

Communication

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J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.6b00014 • Publication Date (Web): 04 Apr 2016 Downloaded from http://pubs.acs.org on April 4, 2016

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Highly Tactic Cyclic Polynorbornene: Stereoselective Ring Expansion Metathesis Polymerization (REMP) of Norbornene Catalyzed By a New Tethered Tungsten-alkylidene Catalyst.

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Supporting Information Placeholder

Abstract: The tungsten alkylidyne ['BuOCO]W \equiv C('Bu)(THF)₂ (1) reacts with CO₂, leading to complete cleavage of one C=O bond, followed by migratory insertion to generate the tungsten-oxo alkylidene **2**. Complex **2** is the first catalyst to polymerize norbornene via Ring Expansion Metathesis Polymerization (REMP) to yield highly *cis-syndiotactic cyclic* polynorbornene.

Ring-opening metathesis polymerization (ROMP) of norbornenes and norbornadienes can lead to a variety of microstructures depending on the resulting tacticity of the polymer (isotactic, syndiotactic, or atactic) and double bond configuration (*cis* or *trans*).¹ Highly tactic polymers often present more well-defined properties, and therefore more value, than their atactic analogs.^{1c,2} However, stereocontrolled ROMP of cyclic monomers still poses a challenge in polymer chemistry. Well-defined alkene metathesis catalysts of tungsten,³ molybdenum,³ and ruthenium^{1c,4} were only recently discovered to initiate ROMP of norbornene monomers with high stereocontrol of tacticity and *cis/trans* ratio.

Perhaps even more challenging than stereocontrolled ROMP is the synthesis of cyclic polymers. Cyclic polymers exhibit remarkably different physical properties (e.g., lower intrinsic viscosity, higher glass transition temperature) compared to their linear counterparts of similar molecular weight.⁵ Despite their interesting properties, laborious synthesis required for cyclic polymers have hindered development of this research field. Methods for the synthesis of cyclic polymers usually involve intramolecular coupling between the chain ends of linear precursors;⁶ however, the inherent limitation of this method is the requirement of dilute conditions and long reaction times.⁷ Recent discoveries in catalytic production of cyclic polymers offer exciting new avenues for their efficient production.8 Grubbs' ring-expansion metathesis polymerization (REMP) strategy overcomes some of the challenges in cyclic polymer synthesis.9 REMP utilizes a cyclometalated alkylidene metal complex as the catalyst.^{9a,10} In this case, the two ends of the growing polymer remains attached to the metal throughout the polymerization process, thus releasing a cyclic polymer upon intramolecular chain transfer.⁹ Cyclic dendronized polymers¹¹ and cyclic brush polymers¹² employing norbornenebased macromonomers were synthesized via REMP using cyclic ruthenium catalysts;¹³ however, control over both tacticity and the cis/trans ratio is either not reported or absent.

Figure 1 outlines the design features of catalyst **2**. The catalyst combines the concept of tethering a M=C bond to a substitutional-

ly inert ancillary ligand to promote REMP,^{9,13} with a tungsten oxo-alkylidene fragment known to promote Z-selective ROMP. (Figure 1).¹⁴ Herein, we report the first catalyst to promote stereocontrolled REMP to yield *cis*-syndiotactic cyclic polynorbornene.



Figure 1. Tethered tungsten-oxo alkylidene catalyst **2** design concept.

Catalyst synthesis and characterization.

Previously reported, the tungsten alkylidyne ['BuOCO]W \equiv C('Bu)(THF)₂ (1) supported by a trianioninc pincer ligand¹⁵ is the precursor for a highly active catalyst for polymerization of alkynes to give cyclic polymers.¹⁶ Treating 1 with CO₂ at 55 °C for 12 h generates the tungsten oxo alkylidene complex 2, and the dinuclear species 3, in a 9:2 ratio, respectively (Scheme 1).

Scheme 1. Synthesis of complexes 2 and 3.



Complex 2 crystallizes preferentially in C_6D_6 , resulting in single crystals amenable to X-ray diffraction. The tungsten ion in complex 2 (Figure 2) is square pyramidal ($\tau = 0.12$).¹⁷ The oxo

group occupies the axial position (W1-O4 = 1.6948(15) Å) and the alkylidene (W1=C21 = 1.9503(19) Å), a THF ligand, and two aryloxides reside in the basal plane.



Figure 2. Left: Solid-state structure of 2 with H atoms, solvent molecules, and disorder on the coordinated THF omitted for clarity. Right: Solid-state structure of 3 with H atoms are omitted for clarity. Thermal ellipsoids drawn at 50% probability.

Scheme 2 depicts the proposed pathway for the formation of catalyst **2**. Carbonyl addition to tungsten alkylidynes bearing trianionic pincer ligands was recently reported by our group.¹⁸ Thus, the first step involves cycloaddition and cleavage of CO_2 across the alkylidyne to give a tungstenoxo-ketene intermediate. It is noteworthy to mention here that the cleavage of CO_2 across a metal-carbon triple bond is unprecedented, with only cycloaddition, but not cleavage, achieved by Fischer.¹⁹ In contrast, CO_2 cycloaddition and cleavage across both early²⁰ and late²¹ metal-carbon double bonds is more common. Strong support for the ketene intermediate comes in the form of an isolable analog employing an ONO³⁻ trianionic pincer ligand.²² However, in this OCO³⁻ case, the ketene moiety is unstable and insetts into the metal-aryl bond of the pincer ligand to give **2**.

Scheme 2. Proposed pathway for the formation of complex 2



Complex 3 is independently isolable from complex 2. Further heating of the initial reaction mixture leads to complete conversion of 2 to 3, as monitored by NMR spectroscopy. The initial formation of complex 2 and 3 in a 9:2 ratio and the eventual conversion of complex 2 into 3 upon heating, suggests the reaction is reversible and that complex **3** forms via attack at the α -carbon of the ketenylide and subsequent loss of CO. Consistent with the mechanism, a sample of the headspace reveals CO as determined by GC-MS (see ESI). Slow evaporation of a concentrated solution of 3 in a pentane/Et₂O mixture yields single crystals suitable for X-ray diffraction. One of the aryloxides from the trianionic OCO^{3-} pincer ligand bridges the two tungsten atoms (W_{1A} and W1B, Figure 2). Bridges created by trianionic pincer ligands were noted in two previous structures by our group²³ and Bercaw's.²⁴ Alkylidene W_{1A} - C_{1A} and W_{1B} - C_{1B} bond lengths of 1.884(4) and 1.885(4) Å are slightly shorter by 0.021(4) than the W=C double bond in the only related tetraanionic pincer OCO4- Walkylidene.²⁵ The empirical formula of dimer **3** implies the loss of CO from 2; however, the mechanism of this transformation is still under investigation. Addition of a few drops of THF to the reaction mixture of 2 and 3 prevents the conversion of 2 into 3 even upon heating, implying loss of THF is an integral step in the formation of 3.

REMP and evidence for stereoselectivity.

Treating **2** (1 mol %) with norbornene at room temperature yields *cis*-selective cyclic polynorbornene (>98% by ¹H NMR spectroscopy) after 7 h (Scheme 3). The reaction was quenched by dropwise addition of the reaction mixture into stirring methanol. The resulting polymer was isolated by filtration and dried under vacuum. Adding **3** (1 mol %) to norbornene at room temperature for 7 h yields polynorbornene in only 42% yield, with no *cis*-selectivity. Table 1 lists polymerization results as a function of the ratio of monomer to catalyst.

A mixture of 2 and 3 maintains the selectivity of 2 when treated with norbornene, suggesting initiation with catalyst 2 and propagation of the monomer are much faster than initiation by the more hindered complex 3. Evidence for fast propagation relative to initiation comes from a sealed NMR tube polymerization experiment. Combining norbornene and 2 in C_6D_6 results in polymer formation but the ¹H NMR spectrum of the reaction mixture exhibits signals attributable to unreacted catalyst 2 (see Figure S17), thus indicating $k_p > k_i$.

Table 1. Polymerization of norbornen $e^{[a]}$ by catalyst 2 with different monomer/catalyst ratio

[mon/cat] ₀	[monomer]0 ^[b]	yield (%)	%cis ^[c]	$M_n^{[d]}(kDa)$	$M_{\rm w}/M_{\rm n}^{\rm [d]}$
25:1	0.1	97	97	126	1.24
50:1	0.1	97	97	197	1.25
100:1	0.1	92	98	248	1.21
200:1	0.1	60	97	578	1.29

^[a] The appropriate amount of a 1 mg/mL solution of catalyst dissolved in toluene is added to 40 mg of norbornene dissolved in toluene and stirred for 7 h at room temperature. ^[b] mol.L⁻¹. ^[c] Determined by ¹H NMR spectroscopy. ^[d] Determined by size exclusion chromatography.

Scheme 3. Polymerization of norbornene by catalyst 2 to generate cyclic polynorbornene.



Cyclic polynorbornene produced with catalyst 2 is syndiotactic (>98%), as determined by a comparison to ¹³C NMR data of previously reported syndiotactic *linear* polynorbornene.²⁶ Tacticity is also supported by post-functionalization of polynorbornene via bromination, as recently described by Schrock and coworkers.^{26b} The brominated polymer exhibits two doublets at 3.84 ppm (J =11.2 Hz) and 3.81 ppm (J = 10.3 Hz) (ESI, Figure S24, top). Consistent with reported cis, syndiotactic polynorbornene, irradiating the methine protons at 2.61 ppm results in two singlets (ESI, Figure S24, bottom).^{26b} Further evidence for high syndiotacticity comes from polymerization of the chiral monomer bis((menthyloxy)carbonyl)norbornadiene (BMCNBD). COSY NMR is able to distinguish between isotactic and syndiotactic poly(BMCNBD). In the case of a *cis* isotactic sample, the olefinic protons are inequivalent, and therefore couple in a COSY NMR spectrum. However, a cis syndiotactic poly(BMCNBD) contains equivalent olefinic protons related by a C₂ axis, and thus do not couple.²⁷ Poly(BMCNBD) produced by 2 does not exhibit any coupling between the olefinic protons, indicating the polymer is syndiotactic (Figure S22).

Since the alkylidene in **2** is tethered to the ligand backbone, REMP is the expected mechanism of polymerization (Scheme 4). Through REMP, the growing polymer chain remains attached by both ends to the catalyst throughout the polymerization process 1

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(see intermediate **A**), and releases a cyclic polynorbornene after undergoing intramolecular chain transfer via backbiting. Though less probable, backbiting can occur to regenerate initiator **2**, or instead; backbiting can occur at any of the other C=C bonds to give intermediate **B**. The proposed mechanism is consistent with the observation of slow initiation/fast propagation since metathesis within complex **2** occurs at a disubstituted, sterically hindered (^fBu) alkylidene, whereas; after the initial ring opening event the new alkylidene is mono-substituted and relatively unhindered.

Scheme 4. Proposed mechanism of REMP of norbornene to give highly *cis* and syndiotactic cyclic polynorbornene.



Size exclusion chromatography (SEC) equipped with multi-angle light scattering (MALS) and viscosity detectors provide compelling data for a cyclic topology. Cyclic polymers have lower intrinsic viscosities and smaller hydrodynamic volumes than their linear analogs. Catalyst that produce linear polynorbornene with high *cis* selectivity (>95%) and syndiotacticity (>95%) are known,²⁸ and a sample was synthesized utilizing Grubbs catalyst Ru(NHC(Ad)(Mes))(=CH(PhOⁱPr))(\eta²-NO₃) (4).²⁹

Table 2. M_n , M_w/M_n , *cis*-selectivity and tacticity of cyclic/linear poly(NBE)

Catalyst	$M_{\rm n}^{\rm [a]}({\rm kDa})$	$M_{\rm w}/M_{\rm n}$	%cis ^[b]	Tacticity ^[c]
2 (cyclic)	113	1.16	>98	syndiotactic
4 (linear)	114,	2.34	>95	syndiotactic
^[a] Absolute m	olecular weights de	etermined b	v SEC-MA	LS. ^[b] Determined

by ¹H NMR spectroscopy. ^[c] Determined by ¹³C NMR spectroscopy.



Figure 3. Plot of log of molar mass versus elution volume.



Figure 4. Mark-Houwink-Sakurada plot, $\log [\eta]$ versus $\log M$

A plot of log of molar mass versus elution volume (Figure 3) shows that the cyclic polynorbornene samples with the same molar mass elute later than their linear counterparts, consistent with their smaller hydrodynamic volume. A Mark-Houwink-Sakurada (MHS) plot (log $[\eta]$ versus log M, where $[\eta]$ is the intrinsic viscosity and M is the viscosity-average molar mass (Figure 4) confirms the lower intrinsic viscosity of the cyclic polymers relative to the linear polymers. The experimental ratio $[\eta]_{cvclic}/[\eta]_{linear}$ of 0.34 over a range of molecular weights are in good agreement with the theoretical value of 0.4.9a Additionally, MHS parameters a of 0.76 and 0.71 for the linear and cyclic samples, respectively, were determined from the slope of the MHS plots. This result indicates that both polymers behave as flexible random coils in solution, meaning the observed differences are caused by different behavior of the polymers in solution. In addition a plot of mean square radius of gyration ($\langle R_g^2 \rangle$) versus molar mass (see ESI Figure S27) obtained for cyclic and linear samples of polynorbornene provides a $\langle R_g^2 \rangle_{cyclic} / \langle R_g^2 \rangle_{linear}$ ratio of 0.4±0.1, which is within the experimental error of the theoretical value of $0.5.^{30}$

In summary, tethering an alkylidene to a substitutionally inert ancillary ligand is an effective design for creating catalysts capable of REMP. Unique to this system, CO₂ cleavage across the metal-carbon triple bond of complex 1 leads to the tethered alkylidene catalyst 2. Though other tethered group VI alkylidene complexes are known,^{10a} complex 2 is the first to function as a REMP catalyst. Comparing the polymers produced by catalyst 2, against cis and syndiotactic rich linear analogs permits their conclusive assignment as cyclic polymers. To the best of our knowledge this is the first catalyst to produce cyclic polynorbornene with such high stereocontrol.¹³ The *cis*-selectivity is presumably due to the steric congestion imposed by the ^tBuOCO⁴⁻ ligand, and the observed syndiotacticity indicates addition of the monomer occurs with alternating stereoselectivity. The monomer adds to one face of the M=C bond first, and in the next addition, it adds to the opposite face of the alkylidene. This type of "stereogenic metal control" occurs when the configuration of the metal center changes after each monomer addition.^{1a} Complex 2 provides new avenues for exploration of not only cyclic polymers, but also catalyst design. Considering the extensive history of early-metal alkylidenes, surely other tethered versions can be designed to initiate REMP.

ASSOCIATED CONTENT

Supporting Information

Full experimental procedures, NMR spectra, X-ray crystallographic and polymer characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

This material is based upon work supported by the National Science Foundation CHE-1265993 (ASV). KAA acknowledges the NSF (CHE-0821346) for the purchase of X-ray equipment.

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