

# Hydrazine-Catalyzed Ring-Opening Metathesis Polymerization of Cyclobutenes

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**ABSTRACT:** Materials formed by the ring-opening metathesis polymerization (ROMP) of cyclic olefins are highly valued for industrial and academic applications but are difficult to prepare free of metal contaminants. Here we describe a highly efficient metal-free ROMP of cyclobutenes using hydrazine catalysis. Reactions can be initiated via *in situ* condensation of a [2.2.2]-bicyclic hydrazine catalyst with an aliphatic or aromatic aldehyde initiator. The polymerizations show living characteristics, achieving excellent control over molecular weight, low dispersity values, and high chain-end fidelity. Additionally, the hydrazine can be used in substoichiometric amounts relative to the aldehyde chain-end while maintaining good control over molecular weight and low dispersity values, indicating that a highly efficient chain transfer mechanism is occurring.

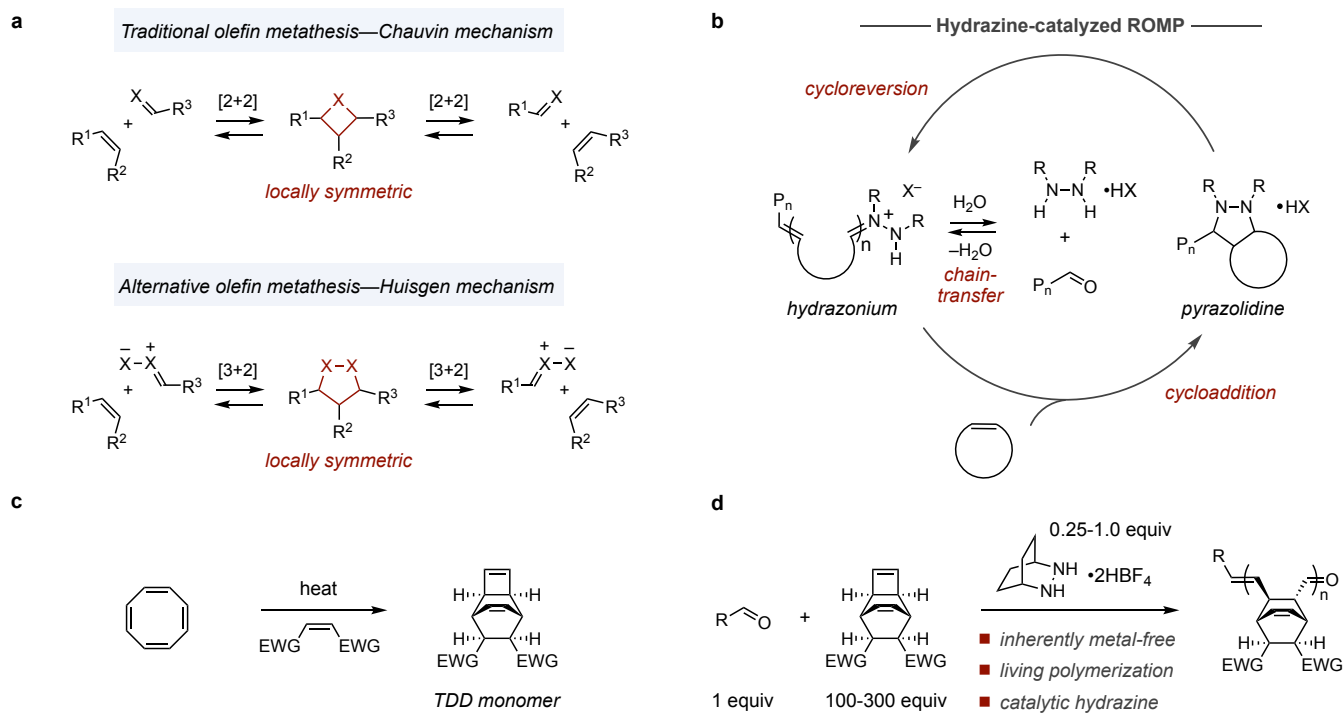
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Ring-opening metathesis polymerization (ROMP) of cyclic olefins enables the synthesis of useful materials that are all but impossible to prepare by other means.<sup>1</sup> For example, a variety of commercial polymers, such as Vestenamer®, Norsorex®, Telene®, Metton®, Zeonex®, and Zeonor®<sup>2</sup> are produced on large scale with ROMP, while more specialized materials are being investigated for applications ranging from drug delivery<sup>3</sup> to photolithography.<sup>4</sup> The chemistry that underwrites these polymerizations is the olefin metathesis reaction in which metal alkylidenes react with olefins, thereby shuffling their alkylidene fragments to generate new olefin products. Among the most important catalytic systems for olefin metathesis are those based on W,<sup>5</sup> Ti,<sup>6</sup> Mo,<sup>7</sup> and Ru.<sup>8</sup> While the value of ROMP has been apparent for many decades, there has been a strong desire to find ROMP catalysts that are based on more earth-abundant, less expensive, and less toxic elements. In this regard, intriguing recent developments in the use of iron catalysts have been reported,<sup>9</sup> although the applicability of these systems is still an open question. On the other hand, there are some polymer applications for which the presence of metal contaminants is unacceptable, such as in the areas of drug delivery, biomedical implants, or microelectronics, which thus necessitates often difficult purification procedures.<sup>10</sup> For this reason and others, it would be of great interest to use abundant main-group elements to achieve olefin ROMP. Unfortunately, designing functionality that effectively mimics the reactivity of metal alkylidenes is not trivial. Creative work by Boydston using

photocatalysis for certain ROMP reactions notwithstanding,<sup>11</sup> the development of a broadly applicable olefin ROMP strategy that uses simple, organic catalysts remains an open challenge.

We have developed a strategy for olefin ROMP that has the potential to fill this gap. Our approach replaces the classic “Chauvin mechanism”<sup>12</sup> for olefin metathesis involving [2+2] cycloadditions/cycloreversions of metal alkylidenes with a [3+2] manifold involving 1,3-dipoles, the so-called “Huisgen mechanism” (Figure 1a).<sup>13</sup> This strategy makes use of readily available hydrazine catalysts that condense with aldehydes to form hydrazonium ions (protonated azomethine imines), which then achieve double bond metathesis via reversible 1,3-dipolar cycloadditions (Figure 1b). We have shown that this alternative metathesis strategy can effect a range of double-bond metathesis reactions including ring-opening and ring-closing carbonyl-olefin metathesis.<sup>14</sup> Recently, we also demonstrated the use of this strategy for the ROMP of cyclopropenes.<sup>15</sup> However, we observed significant monomer decomposition at the temperatures required for efficient polymerization, precluding our assessment of this polymerization as a controlled process. It was thus unclear whether hydrazine-catalyzed ROMP could be used to make larger, more well-defined polymers derived from less strained but more stable monomers. Here, we demonstrate that hydrazine-catalysis can be highly effective for the well-controlled ROMP of cyclobutene monomers.

Cyclobutene ROMP is relatively underexplored in comparison to other strained olefins, such as norbornene, likely due to the paucity of strategies to synthesize cyclobutenes on scale. However, *endo*-tricyclo[4.2.2.0<sup>2,5</sup>]deca-3,9-dienes (TDDs) are a class of thermally stable cyclobutenes that are easily synthesized via the one-pot 6- $\pi$  electrocycloaddition/[4+2]-cycloaddition between 1,3,5,7-cyclooctatetraene and various dienophiles (Figure 1c). This simple reaction provides ready access to TDD monomers suitable for ROMP.<sup>16</sup> As described herein, we have found that hydrazine-catalyzed ROMP of TDD monomers proceeds with high efficiency, resulting in polymers with excellent control over molecular weight, low dispersity values, and high chain-end fidelity (Figure 1d). Importantly, these materials are inherently metal-free, and so require no special purification to remove such impurities.



**Figure 1.** Ring-opening metathesis polymerization (ROMP). a. Chauvin vs Huisgen mechanism for olefin metathesis. b. General design of a hydrazine-catalyzed ROMP reaction. c. Scalable synthesis of TDD monomers. d. Hydrazine-catalyzed TDD ROMP.

**Table 1.** Optimization of hydrazine-catalyzed ROMP of TDD 1.

**3**

**4**

**5**

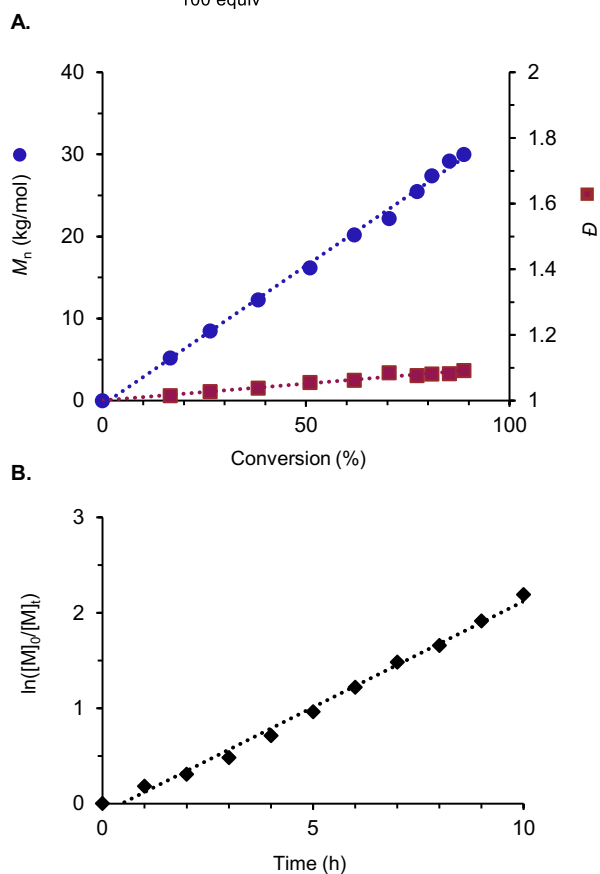
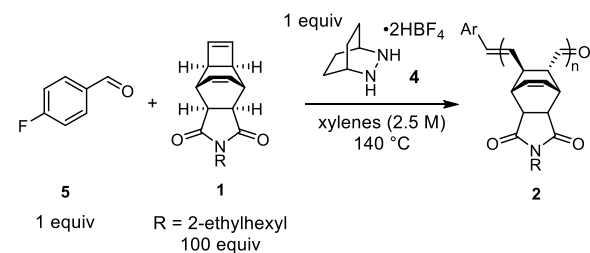
entry <sup>a</sup>	initiator	monomer (equiv)	TFA (equiv)	conv (%)	$M_n^{\text{theo}}$ (kg/mol)	$M_n^{\text{exp}}$ (kg/mol)	$\mathcal{D}$
1	<b>3</b>	100	—	48	15.1	14.8	1.08
2	<b>3</b>	100	1	96	30.2	31.5	1.07
3	<b>4 + 5</b>	100	1	96	30.2	32.3	1.04
4	<b>4 + 5</b>	100	2	96	29.6	33.2	1.04
5 <sup>b</sup>	<b>4 + 5</b>	200	2	98	58.42	62.2	1.07
6 <sup>c</sup>	<b>4 + 5</b>	300	3	94	90.0	90.7	1.09
7	<b>4</b>	100	1	0	—	—	—
8	<b>5</b>	100	1	0	—	—	—

<sup>a</sup> Conditions: aldehyde **5** (1.0 equiv), monomer **1**, and catalyst **4** (1.0 equiv) were heated in a sealed vial under an  $N_2$  atmosphere for 4 h. Conversion determined by  $^1H$  NMR analysis.  $M_n^{\text{exp}}$  and  $\mathcal{D}$  determined on purified products via SEC-MALS. <sup>b</sup> Reaction time = 6 h. <sup>c</sup> Reaction time = 8 h.

For our initial explorations, we selected TDD **1**<sup>17</sup> derived from *N*-2-ethylhexyl succinimide (Table 1), due to the increased solubility and decreased melting point typically seen in monomers containing a 2-ethylhexyl substituent. Our initial attempt entailed the reaction of hydrazonium **3** with TDD **1** (100 equiv) neat at 140 °C. While the resulting polymer **2** exhibited a low dispersity value ( $\mathcal{D}$ ) as well as excellent matching of its number-average molecular weight ( $M_n^{\text{exp}}$ ) with the theoretical value ( $M_n^{\text{theo}}$ ), these conditions led to only modest conversion of monomer to polymer (entry 1). Discoloration of the reaction mixture along with  $^1H$  NMR analysis led us to conclude that the poor performance was due to oxidation of the hydrazine to the corresponding diazene with adventitious oxygen. Because such oxidations are known to be facile with free-base hydrazines, we examined the addition of exogenous acid to help ensure protonation of the hydrazine. Indeed, the addition of one equivalent of TFA resulted in 96% conversion of monomer, producing a polymer with excellent agreement between  $M_n^{\text{exp}}$  and  $M_n^{\text{theo}}$  and a low  $\mathcal{D}$  (entry 2). We also found that the ROMP of **1** proceeds well by mixing hydrazine salt **4** and one equivalent of an aldehyde (e.g. **5**, entry 3). Again, one equivalent of TFA was necessary for high conversion, but increasing TFA loading beyond one equivalent had no additional benefit (entry 4). We were able to target a range of molecular weights by altering the cyclobutene to aldehyde ratio (entries 4-6), as long as we kept the amount of TFA at one equiv per 100 equiv of monomer. In each case, the molecular weight distribution exhibited a low  $\mathcal{D}$ , and the  $M_n^{\text{exp}}$  matched well with  $M_n^{\text{theo}}$ , suggesting that one aldehyde molecule leads to one polymer chain. Importantly, no reaction occurred in the absence of hydrazine **4** or aldehyde **5**, demonstrating that this is not a Brønsted acid-mediated process (entries 7 and 8).

When monitoring the reaction, we observed a linear relationship between  $M_n^{\text{exp}}$  and monomer conversion, which

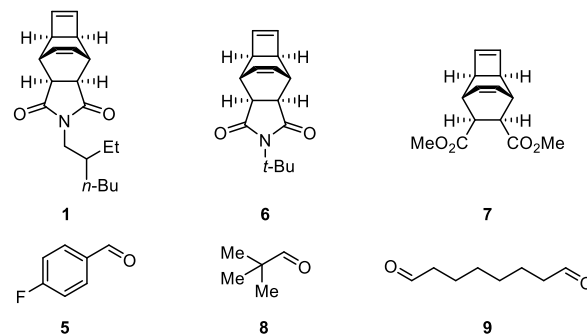
demonstrates that this polymerization proceeds through a chain-growth process (Figure 2a). Furthermore, plotting the natural log of monomer depletion versus time showed a linear relationship corresponding to well-behaved first-order kinetics (Figure 2b). Together, these results support that this reaction is characteristic of a well-controlled polymerization.



**Figure 2.** Kinetic profile of hydrazine ROMP of cyclobutene **1**.

We found that a variety of TDD monomers, including those with imide (**1** and **6**) or ester functionalities (**7**), result in efficient polymerization (Table 2). In addition, polymerization could be initiated from different types of aldehydes, including aromatic (**5**), aliphatic (**8**), and linear aliphatic dialdehydes (**9**). Notably, dialdehyde **9** leads to the productive ROMP of monomer **1**, forming a telechelic polymer.

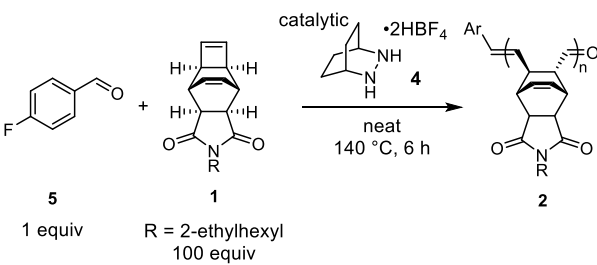
**Table 2.** Scope investigations for hydrazine-catalyzed cyclobutene ROMP.



entry <sup>a</sup>	monomer	aldehyde	TFA (equiv)	conv (%)	$M_n^{\text{theo}}$ (kg/mol)	$M_n^{\text{exp}}$ (kg/mol)	$D$
1	<b>1</b>	<b>5</b>	1	96	30.2	32.3	1.04
2 <sup>b</sup>	<b>1</b>	<b>8</b>	1	97	30.5	31.8	1.05
3 <sup>c</sup>	<b>1</b>	<b>9</b>	2	99	31.2	35.3	1.06
4 <sup>d</sup>	<b>6</b>	<b>5</b>	1	97	25.1	33.9	1.14
5	<b>7</b>	<b>5</b>	2	98	24.5	38.6	1.06

<sup>a</sup> Conditions: aldehyde (1.0 equiv), monomer (100.0 equiv) and catalyst **4** (1.0 equiv) were added to a sealed vial and heated for 4 h under an N<sub>2</sub> atmosphere. Conversion determined via <sup>1</sup>H NMR analysis.  $M_n^{\text{exp}}$  and  $D$  determined on purified products via SEC-MALS. <sup>b</sup> Reaction performed using 1.0 equiv of a preformed initiator via condensation of catalyst **4** with aldehyde **8**. <sup>c</sup> Reaction performed using 1.0 equiv of a preformed initiator via condensation of catalyst **4** with aldehyde **9**. <sup>d</sup> Reaction run in 1,2-dichlorobenzene (1.0 M) for 12 h.

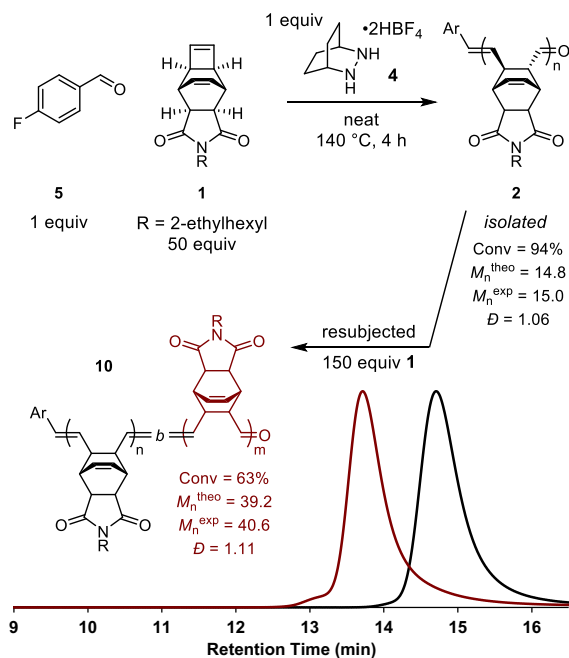
The low  $D$ s observed for these polymerizations suggest that initiation is faster than propagation. Furthermore, because the hydrazine/aldehyde condensation step is reversible, we hypothesized that chain transfer by hydrolysis of the growing chain-end followed by recondensation of the hydrazine with another polymer should enable the use of catalytic loadings of hydrazine **4**. To test this hypothesis, we combined aldehyde **5**, cyclobutene monomer **1**, TFA, and 25 mol% of hydrazine catalyst **4** (Table 3, entry 1). Under these conditions, we observed efficient polymerization to 86% conversion in 6 h, generating a polymer with a narrow  $D$  of 1.09 and good agreement between  $M_n^{\text{exp}}$  and  $M_n^{\text{theo}}$ . Importantly, the addition of 20 equivalents of water resulted in better agreement between  $M_n^{\text{exp}}$  and  $M_n^{\text{theo}}$  (entry 2), further supporting our hypothesis that chain transfer is likely occurring by a hydrolysis/recondensation mechanism. The addition of water did not impact the kinetics of the polymerization.

**Table 3.** Demonstration of catalytic hydrazine.


entry <sup>a</sup>	hydrazine (mol %)	monomer (equiv)	H <sub>2</sub> O (equiv)	conv (%)	M <sub>n</sub> <sup>theo</sup> (kg/mol)	M <sub>n</sub> <sup>exp</sup> (kg/mol)	D
1	25	100	-	86	27.0	38.6	1.09
2	25	100	20	77	24.2	31.6	1.08

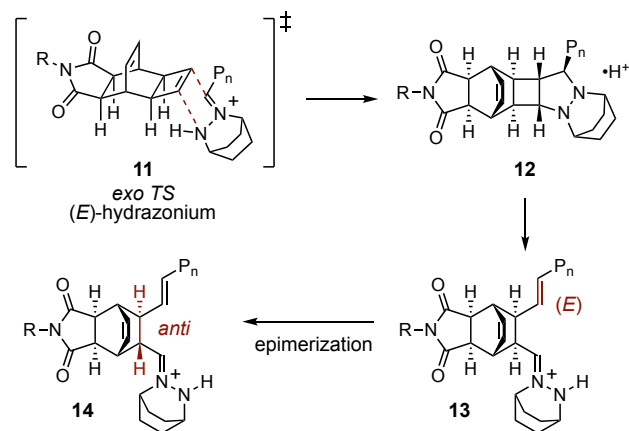
<sup>a</sup> Conditions: aldehyde **5** (1.0 equiv), monomer **1** (100.0 equiv) and catalyst **4** (0.25 equiv) were added to a sealed vial and heated for 6 h under an N<sub>2</sub> atmosphere. Conversion determined via <sup>1</sup>H NMR analysis. M<sub>n</sub><sup>exp</sup> and D determined on purified products via SEC-MALS.

The resulting chain-end provides an opportunity for functionalization and chain extension after polymerization. Subjecting the isolated polymer **2** (M<sub>n</sub><sup>exp</sup> = 15 kg/mol) to the standard conditions and 150 equivalents of additional monomer generated a 41 kg/mol polymer with a D = 1.11 (Figure 3, **10**). Importantly, the polymer underwent a unimodal shift to higher molecular weights with excellent matching between M<sub>n</sub><sup>exp</sup> and M<sub>n</sub><sup>theo</sup> and a low D, indicating efficient chain extension and high chain-end fidelity.

**Figure 3.** Demonstration of polymer chain extension.

Previous studies from our group have shown that the ring-opening carbonyl-olefin metathesis of TDDs<sup>14g</sup> or other cyclic olefins<sup>14a,d</sup> is highly stereoselective, resulting in only

*trans* olefins. This outcome is a result of the preference for cycloaddition of the (*E*)-hydrazonium isomer via an *exo*-transition state, leading to cycloadduct **12**<sup>14</sup> and thence (*E*)-olefins via stereospecific cycloreversion to hydrazonium **13** (Figure 4). In addition, despite the necessarily *syn* configuration of the fused-ring cyclobutene stereocenters of the TDD monomer, the relative orientation of these sites upon ring-opening is exclusively *anti*, resulting from epimerization of the intermediate hydrazonium ion (or the free aldehyde) to the more stable configuration **14**. Consistent with our previous study,<sup>14g</sup> NMR analysis of polymer **2** reveals that the relative orientation of the allylic protons is indeed *anti*.<sup>18</sup>

**Figure 4.** Stereochemical rationale.

In summary, we have developed an efficient hydrazine-catalyzed ROMP of TDD monomers. The reaction occurs via a chain-growth mechanism with living characteristics. The resulting polymers show good agreement between M<sub>n</sub><sup>exp</sup> and M<sub>n</sub><sup>theo</sup>, low Ds, and high chain-end fidelity. Most importantly, the polymers are obtained inherently free of metal contaminants, obviating the need for the purification procedures that are typically needed to remove these impurities. As such, this chemistry should facilitate the use of ROMP in applications that require metal-free materials. Furthermore, while this reaction does not currently allow for the polymerization of common monomers such as norbornenes, we expect that the design of more reactive hydrazine catalysts should enable a broader application of this process.

## AUTHOR INFORMATION

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**Acknowledgments:** Financial support for this work was provided by NIGMS (R35 GM127135). This work made use of the Cornell University NMR Facility, which is supported, in part, by the NSF through MRI award CHE-1531632. This work made use of the Cornell Center for Materials Research Shared Facilities that are supported by the NSF MRSEC program (DMR1719875).

**Supporting Information Available:** Experimental procedures and product characterization data including  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, and HRMS for all new compounds; GPC, TGA, and DSC data for selected polymers.

## References

- (a) Sutthasupa, S.; Shiotsuki, M.; Sanda, F. Recent advances in ring-opening metathesis polymerization, and application to synthesis of functional materials. *Polym. J.* **2010**, *42*, 905–915. (b) Bielawski, C. W.; Grubbs, R. H. in *Controlled and Living Polymerizations* (Eds.: A.H.E. Mller, K. Matyjaszewski), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, **2009**, pp. 297–342. (c) Smith, D.; Pentzer, E. B.; Nguyen, S. T. Bioactive and therapeutic ROMP polymers. *Polymer Revs.* **2007**, *47*, 419–459.
- Mol, J. C. Industrial applications of olefin metathesis. *J. Mol. Catal. A: Chemical* **2004**, *213*, 39–45.
- Johnson, J. A.; Lu, Y. Y.; Burts, A. O.; Xia, Y.; Durrell, A. C.; Tirrell, D. A.; Grubbs, R. H. Drug-loaded, Bivalent-bottle-brush polymers by graft-through ROMP. *Macromolecules* **2010**, *43*, 10326–10335.
- Weitekamp, R. A.; Atwater, H. A.; Grubbs, R. H. Photolithographic olefin metathesis polymerization. *J. Am. Chem. Soc.* **2013**, *135*, 16817–16820.
- (a) Schrock, R. R.; Feldman, J.; Cannizzo, L. F.; Grubbs, R. H. Ring-opening polymerization of norbornene by a living tungsten alkylidene complex. *Macromolecules* **1987**, *20*, 1169–1172. (b) Autenrieth, B.; Jeong, H.; Forrest, W. P.; Axtell, J. C.; Ota, A.; Lehr, T.; Buchmeiser, M. R.; Schrock, R. R. Stereospecific ring-opening metathesis polymerization (ROMP) of *endo*-dicyclopentadiene by molybdenum and tungsten catalysts. *Macromolecules* **2015**, *48*, 2480–2492. (c) Schrock, R. R. Recent advances in high oxidation state Mo and W imido alkylidene chemistry. *Chem. Rev.* **2009**, *109*, 3211–3226.
- (a) Gilliom, L. R.; Grubbs, R. H. Titanacyclobutanes derived from strained, cyclic olefins: the living polymerization of norbornene. *J. Am. Chem. Soc.* **1986**, *108*, 733–742. (b) Risse, W.; Grubbs, R. H. Block and graft copolymers by living ring-opening olefin metathesis polymerization. *J. Mol. Catal.* **1991**, *65*, 211–217. (c) Dono, K.; Huang, J.; Ma, H.; Qian, Y. Ring opening metathesis polymerization of dicyclopentadiene catalyzed by titanium tetrachloride adduct complexes with nitrogen-containing ligands. *J. Appl. Polym. Sci.* **2000**, *77*, 3247–3251.
- Schrock, R. R. Synthesis of stereoregular polymers through ring-opening metathesis polymerization. *Acc. Chem. Res.* **2014**, *47*, 2457–2466
- (a) Vougioukalakis, G. C.; Grubbs, R. H. Ruthenium-based heterocyclic carbene-coordinated olefin metathesis catalysts. *Chem. Rev.* **2010**, *110*, 1746–1787. (b) Ogba, O. M.; Warner, N. C.; O’Leary, D. J.; Grubbs, R. H. Recent advances in ruthenium-based olefin metathesis. *Chem. Soc. Rev.* **2018**, *47*, 4510–4544. (c) Yasir, M.; Liu, P.; Tennie, I. K.; Kilbinger, A. F. M. Catalytic living ring-opening metathesis polymerization with Grubbs’ second- and third-generation catalysts. *Nat. Chem.* **2019**, *11*, 488–494.
- (a) Belov, S.; Mathivathanan, L.; Beazley, M. J.; Martin, W. B.; Bukhryakov, K. V. Stereospecific ring-opening metathesis polymerization of norbornene catalyzed by iron complexes. *Angew. Chem. Int. Ed.* **2021**, *60*, 2934–2938. (b) Takebayashi, S.; Iron, M.A.; Feller, M. *et al.* Iron-catalysed ring-opening metathesis polymerization of olefins and mechanistic studies. *Nat. Catal.* **2022**, *5*, 494–502.

10. (a) Vougioukalakis, G. C. Removing Ruthenium Residues from Olefin Metathesis Reaction Products. *Chem. Eur. J.* **2012**, *18*, 8868–8880. (b) Sui, X.; Wang, C.; Gutekunst, W. R. Sequestration of ruthenium residues via efficient fluorosilyne termination. *Polym. Chem.* **2023**, *14*, 3160–3165.
11. (a) Lu, P.; Kensity, V. K.; Tritt, R. L.; Seidenkranz, D. T.; Boydston, A. J. Metal-free ring-opening metathesis polymerization: from concept to creation. *Acc. Chem. Res.* **2020**, *53*, 2325–2335. (b) Ogawa, K. A.; Goetz, A. E.; Boydston, A. J. Metal-Free Ring-Opening Metathesis Polymerization. *J. Am. Chem. Soc.* **2015**, *137*, 1400–1403.
12. (a) Jean-Louis Herisson, P.; Chauvin, Y. Catalyse de transformation des oléfines par les complexes du tungstène. II. Télomérisation des oléfines cycliques en présence d'oléfinés acycliques. *Makromol. Chem.* **1971**, *141*, 161–176. (b) Katz, T. J.; McGinnis, J. The Mechanism of the Olefin Metathesis Reaction. *J. Am. Chem. Soc.* **1975**, *97*, 1592–1594. (c) Grubbs, R. H.; Burk, P. L.; Carr, D. D. Consideration of the Mechanism of the Olefin Metathesis Reaction. *J. Am. Chem. Soc.* **1975**, *97*, 3265–3267.
13. Huisgen, R. Kinetics and Mechanism of 1,3-Dipolar Cycloadditions. *Angew. Chem. Int. Ed.* **1963**, *2*, 633–696.
14. (a) Griffith, A. K.; Vanos, C. M.; Lambert, T. H. Organocatalytic carbonyl-olefin metathesis. *J. Am. Chem. Soc.* **2012**, *134*, 18581–18584. (b) Lambert, T. H. Development of a hydrazine-catalyzed carbonyl-olefin metathesis reaction. *Synlett* **2019**, *30*, 1954–1965. (c) Zhang, Y.; Jermaks, J.; MacMillan, S. N.; Lambert, T. H. Synthesis of 2*H*-Chromenes via Hydrazine-Catalyzed Ring-Closing Carbonyl-Olefin Metathesis. *ACS Catal.* **2019**, *9*, 9259–9264. (d) Jermaks, J.; Quach, P.; Seibel, Z. M.; Pomerole, J.; Lambert, T. H. Ring-Opening Carbonyl-Olefin Metathesis of Norbornenes. *Chem. Sci.* **2020**, *11*, 7884–7895. (e) Zhang, Y.; Sim, J. H.; MacMillan, S. N.; Lambert, T. H. Synthesis of 1,2-Dihydroquinolines via Hydrazine-Catalysed Ring-Closing Carbonyl-Olefin Metathesis. *Org. Lett.* **2020**, *22*, 6026–6030. (f) Cho, E. K.; Quach, K. P.; Zhang, Y.; Sim, J. H.; Lambert, T. H. Polycyclic Heteroaromatics via Hydrazine-Catalyzed Ring-Closing Carbonyl-Olefin Metathesis. *Chem. Sci.* **2022**, *13*, 2418–2422. (g) Holl, M. G.; Lambert, T. H. Ring-Opening Carbonyl-Olefin Metathesis of Cyclobutenes. *ACS Catal.* **2022**, *12*, 4813–4817.
15. Quach, P. K.; Hsu, J. H.; Keresztes, I.; Fors, B. P.; Lambert, T. H. Metal-Free Ring-Opening Metathesis Polymerization with Hydrazonium Initiators. *Angew. Chem. Int. Ed.* **2022**, *134*, e202203344.
16. For examples of the metal-catalyzed ROMP of TDD monomers see: (a) Asano, Y.; Aoi, H.; Ohtani, H.; Matsuoka, S.; Suzuki, M. Ring-Opening Metathesis Polymerization of Ester-Functionalized Endo-Tricyclo[4.2.2.0<sub>2,5</sub>]Deca-3,9-Dienes and Thermal Properties of the Resulting Polymers. *Polym. Chem.* **2023**, *14*, 1736–1742. (b) Edwards, J. H.; Feast, W. J.; Bott, D. C. New Routes to Conjugated Polymers: 1. A Two Step Route to Polyacetylene. *Polymer* **1984**, *25*, 395–398. (c) Stelzer, F.; Brunthaler, J. K.; Leising, G.; Hummel, K. Synthesis and Polymerization of Tricyclo[4.2.2.0<sub>2,5</sub>]Deca-3,7,9-Triene and Tricyclo[4.2.2.0<sub>2,5</sub>]Deca-3,9-Diene-7,8-Dicarboxylic Anhydride. *J. Mol. Catal.* **1986**, *36*, 135–143. (d) Charvet, R.; Novak, B. M. New Functional Monomers for Well-Controlled ROMP Polymerizations. *Macromolecules* **2001**, *34*, 7680–7685. (e) Song, J.-A.; Park, B.; Kim, S.; Kang, C.; Lee, D.; Baik, M.-H.; Grubbs, R. H.; Choi, T.-L. Living Polymerization Caught in the Act: Direct Observation of an Arrested Intermediate in Metathesis Polymerization. *J. Am. Chem. Soc.* **2019**, *141*, 10039–10047. (f) Kim, K. O.; Choi, T.-L. Synthesis of Dendronized Polymers via Macromonomer Approach by Living ROMP and Their Characterization: From Rod-Like Homopolymers to Block and Gradient Copolymers. *Macromolecules* **2013**, *46*, 5905–5914. (g) Kim, K. O.; Shin, S.; Kim, J.; Choi, T.-L. Living Polymerization of Monomers Containing Endo-Tricyclo[4.2.2.0<sub>2,5</sub>]Deca-3,9-Diene Using Second Generation Grubbs and Hoveyda–Grubbs Catalysts: Approach to Synthesis of Well-Defined Star Polymers. *Macromolecules* **2014**, *47*, 1351–1359. (h) Dutertre, F.; Bang, K.-T.; Vereroudakis, E.; Loppinet, B.; Yang, S.; Kang, S.-Y.; Fytas, G.; Choi, T.-L. Conformation of Tunable Nanocylinders: Up to Sixth-Generation Dendronized Polymers via Graft-Through Approach by ROMP. *Macromolecules* **2019**, *52*, 3342–3350.

17. Yoon, K.-Y.; Shin, S.; Kim, Y.-J.; Kim, I.; Lee, E.; Choi, T.-L. One-Pot Preparation of 3D Nano- and Microaggregates via In Situ Nanoparticlization of Polyacetylene Diblock Copolymers Produced by ROMP. *Macromol. Rapid Commun.* **2015**, *36*, 1069–1074.
18. Although our previous studies strongly indicate the formation of exclusively (*E*)-olefins, we have been unable to definitively determine olefin geometry and polymer tacticity due to a lack of reference compounds.

### TOC graphic

