ROMP of Cyclooctadiene and Cyclooctene with Dihydrofuran: Influence of Ru Fischer Carbene

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Supporting Information Placeholder

ABSTRACT: Vinyl ethers are commonly used to deactivate Grubbs catalysts and terminate ring opening metathesis polymerization (ROMP) by forming Fischer carbene species with attenuated metathesis reactivity. However, we recently demonstrated that a cyclic enol ether, 2,3-dihydrofuran (DHF), can in fact be homopolymerized or copolymerized with norbornene derivatives. 1,5-Cyclooctadiene (COD) and cyclooctene (COE) consist of an important class of ROMP monomers, and we describe here the first study of their copolymerization with DHF. Addition of DHF greatly suppressed the ROMP activity of COD and COE, and resulted in significant alkene isomerization of COD. Chloranil was found to be an effective additive to prevent the undesired isomerization and promote copolymerization. As a result, high molecular weight COD/COE and DHF copolymers were synthesized. Hydrolysis of the enol ether main chain linkages yields polyalkenamers with alcohol and aldehyde end groups. This study encourages further exploration of the *in situ* formed Ru Fischer carbene species in ROMP to access new types of degradable polymers.

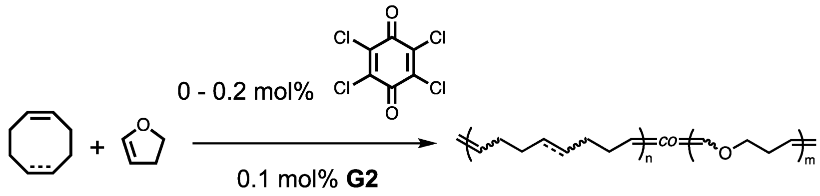
Ring opening metathesis polymerization (ROMP) is one of the most explored polymerization methods, allowing synthesis of polymers with diverse functionalities and architectures from cyclic alkenes. In ROMP and other olefin metathesis reactions with widely used Grubbs catalysts, addition of vinyl ethers has been the standard step to quench the catalyst and terminate the polymerization or reaction for three decades.[1-6] Vinyl ethers rapidly react with Grubbs catalysts to form Ru Fischer carbene species, which show greatly suppressed reactivity toward electron-neutral alkenes, but exhibit activity towards strained alkenes, such as norbornene .[7-10]

We recently showed that 2,3-dihydrofuran (DHF), a commercially available cyclic enol ether, can undergo surprisingly facile ROMP, enabled by the maintained activity of Ru Fischer carbenes towards electron-rich alkenes, yielding a new type of depolymerizable and hydrolytically degradable poly(enol ether).[11] We further demonstrated that DHF is effectively copolymerized with a variety of norbornene derivatives.[12] The *in situ* formed Ru Fischer carbene complex attenuates the otherwise extremely rapid propagation of norbornenes, allowing for even incorporation of the degradable enol ether linkage throughout the copolymers.[12] DHF has since been copolymerized with diynes,[13-14] dicyclopentadiene,[15-16] fluorinated norbornenes,[17] benzoxazine functionalized norbornenes,[18] biomass-derived norbornenes,[19] and oxonorbornenes.[20] Degradable ROMP copolymers have also been synthesized with DHF under catalytic conditions using vinyl ethers as chain transfer agents.[21-22]

While copolymerizations of DHF with highly reactive monomers are rapidly emerging to generate degradable polymers, the activity of *in situ* generated Fischer carbenes towards less strained cyclic alkenes has yet to be explored in the context of copolymerization. 1,5-cyclooctadiene (COD) and cyclooctene (COE) are a class of common ROMP monomers with only moderate ring strain,[23] and ROMP of COD yields nominally polybutadiene with a perfect 1,4-addition microstructure. ROMP of COD initiated by pre-formed Fischer carbene catalysts has been described to proceed at 60°C, albeit at a greatly reduced rate compared to ROMP using analogous benzylidene catalysts.[9] However, a consistent source of electron-rich alkenes was not maintained throughout the polymerization. This suggests that the initial Fischer carbene species had been fully converted to alkylidene after initiation. Accordingly, study of the copolymerization activity of COD with an electron-rich monomer, like DHF, would provide more insight into the reactivity of Fischer carbenes towards moderately strained, electron neutral ROMP monomers by maintaining a higher concentration of Fischer carbenes throughout the duration of the copolymerization.

Herein, we report the first study on ROMP of moderately strained COD and COE in the presence of DHF. The *in situ* formed Ru Fischer carbene complex significantly attenuated the monomer reactivity, but we found that addition of an electron-poor quinone boosts the reactivity to yield high molecular weight copolymers containing degradable enol ether linkages. This study provides new fundamental insight into the reactivity of Fischer carbene complexes through characterization of copolymerization kinetics and copolymer microstructures.

Table 1. ROMP copolymerization of COD or COE with DHF[a]



entry	COX	$[COX]_0$:$[DHF]_0$	[chloranil]:$[G2]_0$	Temp. (°C)	t (h)	% COX conv. [b]	% DHF conv. [b]	% DHF in polymer [b]	$M_{n,\,MALLS}$ [c] (kDa)	Đ [c]
1	COD	95:5	0:1	rt	24	< 5	0	0	-	-
2	COD	85:15	0:1	60	24	48	68	15	-	-
3	COD	70:30	0:1	60	24	15	23	33	-	-
4	COD	50:50	0:1	60	24	8	20	68	-	-
5	COD	95:5	2:1	60	4	100	-[d]	3	101	1.98
6	COD	85:15	2:1	60	4	95	74	11	71	1.71
7	COD	70:30	2:1	60	4	76	53	15	70	1.65
8	COE	95:5	2:1	60	4	93	-[d]	3	52	1.57
9	COE	85:15	2:1	60	4	62	57	11	46	1.49

[a] ROMP was run at [total monomer]$_0$:[**G2**]$_0$ = 1000:1 without solvent, under N_2 atmosphere. [b] Determined by ^{1}H-NMR spectroscopy. [c] Determined by GPC-MALLS analysis in THF. [d] DHF loading was too small to measure conversion accurately.

ROMP of COD typically proceeds smoothly at room temperature, reaching complete conversion within 10 min using 2nd generation Grubbs catalyst ([(SIMes)Ru(=CHPh)(PCy_3)Cl_2]; **G2**). In the initial attempt of COD-DHF copolymerization using **G2**, we found that even the addition of only 5 mol% DHF to COD inhibited polymerization at room temperature with < 5% conversion of COD to polymer after 24 h, reflecting the strongly suppressed metathesis reactivity of the *in situ* formed Ru Fischer carbene toward less strained cyclic alkenes than norbornene derivatives (Table 1, entry 1). We then raised the polymerization temperature to 60 °C. For a mixture of 85 mol% COD and 15 mol% DHF without added solvent and with 0.1 mol% **G2** (relative to the total of both monomers), 48% conversion of COD and 68% conversion of DHF to copolymer were observed at 60 °C after 24 h. Surprisingly, several new small molecule signals between 5.85 ppm and 5.3 ppm also appeared (Figure 1). These signals were identified as 1,4-COD and 1,3-COD, and were formed at 18% and 16%, respectively (Figure 1, Table S1). Increasing DHF loadings led to significantly increased isomerization to 1,3-COD and decreased conversion to polymer, while formation of 1,4-COD remained low (Table 1, entries 2-4). 1,3-COD is the least strained and thermodynamically most stable COD isomer,[24] and therefore 1,4-COD is likely an intermediate during the consecutive isomerization to form the more stable 1,3-COD, thus only being observed in small amounts.

Previously, COD isomerization to a mixture of 1,4-COD and 1,3-COD has only been observed in the presence of isomerization catalysts such as a Ru–H Pincer complex,[25] a biscarbene Rh(I)–H complex,[26] various transition metal carbonyl complexes,[27] and a dichlorobis(triphenylphosphine)Pt(II) complex.[28] COD isomerization has not been reported in its typical ROMP, even at elevated temperatures. Therefore, the observed isomerization was presumably promoted by the decomposition of the *in situ* formed

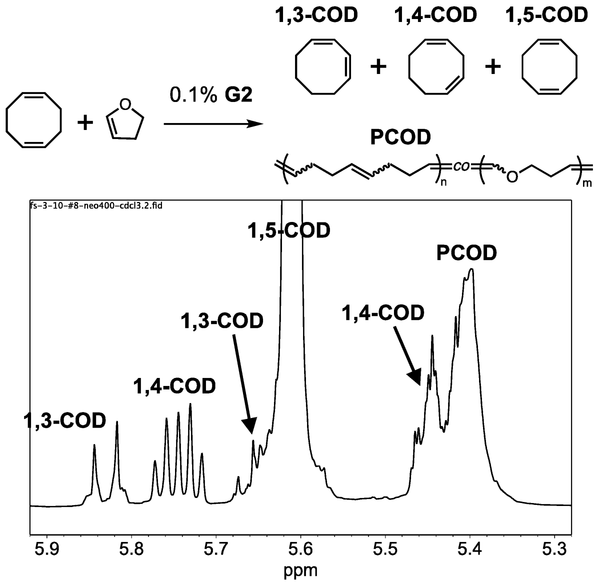


Figure 1. Peak assignment of 1,3-COD, 1,4-COD, 1,5-COD, or PCOD in an ^{1}H-NMR spectrum of P(COD-*co*-DHF) synthesized with 15% DHF loading, without chloranil, at 60 °C for 4 h.

Ru Fischer carbene species. This is consistent with observations made by Grubbs and coworkers that Ru Fischer carbene complexes showed much shorter half-life at 55 °C than the benzylidene counterpart, and thermal decomposition of a Fischer carbene $(PCy_3)_2Cl_2Ru=C(H)OEt$ cleanly generated a hydride species.[9]

Alkene isomerization is known to occur in Ru catalyzed metathesis reactions especially at elevated temperatures[29-30] or when terminal alkenes,[30-32] allyl ethers,[33] or allyl amines[33] are involved. The isomerization is believed to be catalyzed by a Ru–H species formed from the decomposition of Grubbs catalysts. Specific structures of the decomposed Ru species that induce catalytic isomerization reactions are poorly understood. Nishida and coworkers, however, demonstrated that a Ru Fischer carbene formed by the reaction of **G2** with a silyl enol ether quantitatively converts to a Ru–H complex at high temperatures.[32] They attributed the observed isomerization activity using **G2** in the presence of a silyl enol ether to the Ru–H species. Isomerization is often undesired in olefin metathesis. Electron deficient quinones have been found to be effective additives to fully prevent isomerization in ring closing metathesis[33] and cross metathesis.[31, 34] Presumably, the quinone prevents isomerization activity by reacting with the Ru–H species to form the corresponding hydroquinone.[33] Accordingly, we were curious if addition of an electron deficient quinone to DHF and COD copolymerization would prevent COD isomerization or even promote its conversion to polymer.

Excitingly, we found that addition of chloranil (i.e., tetrachloro-1,4-benzoquinone) greatly suppressed the isomerization, enhanced the polymerization rate, and increased final conversion to copolymer. With an initial DHF loading of 15%, the polymerization took over 20 h at 60 °C to surpass 40% conversion of COD to copolymer in

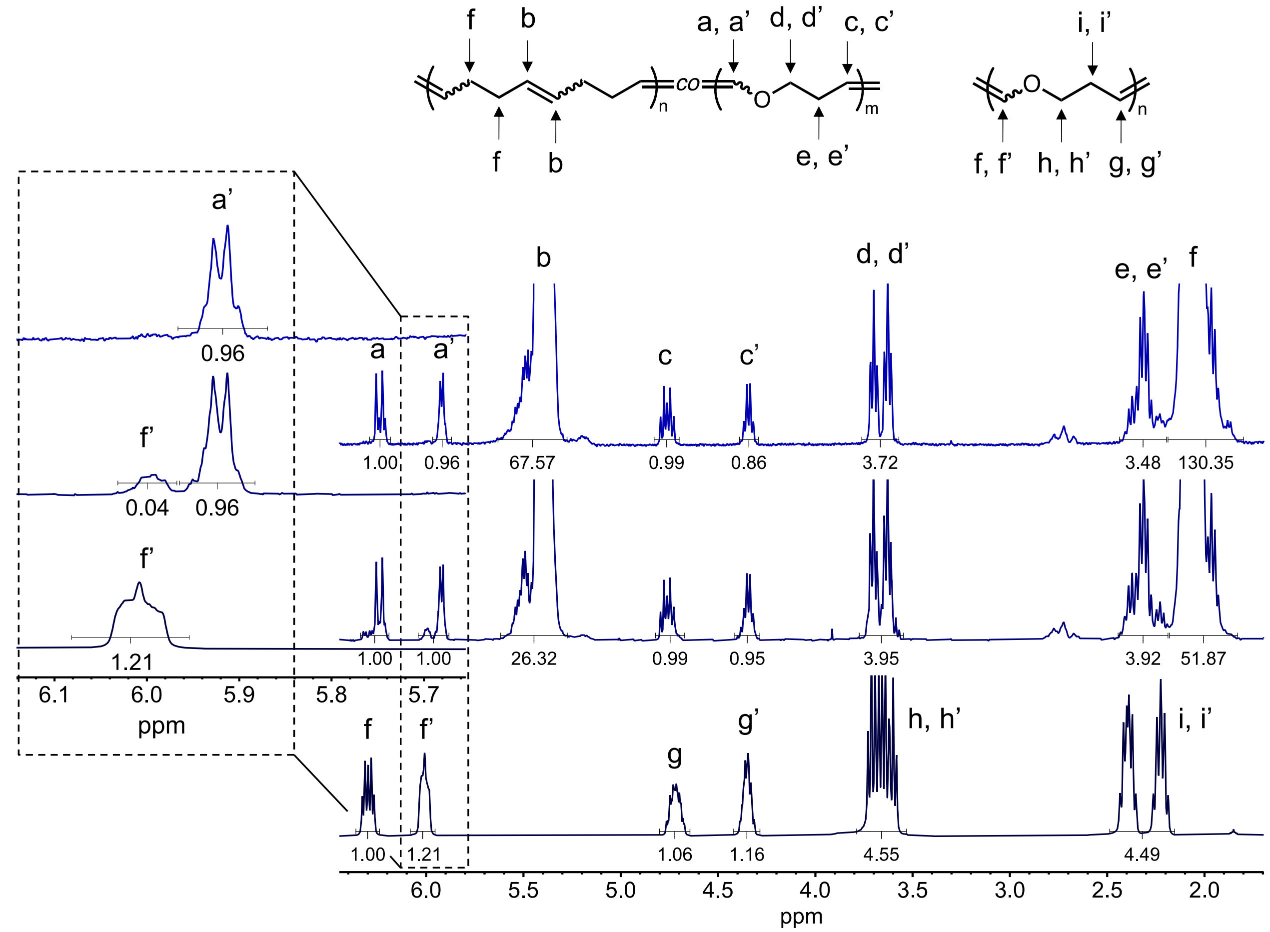


Figure 3. ^1H NMR spectrum of P(COD-*co*-DHF), synthesized with 15% DHF loading. Middle: ^1H NMR spectrum of P(COD-*co*-DHF), synthesized with 30% DHF loading. Bottom: ^1H-NMR spectrum of PDHF homopolymer. Signals corresponding to PDHF homoaddition, f and f', are present in the ^1H-NMR spectrum of P(COD-*co*-DHF) at 30% DHF loading but absent at 15% DHF loading.

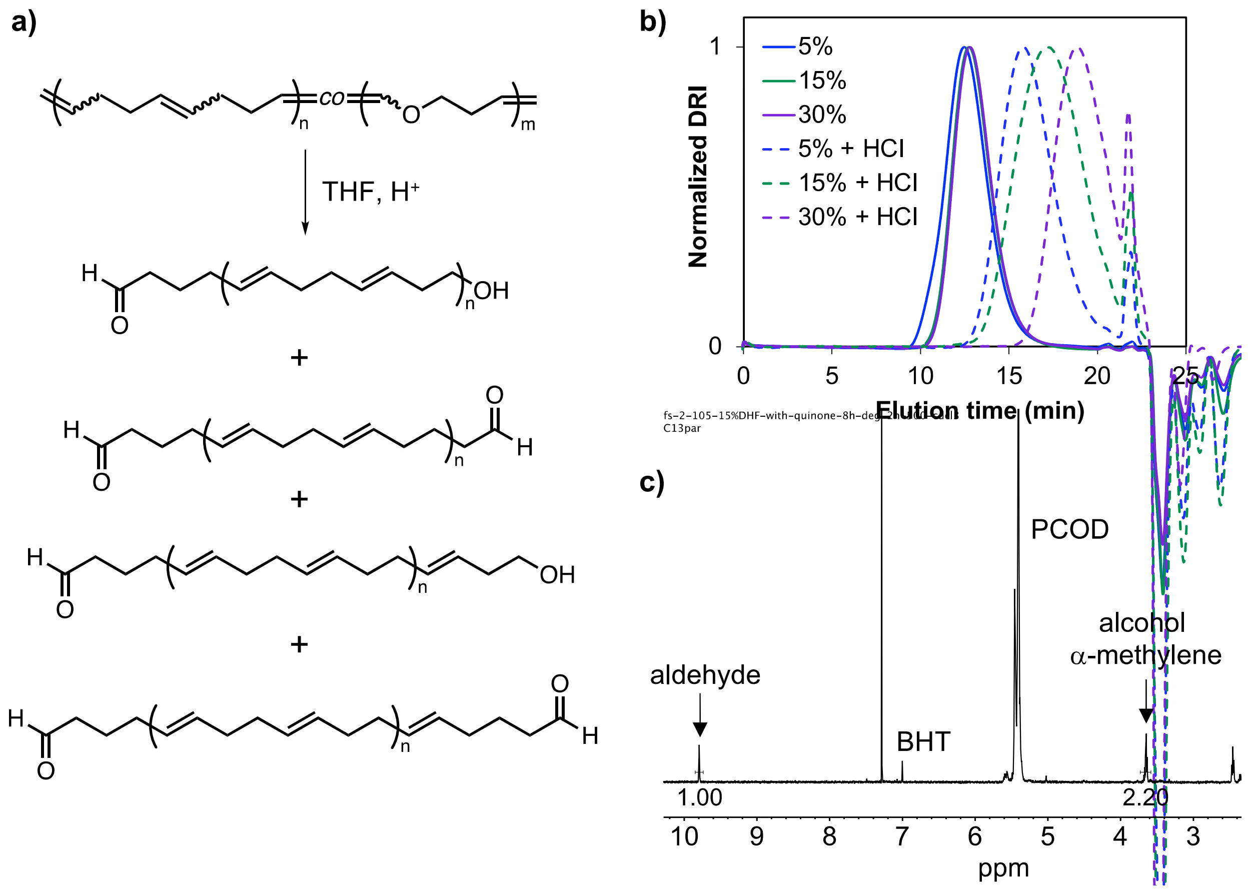


Figure 4. a) Acid-catalyzed degradation of P(COD-*co*-DHF) copolymers results in a combination of aldehyde-alcohol and dialdehyde species due to chain transfer. Structures were identified using Kendrick analysis of a MALDI spectrum of acid catalyzed degradation products (see Supporting Information, Figures S3 and S4). b) GPC traces of P(COD-*co*-DHF) copolymers with 5%, 15%, or 30% DHF loading (denoted by 5%, 15%, and 30%), along with their acid-catalyzed degradation products shown as dashed lines. c) ^{1}H-NMR spectrum of degradation products of a P(COD-*co*-DHF) sample synthesized with 15 mol% DHF. The presence of a terminal aldehyde, **a**, and α-methylene group, **b**, adjacent to a terminal alcohol is confirmed.

absence of chloranil (Figure 2). In the presence of 2 equiv of chloranil relative to **G2**, COD reached 40% conversion to copolymer within 1 h, and >90% conversion after 4 h. At DHF loadings of 5%, 15% and 30%, COD conversion to copolymer reached 100%, 95%, and 76%, respectively, at 60 °C after 4 h. No isomerization was observed at 5% or 15% DHF loading, and less than 5% total conversion to COD isomers was observed at 30% DHF loading (Table S1). Copolymer composition was determined by analyzing the ^{1}H-NMR resonances of the isolated P(COD-*co*-DHF). The composition of DHF in the copolymers was consistently less than in the feed ratio, because of the lower DHF conversions compared to COD, but the DHF composition in the copolymers was consistent with calculated copolymer composition based on the feed ratio and conversions of each monomer. As a result, with initial DHF feed loadings of 5%, 15%, and 30%, the DHF composition in the copolymers was found to be 3%, 11%, and 15%, respectively.

We also investigated the copolymerization of COE with DHF. At DHF loadings of 5% and 15%, COE reached 52% and 46% conversion, respectively, even in the presence of chloranil (Table 1, entries 8-9). We attribute the lower conversion of COE compared to COD to the lower ring strain of COE. The resultant P(COE-*co*-DHF) copolymers had DHF compositions of 3% and 11%, corresponding to initial DHF loadings of 5% and 15%, respectively.

We then quantified the stereochemical distribution of the alkenes in the P(COD-*co*-DHF) copolymers via ^{1}H-NMR spectroscopy. Four distinct enol ether alkene peaks at 6.26 ppm, 5.93 ppm, 4.79 ppm, and 4.37 ppm were identified with roughly equal integrations, indicating an *E/Z* ratio of ≈ 1:1 regardless of DHF loading (Figure 3, Figure S2). This ratio is consistent with the observation in PDHF homopolymers, and reflects nearly the same ground-state energies for *E*- and *Z*-enol ether alkenes.[11] Typically, at equilibrium using **G2**, PCOD homopolymers exhibit about 70-90% *E*-alkene content due to the lower ground-state energy of *E*-alkenes relative to *Z*-alkenes.[35] But the fraction of *E*-alkenes arising from the PCOD component of P(COD-*co*-DHF) copolymers decreased considerably from 63% to 24% when increasing DHF loading from 5% to 30% (Figure S1). This observed trend demonstrates the reduced catalyst activity of the Ru Fischer carbene towards electron neutral, unstrained alkenes, which suppresses the extensive secondary metathesis observed in typical ROMP of COD using **G2** and prevents the backbone alkene stereochemistry from reaching equilibrium in the copolymerization. To probe whether chain transfer via secondary metathesis of electron-neutral alkenes still occurs in the copolymerization system, cis-3-hexene was added as a chain transfer agent (CTA) to copolymerizations with 5% or 15%

DHF after complete COD conversion was reached, and the reaction was allowed to equilibrate at 60 °C (Figure S10, Table S4). Molecular weight reduction was observed at both DHF loadings, indicating that chain transfer on electron-neutral alkenes still occurred, likely catalyzed by Ru alkylidene species present, but is attenuated compared to typical ROMP of COD. Additionally, under the same CTA loading, the polymerization containing 15% DHF equilibrated at a higher molecular weight than with 5% DHF, suggesting that the extent of chain transfer was further suppressed by the higher DHF loading.

Despite the attenuated catalyst activity, high molecular weight copolymers could be synthesized. P(COD-*co*-DHF) at 5, 15, and 30% DHF loadings gave M_n's of 101, 71, and 70 kDa, respectively. Due to lower monomer conversion, P(COE-co-DHF) at 5% and 15% DHF loadings gave M_n's of 52 and 46 kDa, respectively (Figure S11). At all compositions, the copolymers gave monomodal molecular weight distributions with dispersities $Đ$ = 1.6-2 (Figure 4b, and Table 1, entries 5-7).

The distribution of DHF throughout the copolymers was then examined by ^{1}H-NMR spectroscopy of the copolymers and GPC analysis of their degradation products. The enol ether alkene region of ^{1}H-NMR spectra of copolymers with 5% or 15% DHF loadings showed no signals corresponding to DHF homodyad (Figure 3). At 30% DHF loading, weak signals at 6.0 ppm corresponding to DHF homodyad was observed and accounted for 4% of the DHF units in the copolymer (Figure 3). Additionally, comparison of GPC traces of copolymers to their degraded counterparts overall shows a clear shift to low molecular weight products after polymer hydrolysis (Figure 4b).

As a result of enol ether hydrolysis, the copolymer degradation products should contain alcohol and aldehyde end groups. Indeed, ^{1}H-NMR analysis clearly showed an aldehyde signal at 9.76 ppm and an alcohol α-methylene signal at 3.62 ppm with the expected integration ratio of 1:2 (Figure 4c). Matrix-assisted laser desorption ionization mass spectrometry (MALDI MS) of degraded polymers and subsequent Kendrick analysis revealed the presence of two distinct types of telechelic polymers: a heterotelechelic fragment bearing an alcohol and an aldehyde chain end, and a homotelechelic fragment bearing two aldehyde end groups (Figure 4a, and Supporting Information Figures S3-S4 and Table S3). The heterotelechelic population is expected from COD-DHF copolymers due to highly regioselective ring-opening and addition of DHF to the growing chain end catalyst. The dialdehyde homotelechelic polymers may only result from the non-directional chain transfer on backbone alkenes of PCOD during the polymerization (Figure S5).

In summary, we describe the first copolymerization between an electron-rich cyclic alkene, DHF, with moderately strained COD and COE using **G2**. The *in situ* formed Fischer carbene exhibited significantly attenuated metathesis reactivity toward COD, and resulted in unexpected alkene isomerization. Addition of an electron-deficient quinone, chloranil, was found to prevent the undesired isomerization and restore the ROMP reactivity, resulting in high molecular weight, hydrolytically degradable P(COD/COE-*co*-DHF) copolymers. Analysis of the copolymers and their degradation products revealed relatively even distribution of DHF units in the copolymers. This study provides new insight into the underexplored Fischer carbene ROMP reactivity with cyclic enol ethers as comonomers, which enables the development of new types of degradable, enol ether containing ROMP polymers.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Synthetic procedures and characterizations, ^{1}H NMR, ^{13}C NMR, and MALDI spectra and analyses, and chain transfer study.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation (CHE-2106511). F.A.S. was supported by a Stanford Graduate Fellowship.

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TOC Figure