Tandem ROMP/Hydrogenation Approach to Hydroxy-Telechelic Linear Polyethylene

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ABSTRACT: Hydroxy telechelic polycycloalkenamers have long been synthesized using ring-opening metathesis polymerization (ROMP) in the presence of an acyclic olefin chain-transfer agent (CTA); however, this route typically requires protected diols in the CTA due to the challenge of alcohol-induced degradation of ruthenium metathesis catalysts that can not only deactivate the catalysts but also compromise the CTA. We demonstrate the synthesis and implementation of a new hydroxyl-containing CTA in which extended methylene spacers isolate the olefin and alcohol moieties to mitigate decomposition pathways. This CTA enabled the direct ROMP synthesis of hydroxy-telechelic polycyclooctene with controlled chain lengths dictated by the initial ratio of monomer to CTA. The elimination of protection/deprotection steps resulted in improved atom economy. Subsequent hydrogenation of the backbone olefins was performed by a one-pot, catalytic approach employing the same ruthenium alkylidene catalyst used for the initial ROMP. The resultant approach is a streamlined, atom-economic, and low-waste route to hydroxy-telechelic linear polyethylene that uses a green solvent, succeeds with miniscule quantities of catalyst (0.005 mol%), and requires no additional purification steps.

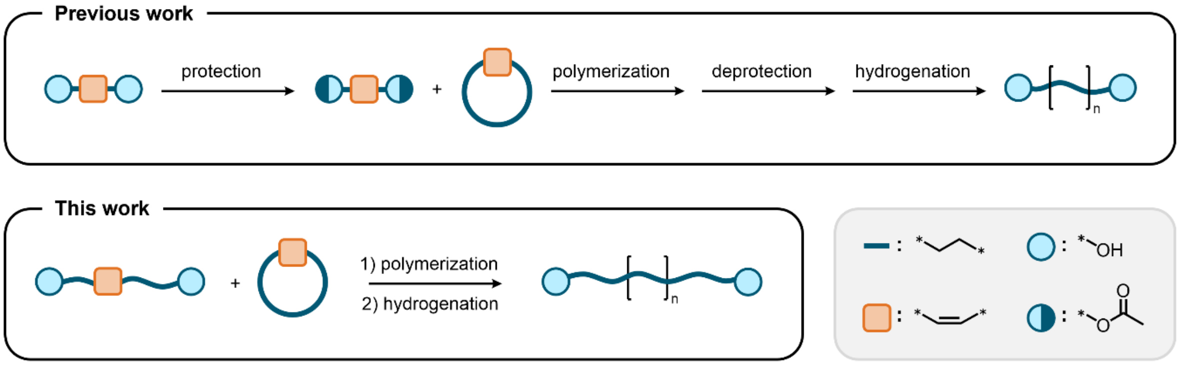
Polyolefins are the predominant class of polymer used globally, with polyethylene (PE) used in a remarkably wide range of applications due to its high thermal/chemical stability, ease of processing, and favorable mechanical properties. As such, there is substantial interest in the development and production of functionalized PE, whether by incorporation of reactive groups during polymerization,[1–6] post-polymerization modification,[7,8,17,18,9–16] or some combination of the two.[19–24] One such strategy is ring-opening metathesis polymerization (ROMP) of cyclic olefins to give polyalkenamers that can be hydrogenated to yield the corresponding polyolefins; the inclusion of a difunctional acyclic alkene as chain-transfer agent (CTA) produces telechelic polyolefins containing the corresponding end groups. The utility of CTAs with varied functionality have been demonstrated in numerous examples,[1,25–33] with the primary requirement being the mutual compatibility of the CTA and the polymerization catalyst, typically ruthenium-based metal carbene derivatives.

One functionality that has proven challenging to directly access in an efficient manner via ROMP with a CTA is that of hydroxyl groups. Initial attempts to polymerize cyclooctadiene with *cis*-2-butene-1,4-diol (C4D) resulted in poor yields and polymers with high *cis* content along the backbone, suggesting deactivation of the catalyst over the course of the reaction.[29] As a result, the majority of ROMP-produced hydroxy-telechelic polyolefins have been synthesized using a protected CTA, typically *cis*-1,4-bis(acetoxy)-2-butene, followed by an additional deprotection step (Scheme 1).[29,34–38] Due to the increasing need for more sustainable chemical processes, the poor atom economy and additional waste of such a protection/deprotection strategy are undesirable. However, high yields with unprotected C4D have only been achieved in the specific case of the cyclic carbonate/olefin monomer 4,7-dihydro-1,3-dioxepin-2-one, which required long reaction times to reach full conversion.[39]

Several mechanisms for the degradation of ruthenium catalysts in the presence of primary alcohols have been proposed; of particular interest in the case of C4D is work by Wolf and co-workers on the interaction of Grubbs 1st generation catalyst (G1) with allylic alcohols.[40] These studies support a decomposition pathway that depends on the ability of allylic alcohols to form enol and aldehyde intermediates in the process of generating the decomposition product, a ruthenium carbonyl complex. These results suggest that this decomposition might be inhibited by increased separation between the olefin and hydroxyl groups, which is further supported by investigations into the metathesis of olefin alcohols that show increasing yields with longer spacers between the olefin and alcohol.[34] In addition, extending the olefin–alcohol distance would prevent the rapid isomerization of allylic alcohols to aldehydes that can occur in the presence of Grubbs metathesis catalysts,[41–47] thereby protecting against loss of the hydroxyl chain-end functionality.

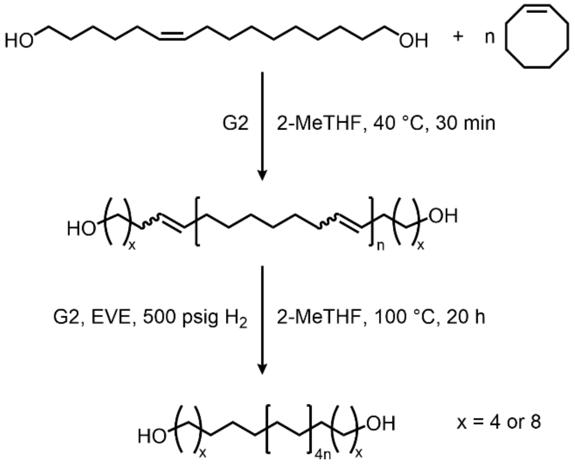
In this work, we explore the effect of such separation by employing a sixteen-carbon diol *cis*-hexadec-6-ene-1,16-diol (C16D) as CTA. This diol is conveniently available in one step from the naturally occurring and inexpensive musk, ω-6-hexadecenlactone, also known as ambrettolide. Using mild reducing conditions, C16D was produced at a multigram scale (Scheme S1). The use of this high-cis olefinic diol as CTA proved effective for generating hydroxy-telechelic polycyclooctene (PCOE) with controlled molar masses, and the elimination of the deprotection step ena-

Scheme 1. Schematic comparison between the previous route to hydroxy-telechelic PE, in which a protected CTA is used in the ROMP of COE, followed by deprotection and then hydrogenation, and the work presented here, in which the use of an extended CTA enables a direct, one-pot synthetic approach.



bled the development of a one-pot, tandem-catalytic route to hydroxy-telechelic linear PE (HTPE, Scheme 2). As shown in Scheme 1, this strategy allows for more direct production of HTPE, reducing both the steps required and waste generated.

Scheme 2. Synthesis of HTPE via simultaneous ROMP of *cis*-cyclooctene and cross-metathesis with *cis*-hexadec-6-ene-1,16-diol, followed by hydrogenation.



To assess the stability of Grubbs 2nd generation catalyst (G2) in the presence of the extended olefin diol, the *cis*/*trans* isomerization of C16D was monitored using a ratio of 100:1 [olefin]$_0$:[G2]$_0$ (Figures 1 and S4). 2-Methyltetrahydrofuran (2-MeTHF) was chosen as solvent due to its bioderived nature and the potential for a catalyst stabilizing effect due to its ability to coordinate with the Ru catalyst, analogous to tetrahydrofuran.[29,48] The initial aliquot at 4 h shows successful isomerization from majority *cis* to majority *trans* (> 80%). After subsequent additions of C16D at 4 h and 24 h (100 additional equivalents to G2 each time), equilibrium was reattained, showing continued catalytic activity. For comparison, C4D was subjected to the same conditions (Figures S5 and S6). While a large *trans* fraction was observed after the initial 4 h, subsequent isomerization of C4D proved slower than in the case of C16D, and a return to equilibrium was not observed within the monitored timeframe. These results suggest catalytic decomposition in the presence of the allylic alcohol compared with C16D.

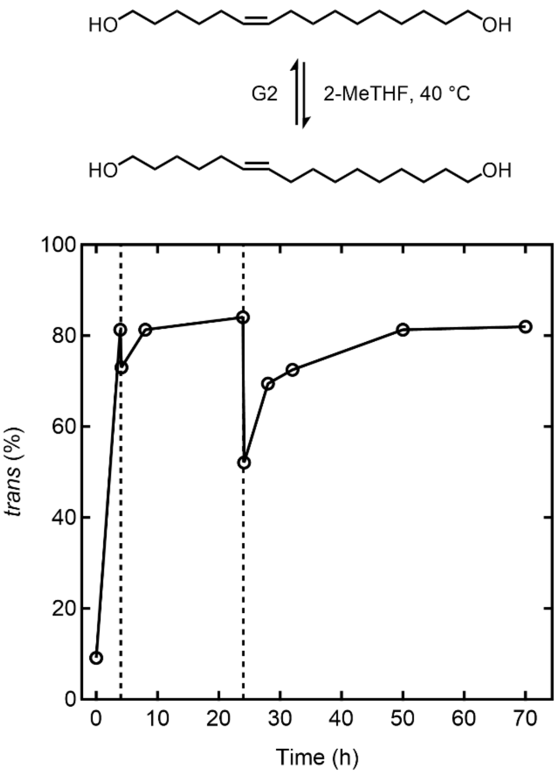


Figure 1. G2-catalyzed isomerization of C16D. Initial [olefin]:[G2] = 100:1. Dashed lines represent addition of 100 equivalents of C16D.

Following these initial results, the ability of C16D to act as a CTA in the ROMP of *cis*-cyclooctene (COE) was investigated. The polymerization of COE in the presence of C16D ([COE]$_0$:[C16D]$_0$ = 100:1, $M_{\text{n, theo}}$ for 100% monomer conversion = $100M_{\text{COE}} + M_{\text{C16D}}$ = 11.3 kg mol^{-1}) occurred rapidly at a very high [COE]$_0$:[G2]$_0$ ratio of 50,000:1, with an aliquot at 15 min showing full conversion of the COE to a polymer with $M_{\text{n, SEC}}$ = 11.6 kg mol^{-1}, $Đ$ = 1.4, and backbone

Table 1. ROMP of COE with varied $[COE]_0$:$[CTA]_0$ ratios.[a]

Entry	$[COE]_0$:$[CTA]_0$	conv. (%)[b]	isolated yield (%)	$M_{n,\,theo}$	$M_{n,\,SEC}$[c]	Đ[c]	$M_{n,\,NMR}$[d]	trans (%)
1	10	≈100	83	1.4	1.9	1.3	2.1	79
2	20	≈100	87	2.5	3.0	1.5	2.8	81
3	50	≈100	91	5.8	5.7	1.4	6.4	81
4	100	≈100	93	11.3	11.9	1.5	12.2	80
5	200	≈100	93	22.2	21.6	1.5	22.7	77
6	500	≈100	92	55.4	50.3	1.6	74.4	80

[a]Conditions: 30 min at 40 °C under Ar atmosphere in 2-MeTHF (1.76 M COE). [b]Conversion of COE to PCOE as calculated from relative integration of resonances for olefinic protons of COE (δ = 5.59–5.70 ppm) and PCOE (δ = 5.32–5.46 ppm). [c]Calculated from MALS-SEC using dn/dc of PCOE in THF as previously determined (0.111 mL g^{-1}).[49] [d]Calculated from relative integration of resonances for olefinic protons (δ = 5.59–5.70 ppm) and methylene protons adjacent to oxygen (3.62–3.70).

trans content of 79% (after isolation by precipitation, see Figure S7). Minimal change in the molar mass was observed over an additional 6 h of polymerization, suggesting that cross metathesis leads to full incorporation of the CTA early in the reaction. This incorporation was further confirmed by ^1H NMR analysis of the purified polymer, which shows a resonance associated with the methylene protons adjacent to the oxygen atoms (Figure 2). Assuming a theoretical number average functionality, F_n, of 2, comparison of the relative integration of these protons to the olefinic protons gives a number average molar mass by NMR spectroscopy of $M_{n,\,NMR}$ = 12.8 kg mol^{-1}, close to that determined by SEC-MALS analysis and thus consistent with a high degree of functionalization.

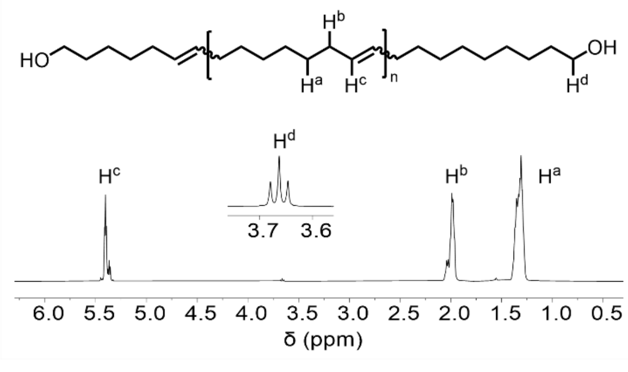


Figure 2. ^1H NMR spectrum of PCOE (synthesized with $[COE]_0$:$[C16D]_0$ = 100:1) in $CDCl_3$; the inset highlights the end group region.

To demonstrate molar-mass control, polymerization of COE was carried out at varied ratios of $[COE]_0$:$[C16D]_0$, from 10:1 to 500:1 (Table 1, Figure S8). The same exceedingly low loading of catalyst ($[COE]_0$:$[G2]_0$ = 50,000:1 (0.002 mol%, 0.015 wt%, or 150 ppm relative to COE)) was used to enable high degrees of hydroxyl functionalization even at the lowest CTA loading (minimum ratio $[C16D]_0$:$[G2]_0$ of 100:1, corresponds to a maximum F_n of 1.98[50]). Despite the small quantities of G2 used, all reactions reached ≈100% conversion of COE within 30 min with commensurately high isolated yields (83–93%), and as with the isomerization study, the resultant PCOE backbone reached an equilibrium *trans* content of ~80%. As expected, the molar masses trend inversely with CTA loading (Figure S9), with close agreement between the values calculated from SEC-MALS and NMR analysis for all but the highest $[COE]_0$:$[CTA]_0$ ratio (500:1). This deviation may be explained by the rapid formation of long, entangled chains, which led to solidification of the reaction that have may prevented full incorporation of the CTA in the polymer over the reaction time.

To further investigate the effect of the CTA olefin–alcohol separation distance on the ROMP of COE, analogous polymerizations were carried out using C4D as the CTA. As expected, polymerizations with this shorter CTA showed poor conversion of the monomer (<30%) and low *trans* backbone content (~50%), consistent with catalyst deactivation (Table S1, Entries 1 and 2). C4D being the source of this deactivation was further supported by decreasing conversions with increasing $[C4D]_0$:$[G2]_0$ ratios. Additionally, incomplete monomer conversion and limited backbone isomerization persisted even when higher catalyst loadings and longer reaction times were employed (Table S1, Entry 3).[39]

Beyond the improved conversions achieved with C16D as CTA, the longer aliphatic chain provides a secondary advantage in the form of greater solubility in nonpolar monomers such as COE. As a result of this increased solubility, the quantity of Me-THF used could be substantially reduced to only the small amount (100 μL) needed to conveniently add the catalyst, and polymerizations at the essentially bulk COE concentrations (≈ 6.7 M) showed little difference in molar mass control and distribution when compared to that generated under more dilute conditions (Figure S10).

An important consequence of direct synthesis (i.e., no deprotection step) of hydroxy-telechelic PCOE is that it facilitates the one-pot synthesis of HTPE, in which the ROMP of COE is immediately followed by hydrogenation of the backbone olefins. Of particular interest with this approach is the ability of ruthenium metathesis catalysts to act as precursors to hydrogenation catalysts under suitable conditions.[51–53] Initial investigation of such a tandem catalytic approach, performed by pressurizing the crude polymerization reaction ($[COE]_0$:$[C16D]_0$ = 100:1, $[G2]_0$ = 0.002 mol%, $[COE]_0$ = 1.76 M) with 500 psig H_2 at 100 °C for 20 h, showed high levels (≈ 97%) of backbone hydrogenation (Figure S11). To achieve full saturation, it was necessary to increase the catalyst loading to $[G2]_0$ = 0.005

mol%; for the largest molar mass investigated ($[COE]_0$:$[C16D]_0$ = 500:1), this loading equates to a maximum F_n of 1.95. Furthermore, to prevent continued metathesis during the hydrogenation step—in particular, the undesired formation of cyclic oligomers at longer reaction times—the Grubbs catalyst was quenched with ethyl vinyl ether immediately following completion of the ROMP. While the resultant Fischer carbene has been demonstrated to be metathesis active under suitable conditions,[54–60] its generation was found to suppress the formation of low-molar-mass species upon dilution in the hydrogenator (necessary to reach minimum volume for stirring, see Figure S12 for SECs) while not interfering with the extent of hydrogenation. The ability of the putative Ru=CH(OR) derivative of G2 to serve as an effective precatalyst for hydrogenation has been heretofore unreported, although the decomposition of analogous Fischer carbenes to Ru hydride species has been established.[59]

As a result of the low solubility of linear PE in 2-MeTHF, the product precipitated out of solution upon hydrogenation and was collected without the need for additional purification by solvent-consumptive reprecipitation steps. The resultant polymer was a semi-crystalline solid with a peak melting temperature of 132 °C, consistent with that expected for linear PE (Figure S13).[61] Full hydrogenation was confirmed by IR spectroscopy, which shows the disappearance of the absorption associated with C=C bending (966 cm^{-1}, Figure 3a), and was further supported by the lack of olefinic resonances in the NMR spectrum (Figure 3b). NMR spectroscopy also shows continued presence of methylene protons adjacent to hydroxyl oxygens with a resonance at 3.41, and similar end-group analysis to that of PCOE gives an $M_{n,\,NMR}$ of 11.4 kg mol^{-1}. Comparison to the value calculated from SEC-MALS (12.4 kg mol^{-1}, calculated using reported dn/dc of PE in 1,2,4-trichlorobenzene at 135 °C,[62] −0.109 mL g^{-1}) demonstrates that a high degree of functionality is maintained throughout the hydrogenation, yielding polyethylene with telechelic hydroxy moieties available for further reactions.

We have demonstrated how the use of a sixteen-carbon diol CTA enables the direct synthesis of hydroxy-telechelic PCOE without the need for additional protection/deprotection of the alcohol end groups. ROMP with this CTA can be performed in the bioderived solvent 2-MeTHF or essentially neat with low catalyst loading, and a range of molar masses can be accessed by varying the ratio of monomer to CTA. By simply pressurizing with H_2 gas, this strategy can be further extended to the production of linear PE via a one pot polymerization–hydrogenation approach. This streamlined route to HTPE not only reduces the effort and time required, but also satisfies the green chemistry principles of reduced waste, improved atom economy, and use of renewable feedstocks in the form of both solvent and CTA.

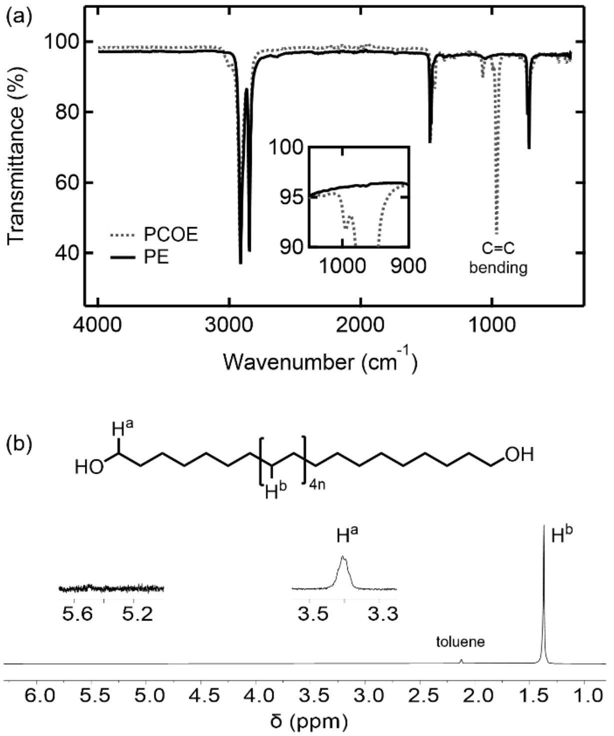


Figure 3. (a) IR spectra of PCOE precursor and PE product (inset shows C=C bending region) and (b) ^1H NMR spectrum of PE (insets show olefinic and end group regions).

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Pitet, L. M.; Hillmyer, M. A. Carboxy-Telechelic Polyolefins by ROMP Using Maleic Acid as a Chain Transfer Agent. *Macromolecules* **2011**, *44*, 2378–2381.

(2) Kobayashi, S.; Kim, H.; Macoscko, C. W.; Hillmyer, M. A. Functionalized Linear Low-Density Polyethylene by Ring-Opening Metathesis Polymerization. *Polym. Chem.* **2013**, *4*, 1193–1198.

(3) Dommanget, C.; D'Agosto, F.; Monteil, V. Polymerization of Ethylene through Reversible Addition–Fragmentation Chain Transfer (RAFT). *Angew. Chemie Int. Ed.* **2014**, *53*, 6683–6686.

(4) Hyatt, M. G.; Guironnet, D. Silane as Chain Transfer Agent for the Polymerization of Ethylene Catalyzed by a Palladium(II) Diimine Catalyst. *ACS Catal.* **2017**, *7*, 5717–5720.

(5) Na, Y.; Dai, S.; Chen, C. Direct Synthesis of Polar-Functionalized Linear Low-Density Polyethylene (LLDPE) and Low-Density Polyethylene (LDPE). *Macromolecules* **2018**, *51*, 4040–4048.

(6) Li, G.; Xu, G.; Ge, Y.; Dai, S. Synthesis of Fluorinated Polyethylene of Different Topologies *via* Insertion Polymerization with Semifluorinated Acrylates. *Polym. Chem.* **2020**, *11*, 6335–6342.

(7) Lu, B.; Chung, T. C. Synthesis of Maleic Anhydride Grafted Polyethylene and Polypropylene, with Controlled Molecular Structures. *J. Polym. Sci. Part A Polym. Chem.* **2000**, *38*, 1337–1343.

(8) Bateman, S. A.; Wu, D. Y. Sulfonyl Azides — An Alternative Route to Polyolefin. *J. Appl. Polym. Sci.* **2002**, *84*, 1395–1402.

(9) Boaen, N. K.; Hillmyer, M. A. Selective and Mild Oxyfunctionalization of Model Polyolefins. *Macromolecules* **2003**, *36*, 7027–7034.

(10) Bae, C.; Hartwig, J. F.; Chung, H.; Harris, N. K.; Switek, K. A.; Hillmyer, M. A. Regiospecific Side-Chain Functionalization of Linear Low-Density Polyethylene with Polar Groups. *Polym. Chem.* **2005**, *44*, 6410–6413.

(11) Ray, A.; Zhu, K.; Kissin, Y. V; Cherian, A. E.; Coates, W.; Goldman, A. S. Dehydrogenation of Aliphatic Polyolefins Catalyzed by Pincer-Ligated Iridium Complexes. *Chem. Commun.* **2005**, 3388–3390.

(12) Bélékian, D.; Cassagnau, P.; Flat, J.-J.; Quinebeche, S.; Autissier, L.; Bertin, D.; Siri, D.; Gigmes, D.; Guillaneuf, Y.; Chaumont, P.; Beyou, E. *N*-Acetoxy-Phthalimide (NAPI) as a New H-Abstracting Agent at High Temperature: Application to the Melt Functionalization of Polyethylene. *Polym. Chem.* **2013**, *4*, 2676–2679.

(13) Zhou, H.; Wang, S.; Huang, H.; Li, Z.; Plummer, C. M.; Wang, S.; Sun, W.; Chen, Y. Direct Amination of Polyethylene by Metal-Free Reaction. *Macromolecules* **2017**, *50*, 3510–3515.

(14) Bunescu, A.; Lee, S.; Li, Q.; Hartwig, J. F. Catalytic Hydroxylation of Polyethylenes. *ACS Cent. Sci.* **2017**, *3*, 895–903.

(15) Williamson, J. B.; Czaplyski, W. L.; Alexanian, E. J.; Leibfarth, F. A. Regioselective C–H Xanthylation as a Platform for Polyolefin Functionalization. *Angew. Chemie Int. Ed.* **2018**, *57*, 6261–6265.

(16) Rakotonirina, M. D.; Baron, M.; Siri, D.; Gaudel-Siri, A.; Quinebeche, S.; Flat, J.-J.; Gigmes, D.; Cassagnau, P.; Beyou, E.; Guillaneuf, Y. Acyloxyimide Derivatives as Efficient Promoters of Polyolefin C–H Functionalization: Application in the Melt Grafting of Maleic Anhydride onto Polyethylene. *Polym. Chem.* **2019**, *10*, 4336–4345.

(17) Plummer, C. M.; Zhou, H.; Li, S.; Zhong, H.; Sun, Z.; Bariashir, C.; Sun, W.; Huang, H.; Liu, L.; Chen, Y. A Direct Functionalization of Polyolefins for Blend Compatibilization by an Insertion of 1,1-Bis(Phenylsulfonyl)Ethylene (BPSE). *Polym. Chem.* **2019**, *10*, 3325–3333.

(18) Chen, L.; Malollari, K. G.; Uliana, A.; Sanchez, D.; Messersmith, P. B.; Hartwig, J. F. Selective, Catalytic Oxidations of C–H Bonds in Polyethylenes Produce Functional Materials with Enhanced Adhesion. *Chem* **2021**, *7*, 137–145.

(19) Makio, H.; Ochiai, T.; Mohri, J.; Takeda, K.; Shimazaki, T.; Usui, Y.; Matsuura, S.; Fujita, T. Synthesis of Telechelic Olefin Polymers via Catalyzed Chain Growth on Multinuclear Alkylene Zinc Compounds. *J. Am. Chem. Soc.* **2013**, *135*, 8177–8180.

(20) German, I.; Kelhifi, W.; Norsic, S.; Boisson, C.; D'Agosto, F. Telechelic Polyethylene from Catalyzed Chain-Growth Polymerization. *Angew. Chemie - Int. Ed.* **2013**, *52*, 3438–3441.

(21) Norsic, S.; Thomas, C.; D'Agosto, F.; Boisson, C. Divinyl-End-Functionalized Polyethylenes: Ready Access to a Range of Telechelic Polyethylenes through Thiol–Ene Reactions. *Angew. Chemie Int. Ed.* **2015**, *54*, 4631–4635.

(22) Yan, T.; Walsh, D. J.; Qiu, C.; Guironnet, D. One-Pot Synthesis of Block Copolymers Containing a Polyolefin Block. *Macromolecules* **2018**, *51*, 10167–10173.

(23) Walsh, D. J.; Su, E.; Guironnet, D. Catalytic Synthesis of Functionalized (Polar and Non-Polar) Polyolefin Block Copolymers. *Chem. Sci.* **2018**, *9*, 4703–4707.

(24) Yan, T.; Guironnet, D. Polyethylene Containing Triblock Copolymers Synthesized by Post-Polymerization Functionalization. *Macromolecules* **2020**, *53*, 4338–4344.

(25) Reyx, D.; Hamza, M.; Campistron, I. Application de La Réaction de Métathèse a La Synthèse de Prépolymères α,ω-Bifonctionnels Partie 3: Mise Au Point Des Conditions d'Obtention de Composés Diéniques et Triéniques Par Cométathèse Du Cyclopentène Avec l'Octène-4 et l'Hexène-3 Dioate de Diméthyle. *J. Mol. Catal.* **1987**, *42*, 289–299.

(26) Chung, T. C.; Chasmawala, M. Synthesis of Telechelic 1,4-Polybutadiene by Metathesis Reactions and Borane Monomers. *Macromolecules* **1992**, *25*, 5137–5144.

(27) Hillmyer, M. A.; Grubbs, R. H. Preparation of Hydroxytelechelic Poly(Butadiene) via Ring-Opening Metathesis Polymerization Employing a Well-Defined Metathesis Catalyst. *Macromolecules* **1993**, *26*, 872–874.

(28) Maughon, B. R.; Morita, T.; Bielawski, C. W.; Grubbs, R. H. Synthesis of Cross-Linkable Telechelic Poly(Butenylene)s Derived from Ring-Opening Metathesis Polymerization. *Macromolecules* **2000**, *33*, 1929–1935.

(29) Bielawski, C. W.; Scherman, O. A.; Grubbs, R. H. Highly Efficient Syntheses of Acetoxy- and Hydroxy-Terminated Telechelic Poly(Butadiene)s Using Ruthenium Catalysts Containing N-Heterocyclic Ligands. *Polymer* **2001**, *42*, 4939–4945.

(30) Annunziata, L.; Fouquay, S.; Michaud, G.; Simon, F.; Guillaume, S. M.; Carpentier, J.-F. Mono- and Di-Cyclocarbonate Telechelic Polyolefins Synthesized from ROMP Using Glycerol Carbonate Derivatives as Chain-Transfer Agents. *Polym. Chem.* **2013**, *4*, 1313–1316.

(31) Diallo, A. K.; Michel, X.; Fouquay, S.; Michaud, G.; Simon, F.; Brusson, J.-M.; Carpentier, J.-F.; Guillaume, S. M. *α*-Trialkoxysilyl Functionalized Polycyclooctenes Synthesized by Chain-Transfer Ring-Opening Metathesis Polymerization. *Macromolecules* **2015**, *48*, 7453–7465.

(32) Michel, X.; Fouquay, S.; Michaud, G.; Simon, F.; Brusson, J.-M.; Carpentier, J.-F.; Guillaume, S. M. *α*,*ω*-Bis(Trialkoxysilyl) Difunctionalized Polycyclooctenes from Ruthenium-Catalyzed Chain-Transfer Ring-Opening Metathesis Polymerization. *Polym. Chem.* **2016**, *7*, 4810–4823.

(33) Vanbiervliet, E.; Fouquay, S.; Michaud, G.; Simon, F.; Carpentier, J.-F.; Guillaume, S. M. From Epoxide to Cyclodithiocarbonate Telechelic Polycyclooctene through Chain-

Transfer Ring-Opening Metathesis Polymerization (ROMP): Precursors to Non-Isocyanate Polyurethanes (NIPUs). *Macromolecules* **2017**, *50*, 69–82.

(34) Hillmyer, M. A.; Nguyen, S. T.; Grubbs, R. H. Utility of a Ruthenium Metathesis Catalyst for the Preparation of End-Functionalized Polybutadiene. *Macromolecules* **1997**, *30*, 718–721.

(35) Pitet, L. M.; Hillmyer, M. A. Combining Ring-Opening Metathesis Polymerization and Cyclic Ester Ring-Opening Polymerization To Form ABA Triblock Copolymers from 1,5-Cyclooctadiene and D,L-Lactide. *Macromolecules* **2009**, *42*, 3674–3680.

(36) Thomas, R. M.; Grubbs, R. H. Synthesis of Telechelic Polyisoprene via Ring-Opening Metathesis Polymerization in the Presence of Chain Transfer Agent. *Macromolecules* **2010**, *43*, 3705–3709.

(37) Pitet, L. M.; Amendt, M. A.; Hillmyer, M. A. Nanoporous Linear Polyethylene from a Block Polymer Precursor. *J. Am. Chem. Soc.* **2010**, *132*, 8230–8231.

(38) Wang, Y.; Hillmyer, M. A. Hydroxy-Telechelic Poly(Ethylene-*Co*-Isobutylene) as a Soft Segment for Thermoplastic Polyurethanes. *Polym. Chem.* **2015**, *6*, 6806–6811.

(39) McGuire, T. M.; Pérale, C.; Castaing, R.; Kociok-Köhn, G.; Buchard, A. Divergent Catalytic Strategies for the *Cis*/*Trans* Stereoselective Ring-Opening Polymerization of a Dual Cyclic Carbonate/Olefin Monomer. *J. Am. Chem. Soc.* **2019**, *141*, 13301–13305.

(40) Werner, H.; Grünwald, C.; Stüer, W.; Wolf, J. Deactivation of the Grubbs Carbene Complex $[RuCl_2(=CHPh)(PCy_3)_2]$ by Allylic Alcohols. *Organometallics* **2003**, *22*, 1558–1560.

(41) Gurjar, M. K.; Yakambram, P. Temperature-Dependent Isomerisation versus Net Fragmentation of Secondary Allylic Alcohols with Grubbs' Catalyst. *Tetrahedron Lett.* **2001**, *42*, 3633–3636.

(42) Paquette, L. A.; Efremov, I. Teubrevin G and Teubrevin H : The First Total Syntheses of Rearranged *Neo*-Clerodanes Including Solutions to the Problems of Chirality Merger and Furan Ring Assembly. *J. Am. Chem. Soc.* **2001**, *6* (9), 4492–4501.

(43) Sworen, J. C.; Pawlow, J. H.; Case, W.; Lever, J.; Wagener, K. B. Competing Ruthenium Catalyzed Metathesis Condensation and Isomerization of Allylic Olefins. *J. Mol. Catal. A Chem.* **2003**, *194*, 69–78.

(44) Nakashima, K.; Okamoto, S.; Sono, M.; Tori, M. Isomerization Reactions of Allylic Alcohols into Ketones with the Grubbs Reagent. *Molecules* **2004**, *9*, 541–549.

(45) Finnegan, D.; Seigal, B. A.; Snapper, M. L. Preparation of Aliphatic Ketones through a Ruthenium-Catalyzed Tandem Cross-Metathesis/Allylic Alcohol Isomerization. *Org. Lett.* **2006**, *8*, 2603–2606.

(46) Greenwood, E. S.; Parsons, P. J.; Young, M. J. Redox Isomerization of Allylic Alcohols and Amides Using Grubbs' Catalyst. *Synth. Commun.* **2006**, No. 33, 223–228.

(47) Schmidt, B.; Hauke, S. Cross Metathesis of Allyl Alcohols: How to Suppress and How to Promote Double Bond Isomerization. *Org. Biomol. Chem.* **2013**, *11*, 4194–4206.

(48) Smoleń, M.; Kędziorek, M.; Grela, K. 2-Methyltetrahydrofuran: Sustainable Solvent for Ruthenium-Catalyzed Olefin Metathesis. *Catal. Commun.* **2014**, *44*, 80–84.

(49) Pitet, L. M.; Chamberlain, B. M.; Hauser, A. W.; Hillmyer, M. A. Synthesis of Linear, H-Shaped, and Arachnearm Block Copolymers By Tandem Ring-Opening Polymerizations. *Macromolecules* **2010**, *43*, 8018–8025.

(50) Bielawski, C. W.; Hillmyer, M. A. Telechelic Polymers from Olefin Metathesis Methodologies. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinham, Germany, 2003; pp 255–282.

(51) Louie, J.; Bielawski, C. W.; Grubbs, R. H. Tandem Catalysis: The Sequential Mediation of Olefin Metathesis, Hydrogenation, and Hydrogen Transfer with Single-Component Ru Complexes. *J. Am. Chem. Soc.* **2001**, *123*, 11312–11313.

(52) Drouin, S. D.; Zamanian, F.; Fogg, D. E. Multiple Tandem Catalysis: Facile Cycling between Hydrogenation and Metathesis Chemistry. *Organometallics* **2001**, *20*, 5495–5497.

(53) Fogg, D. E.; Santos, E. N. Tandem Catalysis: A Taxonomy and Illustrative Review. *Coord. Chem. Rev.* **2004**, *248*, 2365–2379.

(54) van der Schaaf, P. A.; Kolly, R.; Kirner, H.-J.; Rime, F.; Mühlebach, A.; Hafner, A. Synthesis and Reactivity of Novel Ruthenium Carbene Catalysts. X-Ray Structures of $[RuCl_2(=CHSC_6H_5)(P^iPr_3)_2]$ and $[RuCl_2(CHCH_2CH_2\text{-}C,N\text{-}2\text{-}C_5H_4N)(P^iPr_3)]$. *J. Organomet. Chem.* **2000**, *606*, 65–74.

(55) Katayama, H.; Urushima, H.; Nishioka, T.; Wada, C.; Nagao, M.; Ozawa, F. Highly Selective Ring-Opening/Cross-Metathesis Reactions of Norbornene Derivatives Using Selenocarbene Complexes as Catalysts. *Angew. Chemie Int. Ed.* **2000**, *39*, 4513–4515.

(56) Katayama, H.; Yonezawa, F.; Nagao, M.; Ozawa, F. Ring-Opening Metathesis Polymerizations of Norbornene Using Vinylic Ethers as Chain-Transfer Agents: Highly Selective Synthesis of Monofunctional Macroinitiators for Atom Transfer Radical Polymerization. *Macromolecules* **2002**, *35*, 1133–1136.

(57) Louie, J.; Grubbs, R. H. Metathesis of Electron-Rich Olefins: Structure and Reactivity of Electron-Rich Carbene Complexes. *Organometallics* **2002**, *21*, 2153–2164.

(58) Weitekamp, R. A.; Atwater, H. A.; Grubbs, R. H. Photolithographic Olefin Metathesis Polymerization. *J. Am. Chem. Soc.* **2013**, *135*, 16817–16820.

(59) Ahmed, T. S.; Grandner, J. M.; Taylor, B. L. H.; Herbert, M. B.; Houk, K. N.; Grubbs, R. H. Metathesis and Decomposition of Fischer Carbenes of Cyclometalated Z-Selective Ruthenium Metathesis Catalysts. *Organometallics* **2018**, *37*, 2212–2216.

(60) Feist, J. D.; Xia, Y. Enol Ethers Are Effective Monomers for Ring-Opening Metathesis Polymerization: Synthesis of Degradable and Depolymerizable Poly(2,3-Dihydrofuran). *J. Am. Chem. Soc.* **2020**, *142*, 1186–1189.

(61) Fatou, J. G.; Mandelkern, L. The Effect of Molecular Weight on the Melting Temperature and Fusion of Polyethylene. *J. Phys. Chem.* **1965**, *69*, 417–428.

(62) Wagner, H. L.; Hoeve, C. A. J. Effect of Molecular Weight on the Refractive Increment of Polyethylene and *n*-Alkanes. *J. Polym. Sci. Part A-2* **1971**, *9*, 1763–1776.

TABLE OF CONTENTS GRAPHIC