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Isomer-driven polymerization, depolymerization, and reconstruction†

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We report that differences in ring strain enthalpy between *cis* and *trans* isomers of sila-cycloheptene provide a driving force for both polymerization and depolymerization *via* olefin metathesis. A need for new methods to reintroduce the low-strain isomer into the plastic economy inspired the development of a polymerization based on ring-opening/cross-metathesis step polymerization, which afforded perfect sequence control for an alternating copolymer. The chemical principles are a platform for achieving both efficient polymerization and depolymerization with high mass recovery in functional polymers.

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Introduction

Chemical solutions to end-of-life management of post-consumer plastic waste are an emerging and urgent area of research. Currently, less than 10% of plastic waste is mechanically recycled, instead ending in the landfill or incinerator (a linear plastic economy). In contrast to mechanical recycling, which can erode material properties due to changes in molecular weight characteristics arising from mechanical degradation, chemical recycling to monomer transforms plastic waste into feedstocks indistinguishable from petroleum-derived monomer, which can then reform pristine plastics (a more circular plastic economy). Approaches to chemical recycling to monomer include comonomers or end groups in poly(methyl methacrylate) (PMMA) that trigger β -scission, $^{3-9}$ transesterification of poly(ethylene terephthalate), $^{10-13}$ self-immolative polymers, $^{14-16}$ and more. 17

Olefin metathesis-based approaches to polymer deconstruction have been recently reviewed. ¹⁸ An attractive feature of this approach is that the polymer is stable until addition of the metathesis catalyst. Deconstruction can be a depolymerization process that returns the original starting monomer or a reaction yielding a different chemical building block. ¹⁹ Polymerization thermodynamics are critical: ^{20–23} if ringopening metathesis polymerization (ROMP) is highly exother-

mic due to significant strain release, the reverse reaction (ringclosing metathesis (RCM) depolymerization) is challenging to

effect. Chemical recycling to monomer by olefin metathesis was until recently limited to monomers with low-to-moderate

ring strain,22 while polymeric materials derived from higher

strain monomers like norbornene and cis-cyclooctene²⁴ were

not depolymerizable to monomer. Recently, structural modifi-

cations to cis-cyclooctene enabled chemical recycling to

monomer by modulating ring-strain enthalpy (RSE) and polymerization–depolymerization thermodynamics. ^{21,25}

Exploiting the differences in RSE between cis and trans geo-

Herein, we demonstrate isomer-driven polymerization, depolymerization, and reconstruction of sila-cycloheptene by multiple olefin metathesis mechanisms. We recently reported the geometrically-selective synthesis of both the *cis* and *trans* isomers of sila-cycloheptene 1 in which *trans*-1 was high strain (*ca.* 10 kcal mol⁻¹) and readily underwent ROMP.²⁷ P1 is a novel example of a hybrid polymer incorporating both C and Si into the backbone. We showed *via* single molecule force spectroscopy that the Si incorporation into P1 reduced single chain elasticity relative to all-carbon polymer backbones,

additional chemical methods to reintroduce the low-strain

isomer into the plastic economy.

metric isomers of the same cycloalkene has potential to broaden the scope of polymeric materials amenable to olefin metathesis polymerization–depolymerization, as shown by Wang *et al.* in a "closed-loop" photoisomerization-ROMP-RCM cycle of fused bicyclic cyclooctene monomers. ²⁶ However, olefin photoisomerization has limitations: high-energy light is typically needed (*e.g.*, 254 nm) and the amount of *cis* isomer that can be converted to *trans* isomer is fundamentally limited by the photostationary *trans*: *cis* ratio. This means that not all the chemical matter recovered by depolymerization to the *cis*-isomer can reenter the cycle, highlighting the need for

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resulting in a softer, less stiff polymer strand, which was hypothesized to arise from force-induced changes in geometry and conformation at Si.²⁸ While *trans-*1 was a good ROMP monomer, low strain *cis-*1 (*ca.* 1–2 kcal mol⁻¹) did not polymerize. DFT calculations predicted that metathesis initiation is kinetically accessible for *cis-*1, but ROMP is endothermic.

We now report well-controlled ROMP of *trans-*1 to afford a high molecular weight (>300 kg mol⁻¹) homopolymer **P1** that is stable in the absence of a metathesis initiator but undergoes 100% depolymerization to low-strain *cis-*1 upon addition of an appropriate initiator (Fig. 1). To reuse the low-strain isomer, we hypothesized that ring-opened *cis-*1 could be captured in a selective cross-metathesis reaction, resulting in a novel tandem ring-opening/cross-metathesis (RO-CM) olefin metathesis polymerization that is sequence-controlled. We show that recovered *cis-*1 participates in RO-CM with butanediol diacrylate (BDA) to afford a perfectly alternating copolymer **P2**. This work demonstrates the ability of isomerism to drive novel polymer design, optimize reactivity, mass recovery, and reuse, as well as the role of Si for C replacement²⁹ in modulating monomer ring strain, polymerization thermodynamics, and polymer properties.

Results and discussion

Our initial efforts focused on identifying if molecular weight characteristics are important in depolymerization of P1 as our initial publication reported a high molecular weight and high

Fig. 1 Intrinsic differences in ring strain of *trans-* and *cis-***1** enable polymerization, depolymerization, and reconstruction by multiple olefin metathesis mechanisms. ROMP = ring-opening metathesis polymerization; RCM = ring-closing metathesis; ROIMP = ring-opening-insertion metathesis polymerization; RO-CMP = ring-opening/cross-metathesis polymerization.

novel tandem olefin polymerization

dispersity polymer ($M_{\rm n}=62.6~{\rm kg~mol}^{-1}$, $M_{\rm w}/M_{\rm n}=3.50$) reflecting a multimodal sample containing both high molecular weight strands and oligomeric fragments.²⁷ The low molecular weight fraction included cyclic oligomers arising from ringclosing macrocyclization, which lack end groups and could complicate end-group selective initiation of depolymerization. To remove the lower molecular weight fraction, *trans-1* was polymerized to ${\bf P1}_{5.03}$ as a polymodal sample then purified *via* recycling size exclusion chromatography (RSEC) and reprecipitated in methanol to afford narrow dispersity ${\bf P1}_{1.23}$ (Fig. 2).

Unimodal **P1** can also be synthesized directly, as we have now also identified improved ROMP conditions. Hypothesizing that the formation of lower molecular weight oligomers arose from secondary metathesis reactions, we sought to rigorously purify *trans*-1 by recrystallization to remove any olefinic contaminants from synthesis (*e.g.*, *trans*-1,4-dichlorobutene). With highly purified starting material and a much shorter reaction time of 10 minutes, **P1** was synthesized in high molecular weight and in a unimodal distribution ($M_n = 92.9 \text{ kg mol}^{-1}$, $M_w/M_n = 1.14$, Scheme 1a).

Upon treatment of P1_{1.23} with 1 mol% of the metathesis initiator G1, we observed after 16 hours by ¹H NMR spectroscopy the growth of peaks assigned to *cis*-1 (55% conversion) with polymeric material remaining (Fig. 3). Consistent with chain transfer competing with depolymerization by RCM, multimodal P1_{11.1} (containing residual oligomers) depolymerized in only 28% conversion under the same conditions (Fig. S2†).

Monitoring the depolymerization of P1_{1.23} over time by SEC (Fig. 4 and Table 1), we observed a gradual decrease in the amount of P1 and an increase in *cis*-1. Reisolation of P1 at

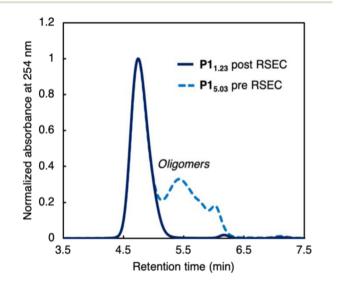


Fig. 2 Size exclusion chromatography (SEC) elugram of P1 before (dashed) and after (solid) purification by recycling SEC, normalized to the largest molecular weight peak at 4.74 min ([P1] = 1.00 mg mL-1, THF, RT) relative to polystyrene standards. P1 (before RSEC) $M_n = 2.03 \text{ kg mol}^{-1}$, $M_w/M_n = 5.03$. P1 (after RSEC) $M_n = 13.0 \text{ kg mol}^{-1}$, $M_w/M_n = 123$

Scheme 1 (a) Optimized polymerization of trans-1 to afford low dispersity P1 and (b) optimized depolymerization of P1 to afford cis-1 in 85% yield.

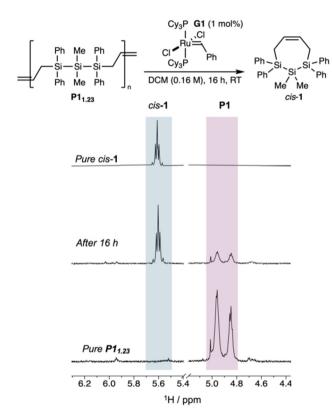


Fig. 3 Cropped ¹H NMR spectra of pure cis-1 (top), after 16 hours of depolymerization (middle), and pure P1_{1.23} (bottom) showing 55% depolymerization to cis-1.

each time point showed that $M_{\rm n}$ decreased from 11.9 kg mol⁻¹ to 6.92 kg mol⁻¹ while dispersity increased modestly from 1.30 to 1.81 (Table 1). Deconstruction at random internal sites would result in many more short oligomers and a much broader $M_{\rm w}/M_{\rm n}$ than we observed here, suggesting a possible end-to-end depolymerization. At the same time, the modest increase in dispersity suggested that chain transfer might also

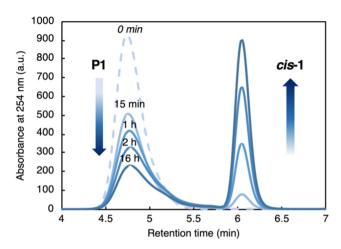


Fig. 4 SEC elugrams of recovered P1 over time ([P1] = 0.75 mg mL^{-1} , THF, RT). See Table 1 for molecular weight characteristics of recovered P1.

Table 1 Molecular weight characteristics of recovered P1 over time^a

Reaction time	$M_{\rm n}^{\ b} \left({\rm kg \ mol}^{-1} \right)$	$M_{\rm w}/M_{\rm n}^{\ b}$	
0	11.9	1.30	
15 min	9.55	1.51	
1 h	8.0	1.68	
2 h	7.12	1.79	
16 h	6.92	1.81	

^a Depolymerization of P1 performed at room temperature over 16 h with a concentration of 0.16 M in DCM and 1 mol% G1. b Determined by size exclusion chromatography relative to polystyrene standards at 254 nm (THF, [P1] = 0.75 mg mL⁻¹, 40 °C, 0.35 mL min⁻¹, 10 μL injection).

be occurring between strands, reducing the efficiency of depolymerization.

We investigated other metathesis initiators. While G3 improved the depolymerization efficiency compared to G1, resulting in 86% depolymerization of P1 to cis-1, the best conditions employed 1 mol% of G2 and increased depolymerization efficiency to 100% conversion to cis-1 (Table 2, entries 2

Table 2 Conversion of P1 to cis-1 under different conditions

Entry	$M_{\rm w}/M_{\rm n}$ of starting P1	Cat. ^a	mol%	Temp. (°C)	% NMR yield ^b cis- 1
1	1.23	G1	1	23	55
2	1.23	G2	1	23	100
3	2.13	G2	1	23	100 (85% isolate yield)
4	1.23	G3	1	23	86
5	11.1	G1	1	23	28
6	11.1	G1	3	23	38
7	11.1	G1	5	23	37
8	11.1	G1	1	50	36
9	8.61	G2	1	23	84

^a Catalyst used for depolymerization. ^b Determined from the relative integration of the polymer olefinic protons and the olefinic protons of *cis*-1.

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and 3), with no remaining high molecular weight polymer. In general, higher loadings of metathesis promoter and higher temperatures led to higher quantities of recovered *cis-*1 (entries 5–7). Scaling up the best conditions, we were able to depolymerize 80 mg of **P1** to 100% conversion by ¹H NMR and with 85% isolated yield of *cis-*1 (Table 2, entry 3). We hypothesize that the higher depolymerization efficiency with **G2** is related to its generally higher reactivity relative to **G1** ³⁰ and employing **G2** instead of **G1** also increased the depolymerization efficiency of high dispersity material (compare entries 5 and 9).

Having identified the circumstances leading to complete depolymerization of **P1** to *cis-***1**, we considered potential reuse scenarios for this low-strain cycloalkene. Entropy-driven ROMP can be an effective method for polymerization of low-strain cycloalkenes but requires high concentrations³¹ and *cis-***1** is a crystalline solid that is poorly soluble in CH_2Cl_2 , $CHCl_3$ and other solvents (Table S1†). We considered alkene photoisomerization, but photochemical silylene extrusion³² is possible for *cis-***1**. In addition, the amount of *trans* isomer available from the *cis* isomer is limited by the photostationary *trans: cis* ratio. 33,34

For these reasons, we sought an alternative polymerization method for cis-1. Prior calculated free energy profiles for initiation of cis- and trans-1 ROMP with G2 27 indicated that cis-1 is kinetically able to form a ring-opened, Ru-terminated structure similar to A (Fig. S3†).35 While the reaction of A with cis-1 to form a homopolymer via ROMP (a chain polymerization) is endothermic and not observed, we hypothesized that intermediate A could instead be captured in cross-metathesis. Reaction of A with a bifunctional Type 2 olefin B2 would release the metathesis catalyst and difunctional molecule AB, which we anticipated would be a suitable step polymerization monomer³⁶ via selective cross-metathesis between terminal alkene and acrylate end groups.37,38 Formation of the low energy α,β-unsaturated ester provides the driving force for ring-opening/cross-metathesis (RO-CM). While RO-CM is a tandem reaction extensively developed for small molecule synthesis, 39,40 it does not appear that RO-CM step polymerization has previously been reported. The polymerization by selective cross-metathesis of linear monomers with a terminal alkene and an acrylate supports our hypothesized mechanism.37,38 It is plausible that both RO-CM and the reverse order of fundamental steps (cross metathesis/ringopening, CM-RO) operate simultaneously, although CM-RO would require G2 to react first with B2 and then ring open cis-1 41,42 while the reaction of G2 with acrylates is slower than with more activated olefins.

To test the hypothesized RO-CM reactivity, we carried out two small molecule studies in which we reacted *cis-*1 with 1-hexene (Type 1 olefin) or methyl acrylate (Type 2 olefin). With 1-hexene, we only observed the formation of the homodimerization product 4-decene and residual *cis-*1 (Fig. S4†). But in the presence of excess methyl acrylate, the ring-opened structure 2 was isolated in 61% yield after purification by silica gel chromatography (Scheme 2). The RO-CM product 2 has

Scheme 2 Model reaction for ring opening-cross metathesis (RO-CM) of *cis-***1** and methyl acrylate.

exclusively the *trans* olefin geometry, as determined by the coupling constants of the olefinic peaks δ 6.81 (J_{1H-1H} = 15.5 Hz) and δ 5.39 (J_{1H-1H} = 15.4 Hz) (Fig. S5†).

Expanding from molecular RO-CM, we then investigated the RO-CM step polymerization of *cis-*1 and 1,4-butanediol diacrylate (BDA) (Fig. 5b). We observed 91% consumption of *cis-*1 within 4.5 hours. By precipitation from hexanes, we obtained polymer **P2** ($M_{\rm n}=3.31~{\rm kg~mol}^{-1},~M_{\rm w}/M_{\rm n}=1.87$). Structural characterization supported incorporation of both monomers. ATR-IR spectroscopy (Fig. S5†) indicated the presence of an α,β -unsaturated carbonyl at 1706 cm⁻¹, as well as a SiMe functional group at 1257 cm⁻¹.

Since cis-1 is a poor ROMP monomer and BDA is a poor ADMET monomer, RO-CM predicts an alternating copolymer due to faster crosspolymerization than homopolymerization. Structural characterization supported assignment of **P2** to a highly alternating polymer (>99% alteration) based on 1 H NMR spectroscopy (Fig. 6) in which neither the singlet consistent with a fumarate resonance nor the lower field resonances of a diallyl silane were observed. The major peaks were assigned to the alternating copolymer and were consistent with an (E)-geometry. Resonances consistent with both acrylate and styrenic end groups were identified and full details of copolymer structural characterization are reported in the ESI.† We note that **P2** can itself be deconstructed at end of life by ester hydrolysis.

To understand the impact of BDA incorporation onto the properties of a hybrid carbosilane polymer, we measured the glass transition temperature ($T_{\rm g}$) of P2. While the homopolymer P1 exhibits a glass transition temperature a little above room temperature (ca. 35 °C), the alternating copolymer P2 had a $T_{\rm g}$ ca. 13 °C. The lower $T_{\rm g}$ may reflect the additional incorporation of the flexible butane chain and a lower overall aromatic side chain content. In recent years, the role of sequence control has emerged as a tactic for modulating the glass transition temperature of a copolymer. The onset of thermal decomposition occurred at ca. 300 °C, consistent with other Si–Si containing polymers. The open control is a containing polymers.

This tandem ring-opening and selective cross-metathesis polymerization has the advantage of very high sequence control, a grand challenge in polymer synthesis. ^{45,46} The copolymerization of cycloalkenes and α,ω -diene monomers related to Type 1 olefins is known, but not sequence controlled. ^{47,48} Alternating copolymerization by olefin metathesis has been reported with cyclohexene and electron-poor strained cycloalkenes (*e.g.*, cyclobutenecarboxamide). ⁴⁹ The most similar reac-

Fig. 5 (a) Proposed mechanism for ring-opening/cross-metathesis step polymerization yielding highly alternating copolymers. (b) Synthesis of P2 via RO-CM step polymerization.

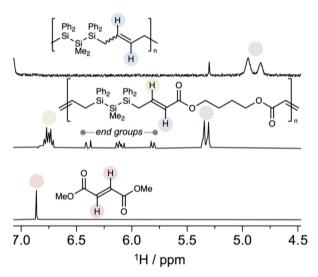


Fig. 6 Cropped ¹H NMR spectra (CDCl₃, 400 MHz) comparing the olefinic regions of P1 (top), P2 (middle), and dimethyl fumarate (bottom). There is no evidence of signals consistent with consecutive homopolymerization repeat units, supporting a highly alternant copolymer microstructure.

tion to ours is ring-opening-insertion metathesis polymerization (ROIMP). ROIMP is the copolymerization of cycloalkenes and diacrylates to yield highly alternant copolymers, 50-53 but ROIMP proceeds by a distinctly different mechanism involving first rapid cycloalkene ROMP (e.g., cis-cyclooctene), followed by insertion of BDA or other diacrylate into the homopolymer by a slower secondary metathesis process.

In the current work, the lack of cis-1 homopolymerization and the well-precedented slow rate of acrylate dimerization are not consistent with a ROIMP mechanism involving insertion of a second monomer into a homopolymer. A series of control experiments suggested that cis-1/BDA RO-CM copolymerization proceeds by a mechanism that is distinct from ROIMP and that these differences result in meaningful impacts on polymer microstructure e.g., sequence control.

First, we evaluated the reactivity of trans-1 and BDA under the same conditions employed for cis-1. We observed a mixture that consisted predominantly of P1 and unreacted BDA, with evidence of smaller amounts of dimeric BDA and P2 (Fig. S6†). This is distinctly different from the outcome with cis-1, where no homopolymers were observed, and is consistent with high strain trans-1 being suitable for ROIMP while low strain cis-1 reacts via RO-CM step polymerization.

Second, we noted that Choi and Grubbs reported that polycyclooctene could be used directly as a substrate for ROIMP, supporting the hypothesis that the homopolymer is an intermediate. If ROIMP was operative for the copolymerization of cis-1/BDA, P1 should react with BDA to yield P2. However, the reaction between homopolymer P1 and BDA afforded only residual P1 and small quantities of the BDA dimer/oligomer, but no spectroscopic evidence of either cis-1 or P2 (Fig. S10†).

Third, a consequence of the ROIMP mechanism is that extended homopolycycloalkene segments were found at early time points (e.g., 20 min).50 For cis-1/BDA copolymerization, high alternation of 82.0% was observed after 15 minutes (Fig. S11†). This points to the very high selectivity for crossmetathesis rather than homopolymerization.

Conclusions

The isomer-driven metathesis reactivity reported herein highlights how subtle differences in structure, thermodynamics, and kinetics can be exploited in the well-controlled, serial

polymerization/depolymerization/reconstruction pathways. Only the trans isomer of sila-cycloheptene 1 undergoes ROMP by chain polymerization, driven by strain release. The reverse ring-closing metathesis reaction yields only the low-strain cis isomer of 1, driven by the entropic benefit of depolymerization, and leading to 100% selectivity for a single product and 100% conversion in chemical recycling. The use of cycloalkene geometric isomerism to affect the position of polymer thermodynamics is recently emerging, building onto the use of cis/ trans relative configuration at tetrahedral stereoegenic centers. 54,55 We reintroduce cis-1 into polymeric materials by a novel tandem olefin metathesis pathway involving ringopening/cross-metathesis step polymerization. Tandem olefin metathesis reactions remain rare in macromolecular synthesis due to poor control,⁵¹ but herein we achieved perfect selectivity for the cross-metathesis reaction and obtained a highly alternant copolymer from cis-1 and the diacrylate BDA. The resulting polymer was fully characterized by ATR-IR, ¹H, ¹³C, ²⁹Si, COSY, and HSQC NMR spectroscopy to determine polymer microstructure.

That a 7-membered ring can switch from a high to a low-strain reactivity manifold is enabled not only by controlling olefin geometry, but also by the ability of Si for C replacement to modulate ring conformation and geometry (trans-cycloheptene is unstable >-40 °C). The work described herein show-cases that subtle structural modifications can have dramatic effects on chemical reactivity relevant to polymer end-of-life management.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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