strain Energy of Cyclic Olefin Monomers for Ring-Opening Metathesis Polymerization

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ABSTRACT: Ring-opening metathesis polymerization (ROMP) is an effective method for synthesizing high molecular weight, functional polymers, but the technique is limited by its reliance on high ring strain cyclic olefins. As a result, the most common monomers are norbornene derivatives. The reliance on this one molecular framework for efficient ROMP of functionalized materials limits the obtainable properties of ROMP polymers. In this work, we investigate new bicyclic monomers synthesized via epoxidation of commercial dienes. DFT estimates of these monomers' ring strains suggests a particular increase in strain for cyclic olefins containing allylic epoxides. We found that the eight-membered (**COO**) and five-membered (**CPO**) cyclic olefins were particularly effective for ROMP. **CPO** was of especially intriguing due to its excellent polymerizability when compared to the limited reactivity of other five-membered rings. The resulting polymers of both monomers displayed T_g s well below room temperature. Interestingly, poly(**3,4-COO**) showed both high stereo- and regioregularity while poly(**CPO**) showed little regularity. Both polymers could be readily modified via post-polymerization ring-opening of the reactive allylic epoxides. With the advantages of high epoxide density in poly(**CPO**), we see **CPO** as an exciting new ROMP monomer that is easily synthesized, can be polymerized to high conversion at room temperature, and may be facily modified to yield a wide range of functional materials.

Introduction

Ring-opening metathesis polymerization (ROMP) is a powerful method for synthesizing polymers via the ring-opening of cyclic olefins.¹⁻² With the wide availability of commercial homogeneous metathesis initiators, ROMP has become an accessible tool for synthesizing functional polymers, with applications ranging from industrial production of rubbers³ to emergent systems for drug delivery⁴ and gas separation.⁵ However, because olefin metathesis is an equilibrium process, reaching high degrees of conversion typically requires the use of monomers with significant ring strain. While high strain (> 20 kcal mol⁻¹) monocyclic cyclopropenes⁶⁻⁹ and cyclobutenes¹⁰⁻¹¹ have been explored, the synthetic challenge of accessing these monomers has resulted in few examples in the literature.

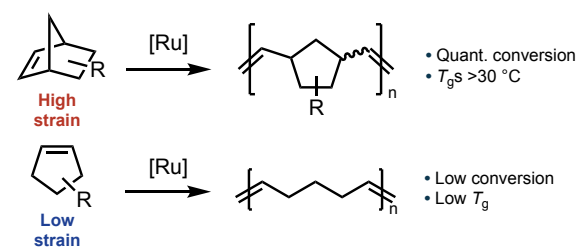
Although low-strain monomers, such as cyclopentene (**CPen**), are polymerizable, low ring strains require low temperatures and high monomer concentrations to achieve significant conversion to polymer.¹²⁻¹⁶ In work by Kennemur and coworkers, DFT calculations were used to assess the strain energies of a number of substituted cyclic five-membered rings.¹⁷ Of the 73 CPE derivatives investigated, only 7 derivatives had larger ring strains than unsubstituted **CPen**. Even when computational methods do suggest **CPen** derivatives have higher strain energies than **CPen**, the achieved monomer conversion has not been significantly greater.¹³

Due to these limitations of monocyclic olefins, the most common monomers for ROMP are bicyclic species, typically norbornenes (**NBEs**), which are easily synthesized via the Diels–Alder reaction. While several steps are required to obtain high purity monomers such as the fast-polymerizing *exo*-norbornene imides, these manipulations are easily performed by most synthetic polymer groups, and monomers may be easily functionalized to meet one's particular need. Unfortunately, due to the presence of a cyclopentene ring in the backbone, polynorbornenes generally have high glass transition

temperatures (T_g s) and are highly hydrophobic without the addition of solubilizing groups such as oligo ethylene glycol chains¹⁸⁻¹⁹ or zwitterions²⁰ (Figure 1).

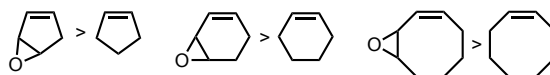
Taking inspiration from these strained bicyclic compounds, our group sought to explore the ROMP of other bicyclic monomers. While substitutions of **CPen** in general have not been effective in significantly increasing strain energy, we believed the inclusion of fused rings would result in species with higher strain energies.

Conventional ROMP Monomers



This Work

Increased strain energies



Enhanced polymerizability

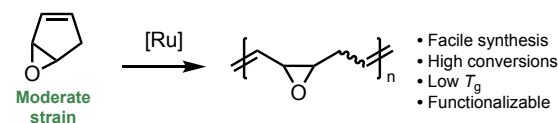


Figure 1. Comparison of conventional ROMP with allylic epoxide cyclic olefins, which show increased strain energies, are readily polymerized, and can be functionalized post-polymerization via epoxide ring-opening.

Similarly to the case of norbornenes, fused ring systems restrict the conformations accessible to these cyclic olefins, resulting in significant torsional strain. While previous work has demonstrated that *trans*-fused ring systems synthesized from 1,5-cyclooctadiene produced monomers with lower ring strains than cyclooctene (**COct**),²¹ we believed that synthesizing monomers instead from 1,3-cycloalkadienes with *cis*-fused rings might instead result in higher strain species.

We chose to focus our investigation on epoxidized cyclic olefins as opposed to other bicyclic systems due to their relative ease of synthesis. Additionally, unlike other cyclic species, epoxides may be readily ring-opened with a range of nucleophiles.²² Incorporating epoxides into the polymer backbone would provide a functional handle to enable facile post-polymerization modifications.

In this study, we examined the effects of epoxides on the strain energies and polymerizability of cyclic olefins. In all cases, the inclusion of allylic epoxides increased the strain energy relative to that of the unfunctionalized cyclic olefin. Of particular note, the epoxidized five-membered ring could be polymerized with 94% conversion at 1 M at 25 °C. The resulting polymers with allylic epoxides in the backbone were easily modified post-polymerization using a range of nucleophiles, resulting in a densely functionalized polymer.

Results and Discussion

Computational Studies

We began by computationally investigating the strain energies of NBE, a series of monocyclic olefins, **CPen**, **CHex**, and **COct**, and a number of epoxidized derivatives (Figure 2). For the six- and eight-membered rings, we considered oxides synthesized via epoxidizing both conjugated and non-conjugated cyclic dienes. The theoretical strain energies of these molecules was investigated via DFT at the M06L/def2-svp level of theory.²³ Ring strain energies were estimated by calculating the ΔH values for the homodesmotic reaction of the cyclic olefin and ethylene to give a ring opened species. The enthalpies of the lowest energy conformers were used for these calculations. For small rings such as those investigated here, the ΔH values for the ethenolysis reaction provide a reasonable approximation of the strain energy of the system.²⁴

The calculated strain energy values of the hydrocarbons showed decent agreement with previously-determined strain energy values.^{12-13, 17, 25} The strain energy of 6.6 kcal mol⁻¹ calculated for **CPen** was only 1.0 kcal mol⁻¹ greater than the value experimentally determined by Tuba and Grubbs.¹² To the best of our knowledge, the experimental strain energies for other cyclic olefins as determined by variable temperature ROMP studies have not been reported. Importantly, our calculated strain energies were in agreement with general trends in polymerizability (namely, higher strain **COct** is polymerized with higher conversion while low strain **CHex** is considered un-polymerizable²⁶).

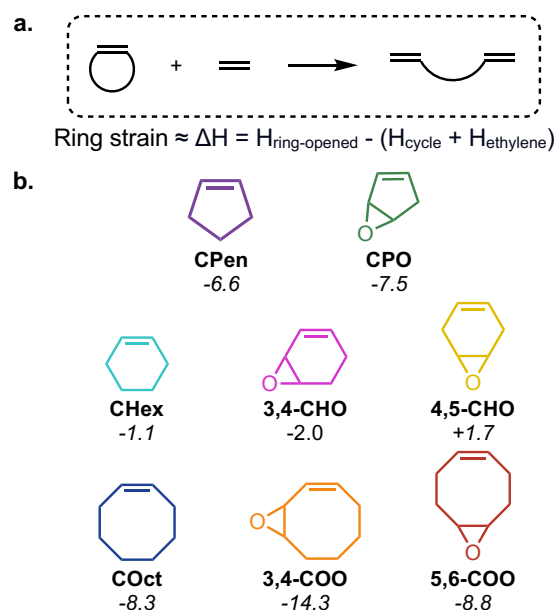
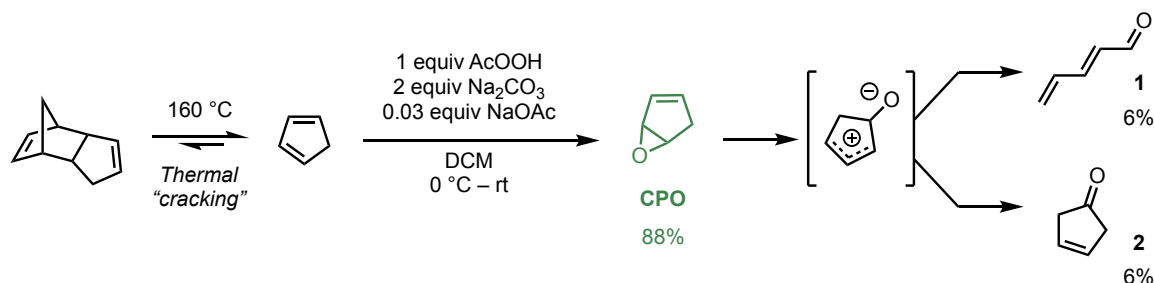


Figure 2. a. The homodesmotic reaction between a cyclic olefin and ethylene to give a ring-opened species used to estimate the ring-strain energy of a series of cyclic olefins. b. A series of cyclic olefins investigated for ROMP, including epoxidized cyclic olefins and their unfunctionalized analogues, along with the ΔH values for the ethenolysis reaction in kcal mol⁻¹ calculated via DFT.

The effects of epoxidation on the calculated strain energies were particularly intriguing. The epoxidized five-membered ring **CPO** had a ΔH value of -7.5 kcal mol⁻¹, nearly 1 kcal mol⁻¹ more strained than unfunctionalized **CPen**. For the **CHex** and **COct** derivatives, the substitution pattern of the epoxide greatly affected the compounds' strain energies. The ΔH value for **3,4-CHO** was determined to be -2.0 kcal mol⁻¹, a greater strain energy than that of **CHex**. However, **4,5-CHO** showed a positive ΔH value of 1.7 kcal mol⁻¹. Similarly, **3,4-COO** had a ΔH value of -14.3 kcal mol⁻¹, making it more strained than the unfunctionalized **COct** by 6 kcal mol⁻¹. **5,6-COO** on the other hand shows only a modest increase in strain energy of 0.5 kcal mol⁻¹ from **COct**. These calculations suggested that the three allylic epoxide cyclic olefins would be more effective ROMP monomers than their unsubstituted analogues.

Synthesis of Epoxidized Monomers

With these promising DFT calculations in hand, we sought to synthesize the 5 epoxidized bicyclic species in order to assess their ability to polymerize. Both **CHO** and **COO** isomers could be synthesized from commercially available cyclic dienes with either mCPBA or peracetic acid used as the oxidant. All four could be purified via flash chromatography on silica gel, though higher yields were acquired if the silica was first treated with triethylamine due to the epoxides' susceptibility to acid-catalyzed ring opening.²⁷



Scheme 1. The synthesis of **CPO**.

The route to accessing **CPO** began with the thermal cracking of inexpensive dicyclopentadiene into cyclopentadiene (Scheme 1). The distilled cyclopentadiene could be safely stored in a $-50\text{ }^{\circ}\text{C}$ freezer over several weeks, making it unnecessary to use cracked cyclopentadiene immediately. The oxidation of cyclopentadiene proved more challenging than anticipated. Unlike the other dienes, mCPBA was not found to be a useful oxidant, resulting in complete conversion of cyclopentadiene into a complex mixture of products, none of which could be identified as the desired product (Figure S1). We instead adopted a regularly employed procedure using a peracetic acid solution.²⁸⁻³² Despite many attempts at optimization, significant amounts of aldehyde **1** and cyclic ketone **2** were produced during the course of the reaction (Scheme 1, Figure S2). The isomerization has been hypothesized to proceed via a zwitterionic intermediate in the absence of acid.³³ While **2** is unlikely to interfere with ROMP of **CPO**, due to our concerns that **1** would participate in chain transfer, we proceeded to successfully purify the mixture with an (aminomethyl) polystyrene resin, furnishing pure **CPO** following distillation under reduced pressure.

ROMP of Epoxidized Monomers

With these monomers in hand, we set off to test their efficacy in polymerization via ROMP. We prepared 1 M solutions of cyclic alkenes **CPen** and **COct** as well allylic epoxides **CPO** and **3,4-COO** in degassed CDCl_3 in NMR tubes with pierceable septa caps (Figure 3a). Polymerization was initiated by adding 1 equiv of metathesis catalyst **G3** to 500 equiv monomer. Monomer conversion was monitored *in situ* via ^1H NMR spectroscopy. 8-membered rings **COct** and **3,4-COO** showed rapid conversion into polymer, with no detectable monomer remaining after 30 minutes. **COct** showed a faster initial polymerization rate than **3,4-COO**, likely due to either the increased sterics or potential chelation of the epoxide. As both monomers were calculated to have relatively high strain energies, it is unsurprising that at a starting concentration of 1 M the monomer-polymer equilibrium could not be observed (Figure 3b).

Under these same conditions, **CPen** reached an equilibrium monomer concentration of 0.88 M. The equilibrium ring-chain concentration ($[M]_{\text{eq}}$) may be determined using eq 1.

$$\ln([M]_{\text{eq}}) = \frac{\Delta H_p^\circ}{RT} - \frac{\Delta S_p^\circ}{R} \quad \text{eq 1}$$

R is the gas constant, T is temperature in K, and ΔH_p° and ΔS_p° are the experimental changes in enthalpy and entropy of polymerization, respectively. Using the experimentally-determined thermodynamic values for ROMP of **CPen** from Tuba and Grubbs, the equilibrium concentration at $25\text{ }^{\circ}\text{C}$ is calculated to be 0.86 M, closely matching our experimental result.

Unlike **CPen**, however, **CPO** shows rapid conversion into polymer, reaching an equilibrium monomer concentration of 0.06 M. By solving eq 1 for the thermodynamic parameters for the ROMP of **CPO** using variable temperature ^1H NMR study, we determined the ΔH_p and ΔS_p values for **CPO** to be $-7.1\text{ kcal mol}^{-1}$ and 18.6 cal mol^{-1} , respectively (Figure S3). Notably, the ΔH_p value closely matched our DFT result and the ΔS_p value was rather close to that of **CPen**. These data suggest that the increased polymerizability of **CPO** relative to **CPen** primarily is due to the greater strain energy of **CPO** induced by the inclusion of an allylic epoxide.

While **CHex** is generally considered unpolymerizable, particularly at similarly low concentrations, we nevertheless attempted the polymerizability of the 6-membered rings as well. **G3** was added to concentrated solutions of **CHex**, **3,4-CHO**, and **4,5-CHO**. While

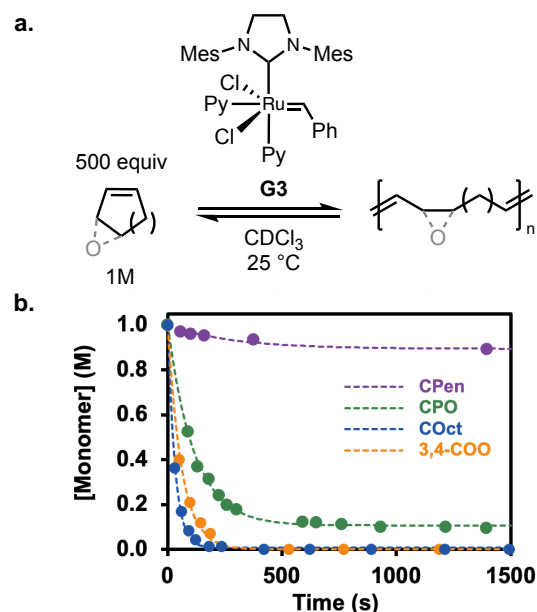


Figure 3. a. Scheme of the polymerization of cyclic olefins with **G3**. b. Plot of the conversion of monomer to polymer determined by ^1H NMR spectroscopy over time. Conditions: $[M]_0 = 1\text{ M}$ in CDCl_3 , $[\text{G3}]_0/[M]_0 = 500$.

no conversion was detected for **CHex**, the equilibrium concentration for **3,4-CHO** and **4,5-CHO** was found to be 3.4 and 4.5 M, respectively (Figure S4). Together, these experimental results again suggest the specifically allylic placement of the epoxide increases the ring strain and thereby polymerizability of otherwise unpolymerizable cyclic olefins.

With both **3,4-COO** and **CPO** shown to readily polymerize, we targeted polymers of different intended degrees of polymerization (DP) by changing the ratio of monomer to **G3**. After the desired polymerization time, samples were quenched with excess ethyl vinyl ether and analyzed via ^1H NMR spectroscopy and GPC. For **3,4-COO**, a linear relationship between theoretical molecular weight and M_n determined by GPC, with respect to polystyrene standards, was observed for intended DPs from 100 to 500 (Table 1, Entries 1–4, Figure S5). However, a lower-than-expected M_n GPC was observed when an intended DP of 1000 was targeted. Similarly, we observed that the polymers' dispersities increased from 1.41 to 1.78 as the intended DP was increased, suggesting an increased prevalence of cross metathesis and overall a worse controlled polymerization at high monomer to catalyst ratios.

Poly(**CPO**)s with DPs from 100 to 5000 were likewise targeted. Conversions for all samples were $>90\%$ for all samples except for DP = 5000, though the concentration was increased to achieve DPs greater than 1000 within 2 h (Table 1, Entries 5–7, 9–11, Figure S6). A linear relationship between $M_{n,\text{theo}}$ and $M_{n,\text{GPC}}$ was found for intended DPs from 100 to 1000, with some deviation observed for particularly high DP samples. Unlike what was observed for the poly(**3,4-COO**) samples, there was no direct relationship between molecular weight and dispersity, with most samples having moderate dispersities between 1.4 and 1.6. We found little effect of conducting the polymerization at $0\text{ }^{\circ}\text{C}$, with a slightly higher conversion and molecular weight observed relative to room temperature but minimal change in dispersity (Table 1, Entry 8, Figure S7). Likewise, we found no difference in dispersity whether the polymerization was allowed to proceed for 20 min or 1 h (Figure S8). Although these overall differences in dispersity are small, we hypothesize that the

Table 1. ROMP of **CPO** and **3,4-COO**

Entry ^a	Monomer	[M] ₀	Cat.	[M] ₀ /[cat.] ₀	Time (h)	Temp. (°C)	Conv. (%) ^b	M _{n,theo} (kDa) ^b	M _{n,GPC} (kDa) ^c	Đ ^c
1	COO	1	G3	100	1	20	>98	12.5	10.9	1.41
2	COO	1	G3	250	1	20	>98	31.2	40.6	1.59
3	COO	1	G3	500	1	20	>98	62.2	70.7	1.64
4	COO	1	G3	1000	2	20	>98	124.3	108.9	1.78
5	CPO	1	G3	100	1	20	94	7.8	5.6	1.50
6	CPO	1	G3	250	1	20	94	19.4	13.4	1.62
7	CPO	1	G3	500	1	20	94	38.7	25.0	1.44
8	CPO	1	G3	500	1	0	95	39.1	31.9	1.53
9	CPO	1	G3	1000	1	20	93	76.5	47.2	1.59
10	CPO	2	G3	2500	2	20	96	197.1	107.3	1.44
11	CPO	4	G3	5000	2	20	81	332.6	155.7	1.59
12	CPO	1	G1	500	1	20	22	9.1	13.7	1.45
13	CPO	1	G2	500	1	20	45	18.6	32.4	1.81
14	CPO	1	HG	500	1	20	95	39.1	16.3	1.40
15	CPO	1	Z	500	1	20	4	1.7	—	—

^aPolymerizations were conducted using degassed THF in scintillation vials equipped with pierceable septa caps. Catalyst was prepared as stock solution in THF and injected into monomer vials to initiate polymerization. Polymerizations were quenched via addition of ethyl vinyl ether. ^bMonomer conversion and M_{n,NMR} were calculated based on relative integration of remaining monomer and polymer olefin signals by ¹H NMR spectroscopy. ^cM_{n,GPC} calculated with GPC calibration curve using polystyrene standards.

greater concentration of backbone epoxides in poly(**CPO**) may better prevent cross metathesis than poly(**3,4-COO**).

We additionally screened several other Grubbs-type metathesis catalysts for the polymerization of **CPO**. All polymerizations were conducted at [CPO]₀ = 1 M in THF with a [CPO]₀/[cat.] ratio of

500 (Figure 4, Table 1, Entries 11–15). Both **G1** and **G2** catalysts showed less monomer conversion than **G3**. Notably, both also showed relatively higher M_n values, suggesting incomplete initiation relative to **G3**. This may also explain the significantly higher dispersity of 1.81 for the **G2** polymer.³⁴ While the Hoveyda-Grubbs (**HG**) catalyst showed similar conversion to **G3**, its M_n value was significantly lower, due to the greater amount of low molecular weight cyclic species observed by GPC.³⁵ Finally, while ¹H NMR spectroscopy suggested use of the Hoveyda-Grubbs Z-olefin-selective catalyst (**Z**),³⁶ relatively little conversion was observed, with little additional conversion even at extended times.

The thermal properties of these materials were investigated via DSC (Figure S10). The T_g for poly(**COct**) and poly(**CPen**) were not observed in the temperature range examined.³⁷⁻³⁸ However, both showed significant melting peaks with maxima at 13.6 and 62.2 °C, respectively. Poly(**3,4-COO**) and poly(**CPO**) have T_gs of -21.1 and 1.1 °C, respectively, with the higher T_g for poly(**CPO**) likely due to the greater concentration of backbone epoxides. Unlike poly(**COct**) and poly(**CPen**), neither of the epoxidized polymers demonstrate melting or crystallization temperatures.

Regio- and Stereoselectivity

¹H and ¹³C NMR spectroscopy of poly(**3,4-COO**) and poly(**CPO**) was used to interrogate the stereo- and regioselectivity of the polymerization of the two epoxidized monomers. Given both monomers were racemic mixtures, we chose to focus our attention not on the stereochemistry of the epoxides but rather olefin configuration.

Previously, 3-substituted cyclooctenes have been found to have >96% regioselectivity (head-to-tail arrangements) with >93% incorporation of trans olefins.³⁹ From the analysis of the olefin region of the ¹H NMR spectrum of poly(**3,4-COO**), we observe high regio- and stereoselectivity (Figure 5a). The head-to-tail content is 92% while the *trans* olefin content is 80%. Qualitatively, the sharp, well-

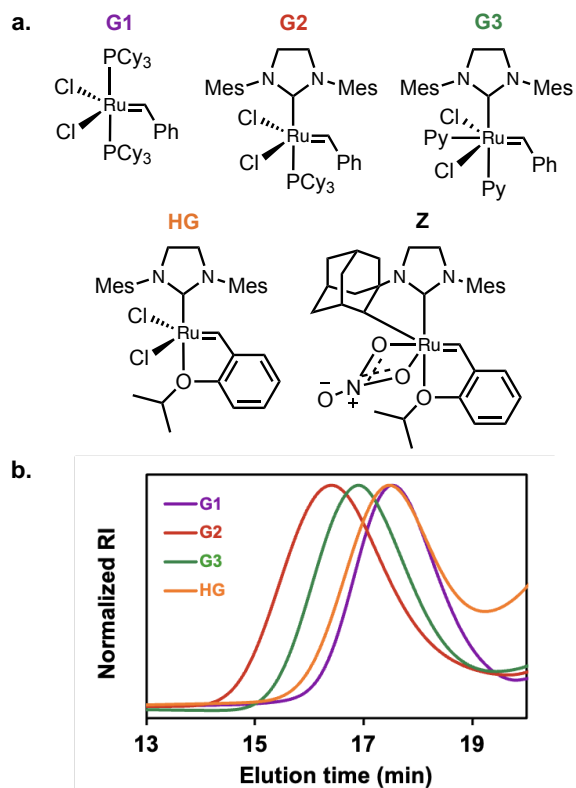


Figure 4. a. Different Grubbs-type initiators screened for the polymerization of **CPO**. b. GPC traces for poly(**CPO**)s polymerized with different initiators.

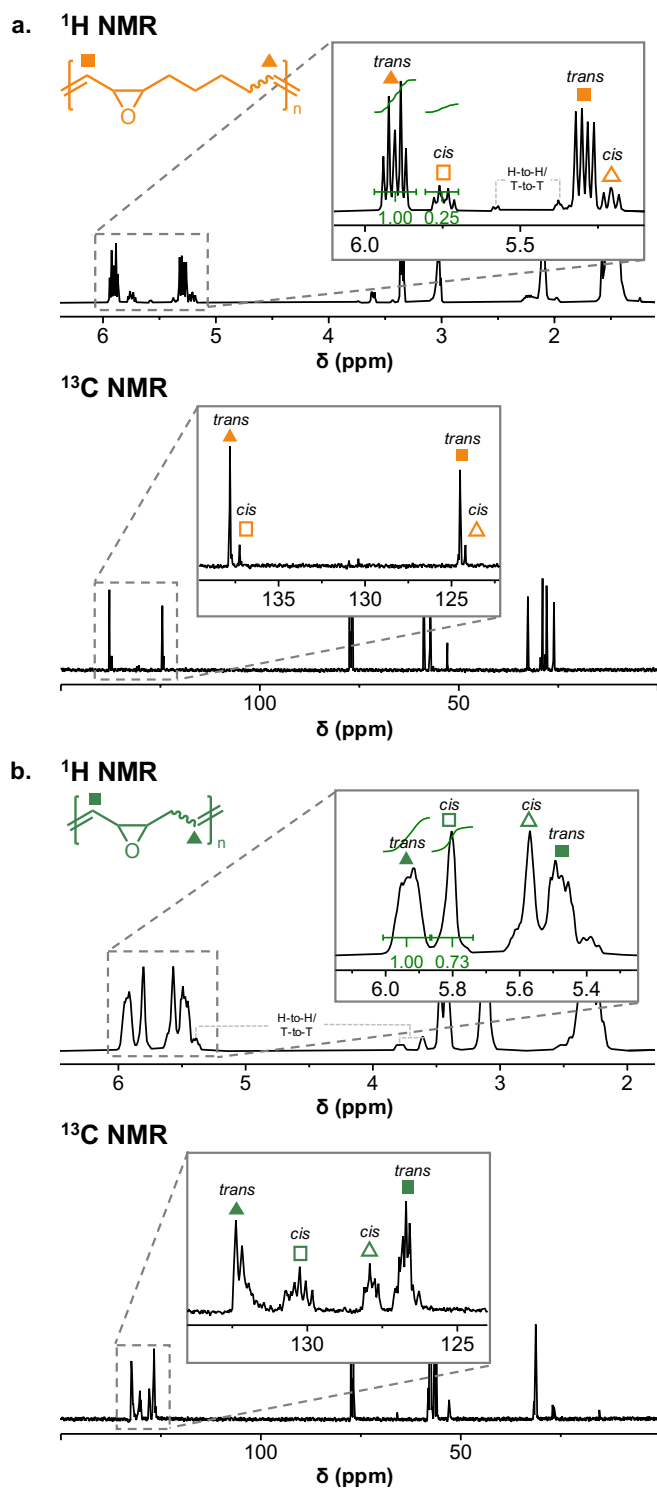


Figure 5. a. ¹H and ¹³C NMR spectra of poly(3,4-COO). b. ¹H and ¹³C NMR spectra of poly(CPO).

resolved ¹H NMR signals support the high degree of regularity of these polymers. Additionally, the ¹³C NMR signals similarly suggest high regularity. As the high regioselectivity of 3-substituted cyclooctenes was thought to be due to the steric clash between the substituent and the NHC ligand on the Grubbs catalyst,⁴⁰ the use of a less bulky epoxide may explain the decreased selectivity of the polymerization of COO.

When analyzing the poly(CPO) sample, we found significantly less regio- and stereospecificity (Figure 5b). We found a significantly lower head-to-tail ratio of 85% based on ¹H NMR analysis.

Additionally, only 58% of backbone olefins were *trans*. The ¹³C NMR spectrum of poly(CPO) provides evidence of significantly more olefin carbons than for poly(3,4-COO). In part this may be due to the increased amount of head-to-head monomer linkages. Additionally, the decreased number of carbons per repeat unit makes the ¹³C NMR signals more susceptible to differences in epoxide stereochemistry due to the use of a racemic CPO. Further investigation is warranted to investigate the causes for greater irregularity in the polymerization of CPO. We hypothesize that due to the small ring size of CPO, the relative steric differences between the epoxide and methylene groups alpha to the olefin result in poorer regio- and stereochemical control.

Copolymerizations of CPO and CPen

Poly(CPO) contains a greater concentration of backbone epoxides than poly(3,4-COO). In order to synthesize polymers with tunable concentrations of epoxides, we attempted the copolymerization of CPO with CPen. Polymerizations were performed using G3 as an initiator at an overall monomer concentration of 1 M. CPO:CPen ratios were varied from 2:1, 1:1, and 1:2. In all cases the polymerizations were performed below the homopolymerization equilibrium concentration of CPen. Table 2 shows the results of these successful copolymerizations (Table 2, Entries 1–3, Figure 12). Unsurprisingly, a greater amount of the high-strain CPO was incorporated into the polymer than CPen. However, between 23% and 45% of CPen was polymerized into each, showing greater polymerizability when copolymerized with CPO than when homopolymerized under identical conditions. This is likely due to both the greater entropy of mixing in these copolymerization systems, leading to greater polymerizability of both monomers, but essentially a “trapping” of the less polymerizable CPen between more polymerizable CPO units within the polymer. Interestingly, when the monomer concentration for a 1:2 copolymerization was increased to 2 M, the incorporation of CPen decreased to 23%, perhaps due to the increased favorability of incorporation of CPO into the chain (Table 2, Entry 4, Figure S13). Additionally, the incorporation of any CPen into the polymer resulted in the disappearance of a *T_g* within the observed temperature range from -50–50 °C (Figure S14).

Post-Polymerization Modification of Polymers

The presence of backbone epoxides in these polymers presented a unique opportunity to leverage this reactive functional group to easily modify these polymers with a desired nucleophile. This would allow one pre-polymer to be easily diversified into a range of different materials depending on the desired application. For our post-polymerization modification studies, we targeted lower molecular weight samples of ROMP polymers with allylic epoxides poly(3,4-COO) and poly(CPO) as well as a sample of poly(5,6-COO) which contained non-allylic epoxides. To test the efficacy of these

Table 2. Copolymerization of CPO and CPen

Entry ^a	CPO: CPen	CPO (%)	CPen (%)	<i>M_n</i> GPC (kDa) ^b	<i>D</i> ^b
1	2:1	77	23	17.7	2.68
2	1:1	66	34	16.0	2.39
3	1:2	55	45	19.3	2.44
4	1:2	77	23	22.7	2.85

^aConditions: [CPO + CPen]₀ = 1 in CHCl₃, [CPO + CPen]₀/[G3] = 500, rt, 1 h. ^b*M_n* GPC calculated with GPC calibration curve using polystyrene standards.

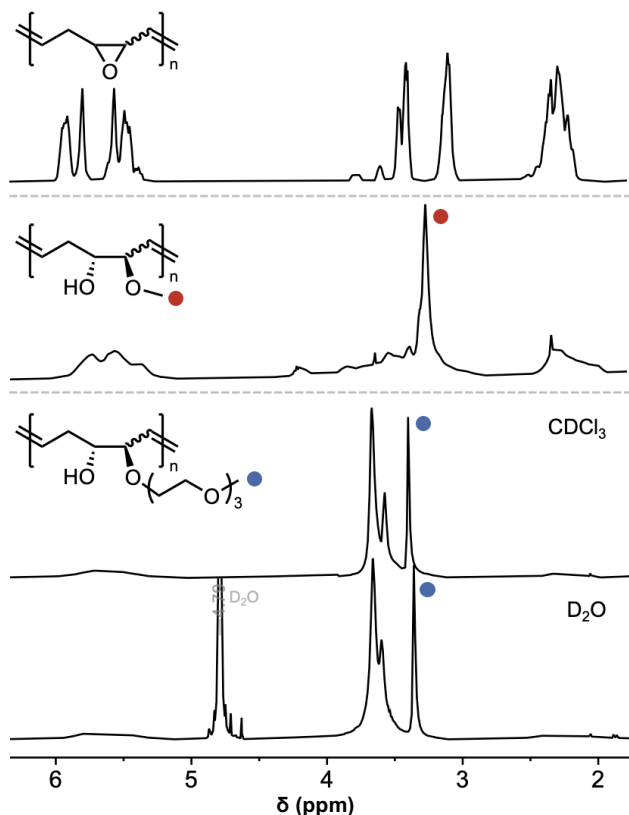


Figure 6. ^1H spectra of poly(CPO) and polymers with the addition of methanol and methoxy triethylene glycol.

modifications, each polymer sample was prepared as a 0.1 M solution in CDCl_3 , to which 5 equiv of methanol added per repeat unit as well as a catalytic amount of sulfuric acid. After 3 h, ^1H NMR spectra were acquired of the resulting polymers.

Based on ^1H NMR analysis, the samples of poly(**3,4-COO**) and poly(**CPO**) both demonstrated high amounts of functionalization of 90% and 95%, respectively (Figures S15, S16, and 6). Interestingly, under these same conditions, poly(**5,6-COO**) showed a negligible degree of functionalization (Figure S17), demonstrating the enhanced reactivity of allylic epoxides.

We additionally demonstrated the ring-opening of poly(**CPO**) with methoxy triethylene glycol, resulting in a polymer that was soluble both in CDCl_3 and D_2O (Figure 6). We envision this easy modification to be a facile route to water-soluble soft materials and potentially to the synthesis of amphiphilic polymers were block copolymers with **CPO** to be obtained.

Conclusions

In this work, we demonstrated that the inclusion of epoxides in five-, six-, and eight-membered cyclic olefins increases the strain energy of these cycles, making them more amenable to ROMP. Allylic epoxides in particular result in the greatest increase in strain energy and also allow the resulting polymers to readily be modified post-polymerization via nucleophilic ring-opening. We envision this class of monomers, particularly **CPO**, as a readily-accessible, highly polymerizable ROMP monomer that could be easily prepared by many synthetic polymer labs to make a range of useful functional materials with a common pre-polymer. This work further opens the possibility to study the effects of other fused bicyclic monomers on the polymerizability of other medium-sized, lower strain cyclic olefins.

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Notes

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