cis-Selective Acyclic Diene Metathesis Polymerization using Bulky Cyclometalated Ruthenium Carbene Catalysts

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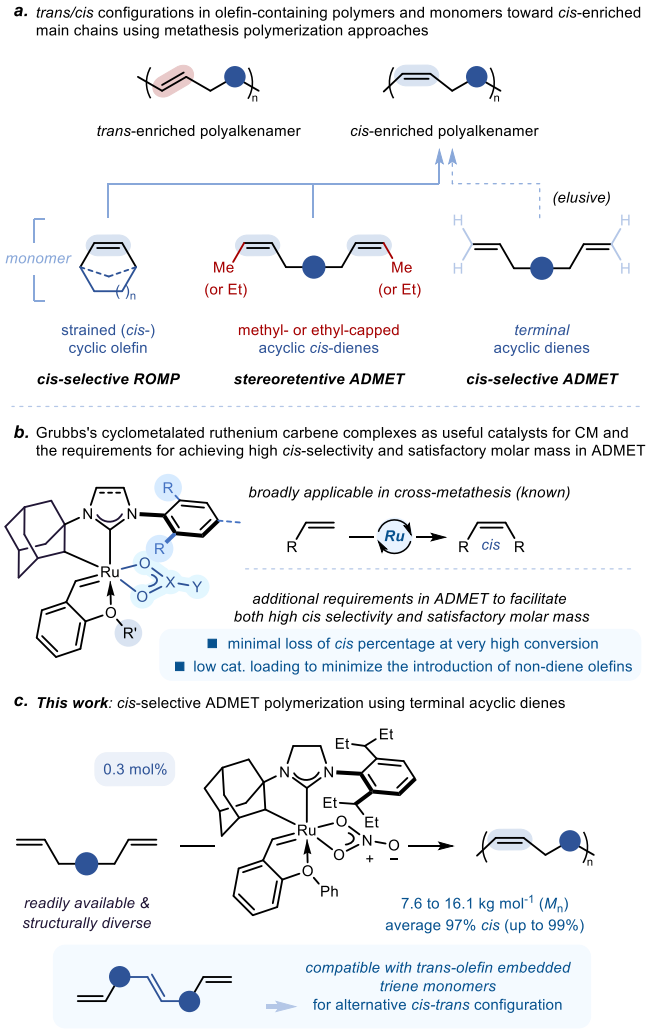
Supporting Information Placeholder

ABSTRACT: The regulation of *cis*-*trans* configuration is important for investigating the structure-property relationship and fine-tuning the properties of olefin-containing polymers. While classic metathesis polymerization typically yields *trans*-enriched polymer backbones, the selective construction of all-*cis*-configured polyalkenamers was previously restricted to the use of strained cyclic olefins or methyl/ethyl-capped acyclic *cis*-dienes as monomers. Here, we reported an efficient and diverse-oriented *cis*-selective ADMET using readily available terminal acyclic dienes, which achieves a high *cis*-percentage of up to 99% and satisfactory molar mass by a bulky cyclometalated ruthenium-carbene catalyst. This method is further compatible with *trans*-olefin embedded triene monomers, providing a convenient tool for constructing alternative *cis*-*trans* configurations in polyalkenamers. A *cis*-ADMET-prepared and **G2**-degradable polymer was also explored. This work expands the possibilities for precision polymer synthesis and may offer new avenues for material design.

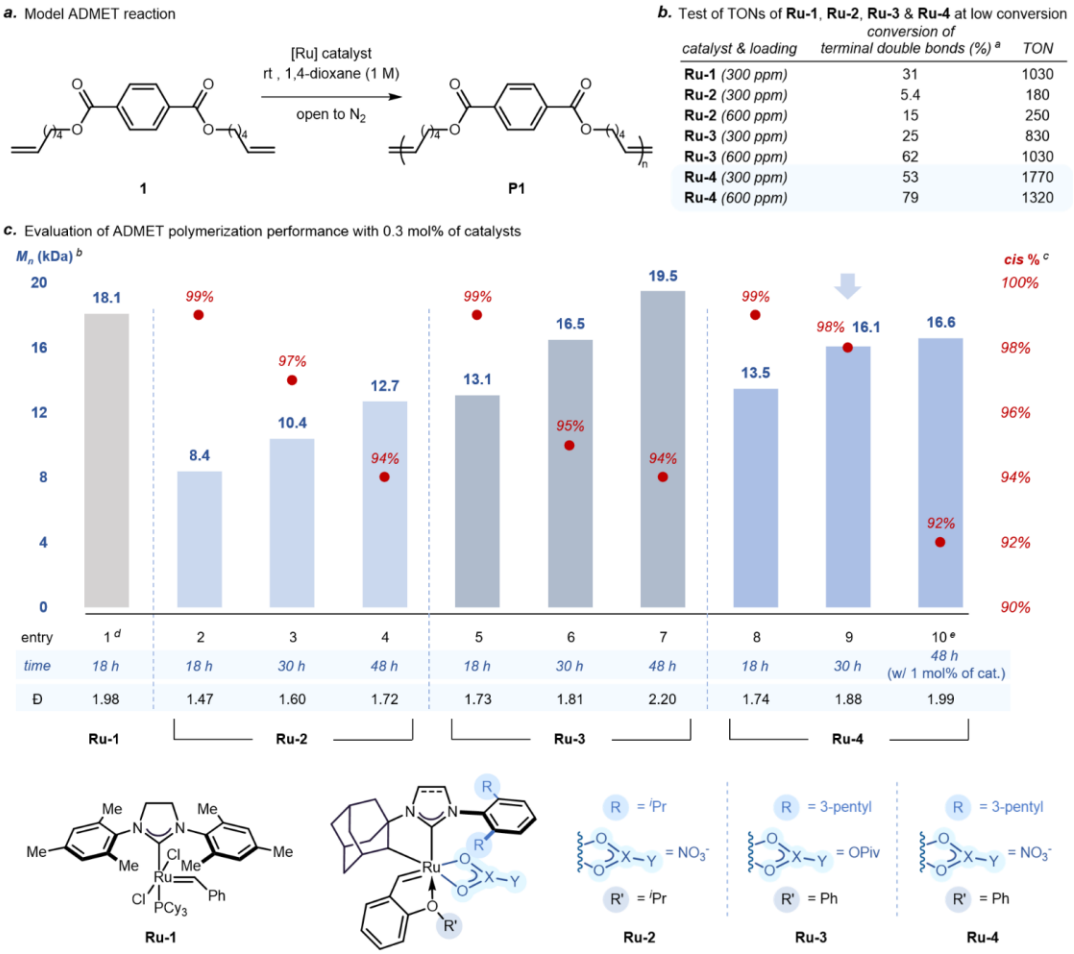
Evidenced by the extensive studies on polyisoprenes with all-*cis*, all-*trans*, or mixed *cis*-*trans* structures,[1] the regulation of *cis*-*trans* configuration of main-chain double bonds offers an important stereochemical handle for adjusting and enhancing properties of polymers with repeating alkene units.[2] Among various approaches towards olefin-containing polymers, olefin metathesis-based polymerization methods, including both ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET) polymerization, are ubiquitously practiced due to its broad structural and functional group compatibility.[3] Often, the formation of sterically less congested olefins is thermodynamically preferred, yet, the nature of double bond formation at a metal center renders metathesis polymerization with valuable opportunities to kinetically tune the stereochemistry of the resulting olefin.[4] The selective formation of thermodynamically less favored olefin configurations, such as *cis*-1,2-disubstituted olefins, could be realized by a series of elegantly developed Mo, W, and Ru catalysts.[5-8] Therefore, while a classic metathesis polymerization often results in mixed olefin configurations favoring the *trans* form, *cis*-enriched polymer backbones are accessible (Scheme 1a).[9] For example, significant progress has been made in *cis*-selective ROMP, leading to nearly perfect stereochemical control[10] and tailored polymer properties including light-responsiveness and improved shear stability.[11] Further, an ADMET-based approach to *cis*-polymer backbones has been elegantly demonstrated recently by using a stereoretentive Ru-dithiolate catalyst, which largely broadens the scope of attainable *cis*-polyalkenamers beyond *cis*-selective ROMP.[12] While both

Scheme 1. Approaches toward *cis*-enriched polyalkenamers *via* metathesis polymerization and catalyst requirements for facilitating effective *cis*-selective ADMET.



approaches are efficient, the olefinic monomers are limited to strained cyclic olefins or special methyl/ethyl-capped acyclic *cis*-dienes. The use of simple terminal acyclic dienes[13] in the selective construction of *cis*-polyalkenamers remains elusive, despite that this classic type of monomers is not only structurally diverse but

Scheme 2. Evaluation of *cis*-selective ADMET with various catalysts.



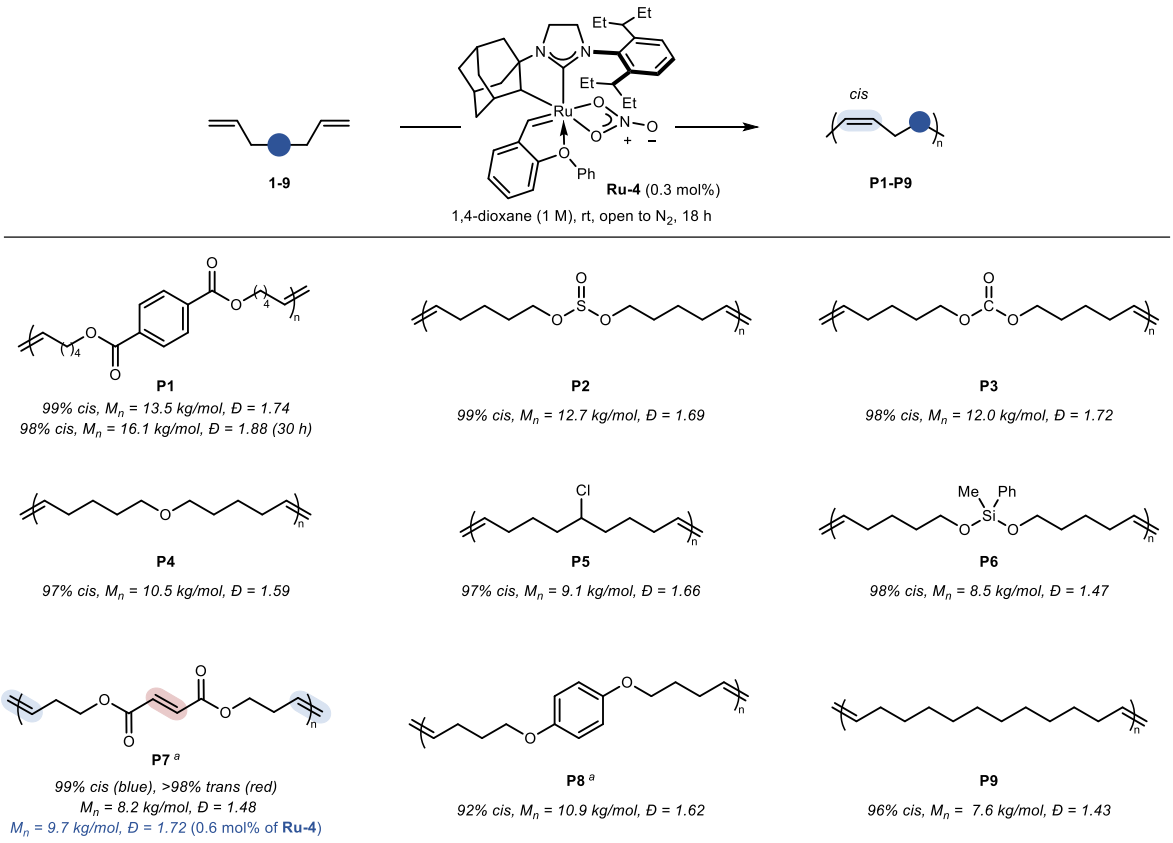
[a] Determined by ^{1}H NMR analysis of the crude reaction mixture. [b] Determined by size exclusion chromatography (SCE) in THF against polystyrene standards. [c] Determined by ^{1}H NMR analysis of purified polymers. [d] *cis*-percentage = 16%. [e] Using 1 mol% of **Ru-4**. For details, see *Supporting Information*.

also readily available. Hence, it would be highly desirable if *cis*-selective ADMET polymerization of terminal dienes could be realized with the same degree of stereochemical accuracy as previous studies using *cis*-substrates, which would streamline the production of a wide array of stereocontrolled polymers for diverse applications.[14]

The desired *cis*-selective ADMET requires the selective construction of *cis*-double bonds between terminal alkenes during polycondensation. Among several classes of stereoselective metathesis catalysts, the cyclometalated ruthenium carbene catalysts were first discovered by the Grubbs group,[7a] which quickly expand to a family of catalysts with different chelating structures, NHC backbones, aryl side arms, and anionic ligands.[15] These catalysts have been well explored for *cis*-selective CM and ROMP with broad compatibility, and a proposed *cis*-selective ADMET would share a similar mechanistic profile as *cis*-selective CM, with the olefin substituents pointing away from the NHC side arm during side-bound cycloaddition/reversion and resulting in *cis*-olefin configuration.[16] However, additional requirements are necessary to facilitate the achievement of both high *cis* selectivity and satisfactory molar mass in *cis*-ADMET (Scheme 1b). First, since the Ru-carbene catalyst releases a non-diene olefin (typically a substituted styrene) after the initial catalytic cycle, a sufficiently low catalyst loading with a high turnover number (TON) is preferred for both practicality and a high molar mass.[17] Second, it is often observed that *cis*-selectivity drops significantly in late stages of CMs (e.g., >90% conversion of terminal double bonds), potentially due to the accumulation of decomposed organometallic species and/or increased reprocessing of generated *cis*-olefins. Therefore, the desired catalyst for *cis*-ADMET should be able to not only induce high kinetic *cis*-selectivity during bond formation but also maintain it while pushing the reaction towards almost full conversion. Interestingly, if the catalysts can also perfectly distinguish the reactivity of terminal and *cis*-olefins from that of main-chain *trans*-olefins,[18] linear *trienes* containing embedded *trans*-double bonds could potentially serve as an effective monomer. This may enable the formation of an alternative *cis-trans* main-chain configuration that is difficult to access conventionally. Here, we report *cis*-selective ADMET polymerization of terminal acyclic dienes, which exhibits a broad scope among functionalized skeletons and a high *cis*-selectivity of up to 99%.[19] We also showcased the convenient synthesis of *cis*-a-*trans* polyalkenamers from triene monomers and the full degradation of one of these polymers using **G2** (Scheme 1c).

Di(hex-5-en-1-yl) terephthalate (**1**) was selected as a model substrate to investigate the proposed *cis*-selective ADMET polymerization (Scheme 2a). A group of catalysts was evaluated, including **G2** (**Ru-1**) and the "classic" cyclometalated Ru-carbene catalyst **Ru-2** bearing a Dipp NHC-side arm. We also synthesized the recently developed **Ru-3** and **Ru-4** featuring a bulkier Dipep side arm and a faster-initiation OPh auxiliary, which have been found superior in several challenging CM and cascade polymerization reactions. [15e, 15f, 20] TONs of these catalysts were first evaluated at low-

Scheme 3. Scope for *cis*-selective ADMET using Ru-4.

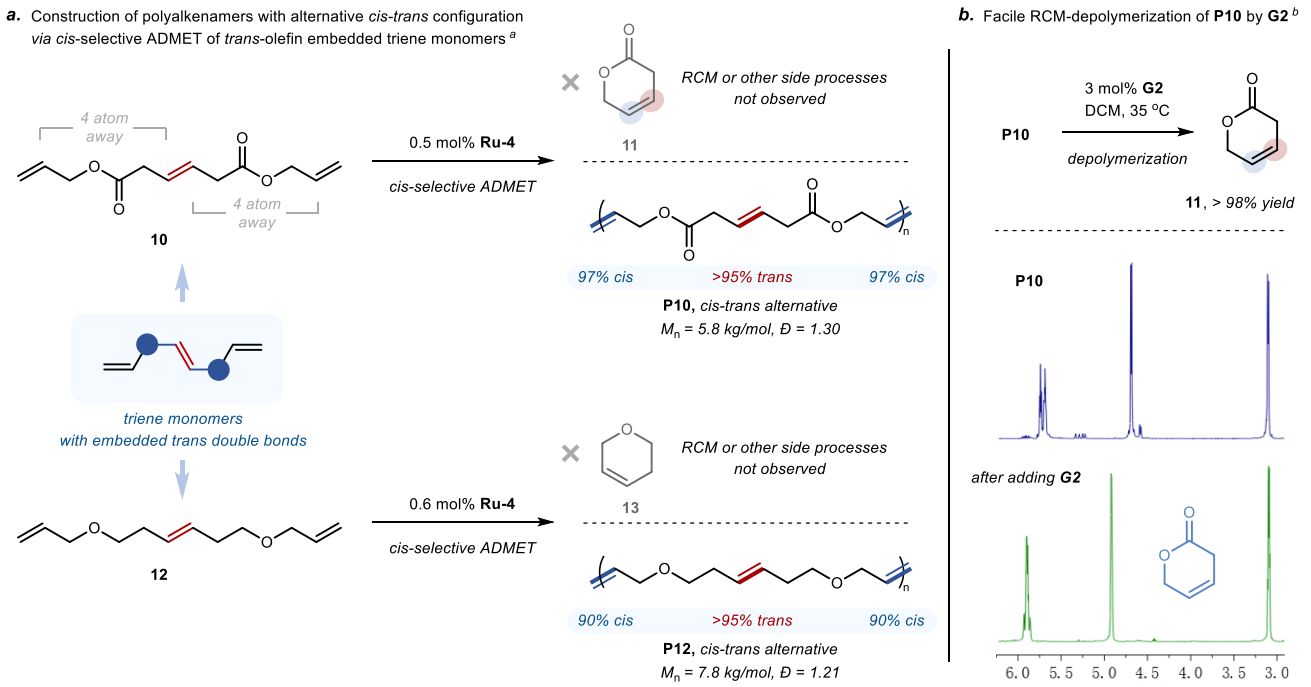


[a] Conducted in 1,2-dichlorobenzene. For details, see *Supporting Information*.

to-medium conversion using monomer **1**, with a catalyst loading of either 300 or 600 ppm (Scheme 2b). The reactions were monitored until the conversion of terminal double bonds ceased to increase. While **G2** showed a TON of 1030 at 300 ppm loading, the use of the "classic" cyclometalated **Ru-2** catalyst only resulted in a 5.4% conversion and a TON of 180. The bulkier pivalate catalyst **Ru-3** and nitrate catalyst **Ru-4** exhibit higher effectiveness, achieving TONs of 830 and 1770 at the same catalyst loading, respectively. **Ru-2**, **Ru-3**, and **Ru-4** were further examined with a catalyst loading of 600 ppm to minimize the potential influence of impurities in monomer **1**, and the measured TONs varied similarly to those with 300 ppm of catalysts. The use of 1000 ppm of **Ru-4** was sufficient in generating **P1** with a molar mass of 8.9 kg mol^{-1}. However, to facilitate the access to higher molar masses and an impartial assessment of the catalyst-dependent relationship between molar mass and *cis*-percentage, a unified catalyst loading of 0.3 mol% was utilized to investigate the ADMET of **1** with various catalysts (Scheme 2c). As a benchmark, the use of **Ru-1** furnished **P1** with a *cis*-percentage of 16% and a molar mass of 18.1 kg mol^{-1} (entry 1). When **Ru-2** was used, a remarkable *cis*-percentage of 99% was observed after 18 hours. However, only 93% of the terminal alkenyl group had reacted, resulting in a relatively low molar mass of **P1** (8.4 kg mol^{-1}). While extending the reaction time did result in higher molar masses, a significant and continuous decrease in *cis*-percentage was observed over time. For example, only a 97% *cis* ratio was achieved when the molar mass of **P1** reached 10.4 kg mol^{-1}, which further decreased to 94% when the molar mass increased to 12.7 kg mol^{-1} (entries 2-4). With a bulkier NHC side arm and a faster initiation rate, **Ru-3** bearing a pivalate anion catalyzed a more efficient *cis*-selective ADMET than **Ru-2**, producing **P1** with a molar mass of 13.1 kg mol^{-1} after 18 hours and 19.5 kg mol^{-1} after 48 hours. However, a significant drop in *cis*-percentage (from 99% to 95%) was still observed during the time frame of 18 to 30 hours (entries 5-7). Finally, the use of **Ru-4**, a bulkier catalyst with a nitrate anion, led to optimal *cis*-selective ADMET polymerization of **1** that exhibited fast polymerization kinetic, satisfactory molar masses, and slow erosion of stereoselectivity. After 18 hours of reaction with **Ru-4**, **P1** was generated with a molar mass of 13.5 kg mol^{-1} and a *cis*-percentage of 99%. The molar mass continued to increase to 16.1 kg mol^{-1} over the following 12 hours, and the *cis*-percentage only slightly decreased to 98% (entries 8 and 9). It is noteworthy that the ADMET reaction based on a stereoretentive mechanism using the corresponding ethyl-capped *cis*-diene could only afford **P1** with 94% *cis* selectivity and a molar mass of 15.9 kg mol^{-1},[12] which highlights the effectiveness of the current approach based on terminal dienes. The effect of a higher **Ru-4** loading (1 mol%) was investigated, resulting in a similar molar mass (16.6 kg mol^{-1}) but reduced stereoselectivity (92% *cis*) after a prolonged reaction time (entry 10).

Under the optimal condition, the scope of the *cis*-selective ADMET was then investigated. Nine different monomers with diverse functional and skeletal features were examined, leading to polyalkenamers with a *cis* percentage ranging from 96% to 99%, except for **P8** (Scheme 3). Among these, polyester **P1**, polysulfite **P2**, polycarbonate **P3** and polyether **P4** could all be accessed with molar masses larger than 10 kg mol^{-1} and *cis* percentage over 97%. Chlorinated **P5** and polysiloxane **P6**, which possess additional handles for post-polymerization functionalization and/or remolding, could also be accessed with high *cis*-selectivity (97-98% *cis*).[21a, 21b] Moreover, di(but-3-en-1-yl) fumarate, a readily available terminal diene from fumaric acid, could also be employed. While the newly formed double bonds are 99% *cis*, the electron-deficient *trans*-double bonds are well-preserved in the main-chain of **P7**, providing electro- and radicalphilic reactivity for further elaboration.[21c] Due

Scheme 4. Construction of alternative *cis-trans* configurations from triene monomers and a related depolymerization study

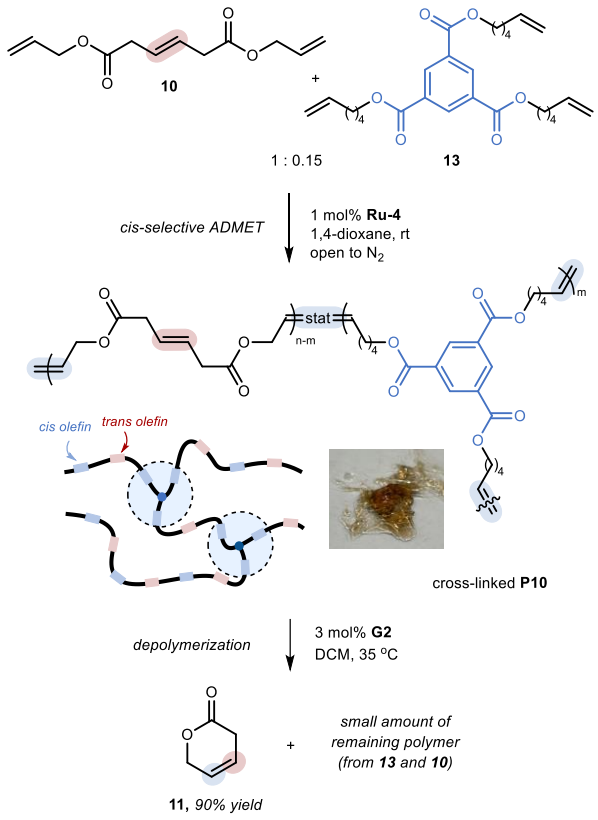


[a] Condition same as Scheme 3 except for higher loadings of **Ru-4**. [b] 3 mol% **G2**, DCM (0.01 M), 35 °C, 6 h. For details, see *Supporting Information*.

to poor solubility, polyether **P8** and unfunctionalized **P9** were prepared in 1,2-dichlorobenzene instead of 1,4-dioxane. Additionally, increasing the catalyst loading from 0.3 mol% to 0.6 mol% could increase the molar mass of **P7** from 8.2 kg mol^{-1} to 9.7 kg mol^{-1}. The thermal properties of the synthesized *cis*-polyalkenamers were measured using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), and found to be consistent with the previous assessment.[12] Among them, the melting temperature (T_m) of the all-*cis* **P1** could be measured and found lower than a *trans*-enriched **P1.**[12]

Besides thermal properties, we further aim to evaluate the chemoselectivity of the *cis*-selective ADMET against main-chain *trans* olefins. As **Ru-4** demonstrates high stereoselectivity in forming *cis*-olefins during ADMET, assuming that 1,2-disubstituted trans-double bonds in monomers could be completely left alone, a convenient approach towards well-defined polyalkenamers with precisely-positioned *cis-trans* configuration could be envisioned (Scheme 4a). As a model substrate, triene **10** with a centered *trans*-double bond was prepared in a single step from trans-*β*-hydromuconic acid, which is unsuitable for ADMET using conventional catalysts like **G2**. If the chemoselectivity of **Ru-4** is flawed and the centered *trans* double bond cannot be completely left untouched, the formation of but-3-enoate and/or β,γ-unsaturated δ-lactone (**11**),[22] even in a small amount, would be expected as an indicator. To our delight, no lactone **11** or other significant side processes was observed in the ADMET of **10** using **Ru-4**, indicating perfect chemoselectivity. The generated semi-crystalline polyester **P10**, with a medium molar mass of 5.8 kg mol^{-1}, possesses a precise *cis*-a-*trans* configuration, a non-trivial feature that makes it valuable for structure-property investigations and as models for imprecise systems. Besides, we found that **P10** underwent facile depolymerization in the presence of **G2** and furnished **11** in >98% yield, thus representing an intriguing switch between an ADMET polymerization and an RCM depolymerization (Scheme 4b). The well-tolerance of main-chain *trans*-double bonds appears to be universally useful for constructing stereo-controlled polymers. In another case, polyether **P12**, with an alternatively configured main chain, could also be produced through the same **Ru-4**-catalyzed ADMET from triene **12**.[23]

Scheme 5. Synthesis and depolymerization of a cross-linked *cis*-ADMET-derived polymer.



The high *cis*-selectivity of **Ru-4** could be further utilized to construct a cross-linked ADMET polymer that is **G2**-degradable (Scheme 5). A model study performed with triene **10** and 4 mol% of crosslinker **13** revealed that the terminal double bonds in **10** and **13** had similar reactivity at 80-85% conversion. Accordingly, treatment of **10** with an increased amount of **13** (15 mol%) and **Ru-4** (1 mol%) was further carried out, leading to a cross-linked **P10** with alternatively placed *cis*- and *trans*-double bonds and a gel content of 22%. Nevertheless, treatment of the gel-like material with 3 mol% of **G2** in DCM led to its facial degradation, generating **11** in 90% yield.

In summary, we have developed an efficient *cis*-selective ADMET polymerization using readily available terminal acyclic dienes. A diverse range of stereo-controlled polyalkenamers could be produced with a high *cis*-percentage of up to 99%. The use of a bulky cyclometalated ruthenium carbene catalyst at a typical loading of 0.3 mol% is crucial for maintaining high *cis*-selectivity while ensuring satisfactory molar mass. The catalytic system further allows trienes with centrally located *trans*-double bonds to serve as monomers, providing convenient access to polyalkenamers with alternative *cis*-*trans* configurations. The RCM-depolymerization of a *cis*-ADMET-generated polymer was also demonstrated. Overall, this work expands the possibilities for precision polymer synthesis and may find further applications in material design.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This project was supported by the Natural Science Foundation of China (Grant No. 22201015), Beijing Natural Science Foundation (Grant No. 2232005), BNLMS, and Peking University Li Ge Zhao Ning Youth Research Fund for Life Sciences (Grant No. LGZNQN202204). The authors thank Prof. Jianbo Wang (PKU) and Prof. Zi-Chen Li (PKU) for their insightful discussion and suggestions.

REFERENCES

(1) (a) Coates, G. W.; Domski, G. J. Polymerization and Oligomerization of Olefins. In *Organotransition Metal Chemistry: From Bonding to Catalysis*; Univ. Science Books, 2010; pp 1047–1100. (b) Mark, J. E. *Polymer Data Handbook*, 2nd ed; Oxford University Press, 2009. (c) Phuphuak, Y.; Bonnet, F.; Stoclet, G.; Bria, M.; Zinck, P. Isoprene Chain Shuttling Polymerisation between *Cis* and *Trans* Regulating Catalysts: Straightforward Access to a New Material. *Chem. Commun.* **2017**, *53*, 5330–5333.

(2) Worch, J. C.; Prydderch, H.; Jimaja, S.; Bexis, P.; Becker, M. L.; Dove, A. P. Stereochemical Enhancement of Polymer Properties. *Nat. Rev. Chem.* **2019**, *3*, 514–535.

(3) (a) Bielawski, C. W.; Grubbs, R. H. Living Ring-Opening Metathesis Polymerization. *Prog. Polym. Sci.* **2007**, *32*, 1−29. (b) Herz, K.; Elser, I.; Buchmeiser, M. R. Ring-Opening Metathesis Polymerization: Mechanisms In *Macromolecular Engineering: From Precise Synthesis to Macroscopic Materials and Applications*; Wiley-VCH, 2022. (c) Wagener, K. B.; Boncella, J. M.; Nel, J. G. Acyclic Diene Metathesis (ADMET) Polymerization. *Macromolecules* **1991**, *24*, 2649–2657. (d) Schulz, M. D.; Wagener, K. B. ADMET Polymerization. In *Handbook of Metathesis*, 2nd ed.; Wiley-VCH, 2015; pp 315−355. (e) Caire da Silva, L.; Rojas, G.; Schulz, M. D.; Wagener, K. B. Acyclic Diene Metathesis Polymerization: History, Methods and Applications. *Prog. Polym. Sci.* **2017**, *69*, 79–107.

(4) For reviews, see: (a) Fürstner, A. Teaching metathesis "simple" stereochemistry. *Science* **2013**, *341*, 1229713. (b) Hoveyda, A. H.; Khan, R. K. M.; Torker, S.; Malcolmson, S. J. Catalyst-controlled stereoselective olefin metathesis. In *Handbook of Metathesis*; Wiley-VCH: Weinheim, 2015; pp 503−562. (c) Montgomery, T. P.; Ahmed, T. S.; Grubbs, R. H. Stereoretentive olefin metathesis: an avenue to kinetic selectivity. *Angew. Chem., Int. Ed.* **2017**, *56*, 11024−11036.

(5) For selected examples with molybdenum-based complexes, see: (a) Townsend, E. M.; Schrock, R. R.; Hoveyda, A. H. *Z*-selective metathesis homocoupling of 1,3-dienes by molybdenum and tungsten monoaryloxide pyrrolide (MAP) complexes. *J. Am. Chem. Soc.* **2012**, *134*, 11334−11337. (b) Kiesewetter, E. T.; O'Brien, R. V.; Yu, E. C.; Meek, S. J.; Schrock, R. R.; Hoveyda, A. H. Synthesis of *Z*-(pinacolato)allylboron and *Z*-(pinacolato)alkenylboron compounds through stereoselective catalytic cross-metathesis. *J. Am. Chem. Soc.* **2013**, *135*, 6026−6029. (c) Zhang, H.; Yu, E. C.; Torker, S.; Schrock, R. R.; Hoveyda, A. H. Preparation of macrocyclic *Z*-enoates and (*E*,*Z*)- or (*Z*,*E*)-dienoates through catalytic stereoselective ring-closing metathesis. *J. Am. Chem. Soc.* **2014**, *136*, 16493−16496. (d) Yu, E. C.; Johnson, B. M.; Townsend, E. M.; Schrock, R. R.; Hoveyda, A. H. Synthesis of linear (*Z*)-*α*,*β*-unsaturated esters by catalytic cross-metathesis. The influence of acetonitrile. *Angew. Chem., Int. Ed.* **2016**, *55*, 13210−13214.

(6) For selected examples with tungsten-based complexes, see: (a) Jiang, A. J.; Zhao, Y.; Schrock, R. R.; Hoveyda, A. H. Highly *Z*-Selective Metathesis Homocoupling of Terminal Olefins. *J. Am. Chem. Soc.* **2009**, *131*, 16630–16631. (b) Peryshkov, D. V.; Schrock, R. R.; Takase, M. K.; Müller, P.; Hoveyda, A. H. *Z*-Selective Olefin Metathesis Reactions Promoted by Tungsten Oxo Alkylidene Complexes. *J. Am. Chem. Soc.* **2011**, *133*, 20754–20757.

(7) For selected examples with ruthenium-based complexes, see: (a) Endo, K.; Grubbs, R. H. Chelated ruthenium catalysts for *Z*-selective olefin metathesis. *J. Am. Chem. Soc.* **2011**, *133*, 8525−8527. (b) Occhipinti, G.; Hansen, F. R.; Törnroos, K. W.; Jensen, V. R. Simple and Highly *Z*-Selective Ruthenium-Based Olefin Metathesis Catalyst. *J. Am. Chem. Soc.* **2013**, *135*, 3331−3334. (c) Koh, M. J.; Khan, R. K. M.; Torker, S.; Yu, M.; Mikus, M. S.; Hoveyda, A. H. High-value alcohols and higheroxidation-state compounds by catalytic *Z*-selective cross-metathesis. *Nature* **2015**, *517*, 181−186. (d) Xu, C.; Shen, X.; Hoveyda, A. H. In situ methylene capping: a general strategy for efficient stereoretentive catalytic olefin metathesis. The concept, methodological implications, and applications to synthesis of biologically active compounds. *J. Am. Chem. Soc.* **2017**, *139*, 10919−10928.

(8) For a recent review, see: Dawood, K. M.; Nomura, K. Recent Developments in *Z*-Selective Olefin Metathesis Reactions by Molybdenum, Tungsten, Ruthenium, and Vanadium Catalysts. *Adv. Synth. Catal.* **2021**, *363*, 1970–1997.

(9) For selected examples for the construction of *cis*-enriched polyalkenamers besides transition metal-catalyzed metathesis polymerization, see: (a) Yang, X.; Gitter, S. R.; Roessler, A. G.; Zimmerman, P. M.; Boydston, A. J. An Ion-Pairing Approach to Stereoselective Metal-Free Ring-Opening Metathesis Polymerization. *Angew. Chem. Int. Ed.* **2021**, *60*, 13952–13958. (b) Worch, J. C.; Dove, A. P. Click Step-Growth Polymerization and *E*/*Z* Stereochemistry Using Nucleophilic Thiol-Yne/-Ene Reactions: Applying Old Concepts for Practical Sustainable (Bio)Materials. *Acc. Chem. Res.* **2022**, *55*, 2355–2369.

(10) (a) Flook, M. M.; Jiang, A. J.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *Z*-Selective Olefin Metathesis Processes Catalyzed by a Molybdenum Hexaisopropylterphenoxide Monopyrrolide Complex. *J. Am. Chem. Soc.* **2009**, *131*, 7962–7963. (b) Flook, M. M.; Gerber, L. C. H.; Debelouchina, G. T.; Schrock, R. R. *Z*-Selective and Syndioselective Ring-Opening Metathesis Polymerization (ROMP) Initiated by Monoaryloxidepyrrolide (MAP) Catalysts. *Macromolecules* **2010**, *43*, 7515–7522. (c) Schrock, R. R. Synthesis of Stereoregular Polymers through Ring-Opening Metathesis Polymerization. *Acc. Chem. Res.* **2014**, *47*, 2457–2466. (d) Keitz, B. K.; Fedorov, A.; Grubbs, R. H. *cis*-Selective Ring-Opening Metathesis Polymerization with Ruthenium Catalysts. *J. Am. Chem. Soc*. **2012**, *134*, 2040−2043. (e) Khan, R. K. M.; Torker, S.; Hoveyda, A. H. Readily accessible and easily modifiable Ru-based catalysts for efficient and *Z*-selective ring-opening metathesis polymerization and ring-opening/ cross-metathesis. *J. Am. Chem. Soc.* **2013**, *135*, 10258−10261. (f) Koh, M. J.; Khan, R. K. M.; Torker, S.; Hoveyda, A. H. Broadly applicable *Z*- and diastereoselective ring-opening/cross-metathesis catalyzed by a dithiolate Ru complex. *Angew. Chem., Int. Ed.* **2014**, *53*, 1968−1972. (g) Hou, X.; Nomura, K. (Arylimido)Vanadium(V)–Alkylidene Complexes Containing Fluorinated Aryloxo and Alkoxo Ligands for Fast Living Ring-Opening Metathesis Polymerization (ROMP) and Highly *Cis*-Specific ROMP. *J. Am. Chem. Soc.* **2015**, 137, 4662–4665. (h) Hou, X.; Nomura, K. Ring-Opening Metathesis Polymerization of Cyclic Olefins by (Arylimido)Vanadium(V)-Alkylidenes: Highly Active, Thermally Robust *Cis* Specific Polymerization. *J. Am. Chem. Soc.* **2016**, *138*, 11840–11849.

(11) (a) Hsu, T.-W.; Kim, C.; Michaudel, Q. Stereoretentive Ring-Opening Metathesis Polymerization to Access All-*Cis* Poly(*p*-Phenylenevinylene)s with Living Characteristics. *J. Am. Chem. Soc*. **2020**, *142*, 11983–11987. (b) Song, J.-A.; Peterson, G. I.; Bang, K.-T.; Ahmed, T. S.; Sung, J.-C.; Grubbs, R. H.; Choi, T.-L. Ru-Catalyzed, *Cis*-Selective Living Ring-Opening Metathesis Polymerization of Various Monomers, Including a Dendronized Macromonomer, and Implications to Enhanced Shear Stability. *J. Am. Chem. Soc.* **2020**, *142*, 10438–10445.

(12) Hsu, T.-W.; Kempel, S. J.; Felix Thayne, A. P.; Michaudel, Q. Stereocontrolled Acyclic Diene Metathesis Polymerization. *Nat. Chem.* **2023**, *15*, 14–20.

(13) Tindall, D.; Wagener, K. B. Acyclic Diene Metathesis (ADMET) Segmented Copolymers. *Macromolecules* **2004**, *37*, 3328–3336.

(14) (a) Atallah, P.; Wagener, K. B.; Schulz, M. D. ADMET: The Future Revealed. *Macromolecules* **2013**, *46*, 4735–4741. (b) Hopkins, T. E.; Wagener, K. B. ADMET Synthesis of Polyolefins Targeted for Biological Applications. *Macromolecules* **2004**, *37*, 1180–1189. (c) Pribyl, J.; Wagener, K. B.; Rojas, G. ADMET Polymers: Synthesis, Structure Elucidation, and Function. *Mater. Chem. Front.* **2021**, *5*, 14–43. (d) Li, Z.-L.; Lv, A.; Du, F.-S.; Li, Z.-C. Intrachain Cyclization via Postmodification of the Internal Alkenes of Periodic ADMET Copolymers: The Sequence Matters. *Macromolecules* **2014**, *47*, 5942–5951. (e) Wang, X.; Zhao, W.; Nomura, K. Synthesis of High-Molecular-Weight Biobased Aliphatic Polyesters by Acyclic Diene Metathesis Polymerization in Ionic Liquids. *ACS Omega* **2023**, *8*, 7222–7233.

(15) (a) Keitz, B. K.; Endo, K.; Patel, P. R.; Herbert, M. B.; Grubbs, R. H. Improved ruthenium catalysts for *Z*-selective olefin metathesis. *J. Am. Chem. Soc.* **2012**, *134*, 693−699. (b) Rosebrugh, L. E.; Herbert, M. B.; Marx, V. M.; Keitz, B. K.; Grubbs, R. H. Highly active ruthenium metathesis catalysts exhibiting unprecedented activity and *Z*-selectivity. *J. Am. Chem. Soc.* **2013**, *135*, 1276−1279. (c) Herbert, M. B.; Suslick, B. A.; Liu, P.; Zou, L.; Dornan, P. K.; Houk, K. N.; Grubbs, R. H. Cyclometalated *Z*-Selective Ruthenium Metathesis Catalysts with Modified N-Chelating Groups. *Organometallics* **2015**, *34*, 2858–2869. (d) Dumas, A.; Tarrieu, R.; Vives, T.; Roisnel, T.; Dorcet, V.; Baslé, O.; Mauduit, M. A Versatile and Highly *Z*-Selective Olefin Metathesis Ruthenium Catalyst Based on a Readily Accessible N-Heterocyclic Carbene. *ACS Catal.* **2018**, *8*, 3257–3262. (e) Xu, Y.; Wong, J. J.; Samkian, A. E.; Ko, J. H.; Chen, S.; Houk, K. N.; Grubbs, R. H. Efficient *Z*-Selective Olefin-Acrylamide Cross-Metathesis Enabled by Sterically Demanding Cyclometalated Ruthenium Catalysts. *J. Am. Chem. Soc.* **2020**, *142*, 20987–20993. (f) Xu, Y.; Gan, Q.; Samkian, A. E.; Ko, J. H.; Grubbs, R. H. Bulky Cyclometalated Ruthenium Nitrates for Challenging *Z*-Selective Metathesis: Efficient One-Step Access to α-Oxygenated *Z*-Olefins from Acrylates and Allyl Alcohols. *Angew. Chem. Int. Ed.* **2022**, *61*, e202113089.

(16) Liu, P.; Xu, X.; Dong, X.; Keitz, B. K.; Herbert, M. B.; Grubbs, R. H.; Houk, K. N. *Z*-selectivity in olefin metathesis with chelated Ru catalysts: computational studies of mechanism and selectivity. *J. Am. Chem. Soc.* **2012**, *134*, 1464−1467.

(17) Li, H.; Caire da Silva, L.; Schulz, M. D.; Rojas, G.; Wagener, K. B. A Review of How to Do an Acyclic Diene Metathesis Reaction. *Polym. Int.* **2017**, *66*, 7–12.

(18) Cannon, J. S.; Grubbs, R. H. Alkene Chemoselectivity in Ruthenium-Catalyzed *Z*-Selective Olefin Metathesis. *Angew. Chem. Int. Ed.* **2013**, *52*, 9001–9004.

(19) During the preparation of this article, a related *cis*-selective ADMET was reported by Michaudel using **Ru-2**: Kempel, S. J.; Hsu, T.-W.; Nicholson, J. L.; Michaudel, Q. *cis*-Selective Acyclic Diene Metathesis Polymerization of α, ω-Dienes, **2023**, doi:10.26434/chemrxiv-2023-x02qw.

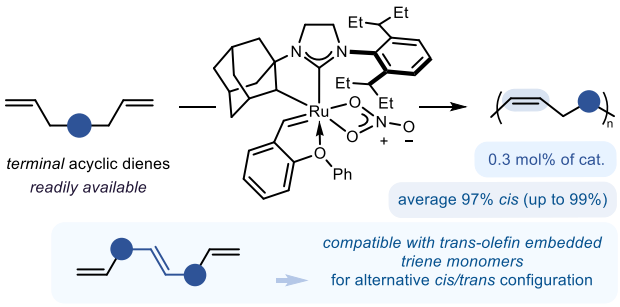
(20) Ryu, H.; Sung, J.-C.; Kim, G.; Xu, Y.; Grubbs, R. H.; Choi, T.-L. Cascade Cyclopolymerization of 5-Ethynyl-1,8-Nonadiyne Derivatives to Synthesize Low Band Gap Conjugated Polyacetylenes Containing a Fused Bicyclic Structure *Angew. Chem. Int. Ed.* **2022**, *61*, e202210244.

(21) (a) Mijangos, C.; Calafel, I.; Santamaría, A. Poly(Vinyl Chloride), a Historical Polymer Still Evolving. *Polymer* **2023**, *266*, 125610. (b) Husted, K. E. L.; Brown, C. M.; Shieh, P.; Kevlishvili, I.; Kristufek, S. L.; Zafar, H.; Accardo, J. V.; Cooper, J. C.; Klausen, R. S.; Kulik, H. J.; Moore, J. S.; Sottos, N. R.; Kalow, J. A.; Johnson, J. A. Remolding and Deconstruction of Industrial Thermosets via Carboxylic Acid-Catalyzed Bifunctional Silyl Ether Exchange. *J. Am. Chem. Soc.* **2023**, *145*, 1916–1923. (c) Hoffmann, C.; Stuparu, M. C.; Daugaard, A.; Khan, A. Aza-Michael Addition Reaction: Post-Polymerization Modification and Preparation of PEI/PEG-Based Polyester Hydrogels from Enzymatically Synthesized Reactive Polymers. *J. Polym. Sci., Part A: Polym. Chem.* **2015**, *53*, 745–749.

(22) Andreana, P. R.; McLellan, J. S.; Chen, Y.; Wang, P. G. Synthesis of 2,6-Dideoxysugars via Ring-Closing Olefinic Metathesis. *Org. Lett.* **2002**, *4*, 3875–3878.

(23) (a) Fokou, P. A.; Meier, M. A. R. Acyclic Triene Metathesis Polymerization with Chain-Stoppers: Molecular Weight Control in the Synthesis of Branched Polymers. *Macromol. Rapid Comm.* **2008**, *29*, 1620–1625. (b) de O. Romera, C.; Cardoso, P. B.; Meier, M. A. R.; Sayer, C.; Araújo, P. H. H. Acyclic Triene Metathesis (ATMET) Miniemulsion Polymerization of Linseed Oil Produces Polymer Nanoparticles with Comparable Molecular Weight to That of Bulk Reactions. *Eur. J. Lipid. Sci. Tech.* **2015**, *117*, 235–241.

TOC Graph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