

# Stereocontrolled Acyclic Diene Metathesis Polymerization

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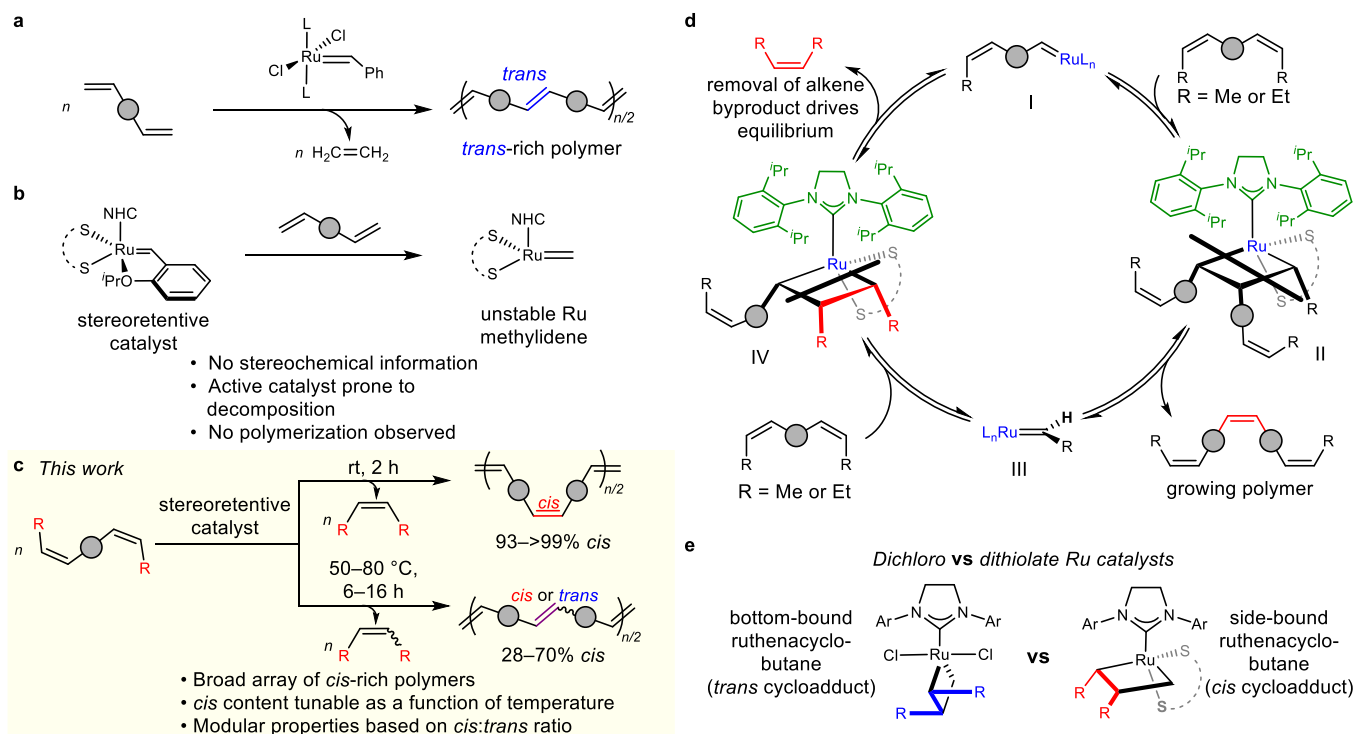
## Abstract

The *cis/trans* geometry of olefins is known to dramatically influence the thermal and mechanical properties of polyalkenamers. Yet, polymerization methods that allow the practitioner to efficiently control this parameter are scarce. Herein, we report the development of a stereoretentive acyclic diene metathesis (ADMET) polymerization that capitalizes on the unique reactivity of dithiolate Ru carbenes combined with *cis* monomers. These Ru catalysts exhibit exquisite retention of the *cis* geometry and tolerate many polar functional groups, enabling the synthesis of all-*cis* polyesters, polycarbonates, polyethers, and polysulfites. Additionally, the stereoretentive ADMET is characterized by low catalyst loadings and tolerance toward *trans* impurities in the monomer batch, which should lend to ready implementation at large-scale. Remarkably, modulation of the reaction conditions including temperature and reaction time leads to an erosion of stereoretention, thereby permitting a stereocontrolled synthesis of polyalkenamers with predictable *cis:trans* ratios. The impact of the *cis:trans* alkene content within the polymer backbone on the thermal properties was clearly demonstrated through differential scanning calorimetry and thermogravimetric analysis. Stereocontrolled ADMET provides a unique synthetic approach toward materials with precise structures and tailored properties.

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Perhaps best exemplified by the numerous modifications of the venerable Wittig and Horner–Wadsworth–Emmons reactions, controlling the *cis* or *trans* (*Z* or *E*) geometry of alkenes in organic molecules has motivated the development of a myriad of synthetic methods to access either isomer selectively <sup>1</sup>. Indeed, the configuration of alkenes dramatically impacts the shape, properties, and reactivity of compounds. Interestingly, despite the importance of this structural parameter on the thermal and mechanical, properties of polymeric materials <sup>2</sup>, few polymerizations allow the practitioner to precisely dictate the *cis:trans* ratio within macromolecules and these processes are limited to a narrow scope of monomers <sup>3–6</sup>. Among the classic examples illustrating the influence of alkene geometry over material properties, *trans*-polyisoprene (*gutta percha*) is a hard, brittle semi-crystalline material, once used in the manufacturing of golf balls <sup>7</sup>, while the more amorphous *cis*-polyisoprene is an elastic material found in latex gloves <sup>8,9</sup>.

Ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET) polymerization are among the most powerful methods to access unsaturated polymers, but typically afford *cis/trans* mixtures or *trans*-rich linkages dictated by the thermodynamic stability of the products <sup>10</sup>. The recent introduction of stereoselective Mo, W, and Ru catalysts has paved the way for kinetic control of the olefin metathesis process, overcoming the product preference for *trans* alkenes <sup>11–16</sup>. While careful catalyst design has afforded impressive *cis* selectivity in a variety of transformations based on olefin metathesis, only a limited number of polymers have been synthesized through stereoselective processes, all through ROMP. For example, dithiolate Ru carbenes uniquely preserve the configuration of the starting olefin throughout the metathesis process <sup>17–19</sup>. Hoveyda and coworkers demonstrated that ROMP of norbornene or cyclooctadiene with this family of stereoretentive catalysts leads to exquisite *cis* selectivity along the polymer backbone <sup>12</sup>. Choi and coworkers expanded the scope of norbornene-type monomers for

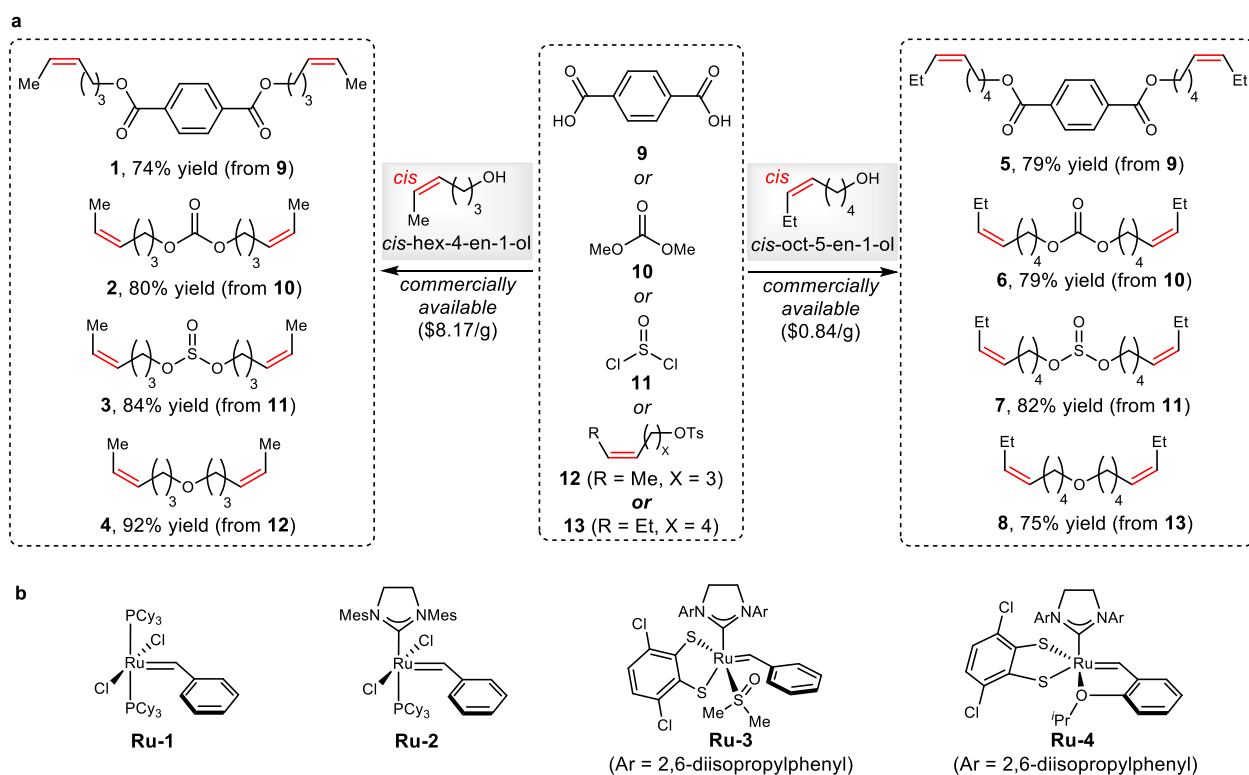


**Fig. 1. Design of stereocontrolled ADMET.** **a.** Typical ADMET polymerizations favor high *trans* alkene content. **b.** Dithiolate Ru catalysts lead to highly unstable Ru methylidenes with terminal diene monomers. **c.** Design of a stereocontrolled ADMET modulated by the reaction temperature. **d.** Proposed stereoretentive ADMET cycle (the initial reaction between the Ru precatalyst and the monomer was omitted for clarity). **e.** Bottom-bound olefin approach with dichloro Ru catalysts compared to side-bound approach with dithiolate Ru catalysts.

stereoretentive ROMP<sup>15</sup>, and reported that the shear stability of the resulting all-*cis* polymers was greatly enhanced relative to that of their all-*trans* counterparts. Recently, we harnessed the reactivity of this family of catalysts in combination with [2.2]paracyclophane diene monomers to synthesize all-*cis* poly(*p*-phenylene vinylene)s (PPVs) with living characteristics and unusually high molar masses<sup>20, 21</sup>. While these examples of stereoretentive ROMP afforded extremely precise polymeric structures (narrow molar mass distributions, perfect *cis* stereoselectivity, etc.), the ROMP process typically requires highly strained monomers thereby narrowing the scope of accessible polymers. Further, these scarce examples only afforded strict *cis* selectivity. Herein, we report the implementation of stereoretentive olefin metathesis into the ADMET process as a versatile method to access all-*cis* polyalkenamers. Additionally, careful optimization of the reaction conditions provided unprecedented stereocontrol over the proportion of *cis* and *trans* alkenes throughout the polymer backbone. Several families of alkene-containing polymers were synthesized with predictable *cis:trans* ratios from 20:80 to >99:1, providing a valuable strategy to tune the thermal properties of several types of polymers.

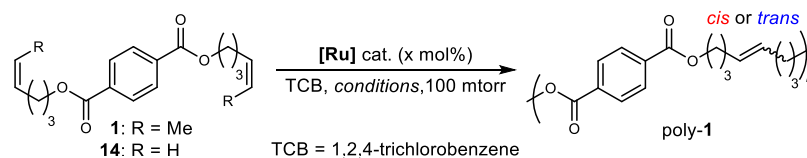
One of the major advantages of ADMET over other polymerizations based on olefin metathesis is the simplicity and ubiquity of the monomer structure characterized by the presence of two terminal alkenes. These  $\alpha,\omega$ -dienes are polymerized following a step-growth mechanism, where removal of ethylene gas is the thermodynamic driving force (Fig. 1a)<sup>22, 23</sup>. Pioneered by Wagener and coworkers<sup>24</sup>, ADMET polymerization has been employed to synthesize an impressive variety of polymers including polyethylene with precise alkyl branching<sup>25</sup>, ionic polymers<sup>26</sup>, and conjugated polymers, albeit with high *trans* alkene content<sup>27</sup>. Developing a stereoselective ADMET would therefore open the door to a cornucopia of stereodefined polymers for a variety of applications, but several pitfalls were identified at the outset of this work. Since ADMET polymerization relies on iterative couplings between terminal dienes that are neither *cis* nor *trans* (Fig. 1b), typical ADMET monomers preclude the stereoretentive mechanism of dithiolate Ru catalysts. Additionally, the Ru methylidene intermediate generated upon reaction of the dithiolate carbene with a terminal alkene is known to readily decompose, likely through a 1,2-shift of the anionic sulfide ligand<sup>14</sup>. Hoveyda and coworkers reported an elegant strategy to circumvent the premature deactivation of the catalyst in

the cross metathesis of terminal alkenes through *in situ* methylene capping with gaseous *cis*-but-2-ene<sup>28</sup>. This approach, however, is not compatible with ADMET, which requires constant removal of volatile alkene by-products to drive the step-growth process. We envisioned that synthesizing capped monomers with pre-installed *cis* geometry would obviate both catalyst decomposition and the need for *cis*-but-2-ene, as well as allow the desired stereoretention (Fig. 1c). While non-terminal dienes have previously been polymerized using ADMET<sup>29</sup>, the retention of alkene configuration of the monomer was not observed with Grubbs' second generation catalyst. The proposed mechanistic cycle of a stereoretentive ADMET is outlined in Fig. 1d. The [2+2] cycloaddition of carbene intermediate **I** with a capped monomer or a growing polymer would afford ruthenacyclobutane **II** and subsequent cycloreversion would lead to the formation of stabilized Ru ethylidene (R = Me) or propylidene (R = Et) intermediate **III**. In contrast to the bottom-bound approach typically observed with dichloro Ru carbenes, the dithiolate ligand is known to enforce a side-bound approach of the monomer with the alkene substituents pointing away from the bulky aryl groups of the NHC ligand (Fig. 1e)<sup>18</sup>. Following cycloreversion, Ru-ethylidene/propylidene **III** would further react with another capped alkene (from a monomer or a growing oligomer) to form ruthenacycle **IV**, whose cycloreversion would regenerate a reactive Ru carbene and expel volatile *cis*-but-2-ene (R = Me) or *cis*-hex-3-ene (R = Et). Removal of either byproduct would drive all equilibria toward a productive cycle.



**Fig. 2. Monomers and Ru catalysts.** **a.** Readily accessible methyl- and ethyl-capped *cis,cis*-monomers from commercially available reagents. **b.** Catalysts screened in stereocontrolled ADMET.

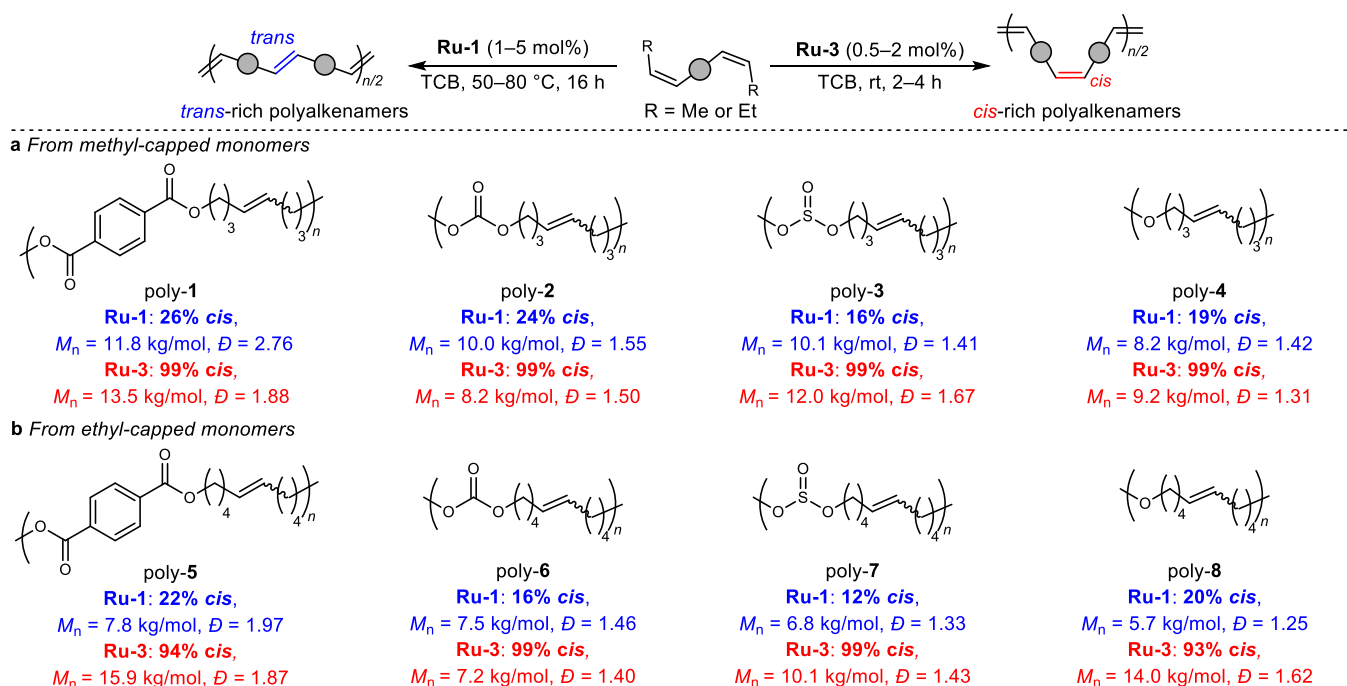
Capitalizing on the inexpensive and readily available *cis*-hex-4-en-1-ol and *cis*-oct-5-en-1-ol<sup>30</sup>, a variety of monomers were synthesized in one or two steps in high yields (Fig. 2a and Supplementary Information)<sup>31-34</sup>. These two groups of monomers (**1-4** and **5-8**) were selected to interrogate the tolerance of dithiolate catalysts to polar monomers containing Lewis basic functional groups, as well as the effect of increasing the size of the capping group (Et vs Me) on the polymerization. As a benchmark of *cis/trans* selectivity, terminal diene **14** was polymerized under standard ADMET conditions using **Ru-1** (Fig. 2b) in 1,2,4-trichlorobenzene at 50 °C under high vacuum (~100 mtorr) for 16 h. The resulting polymer, poly-**1** ( $M_n = 13.1$  kg/mol,  $D = 2.61$ ), was isolated with 23% *cis* content as established by <sup>1</sup>H NMR (Table 1, entry 1 and Supplementary Fig. 4). As expected, the polymerization of **14** with dithiolate

**Table 1.** Optimization of Stereoretentive ADMET with Dithiolate Ru Catalysts

entry	monomer	[Ru] (mol%)	Temperature (°C)	Time (h)	Conversion (%) <sup>a</sup>	$M_n$ (kg/mol) <sup>b</sup>	$\bar{D}$ <sup>c</sup>	<i>cis</i> (%) <sup>d</sup>
1	14	Ru-1 (5)	50	16	100	13.1	2.61	23
2	14	Ru-3 (5)	50	16	—	—	—	—
3	14	Ru-4 (5)	50	16	—	—	—	—
4	1	Ru-1 (5)	50	16	100	4.3	1.50	29
5	1	Ru-1 (5)	80	16	100	11.8	2.76	26
6	1	Ru-2 (5)	50	16	100	13.4	2.00	21
7	1	Ru-3 (5)	50	16	100	13.1	2.13	54
8	1	Ru-3 (5)	50	4	100	12.6	1.74	62
9	1	Ru-3 (5)	50	2	100	11.8	1.81	73
10	1	Ru-3 (0.5)	23	2	100	13.5	1.88	>99
11	1	Ru-4 (0.5)	23	2	100	13.0	1.75	>99
12	1 (95% <i>cis</i> )	Ru-3 (0.5)	23	2	100	7.7	1.63	>99

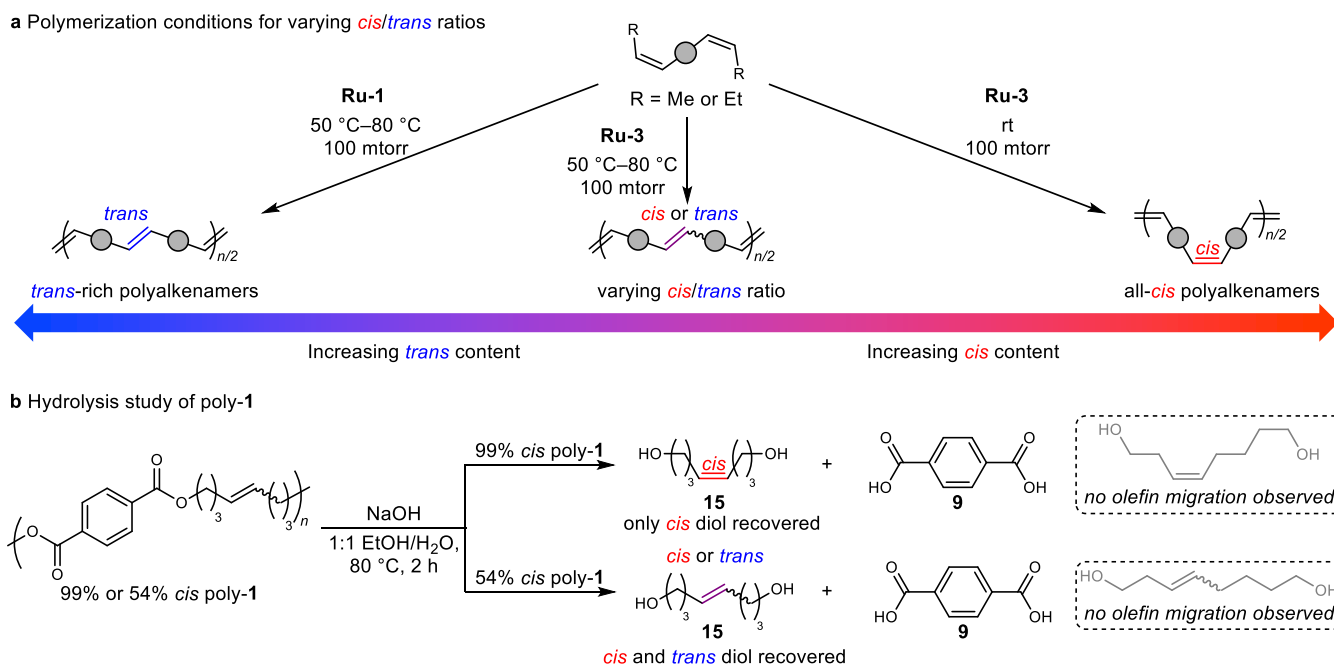
<sup>a</sup>Conversion of monomer determined by <sup>1</sup>H NMR analysis of the crude mixture. <sup>b</sup> $M_n$  determined through size exclusion chromatography (SEC) in THF against polystyrene standards (RI detection). <sup>c</sup> $M_w/M_n$ . <sup>d</sup>Calculated using <sup>1</sup>H NMR analysis.

catalysts **Ru-3** and **Ru-4** (Fig. 2b) did not afford any polymers (Table 1, entries 2 and 3). Switching to methyl-capped monomer **1** did not result in any increase of *cis* content with **Ru-1** (Table 1, entries 4 and 5) nor with **Ru-2** (Table 1, entry 6). Of note, increasing the temperature with **Ru-1** allowed the production of poly-1 with higher molar masses, but did not significantly affect the *cis* content. By contrast, methyl-capped monomer **1** in combination with **Ru-3** afforded poly-1 with 54% *cis* content (Table 1, entry 7). Interestingly, when the reaction time was decreased to 4 h or 2 h, the molar masses of poly-1 did not significantly decrease ( $M_n = 12.6$  kg/mol and 11.8 kg/mol, respectively), but the *cis* selectivity improved to 62% and 73% (Table 1, entries 8 and 9). To our delight, running the polymerization at room temperature to further increase kinetic control over the polymerization and at lower catalyst loading (0.5 mol%) afforded perfect *cis* selectivity ( $M_n = 13.5$  kg/mol,  $\bar{D} = 1.88$ , Table 1, entry 10). The low catalyst loading permitted by the high reactivity of **Ru-3** is promising for large-scale applications. Notably, **Ru-4** furnished an all-*cis* polymer of similar size ( $M_n = 13.0$  kg/mol,  $\bar{D} = 1.75$ ) when subjected to the same conditions (Table 1, entry 11). Finally, the tolerance to *trans* impurities in the monomer batch was probed. Indeed, *trans* alkenes are known to react slower with stereoretentive dithiolate catalysts than the *cis* congeners due to the steric clash between one substituent of the ruthenacycle and the NHC ligand,<sup>19</sup> which would potentially allow the use of less expensive, stereochemically impure



**Fig. 3. Polymer scope of stereocontrolled ADMET.** a. Polymers from methyl-capped monomers (poly-1–poly-4). b. Polymers from ethyl-capped monomers (poly-5–poly-8).

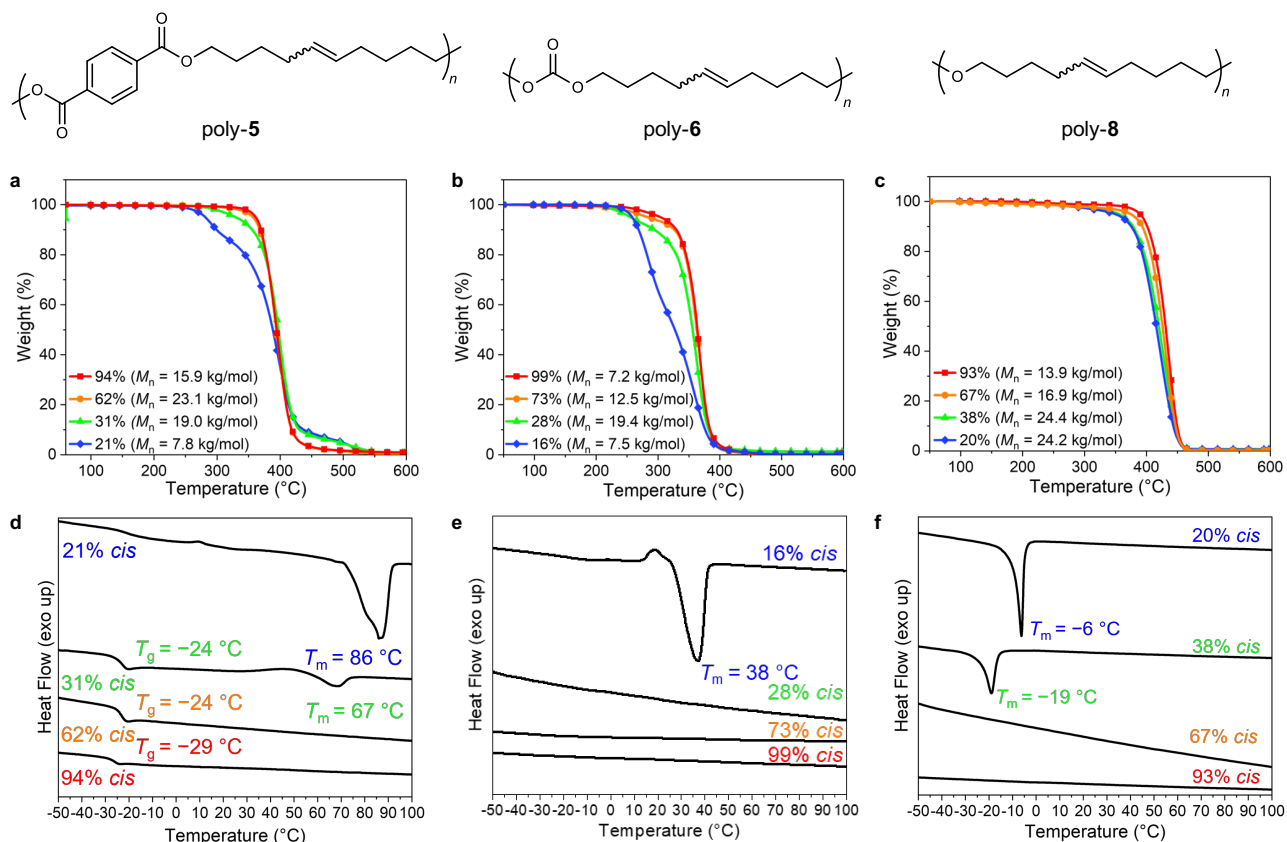
monomers. Impressively, polymerization of 95% *cis* **1** led to poly-1 with >99% *cis* content and a slightly diminished molar mass ( $M_n = 7.7 \text{ kg/mol}$ ,  $\mathcal{D} = 1.63$ , Table 1, entry 12). This finding should open the door to the synthesis of a variety of monomers through diverse synthetic routes (e.g., hydrogenation of alkynes with Lindlar's catalyst, Wittig olefination, etc.) without the need for perfect diastereoselectivities.



**Fig. 4. Selectivity in stereocontrolled ADMET.** a. Preparation of polyalkenamers with different *cis/trans* content via ADMET using different reaction conditions. b. Hydrolysis of poly-1 (99% *cis* from Table 1, entry 10 and 54% *cis* from Table 1, entry 7) indicates that olefin migration does not take place with **Ru-3**.

Under optimized conditions, all-*cis* poly-2, poly-3, and poly-4 were also obtained from monomers 2, 3, and 4, respectively, displaying the excellent functional group tolerance of stereoretentive ADMET (Fig. 3a). These ADMET conditions are also milder compared to traditional ADMET processes that are generally conducted at higher temperatures for several hours or even days. After determining suitable conditions for the polymerization of methyl-capped monomers, the ethyl-capped monomers were found to only require moderate increases in reaction time (4 h instead of 2 h) and catalyst loading (1–2 mol% instead of 0.5 mol%) to access similarly sized all-*cis* polymers, poly-5–8 (Fig. 3b) (see Supplementary Information). The ability to use different capping groups with similarly high *cis* selectivity should broaden the scope of monomers for the stereoretentive ADMET. Importantly, several synthesized polymers are structurally analogous to industrially-relevant polymers such as poly(ethylene terephthalate) (PET) for poly-1 and poly-5.

The lower *cis*-selectivity observed at 50 °C with **Ru-3** prompted an investigation of temperature modulation as a means to dictate the content of *cis* and *trans* olefins in polyalkenamers. Decreasing amounts of *cis* olefins (from ~70% to ~30%) were obtained when the ADMET polymerization was performed at 50 °C or 80 °C for increased reaction times (6–16 h) (Fig. 4a and Supplementary Tables 1–8). Olefin isomerization has been reported in ADMET processes with Ru metathesis catalysts containing an NHC ligand such as **Ru-2**. Several mechanisms have been postulated for this isomerization, including a Ru–H species and metal allyl complexes derived from decomposed catalyst<sup>35–37</sup>. Notably, these pathways generally lead to concomitant alkene migration, which was indeed observed using **Ru-2** (Supplementary Fig. 5). However, hydrolysis of poly-1 revealed that olefin migration does not take place with stereoretentive **Ru-3**, neither at room temperature, nor at higher temperatures (Fig. 4b). Hydrolytic degradation of *cis*-rich poly-1, poly-2, poly-3, poly-5, poly-6, and poly-7 under basic conditions cleanly delivered the *cis* isomer of oct-4-ene-1,8-diol (**15**) or dec-5-ene-1,10-diol (**S8**). While the exact mechanism of isomerization remains unclear, modulation of the *cis/trans* content without olefin migration was successfully performed with all monomers thereby



**Fig. 5. Relationship between polymer stereochemistry and thermal properties.** TGA thermograms of poly-5 (a), poly-6 (b), and poly-8 (c). DSC thermograms of poly-5 (d), poly-6 (e), and poly-8 (f).



providing access to a library of polyalkenamers with tailored backbone geometries from single building blocks. Importantly, the lack of olefin migration engenders more reproducible polymer properties<sup>38</sup>.

The thermal properties of the synthesized polyalkenamers with varying *cis/trans* ratios were analyzed via thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Fig. 5 for selected polymers and supporting information). While the range of molar masses (~7–25 kg/mol) resulting from the ADMET step-growth process renders the deconvolution of the impact of olefin stereochemistry challenging in some cases, comparison of polyalkenamers of similar sizes revealed enhanced stability with an increase in *cis* content (Fig. 5a–c). For poly-5 with 94% *cis* double bonds ( $M_n = 15.9$  kg/mol), a decomposition temperature ( $T_d$ ) recorded at 5% mass loss was observed at 365 °C compared to 360 °C for 62% *cis* ( $M_n = 23.1$  kg/mol) and 355 °C for 31% *cis* ( $M_n = 19.0$  kg/mol) (Fig. 5a). The  $T_d$  of poly-6 decreased by 46 °C when going from 99% *cis* to 16% *cis* for almost identical molar masses (Fig. 5b). Poly-8 exhibited a  $T_d$  of 390 °C for the 93% *cis* polymer ( $M_n = 13.9$  kg/mol) as opposed to 374 °C for a 67% *cis* polymer ( $M_n = 16.9$  kg/mol, Fig. 5c). Analogously, all other synthesized polyalkenamers had thermal stabilities that varied with *cis* content (Supplementary Tables 9–16). DSC revealed a clear influence of *cis*-alkene content on thermal transitions as depicted in the thermograms in Fig. 5d–f, which is in line with reports by Buchard<sup>39</sup> and Dove and Becker<sup>3,40</sup>. In addition to small variations of glass transition temperatures ( $T_g$ ), striking differences in crystalline behavior were observed. For example, *cis*-rich poly-5, poly-6, and poly-8 appeared amorphous via DSC, while the same polyalkenamers with a majority of *trans* olefins exhibited both a melting ( $T_m$ ) and a crystallization temperature ( $T_c$ ). Poly-5 with only 31% and 22% *cis* olefins displayed a  $T_m$  at 67 and 86 °C, respectively (Fig. 5d). The only sample of poly-6 to present a  $T_m$  (38 °C) contained only 16% *cis* linkages (Fig. 5e). Meanwhile, all other samples of poly-6 had no observable thermal transitions. Poly-8 showcased the most diverse thermal profile as a function of alkene stereochemistry. No thermal transitions could be detected with the 93% and 67% *cis* forms, but  $T_m$ 's and  $T_c$ 's were measured for samples with decreased *cis* content (38% and 20%) (Fig. 5f). DSC analysis of the two *trans*-rich poly-8 revealed sharp  $T_m$ 's at –6 °C (20% *cis*) and –19 °C (38% *cis*). Other synthesized polyalkenamers such as poly-7 displayed amorphous characteristics regardless of *cis* content with no thermal transitions detected in the DSC (Supplementary Fig. 22). While the nature of the polar groups and the number of methylenes in the repeating unit clearly impacts the phase transitions of the polyalkenamers, controlling the geometry of alkenes throughout the backbone provides an additional handle to tune the thermal properties of a variety of polymers.

Unprecedented control over the molecular structure and physical properties of polyalkenamers—including polyesters, polycarbonates, polysulfites, and polyethers—has been achieved through stereocontrolled ADMET. This method capitalizes on methyl- or ethyl-capped diene monomers to impart both the stereochemical information and catalyst stability critical to the polymerization process. Over 99% *cis*-selectivity was achieved for a variety of polymers including unsaturated polyesters, polycarbonates, polysulfites, and polyethers, which is a testament to the versatility of this method. The high reactivity of stereoselective dithiolate Ru catalysts towards *cis* monomers led to low catalyst loading (0.5 mol%), rapid reaction at room temperature (2–4 h), and tolerance toward *trans* monomer impurities, which are all attractive features for large-scale implementation. Stereoretention during the polymerization process was found to be sensitive to the reaction conditions, which provided a functional handle to modulate the ratio of *cis:trans* alkene units within the polymer backbone. This unique stereocontrol was harnessed to produce a variety of polyalkenamers with predictable *cis:trans* ratios from 20:80 to >99:1 and to study the influence of alkene geometry over the thermal properties of the macromolecules. Increased thermal stability was generally correlated to increased *cis* olefin content and thermal transitions such as  $T_g$ ,  $T_m$ , and  $T_c$  were greatly affected by the stereochemistry of the alkenes in the backbone. Of note, structural analogs of PET, a high commodity polyester, were prepared and exhibited tunable phase transition temperatures and efficient depolymerization via hydrolysis. This process provides a practical and efficient handle to control material properties for a large variety of olefin-containing polymers, which aligns well with the polymer field's pursuit of precise macromolecular structures for soft materials with designable properties and functionality<sup>41</sup>.

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#### **Author contributions**

T.-W.H., S.J.K., and A.P.F.T. performed research. All authors designed research and analyzed data. Q.M., S.J.K, and T.-W.H. wrote the paper and Supplementary Information. T.-W.H. and S.J.K. contributed equally to this work.

#### **Competing interests**

Authors declare that they have no competing interests.