Introducing "Ynene" Metathesis: Ring-Expansion Metathesis Polymerization Leads to Highly Cis and Syndiotactic Cyclic Polymers of Norbornene

Soufiane S. Nadif,[†] Tomohiro Kubo,[‡] Stella A. Gonsales,[†] Sudarsan VenkatRamani,[†] Ion Ghiviriga,[†,‡] Brent S. Sumerlin,[‡] and Adam S. Veige*,[†,‡]

[†]Center for Catalysis, Department of Chemistry, University of Florida, P.O. Box 117200, Gainesville, Florida 32611, United States
[‡]Center for Macromolecular Science & Engineering and George & Josephine Butler Polymer Research Laboratory, Department of Chemistry, University of Florida, P.O. Box 117200, Gainesville, Florida 32611, United States

S *Supporting Information*

ABSTRACT: Tungsten alkylidynes $[CF_3-ONO]W\equiv CC(CH_3)_3(THF)_2$ (**1**) and $[^tBuOCO]W\equiv CC-(CH_3)_3(THF)_2$ (**3**) react with ethylene. Complex **1** reacts reversibly with ethylene to give the metallacyclobutene (**2**). Complex **3** reacts with ethylene to form the tethered alkylidene (**4**) featuring a tetraanionic pincer ligand. Complexes **1** and **3** initiate the polymerization of norbornene at room temperature. The polymerization of norbornene by **1** is not stereoselective, whereas **3** generates a highly cis and syndiotactic cyclic polynorbornene. Comparison of the intrinsic viscosity, radius of gyration, and elution time of the synthesized cyclic polynorbornene with those of linear analogues provides conclusive evidence for a cyclic topology.

E nyne metathesis involves the reaction between an alkylidene and an alkyne (Scheme 1A).[1] Numerous ruthenium

Scheme 1. Illustration Depicting the Orthogonality of "Enyne" and "Ynene" Metathesis

carbenes[2] and early-metal alkylidenes[3] react with alkynes. However, alkylidynes do not react with alkenes in "ynene" metathesis (Scheme 1B). Fürstner correctly highlighted the difference in reactivity in his recent review of alkyne metathesis: "*Alkyne metathesis is strictly orthogonal to alkene metathesis in the sense that none of the commonly used metal alkylidynes are capable of activating olefins of any kind.*"[4] The apparent orthogonality is important in the application of alkyne metathesis to total synthesis (i.e., it is possible to execute alkyne metathesis in the presence of alkenes).[5] In fact, just one obscure example of ynene reactivity between alkylidynes and alkenes exists.[6] The tungsten alkylidyne $(DME)Cl_3W\equiv CC(CH_3)_3$ reacts with cyclopentene

to produce poly-1-pentenylene.[7] However, the active species is unknown, and the details of the reaction are not well elucidated.

Trianionic pincer ligands[8] can induce unusually nucleophilic metal−carbon triple bonds.[9] Thus, we hypothesized that if a trianionic pincer alkylidyne could be coaxed to undergo cycloaddition with a cyclic olefin, it would inherently lead to a tethered alkylidene and therefore would be poised to initiate ring expansion metathesis polymerization (REMP) to give cyclic polymers, as illustrated in Scheme 2. If successful, this new "ynene" reactivity profile for alkylidynes will open up new opportunities to develop REMP catalysts and cyclic polymers.

Scheme 2. Potential Application of "Ynene" Chemistry To Generate a Tethered Alkylidene Complex Capable of Initiating REMP

tethered alkylidene

Cyclic polymers[10] are a fascinating class of materials that exhibit dramatically different properties (e.g., density,[11] refractive index,[12] T_g[13]) compared with their equivalent linear counterparts. Despite their interesting properties, cyclic polymers remain underdeveloped because of inherent challenges with their preparation, though a few catalysts capable of producing cyclic polymers are known.[14] For example, via a mechanism akin to cyclotrimerization of alkynes, our group reported a highly active catalyst that polymerizes alkynes to produce macrocyclic polyenes.[14f−h] Grubbs reported the first REMP catalyst using a Ru-tethered carbene that polymerizes cyclic olefins.[14c,15] Grubbs' tethered carbene catalyst polymerizes norbornene-type monomers to form dendronized[15b] and brush[15d] cyclic polymers but does not appear to control the polymer microstructure (tacticity, double bond arrangement) to the extent of other ring opening

metathesis polymerization (ROMP) Ru carbenes.[16] Exploiting the fact that diphenolate, binapthalate, and monoaryloxide pyrrolide (MAP) W and Mo alkylidenes exert high stereocontrol in ROMP,[17] we recently designed a tethered W alkylidene that produces the first highly cis and syndiotactic cyclic poly-norbornene (PNB).[18] Herein we exploit the unprecedented "ynene" reactivity of trianionic-pincer-supported W alkylidynes to initiate REMP of norbornene to give highly cis (>99%) and syndiotactic (>95%) cyclic PNB.

The first clue that REMP is possible using trianionic-pincer-supported W alkylidynes came from their reactivity with ethylene. To the best of our knowledge, no reports identify ethylene undergoing cycloaddition with alkylidynes. However, treating the $[CF_3-ONO]^{3-}$-supported tungsten alkylidyne **1** with ethylene at 1 atm in a sealable NMR tube establishes an equilibrium between the corresponding metallacyclobutene and the initial alkylidyne (Scheme 3). Four multiplets at 3.97, 3.69,

Scheme 3. Reactivity of Alkylidynes 1 and 3 with Ethylene
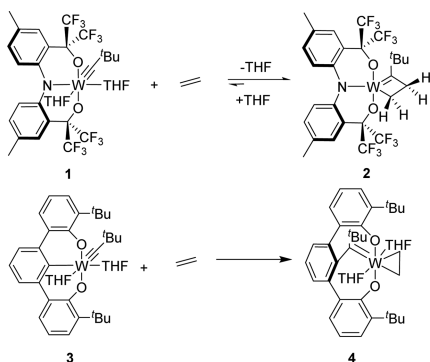
2.84, and 2.32 ppm in the ^{1}H NMR spectrum of **2** are attributable to the diastereotopic protons on the metallacyclobutene. The alkylidene carbon within the metallacycle resonates in a typical position at 280.8 ppm for trianionic-pincer-supported alkylidenes.[9a,19] For reference, the alkylidyne α-carbon in **1** resonates downfield at 313.2 ppm.[19] The reaction is reversible: complex **1** forms when the ethylene is removed from the reaction. It is important to note that Schrock's $(^tBuO)_3W\equiv CC(CH_3)_3$ alkylidyne does not react with ethylene, even at 70 °C. The metal−carbon multiple bond in complex **1** and the amido lone pair on the pincer establish an inorganic enamine[9,19,20] bonding combination, which may be the reason for its enhanced reactivity with ethylene.[9,19,20]

A different reactivity profile occurs with the $[OCO]^{3-}$ W alkylidyne **3**. Treating complex **3** with ethylene provides complex **4** bearing a tetraanionic pincer ligand, as shown in Scheme 3. The same type of rearrangement reaction occurs when complex **3** is treated with alkynes.[14g] Two broad resonances integrating to four protons appear at 2.61 and 1.70 ppm and are attributable to an η^2-ethylene. Slowing the rotation of the ethylene at −65 °C resolves the resonances into two triplets. A ^{1}H NOESY irradiation experiment confirmed that the bound ethylene does not exchange with free ethylene at this temperature. Corresponding carbon resonances for the bound ethylene appear at 38.2 and 15.6 ppm. The alkylidyne carbon in **3** resonates at 297.1 ppm,[14f] but in **4** that carbon atom resonates at 259.1 ppm, which is consistent with a tethered alkylidene. Unlike complex **2**, removing ethylene does not yield the starting material, complex **3**; instead, an intractable mixture results, thus precluding isolation of **4**.

On the basis of the reactivity of complexes **1** and **3** with ethylene, it seemed reasonable that cyclic olefins would also undergo cycloaddition with the metal−carbon triple bond to realize the REMP mechanism described in Scheme 2. Complex **1** reacts very slowly with norbornene to give non-stereoselective cyclic PNB (Scheme 4). Evidence for a cyclic topology comes

Scheme 4. Polymerization of Norbornene by 1 and 5
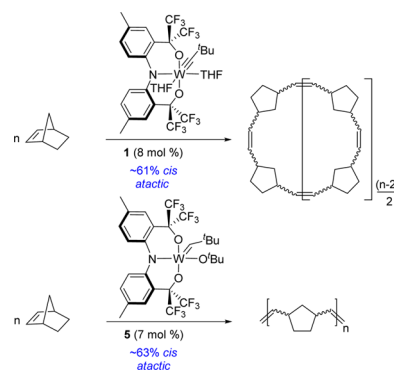
from comparison of the cyclic polymers produced with initiator **1** versus linear non-stereoselective polymers produced with the ONO trianionic pincer alkylidene $[CF_3-ONO]W=CHC-(CH_3)_3(O^tBu)$ (**5**).[19] Catalyst **5** offers the best comparison with **1** since the pincer ligands are identical, but **1** contains an alkylidyne capable of ynene metathesis, whereas **5** contains an alkylidene and therefore is able to produce only linear polymers. Complex **3** rapidly polymerizes norbornene at room temperature (Scheme 5). Moreover, treating a solution of norbornene in

Scheme 5. Polymerization of Norbornene by 1 and 6
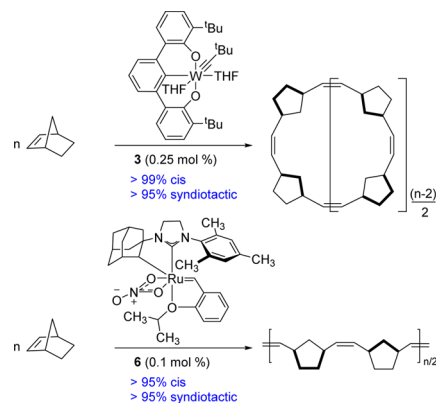
toluene with **3** (0.25 mol %) results in the quantitative formation of highly cis (>99%; ^{1}H NMR) and syndiotactic (>95%; ^{13}C NMR) cyclic PNB within 30 min (Scheme 5). Table 1 lists the results of polymerizations with initiator **3**.

Cyclic PNB produced with initiator **3** is syndiotactic (>95%), as determined by a comparison to ^{13}C NMR data for previously reported syndiotactic *linear* PNB.[21] Polymerizing chiral dicarbomenthoxynorbornadiene (DCMNBD) with complex **3** confirms the assignment of a syndiotactic cyclic polymer. In the case of a cis/isotactic sample, the olefinic protons are inequivalent and therefore couple in a ^{1}H−^{1}H COSY NMR spectrum.[16b,22] Alternatively, in a cis/syndiotactic polymer, the olefinic protons are related by a C_2 axis and thus are equivalent and do not couple. Poly(DCMNBD) produced by initiator **3**

Table 1. Polymerization of Norbornene Catalyzed by 3 under Various Monomer to Catalyst Loadings

[cat/mon]$_0{}^a$	[monomer]$_0{}^b$	yield^e (%)	% cis^c	$M_n{}^d$ (g/mol)	$M_w/M_n{}^d$
1:100	0.1	80	94	118000	1.26
1:200	0.1	83	95	79800	1.22
1:400	0.1	80	94	91500	1.32
1:400	0.05	99	99	425000	1.45

^{a}The appropriate amount of a 1 mg/mL solution of catalyst dissolved in toluene was added to 30 mg of norbornene dissolved in toluene, and the mixture was stirred for 30 min at room temperature. ^{b}In mol·L^{-1}. ^{c}Determined by ^{1}H NMR analysis. ^{d}Determined by size-exclusion chromatography (SEC) using THF as the mobile phase at 35 °C. ^{e}Determined gravimetrically.

does not exhibit coupling between the olefinic protons, indicating that the polymer is syndiotactic (Figure 1). Furthermore, postmodification of the polymer according to literature precedent also indicates that the polymer is syndiotactic (see the Supporting Information (SI)).[21b]
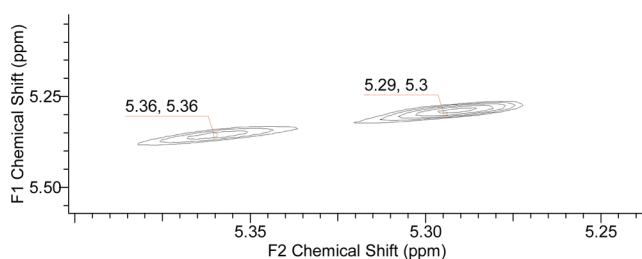
Figure 1. Olefinic proton region of the ^{1}H−^{1}H COSY spectrum of poly(DCMNBD) generated by **3**. The absence of off-diagonal resonances indicates that the sample is exclusively cis/syndiotactic. (Note: the digital resolution is 2 Hz in both dimensions, which is smaller than the expected coupling constant, ∼10 Hz).

Evidence for a cyclic topology. Evidence that polymers produced by complexes **1** and **3** are cyclic comes from comparing them to analogous linear samples produced by **5** and **6**. Here the discussion will focus on the more interesting stereoregular polymers produced with precatalyst **3**. Data supporting a cyclic topology for polymers produced by catalyst **1** are provided in the SI. Linear PNB (Table 2) with a similarly high cis selectivity

Table 2. M_n, M_w/M_n, Cis Selectivity, and Tacticity of Cyclic and Linear Polynorbornene

catalyst	$M_n{}^a$ (g/mol)	$M_w/M_n{}^a$	% cis^b	% syndiotactic^c
3 (cyclic)	125000	1.22	>99	>95
6 (linear)	114000	2.34	>95	>95

^{a}Determined by SEC using THF as the mobile phase at 35 °C. ^{b}Determined by ^{1}H NMR analysis. $^c{}^{13}$C NMR analysis.

(95%) and syndiotacticity (>95%)[23] was synthesized using Grubbs' ruthenium catalyst **6** (Scheme 5).[16a,24] Size-exclusion chromatography (SEC) using multiangle light scattering (MALS) and viscosity detectors provides compelling data for a cyclic topology. Cyclic polymers have smaller hydrodynamic radii than their equivalent linear analogues. Consequently, cyclic polymers have shorter elution times for a given absolute molecular weight during SEC. The differences in the plots of log(molecular weight) versus elution volume in Figure 2A are consistent with linear versus cyclic polymers.
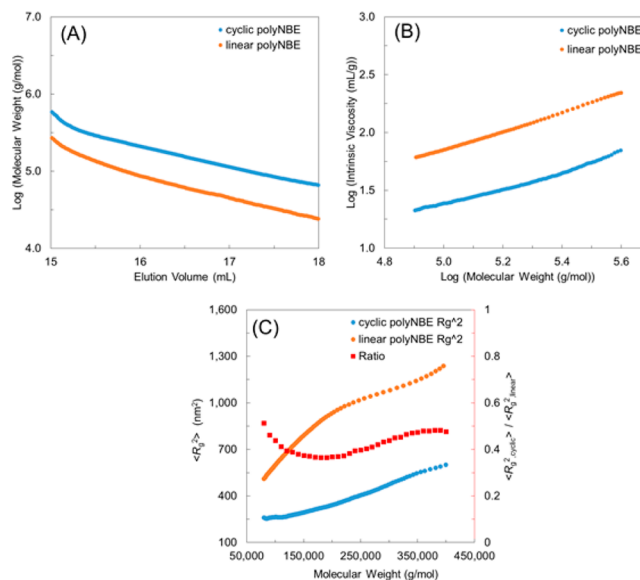

Figure 2. (A) Plots of log(molecular weight) vs elution volume. (B) Mark−Houwink−Sakurada plots, log $[\eta]$ vs log(molecular weight). (C) Plots of mean square radius $\langle R_g{}^2 \rangle$ vs molecular weight.

Furthermore, Mark−Houwink−Sakurada plots (log $[\eta]$ versus log M, where $[\eta]$ is the intrinsic viscosity and M is the viscosity-average molecular weight) (Figure 2B) confirm the lower intrinsic viscosity of the cyclic polymer relative to the linear sample. The two samples have similar values of the Mark−Houwink parameter a (0.75 for the linear sample and 0.66 for the cyclic sample), suggesting that no major conformational differences between the samples exist and that both behave as random coils in solution.[10a] The experimental ratio $[\eta]_{\text{cyclic}}/[\eta]_{\text{linear}}$ over a range of molecular weights agrees with the theoretical value of 0.4 (see Table S5 in the SI).[14c] Finally, the root-mean-square (RMS) radius of gyration for each sample was measured. The cyclic polymers exhibited smaller $\langle R_g{}^2 \rangle$ values for a wide range of molecular weights compared with the linear samples, and the experimentally determined $\langle R_g{}^2 \rangle_{\text{cyclic}}/\langle R_g{}^2 \rangle_{\text{linear}}$ ratio of 0.44 ± 0.07 calculated over the range is within reasonable error limits of the theoretical value of 0.5 (Figure 2C).[25]

Scheme 6 illustrates two plausible mechanisms for how complexes **1** and **3** initiate REMP of norbornene to give cyclic PNB. For both pathways the critical first step is the "ynene" [2 + 2] cycloaddition of norbornene with the metal−carbon triple bond. For complex **1**, subsequent metathesis provides a tethered alkylidene poised for REMP, but the trianionic pincer ligand remains intact. REMP proceeds via sequential cycloaddition of norbornene monomer to the tethered alkylidene to produce cyclic PNB. In contrast, for complex **3**, upon cycloaddition the pincer ligand rearranges to form a tethered alkylidene within a tetraanionic pincer ligand;[14g] this claim is supported by the divergent reactivity observed for **1** and **3** with ethylene. REMP then occurs via sequential cycloaddition of norbornene monomer to the pincer-tethered alkylidene to produce, in the case of **3**, highly cis (99%) and highly syndiotactic (95%) cyclic PNB. Complex **3** has some advantages over the previously published initiator[18] that also produces cis- and syndiotactic-rich cyclic PNB: (1) **3** reacts directly with monomer; (2) **3** is 14 times more active; (3) catalyst loadings of **3** as low as 0.25 mol % provide excellent yields of 99%.

In conclusion, demonstrated for the first time is the [2 + 2] cycloaddition between ethylene and an alkylidyne. Specifically,

Scheme 6. Proposed Mechanisms for REMP of 1 and 3
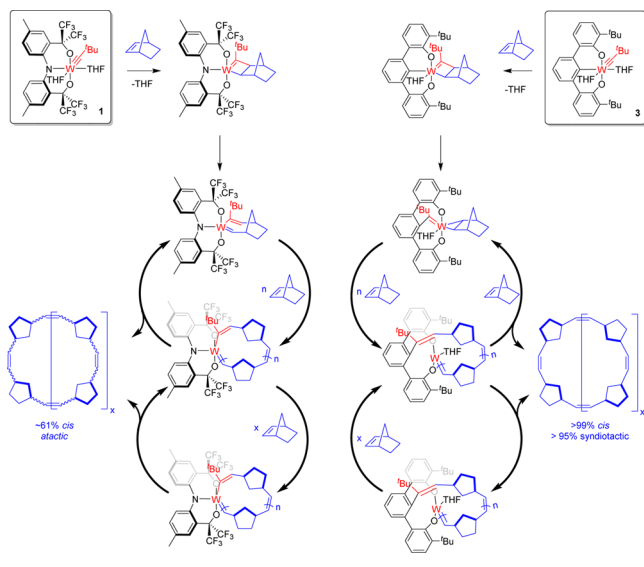
metallacyclobutene **2** forms upon exposure of complex **1** to an atmosphere of ethylene. As a result of the presence of a M−C$_{pincer}$ bond within complex **3**, upon exposure to ethylene the trianionic pincer converts to a tetraanionic pincer containing a tethered alkylidene. Critical to realizing these new REMP catalysts is their ability to undergo ynene metathesis, as both mechanisms result in an inherent tethered alkylidene. Cyclic polynorbornene produced with initiator **3** is stereoregular with highly cis (>99%) and syndiotactic (>95%) repeat units. The combination of a nucleophilic alkylidyne,[9] an electrophilic W^{6+} metal center, and release of strain upon cycloaddition[19] provides enough driving force to enable ynene metathesis. It is conceivable that other metal alkylidynes can access ynene metathesis and initiate REMP, thus providing improved access to polymers with cyclic topologies.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b03247.

Procedures and additional data (PDF)

AUTHOR INFORMATION

Corresponding Author

*veige@chem.ufl.edu

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

REFERENCES

(1) (a) Diver, S. T.; Giessert, A. J. *Chem. Rev.* **2004**, *104*, 1317. (b) Li, J. W.; Lee, D. *Eur. J. Org. Chem.* **2011**, *2011*, 4269. (c) Villar, H.; Frings, M.; Bolm, C. *Chem. Soc. Rev.* **2007**, *36*, 55. (d) Spandl, R. J.; Rudyk, H.; Spring, D. R. *Chem. Commun.* **2008**, 3001.

(2) (a) Collins, S. K.; El-Azizi, Y.; Schmitzer, A. R. *J. Org. Chem.* **2007**, *72*, 6397. (b) Fischmeister, C.; Bruneau, C. *Beilstein J. Org. Chem.* **2011**, *7*, 156. (c) Lippstreu, J. J.; Straub, B. F. *J. Am. Chem. Soc.* **2005**, *127*, 7444.

(3) (a) Zhao, Y.; Hoveyda, A. H.; Schrock, R. R. *Org. Lett.* **2011**, *13*, 784. (b) Singh, R.; Schrock, R. R.; Muller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2007**, *129*, 12654. (c) Lee, Y. J.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 10652.

(4) Fürstner, A. *Angew. Chem., Int. Ed.* **2013**, *52*, 2794.

(5) (a) Furstner, A.; Dierkes, T. *Org. Lett.* **2000**, *2*, 2463. (b) Hoveyda, A. H.; Malcolmson, S. J.; Meek, S. J.; Zhugralin, A. R. *Angew. Chem., Int. Ed.* **2010**, *49*, 34. (c) Mori, M. *Materials* **2010**, *3*, 2087.

(6) *Transition Metal Carbyne Complexes*; Kreibl, F. R., Ed.; Springer: Dordrecht, The Netherlands, 1993.

(7) Weiss, K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 359.

(8) O'Reilly, M. E.; Veige, A. S. *Chem. Soc. Rev.* **2014**, *43*, 6325.

(9) (a) O'Reilly, M. E.; Ghiviriga, I.; Abboud, K. A.; Veige, A. S. *J. Am. Chem. Soc.* **2012**, *134*, 11185. (b) Gonsales, S. A.; Pascualini, M. E.; Ghiviriga, I.; Abboud, K. A.; Veige, A. S. *J. Am. Chem. Soc.* **2015**, *137*, 4840.

(10) (a) Semlyen, J. A. *Cyclic Polymers*, 2nd ed.; Kluwer: Dordrecht, The Netherlands, 2000. (b) Laurent, B. A.; Grayson, S. M. *Chem. Soc. Rev.* **2009**, *38*, 2202. (c) Kricheldorf, H. R. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 251.

(11) Orrah, D. J.; Semlyen, J. A.; Ross-Murphy, S. B. *Polymer* **1988**, *29*, 1455.

(12) Garcia Bernal, J. M.; Tirado, M. M.; Freire, J. J.; Garcia de la Torre, J. *Macromolecules* **1991**, *24*, 593.

(13) Bannister, D. J.; Semlyen, J. A. *Polymer* **1981**, *22*, 377.

(14) (a) Kricheldorf, H. R. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4723. (b) Kricheldorf, R.; L, S.-R. *Macromolecules* **1995**, *28*, 6718. (c) Bielawski, C. W.; Benitez, D.; Grubbs, R. H. *Science* **2002**, *297*, 2041. (d) Jeong, W.; Shin, E. J.; Culkin, D. A.; Hedrick, J. L.; Waymouth, R. M. *J. Am. Chem. Soc.* **2009**, *131*, 4884. (e) Brown, H. A.; Chang, Y. A.; Waymouth, R. M. *J. Am. Chem. Soc.* **2013**, *135*, 18738. (f) Sarkar, S.; McGowan, K. P.; Kuppuswamy, S.; Ghiviriga, I.; Abboud, K. A.; Veige, A. S. *J. Am. Chem. Soc.* **2012**, *134*, 4509. (g) McGowan, K. P.; O'Reilly, M. E.; Ghiviriga, I.; Abboud, K. A.; Veige, A. S. *Chem. Sci.* **2013**, *4*, 1145. (h) Roland, C. D.; Li, H.; Abboud, K. A.; Wagener, K. B.; Veige, A. S. *Nat. Chem.* **2016**, DOI: 10.1038/nchem.2516. (i) Asenjo-Sanz, I.; Veloso, A.; Miranda, J. I.; Pomposo, J. A.; Barroso-Bujans, F. *Polym. Chem.* **2014**, *5*, 6905.

(15) (a) Bielawski, C. W.; Benitez, D.; Grubbs, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 8424. (b) Boydston, A. J.; Holcombe, T. W.; Unruh, D. A.; Frechet, J. M. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **2009**, *131*, 5388. (c) Xia, Y.; Boydston, A. J.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2011**, *50*, 5882. (d) Zhang, K.; Tew, G. N. *ACS Macro Lett.* **2012**, *1*, 574.

(16) (a) Rosebrugh, L. E.; Ahmed, T. S.; Marx, V. M.; Hartung, J.; Liu, P.; López, J. G.; Houk, K. N.; Grubbs, R. H. *J. Am. Chem. Soc.* **2016**, *138*, 1394. (b) Rosebrugh, L. E.; Marx, V. M.; Keitz, B. K.; Grubbs, R. H. *J. Am. Chem. Soc.* **2013**, *135*, 10032.

(17) Schrock, R. R. *Acc. Chem. Res.* **2014**, *47*, 2457.

(18) Gonsales, S. A.; Kubo, T.; Flint, M. K.; Abboud, K. A.; Sumerlin, B. S.; Veige, A. S. *J. Am. Chem. Soc.* **2016**, *138*, 4996.

(19) O'Reilly, M. E.; Ghiviriga, I.; Abboud, K. A.; Veige, A. S. *Dalton Trans.* **2013**, *42*, 3326.

(20) VenkatRamani, S.; Ghiviriga, I.; Abboud, K. A.; Veige, A. S. *Dalton Trans.* **2015**, *44*, 18475.

(21) (a) McConville, D. H.; Wolf, J. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 4413. (b) Hyvl, J.; Autenrieth, B.; Schrock, R. R. *Macromolecules* **2015**, *48*, 3148. (c) Autenrieth, B.; Schrock, R. R. *Macromolecules* **2015**, *48*, 2493. (d) Flook, M. M.; Jiang, A. J.; Schrock, R. R.; Muller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 7962.

(22) O'dell, R.; Mcconville, D. H.; Hofmeister, G. E.; Schrock, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 3414.

(23) Forrest, W. P.; Axtell, J. C.; Schrock, R. R. *Organometallics* **2014**, *33*, 2313.

(24) Keitz, B. K.; Fedorov, A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2012**, *134*, 2040.

(25) Jia, Z. F.; Monteiro, M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 2085.