

# Highly $\beta$ -Selective Cyclopolymerization of 1,6-Heptadiynes and Ring-Closing Enyne Metathesis Reaction Using Grubbs Z-Selective Catalyst: Unprecedented Regioselectivity for Ru-Based Catalysts

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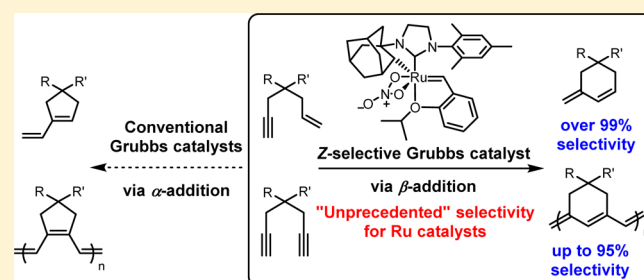
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**S** Supporting Information

**ABSTRACT:** It is well-known that Ru-based Grubbs catalysts undergo a highly selective  $\alpha$ -addition to alkynes to promote *exo*-cyclization during ring-closing enyne metathesis (RCEYM) or to produce conjugated polyenes containing five-membered rings during the cyclopolymerization (CP) of 1,6-heptadiynes. There are a few reports of  $\beta$ -selective addition to alkynes using Schrock catalysts based on Mo but none for readily accessible and easy-to-use Ru-based catalysts. We report the first example of  $\beta$ -selective addition to alkynes using Grubbs Z-selective catalyst, which produces only *endo* products during the RCEYM reaction of terminal enynes

and promotes the CP of 1,6-heptadiyne derivatives to give conjugated polyenes containing a six-membered ring as a major repeat unit. This unique preference for  $\beta$ -selectivity originated from the side-bound approach of alkynes to the catalyst, where the steric hindrance between the chelating N-heterocyclic carbene ligand of the catalyst and the alkynes disfavored  $\alpha$ -addition. To enhance the  $\beta$ -selectivity for CP further, one could increase the size of the substrates on the monomers and lower the reaction temperature to obtain conjugated polyenes containing up to 95% six-membered rings. Moreover, the physical properties of the resulting polymer were analyzed in detail and compared with those of the conjugated polyenes containing only five-membered rings prepared from the same monomer but with a conventional Grubbs catalyst.

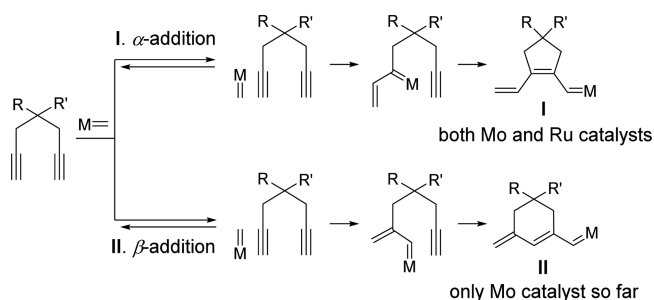


## INTRODUCTION

Cyclopolymerization (CP) of diyne derivatives,<sup>1</sup> along with alkyne polymerization<sup>2</sup> via olefin metathesis reaction, is one of the most powerful and efficient methods for synthesizing conjugated polyenes. Initially, ill-defined catalysts, such as Ziegler-type,<sup>3</sup> MoCl<sub>5</sub>, and WCl<sub>6</sub>, were used.<sup>4</sup> Then, the development of homogeneous Schrock catalysts provided the first groundbreaking contribution to the understanding of the mechanism of CP and the structural information for the resulting conjugated polyenes.<sup>5–9</sup> Recently, the scope of CP was greatly expanded with the development of Ru-based Grubbs catalysts and modified Grubbs catalysts because they were highly active, very user-friendly, and tolerant to air, moisture, and many functional groups.<sup>10–13</sup>

There are two possible pathways for CP:  $\alpha$ -addition and  $\beta$ -addition. The pathway depends on the orientation of the approaching alkylidenes toward the terminal alkynes.<sup>5</sup> For example, 1,6-heptadiyne derivatives undergo CP to give either five-membered rings by  $\alpha$ -addition (Scheme 1, I) or six-membered rings by  $\beta$ -addition (II).<sup>5</sup> Initially, ill-defined catalysts and Schrock catalysts promoted the nonselective addition to alkynes to produce conjugated polyenes with random microstructures containing both five- and six-membered rings as repeat units.<sup>1</sup> Since then, there have been

### Scheme 1. Two Possible Pathways for the Cyclopolymerization of 1,6-Heptadiyne Derivatives



many efforts to control the regioselectivity of the catalyst addition to obtain more regular and well-defined conjugated polyene structures.

The first breakthrough came from the Schrock and Buchmeiser groups, who developed new Mo-based catalyst systems to prepare conjugated polyenes containing either six-<sup>7</sup> or five-membered rings<sup>8</sup> from the CP of 1,6-heptadiyne derivatives by selective  $\beta$ - or  $\alpha$ -addition, respectively.

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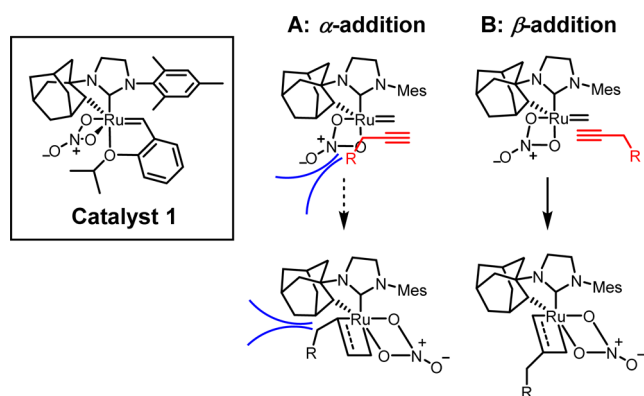
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Subsequently, another groundbreaking result was reported by Buchmeiser and co-workers, who demonstrated the first example of CP using easy-to-use, modified Grubbs catalysts containing electron-withdrawing ligands, such as the trifluoroacetate ligand, and showed that these catalysts produced conjugated polyenes with five-membered ring repeat units exclusively via  $\alpha$ -addition.<sup>8d,10</sup> Recently, our group reported a highly efficient living CP of 1,6-heptadiyne derivatives using third-generation Grubbs catalyst to produce conjugated polyenes with exclusive five-membered ring backbones with excellent molecular weight control and narrow polydispersity index (PDI).<sup>11</sup> With this catalyst, the syntheses of fully conjugated block copolymers and other functional polyenes were also possible.<sup>11–13</sup> However, the formation of conjugated polyenes with six-membered rings by selective  $\beta$ -addition using Ru catalysts has not been achieved. Instead, Ru catalysts could only produce polyenes with six-membered rings from various 1,7-octadiyne monomers by selective  $\alpha$ -addition.<sup>12</sup> Hence, we became interested in the selective  $\beta$ -addition using Ru catalysts because there had been no investigations in this area since the last reports from Schrock's group 20 years ago.<sup>7</sup> Herein, we discuss the preference of  $\beta$ -addition to alkynes using a new Ru-based catalyst containing a chelating N-heterocyclic carbene (NHC) ligand, also known as Grubbs Z-selective catalyst,<sup>14c</sup> and demonstrate the first example of ring-closing enyne metathesis (RCEYM) to produce a six-membered *endo* product exclusively from terminal enynes. In addition, the  $\beta$ -selective CP of 1,6-heptadiyne derivatives is reported to produce conjugated polyenes containing predominantly six-membered ring repeat units with up to 95% selectivity. We developed a plausible model to explain this unprecedented regioselectivity for Grubbs Z-selective catalyst in both RCEYM and CP and provided strategies to enhance the  $\beta$ -selectivity. Lastly, we conducted several characterizations to compare the physical and electronic properties of the polyenes containing five- and six-membered ring microstructures.

## RESULTS AND DISCUSSION

In 2011, Grubbs and co-workers developed a new family of Ru-based catalysts containing chelating NHC ligands that promoted olefin metathesis reactions with high Z-selectivities.<sup>14</sup> In particular, the introduction of adamantyl and nitrate ligands (Grubbs Z-selective catalyst, catalyst **1**, Scheme 2)<sup>14c</sup> dramatically enhanced both the catalytic activity and Z-selectivity in various olefin metathesis reactions, such as

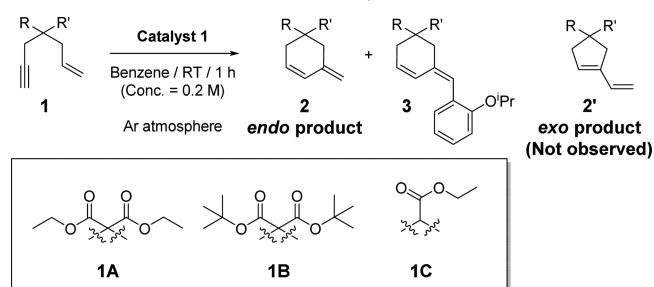
**Scheme 2. Proposed Model for the  $\beta$ -Addition Preference of Catalyst **1****<sup>14c,20</sup>



cross-metathesis,<sup>15</sup> macrocyclic ring-closing metathesis,<sup>16</sup> asymmetric ring-opening cross-metathesis,<sup>17</sup> ethenolysis,<sup>18</sup> and ring-opening metathesis polymerization<sup>19</sup> reactions. Interestingly, DFT calculations revealed that catalyst **1** preferred the side-bound approach<sup>20</sup> to olefins, which was in sharp contrast to the conventional Grubbs catalysts, which favored the bottom-bound approach.<sup>21</sup> As a result, this new approach caused steric repulsions between the substituents on the olefin and chelating NHC ligand, leading to a high Z-selectivity.<sup>20a</sup> With these reports, we envisioned that catalyst **1** might react with the alkynes via  $\beta$ -addition, not  $\alpha$ -addition, because the substituents of the side-bound alkynes would experience a severe steric hindrance with the adamantyl and nitrate ligands during  $\alpha$ -addition (Scheme 2A). However, the substituent on the alkynes could approach catalyst **1** away from the bulky ligands by  $\beta$ -addition, resulting in the least steric hindrance (Scheme 2B). Therefore, one could achieve selective  $\beta$ -addition to alkynes with Ru-based catalysts for the first time if alkynes followed the same mechanism as that for the highly Z-selective olefin metathesis reactions.

Based on the proposed model for selective  $\beta$ -addition, our investigations began with the idea that this unique selectivity of catalyst **1** would undergo the RCEYM reaction from substrate **1** to selectively produce *endo* product **2**, not *exo* product **2'** (Table 1). RCEYM reaction is one of the most useful olefin

**Table 1. RCEYM Using Grubbs Z-Selective Catalysts To Give the *endo* Product Exclusively**



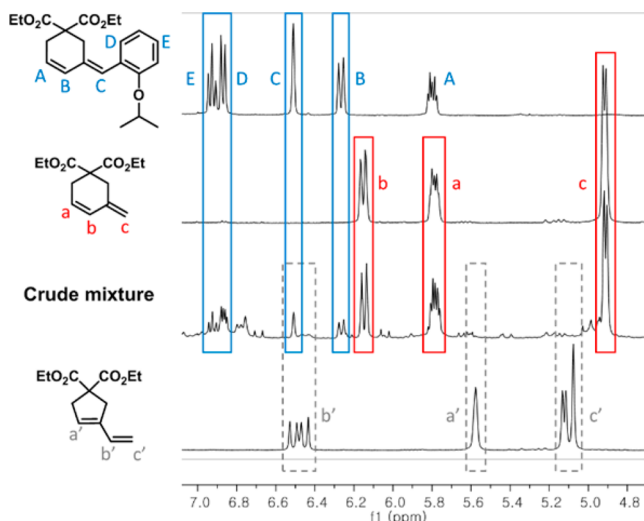
entry	substrate	cat loading (mol %)	conv (%) <sup>a</sup>	isolated yield (%) (2 + 3)
1	1A	10	51	38 (32 + 6)
2		20	>99	64 (56 + 8)
3	1B	10	67	51 (45 + 6)
4		20	>99	72 (64 + 8)
5	1C	10	36	16 (10 + 6)
6		20	60	24 (16 + 8)

<sup>a</sup>Calculated from the <sup>1</sup>H NMR spectrum of a crude reaction mixture.

metathesis reactions that gives cyclic dienes from substrates bearing both alkene and alkyne moieties.<sup>22</sup> It has been well-known that  $\alpha$ -addition of catalysts to the alkyne would produce *exo*-cyclic dienes, while  $\beta$ -addition would produce *endo*-cyclic dienes.<sup>22a</sup> Ru-based Grubbs catalysts showed a strong preference for  $\alpha$ -addition to give *exo* products;<sup>22b,23</sup> in particular, 4,4-substituted hept-1-en-6-yne (**1**) exclusively produced the five-membered *exo* product.<sup>23c</sup> One notable exception was a special Mo catalyst developed by Hoveyda and Schrock that selectively produced *endo* products.<sup>24</sup>

We employed three substituted enynes (**1A–1C**, Table 1) to determine whether the RCEYM of terminal enynes using catalyst **1** would show any regioselectivity. Delightfully, we observed (from the <sup>1</sup>H NMR spectra of the crude reaction

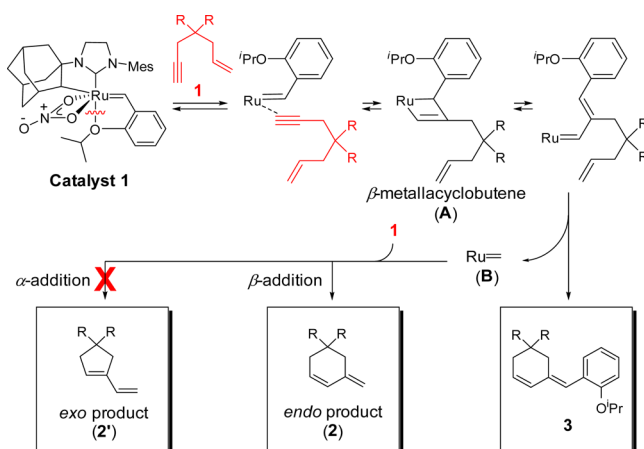
mixtures) that only six-membered *endo* products (**2**) were obtained in all cases, without any signals corresponding to the five-membered *exo* products (**2'**) (Figure 1). In addition, a



**Figure 1.**  $^1\text{H}$  NMR spectra of **3A**, **2A** (top), reaction mixture from entry 2 (middle), and **2'A** (bottom).

small amount of benzylidene-attached products (**3**) containing the six-membered *endo* ring were also obtained (Table 1). This result was in sharp contrast to the previous RCEYM of terminal enynes, which yielded only five-membered *exo* ring products.<sup>23c,24b</sup> Scheme 3 describes the formation of *endo* products

### Scheme 3. Proposed Mechanism of RCEYM Using Catalyst **1**



**2** and **3** using catalyst **1**. Just like the proposed model, catalyst **1** preferentially reacted with the alkyne via  $\beta$ -addition to form the initial  $\beta$ -metallacyclobutene intermediate of **A** (Scheme 3). Then, the new alkylidene initially cyclized to give **3**, a six-membered *endo* product containing benzylidene transferred from catalyst **1**. After this first cycle, Ru methylidene became the active species (**B**) and catalyzed the formation of *endo* product **2**. Although the formation of **3** was inevitable because of the intrinsic structure of catalyst **1**, it is important to note that both **2** and **3** originated from the  $\beta$ -addition of catalyst **1**.

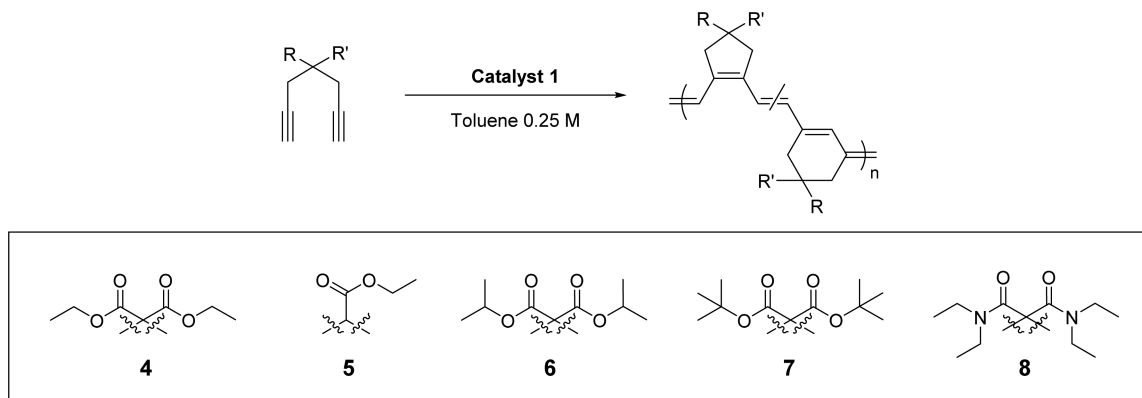
Initially, the ethyl malonate-type enyne (**1A**) showed a 51% conversion in benzene with 10 mol % of catalyst **1** in 1 h, and we isolated a total of 38% of the *endo* products, including 32%

of the pure *endo* product (**2A**) and 6% of the benzylidene-coupled product (**3A**, Table 1, entry 1). Increasing the catalyst loading to 20 mol % further increased the total isolated yield to 69% for the *endo* product (entry 2). When a sterically bulkier *tert*-butyl group was introduced to the substrate (**1B**), the isolated yield of both of the *endo* products increased up to 72% (entries 3 and 4), presumably due to Thorpe–Ingold effects, which facilitated the ring-closing reactions.<sup>12,25</sup> In contrast, the RCEYM of **1C** with a smaller monosubstituent showed a much lower efficiency. The conversion of **1C** was only 36%, and the isolated yield of the total *endo* product was only 16% (entry 5) when treated with 10 mol % of catalyst **1**. Even with 20 mol % of the catalyst, the conversion and the yield of the total *endo* product were 60 and 24%, respectively (entry 6). By in-depth analysis of the crude mixtures, we realized that **1C** also underwent side reactions of undesired alkyne polymerization to generate substituted polyacetylene in an 11% isolated yield.<sup>2,10f</sup> This polymerization was supported by NMR and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) analyses, and the  $M_n$  (number-average molecular weight) of 1.9 kDa was estimated by SEC (size-exclusion chromatography) (Supporting Information Figures S1–S4). This result suggests that there were competing reaction pathways for intramolecular enyne cyclization and intermolecular alkyne polymerization. The former might be disfavored when the substituent is small (Thorpe–Ingold effect),<sup>12</sup> such as in **1C**, and also because alkynes are more reactive than alkenes.<sup>25,26</sup> Despite this side reaction, *endo*-selectivity was still retained without any *exo* products in all cases. All of the results reflected that catalyst **1** underwent exclusive  $\beta$ -addition, regardless of the size of the substituents, even though the efficiency of RCEYM depended on the size of the substituents. In short, we successfully achieved the first *endo*-selective RCEYM of terminal enynes using the user-friendly and commercially available Ru-based catalyst **1** after the pioneering achievement of Hoveyda and Schrock using a Mo catalyst system.<sup>24</sup>

Based on the exclusive formation of the *endo* product from catalyst **1**, we pursued  $\beta$ -selective CP to give conjugated polyenes containing six-membered rings from 1,6-heptadiyne derivatives. Notably, there was only one example of such CP, again from Schrock's group who developed Mo alkylidene-containing sterically bulky carboxylate ligands to enforce  $\beta$ -addition.<sup>5</sup> However, there was no report of such CP using readily accessible Ru-based catalysts. Initially, we examined the reactivity and selectivity of catalyst **1** for the cyclopolymerization of diethyl dipropargylmalonate (DEDPM, **4**) with 2 mol % of catalyst loading (or  $[M]/[C] = 50$ ) at room temperature. We were delighted to find that the conversion to the conjugated polyene after 3 h was 91%. More importantly, the ratio between the five- and six-membered rings on the polymer backbone was 1:3.4 (77% six-membered rings, entry 1, Table 2), determined by  $^{13}\text{C}$  NMR, which showed well-resolved chemical shifts for the carbonyl carbon and the quaternary carbon depending on the ring sizes, that is, five- or six-membered rings.<sup>6</sup> We used the ratio obtained from the signals for the carbonyl carbon as a lower limit (Table 2). Interestingly, this result was in sharp contrast to the previous CP results from the conventional Ru catalysts that produced the conjugated polyenes with only five-membered rings by  $\alpha$ -addition.<sup>10,11</sup>

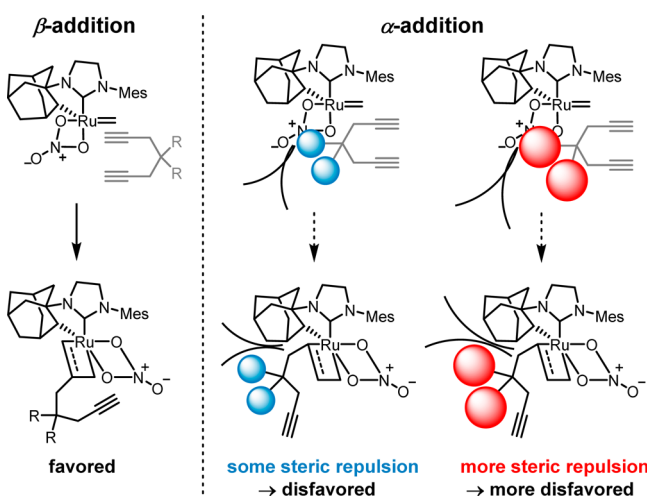
According to our proposed model,  $\alpha$ -addition would be further suppressed with increasing steric repulsions between the substituent on the alkynes and the adamantyl NHC ligand on the catalyst (Figure 2). To test this idea, various monomers

Table 2. Malonate-Type Monomers



entry	monomer	[M]/[C] <sup>a</sup>	temp	time (h)	conv (%) <sup>b</sup>	yield (%) <sup>c</sup>	M <sub>n</sub> theor. (kDa)	M <sub>n</sub> (kDa) <sup>d</sup>	PDI <sup>d</sup>	5/6 <sup>e</sup>	5/6 <sup>f</sup>
1	4	50	rt	3	91	57	10.8	8.6	1.61	1:3.4	1:4.3
2	5	50	rt	3	79	41	6.5	6.6	1.56	1:2.0	nd
3	6	50	rt	3	95	80	12.5	13.1	1.60	1:4.9	1:5.6
4	7	50	rt	3	88	43	12.9	15.6	1.54	1:6.5	1:8.9
5	8	30	rt	3	82	78	7.1	6.9	1.49	1:6.1	nd
6	4	50	-40 °C	48	81	53	8.5	8.0	1.69	1:6.4	1:7.6
7	5	50	-40 °C	72	77	49	6.3	7.9	1.96	1:2.4	nd
8	6	50	-40 °C	48	92	87	12.1	16.4	1.69	1:11.4	1:11.6
9	7	50	-40 °C	36	78	50	11.4	12.5	1.52	1:13.8	1:15.6
10 <sup>g</sup>	7	15	-40 °C	4	>99	55	4.4	8.9	1.53	1:17.8	1:21.0

<sup>a</sup>Monomer-to-catalyst ratio. <sup>b</sup>Calculated from <sup>1</sup>H NMR spectra. <sup>c</sup>Precipitated in hexane at -78 °C. <sup>d</sup>Determined by tetrahydrofuran SEC calibrated using polystyrene standards. <sup>e</sup>Calculated from <sup>13</sup>C NMR spectra based on the signals from the carbonyl carbon. <sup>f</sup>Calculated from <sup>13</sup>C NMR spectra based on the signals from the quaternary carbon. <sup>g</sup>Conducted at 0.1 M.



**Figure 2.** Proposed model for the preference of  $\beta$ -addition in CP using Grubbs *Z*-selective catalyst system.

containing substituents of different sizes at the 4-position were synthesized and examined for the cyclopolymerization (Table 2). Monosubstituted diyne **5** bearing the smallest substituent showed a much lower six-membered ring selectivity (5-ring/6-ring = 1:2.0, entry 2), presumably because the steric repulsion was insufficient for selective  $\beta$ -addition. In contrast, when introducing two isopropyl groups (bulkier than the ethyl group in **4**) to monomer **6**, the six-membered ring selectivity of the resulting polymer increased significantly to 1:4.9 (entry 3). Finally, the introduction of even bulkier *tert*-butyl (**7**) and *N,N*-diethyl amide group (**8**) further increased the selectivity to 1:6.5 and 1:6.1, respectively (entries 4 and 5). In all cases,

molecular weights of the polymers determined by SEC showed reasonable correlation with their theoretical values. The conjugated polyenes were isolated with moderate yields, and their PDIs were relatively broad, presumably due to the slow initiation and some termination. In short, these results demonstrate that the steric factor of the monomers obviously influenced the approach of the alkynes to catalyst **1** and altered the microstructure of the resulting polyenes. Furthermore, this validated our proposed model that the monomers with larger substituents, such as the *tert*-butyl group, effectively induced  $\beta$ -addition to produce six-membered ring-rich conjugated polyenes.

We repeated the CP at lower reaction temperatures down to -40 °C (Table 2, entries 6–10) to further increase the selectivity for  $\beta$ -addition and six-membered ring formation. In the case of monomer **4**, the five- to six-membered ring ratio of the resulting polyenes increased significantly from 1:3.4 to 1:6.4 when compared to the room temperature case (entry 1 vs entry 6). Meanwhile, the polymerization of the smallest monomer (**5**) gave only a small enhancement of the ratio to 1:2.4, even at -40 °C (entry 7). In contrast, **6**, bearing the bulkier substituent (*i*Pr), afforded the conjugated polyene with a much higher  $\beta$ -addition preference (1:11.4, entry 8). Finally, the reaction of the largest monomer (**7**) at -40 °C resulted in the highest six-membered ring selectivity (1:13.8, entry 9). As shown in Figure 3 (and Figure S15), the <sup>13</sup>C NMR spectrum clearly showed the well-resolved signals for both sets of carbonyl and quaternary carbons for easy characterization. Interestingly, the stereochemistry on the olefins in a five-membered ring repeat unit was exclusively *cis*, and this made perfect sense because of the intrinsic nature of Grubbs *Z*-selective catalyst to produce *Z*-olefin (Figure S15). Although CP became much slower at -40

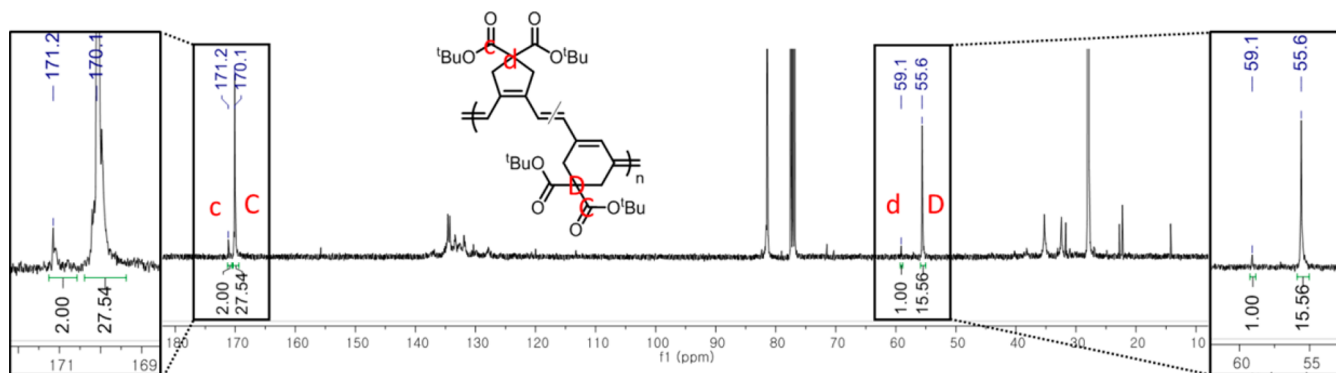


Figure 3.  $^{13}\text{C}$  NMR spectra of the polymer from entry 9 in Table 2.

$^{\circ}\text{C}$  (at least 36 h) than at room temperature, the conversion and  $M_n$  were similar. More importantly, the preference for  $\beta$ -addition increased significantly with the increasing size of the monomers because the kinetic product was favored at a lower temperature, implying that the activation barrier for  $\beta$ -addition was indeed lower than that of  $\alpha$ -addition for catalyst **1**. This result shows the first example of  $\beta$ -selective CP to produce conjugated polyenes containing the six-membered rings with Grubbs catalyst based on Ru metal.

Contrary to the results of RCEYM, which produced only *endo* products via exclusive  $\beta$ -addition,  $\beta$ -selectivity for CP, in general, seemed to be lower than that for RCEYM due to some degree of competing  $\alpha$ -addition, depending on the monomer structures. The different preference for the  $\beta$ -addition selectivity between CP and RCEYM could also be understood from our proposed model modified by the additional steric factors of the growing polymer chain itself (Figure 4). In other

of the polymer chain created an additional steric repulsion between the substituents of the monomers and the polymer chain during the  $\beta$ -addition mode, as depicted in Figure 4. As a result, some competing  $\alpha$ -addition to produce five-membered rings seemed inevitable, even though the major steric repulsion still came from the alkynes and the adamantyl ligand. Poly-7, with a low degree of polymerization (DP) of 15, was synthesized to support this assumption, and this conjugated polyene showed an even higher six-membered ring selectivity (1:17.8) compared to that of poly-7 with DP = 36 (Table 2, entry 10). Now, one can produce conjugated polyenes with up to 95% six-membered ring selectivity using the user-friendly Grubbs catalyst.

It would be worthwhile to investigate the properties of the conjugated polyenes containing six-membered rings in detail and compare them to the analogous polyenes with the five-membered ring structure prepared via  $\alpha$ -addition because there is only one example for the synthesis of these conjugated polyenes via  $\beta$ -addition.<sup>7</sup> To investigate the differences in physical and electronic properties based on the polymer backbone composition, two types of poly-7 of the same  $[M]/[C]$  were prepared: one produced by catalyst **1** (Table 2, entry 9, P(7), 5-ring/6-ring = 1:14) and the other containing a five-membered ring exclusively produced by Grubbs third-generation catalyst (P(7-I)). From their UV-vis spectra in the solution states,  $\lambda_{\text{max}}$  of P(7) appeared at 513 nm without any vibronic peaks,<sup>27</sup> and this value was lower than that of P(7-I) at 588 nm, which corresponds to the 0–0 vibronic peak (547 nm for 0–1 vibronic peak).<sup>11d</sup> This implied that the polymer backbone for P(7-I) was more planar presumably due to the presence of *Z*-olefins in P(7) (Figure S15). However, due to a much broader absorption spectrum for P(7), its optical band gap was lower than that of P(7-I) by 0.1 eV (1.93 and 2.02 eV, respectively) (Table 3 and Figure 5). In contrast, the UV-vis analysis of P(7) in the thin film state revealed a significantly blue-shifted spectrum with a lower  $\lambda_{\text{max}}$  of 484 nm while maintaining the optical band gap (presumably because the bulky substituents distorted much of the backbone planarity of

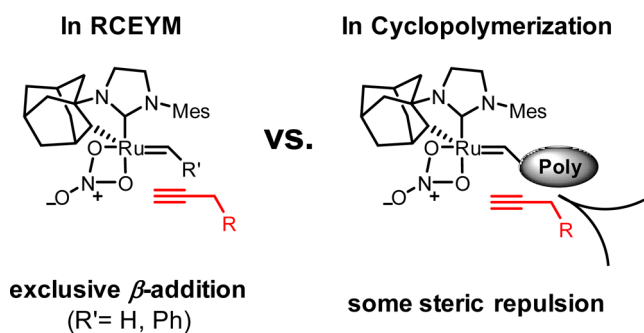


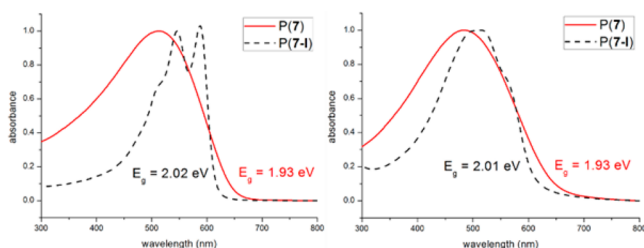
Figure 4. Decreased  $\beta$ -addition preference caused by steric bulkiness of the growing polymer chain.

words, the resting state of the catalytic species in RCEYM was mostly the smallest Ru methylidene and relatively small benzylidene, while the propagation species during CP was the much bulkier alkylidenes containing polymer chains. Therefore, as the polymerization proceeded, this increasing steric bulkiness

Table 3. Comparison of Physical and Electronic Properties of P(7) and P(7-I)

polymer	catalyst	solution		film		$E_{\text{HOMO}}$ (eV) <sup>c</sup>	$T_d$ ( $^{\circ}\text{C}$ ) <sup>d</sup>	$T_g$ ( $^{\circ}\text{C}$ ) <sup>e</sup>
		$\lambda_{\text{max}}$ (nm) <sup>a</sup>	$E_g$ (eV) <sup>a,b</sup>	$\lambda_{\text{max}}$ (nm) <sup>a</sup>	$E_g$ (eV) <sup>a,b</sup>			
P(7)	catalyst <b>1</b>	513	1.93	484	1.93	−4.94	245	110
P(7-I)	Grubbs third gen.	588, 547	2.02	515	2.01	−5.14	242	107

<sup>a</sup>Determined by UV-vis spectroscopy. <sup>b</sup>Calculated from the onset point of the UV-vis spectra. <sup>c</sup>Determined by cyclic voltammetry. <sup>d</sup>Determined by thermogravimetric analysis. <sup>e</sup>Determined by differential scanning calorimetry.



**Figure 5.** UV-vis spectra of P(7) and P(7-I) in a chloroform solution (left) and in the film state (right).

the polymer in the film state, shortening the effective conjugation length of the polymer).<sup>12a,28</sup> A similar blue shift with a lower  $\lambda_{\text{max}}$  of 515 nm was observed for P(7-I) in the film state (Figure 5).

We also measured the highest occupied molecular orbital (HOMO) levels of these two conjugated polymers containing either five- or six-membered ring repeat units by cyclic voltammetry in a dichloromethane solution (Table 3 and Figure S16). For comparison, the HOMO level of P(7) (mostly six-membered rings) was  $-4.94$  eV, whereas that of P(7-I) (exclusively containing five-membered rings) was  $-5.14$  eV. This implied that P(7) was easier to oxidize and would be more air- and moisture-sensitive than P(7-I). The thermal properties of these polymers were also evaluated by thermogravimetric analysis and differential scanning calorimetry, and they showed similar decomposition temperatures ( $245$  °C for P(7) and  $242$  °C for P(7-I)) and glass transition temperatures ( $110$  °C for P(7) and  $107$  °C for P(7-I)) (Table 3 and Figures S17 and S18).

## CONCLUSION

In summary, we demonstrated unprecedented regioselectivity among Ru-based catalysts during the RCEYM of terminal enynes and CP of 1,6-heptadiyne derivatives using the commercially available Grubbs Z-selective catalyst (catalyst 1). This unique catalyst selectively produced *endo* products containing six-membered rings by RCEYM and conjugated polyenes containing six-membered rings as a major repeat unit by CP. This new selectivity originated from the preference of catalyst 1 for  $\beta$ -addition instead of  $\alpha$ -addition because of the side-bound approach instead of the bottom-bound approach. This study is significant because it is the first example of Ru-catalyzed RCEYM and CP to show high six-membered ring selectivity via  $\beta$ -addition, contrary to the previous results that typical Ru-based catalysts gave only five-membered ring structures during analogous RCEYM and CP. We also investigated the determining factors for high  $\beta$ -selectivity in CP and found that the increasing steric bulkiness of the substituents on the monomers and decreasing the reaction temperature enhanced the selectivity for  $\beta$ -addition up to 95%. Several physical properties of the resulting polymer containing mostly six-membered ring repeat units were analyzed and compared with those of the analogous conjugated polyenes containing five-membered rings prepared from the same monomer. We believe that these results will contribute not only to an understanding of the reaction pathway of RCEYM and CP but also to the access of a new potential material prepared by the Grubbs Z-selective catalyst.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b05572.

Experimental details, synthesis characterization data ( $^1\text{H}$  and  $^{13}\text{C}$ NMR, MS, SEC traces), and spectra of the compounds (PDF)

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### Notes

The authors declare no competing financial interest.

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