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Tandem Ring-Opening/Ring-Closing Metathesis Polymerization: Relationship between Monomer Structure and Reactivity

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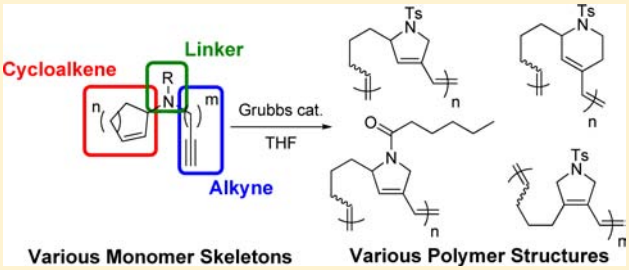
Supporting Information

ABSTRACT: Monomers containing either cycloalkenes with low ring strain or 1-alkynes are poor monomers for olefin metathesis polymerization. Ironically, keeping two inactive functional groups in proximity within one molecule can make it an excellent monomer for metathesis polymerization. Recently, we demonstrated that monomer **1** having cyclohexene and propargyl moieties underwent rapid tandem ring-opening/ring-closing metathesis (RO/RCM) polymerization via relay-type mechanism. Furthermore, living polymerization was achieved when a third-generation Grubbs catalyst was used. Here, we present a full account on this tandem polymerization by investigating how various structural modifications of the monomers affected the reactivity of the tandem polymerization. We observed that changing the ring size of the cycloalkene moieties, the length of the alkynes, and linker units influenced not only the polymerization rates but also the reactivities of Diels–Alder reaction, which is a post-modification reaction of the resulting polymers. Also, the mechanism of tandem polymerization was studied by conducting end-group analysis using ^{1}H NMR analysis, thereby concluding that the polymerization occurred by the alkyne-first pathway. With this mechanistic conclusion, factors responsible for the dramatic structure–reactivity relationship were proposed. Lastly, tandem RO/RCM polymerization of monomers containing sterically challenging trisubstituted cycloalkenes was successfully carried out to give polymer repeat units having tetrasubstituted cycloalkenes.



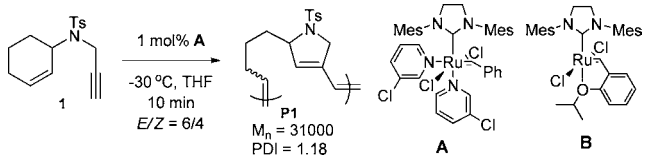
INTRODUCTION

During the last two decades, olefin metathesis reaction has been widely used as an efficient method for synthesizing new molecules by forming new carbon–carbon double bonds.[1] Three major types of the olefin metathesis, ring-opening metathesis (ROM), cross metathesis (CM), and ring-closing metathesis (RCM), were developed as versatile tools in organic synthesis. Similarly, ring-opening metathesis polymerization (ROMP)[2] from ROM, acyclic diene metathesis (ADMET) polymerization[3] from CM, and cyclopolymerization[4] from RCM were developed; these reactions greatly broadened the scope of polymerization methodology and produced a wide variety of polymers from various monomers. However, some monomers hardly undergo polymerization. For instance, cycloalkenes with low ring strain, such as cyclohexenes, hardly polymerize because the equilibrium between ROM and RCM is far more favorable to the monomeric state as cyclohexene.[5,6] Also, the polymerization of 1-alkynes is challenging, especially for ruthenium-based catalysts, because the catalysts undergo α-addition with 1-alkynes, generating sterically shielded 1,1-disubstituted ruthenium carbenes. Therefore, the propagation is retarded, and obtaining high-molecular-weight polymers in high yield becomes difficult.[7,8] Thus, conventional metathesis polymerization of monomers containing these unreactive functional groups is difficult.

In the organic chemistry community, researchers have developed various elegant tandem olefin metathesis reactions by performing relay of two or more metathesis reactions in a single step. This method provided a route for the efficient synthesis of complex organic molecules[9] and natural products.[10] One particular example is tandem enyne RO/RCM reaction, which undergoes relay rearrangement reaction from substrates comprising alkynes and cycloalkenes.[11] The products or intermediates of the enyne metathesis reaction could be further functionalized by consecutive CM or Diels–Alder reactions, thereby increasing the complexity of the molecules.[12,13]

By adopting the concept of tandem metathesis reactions from organic synthesis, we recently reported living tandem RO/RCM polymerization of monomer **1** using the third-generation Grubbs catalyst **A** (Scheme 1).[14] Although **1** contained cyclohexene and propargyl moieties, which were unreactive toward the conventional metathesis polymerization

Scheme 1. Example of Tandem RO/RCM Polymerization



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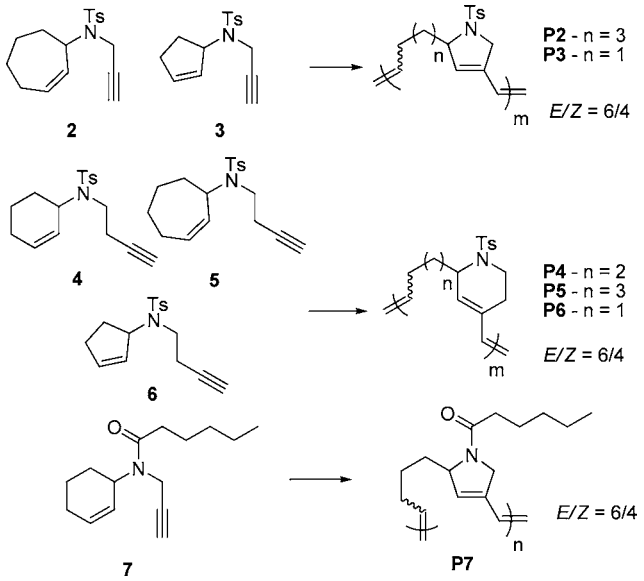
on their own, placing two functional groups in proximity made **1** an excellent monomer that underwent extremely fast polymerization in 1 min at room temperature via regioselective relay tandem RO/RCM reaction. We also achieved controlled polymerization at −30 °C to inhibit the chain-transfer reaction so that polydispersity index (PDI) was narrower than 1.2. Notably, the newly generated alkene showed *E*/*Z* ratio of 6/4, indicating kinetic control of polymerization. The reaction scope of this tandem RO/RCM polymerization was further expanded to include the synthesis of various diblock copolymers by combining the tandem polymerization with either ROMP or cyclopolymerization. In addition, post-functionalization on the newly generated dienes of the polymer backbone was possible by Diels−Alder reaction. Based on this basic skeleton of **1**, one can expand the monomer scope by modifying the structures of **1** so that various new polymers can be prepared by altering the ring sizes, alkyne moieties, and linker groups. Herein, we present a full report on the regioselective tandem RO/RCM polymerization for various monomers and their post-modification by Diels−Alder reaction. In addition, we systematically investigated how each modification of the monomer structures affected reactivities and revealed the details of the mechanism of the tandem polymerization. Notably, all these monomers contained substituted cycloalkenes having low ring strain so their ROMP was impossible,[15] but now we present a new strategy to polymerize these highly challenging monomers via the powerful tandem RO/RCM polymerization.

RESULTS AND DISCUSSIONS

The core skeleton of monomer **1** contains cycloalkene and 1-alkyne as polymerizable groups connected by toluenesulfonyl amide group. To broaden the monomer scope, our initial trial consisted of modifying the ring size of cycloalkenes. As in our previous study, we used the monomer containing cyclohexene that has the lowest ring strain among cycloalkenes. Therefore, other cycloalkenes with relatively higher ring strain, such as cycloheptene and cyclopentene, should undergo tandem RO/RCM polymerization as well, although three-substituted cyclopentenes did not undergo ROMP at all.[15] Cycloheptene derivative (**2**) showed rapid tandem RO/RCM polymerization at room temperature with reactivity comparable to that of **1**. Furthermore, in order to suppress the chain-transfer reaction, the polymerization temperature was lowered to −30 °C and similar to **1**, polymerization of **2** also showed fast propagation and controlled polymerization as PDIs of the polymers were narrower than 1.3, and a linear relationship between monomer-to-initiator ratio (M/I) and molecular weight was observed (Table 1, entries 1−3, Figure 1). Interestingly, when the tandem RO/RCM polymerization of a monomer containing cyclopentene moiety (**3**) was attempted, very sluggish polymerization was observed achieving only 30% conversion even after 12 h of polymerization at room temperature (entry 4). This was puzzling at first because the ring strain of cyclopentene (**3**) was similar to that of cycloheptene (**2**) but was larger than that of cyclohexene (**1**), and therefore, efficient tandem RO/RCM polymerization was expected. To enhance the propagation rate, a second-generation Grubbs−Hoveyda catalyst (**B**) that was thermally more stable was used, and almost complete conversion of **3** was achieved at 50 °C (entry 5). Since the much less reactive monomer **3** was polymerized at a higher temperature, PDI broadening because of the chain-transfer reaction inevitably occurred. Similar to **P1**, the polymer

Table 1. Tandem Metathesis Polymerization of Various Monomers with Different Ring Sizes and Linker Alkynes



entry	monomer (M/I)	temp. (°C)	time	conv.[a]	M_n/PDI[b]
1[c]	**2** (15)	−30	3 min	100%	5.0 k/1.28
2[c]	**2** (30)	−30	5 min	100%	9.1 k/1.28
3[c]	**2** (50)	−30	10 min	100%	12.5 k/1.25
4[c]	**3** (100)	rt	12 h	30%	11.4 k/1.70
5[d]	**3** (50)	50	2 h	98%	13.5 k/1.62
6[c,d]	**4** (50)	50	12 h	<20%	–
7[d]	**5** (50)	50	12 h	0%	–
8[d]	**6** (50)	50	12 h	82%	12.0 k/1.54
9[d]	**6** (50)	65	2 h	100%	15.0 k/1.79
10[c]	**7** (50)	−10	5 min	90%	13.1 k/1.23

[a]Conversion determined by crude ^{1}H NMR. [b]Determined by THF SEC calibrated using polystyrene (PS) standards. [c]**A** was used as catalyst. [d]**B** was used as catalyst.

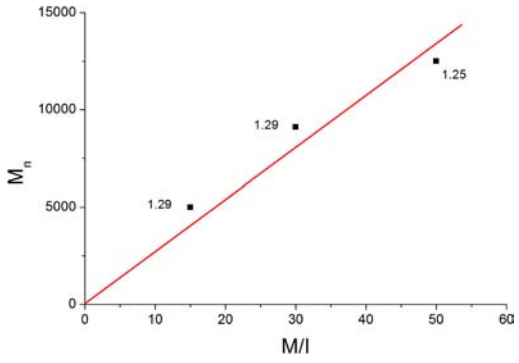


Figure 1. Plot of M_n versus M/I for **P2**. Numbers on the line indicate PDI values.

microstructure showed excellent regiochemistry and the *E*/*Z* ratio on **P2** and **P3** was 6/4.

Next, a structural change was made by changing the length of alkynes. If 1-butynyl group was used instead of propargyl, the polymer unit structure changed from a five-membered ring to a six-membered ring. We investigated how this simple change affected the propagation of the tandem RO/RCM polymerization. Initial trial was done on a monomer **4** containing cyclohexene. However, the polymerization hardly occurred even at 50 or 65 °C (entry 6). No polymer was obtained

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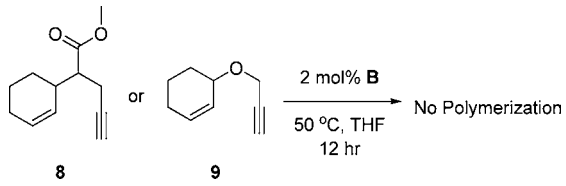
because of low conversion. Even a monomer **5** containing cycloheptene was unreactive and did not undergo polymerization at all (entry 7). Surprisingly, a monomer **6** with cyclopentene underwent tandem RO/RCM polymerization with 82% conversion at 50 °C and, finally, full conversion at 65 °C in 2 h (entries 8 and 9). This result was unexpected, because we initially anticipated that the monomers **4** and **5** would be more reactive than **6** because their propargyl analogs **1** and **2** were more reactive than **3**. However, the reactivity was completely reversed by changing the propargyl group to the homopropargyl group. Overall, the ring closure to make polymers containing six-membered rings was much slower than the five-membered ring cases.[16]

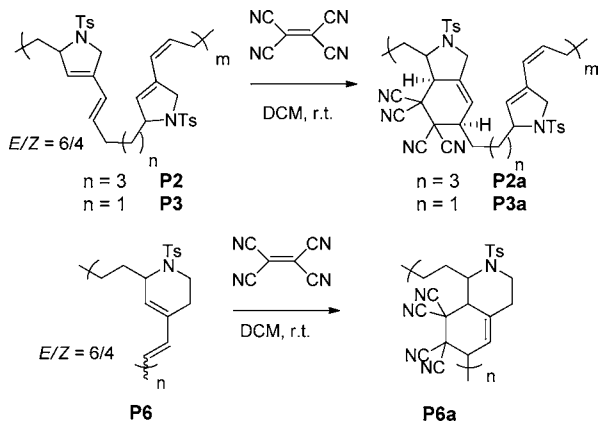
Another key structural factor for the tandem RO/RCM polymerization was the linker unit between cycloalkenes and alkynes. Modifying this linker unit would also change the ring structure of the final polymer unit, and the monomer scope would be expanded. First, sulfonamide was changed to the amide group to give **7**, and it also showed high reactivity and controlled polymerization, thereby affording narrow PDI (entry 10). Nevertheless, the reactivity of **7** was slightly lower than those of **1** and **2**, as polymerization required relatively higher temperature (−10 °C vs −30 °C for **1** and **2**) to achieve high conversion. However, when the linker atom was changed to carbon (**8**) or oxygen (**9**), no polymer was obtained at all even when they were subjected to the forcing conditions by using the catalyst **B** at 50 °C (Scheme 2). This suggested that small change in the linker unit on the monomers also led to huge changes in the tandem polymerization reactivity.

Scheme 2. Unsuccessful Tandem Metathesis Polymerization of Monomers Containing Carbon or Oxygen Linker



Polymers synthesized by the tandem RO/RCM polymerization contain 1,3-diene moiety. A new family of polymers can be prepared by further modifying these functional groups via Diels–Alder reaction.[17] As previously reported, when **P1** with a pyrrolidine unit was reacted with a dienophile, tetracyanoethylene, dienes with *trans*-alkene were fully converted to a Diels–Alder adduct after 48 h, whereas those with *cis*-alkene remained unaltered.[14] Similar post-functionalizations were attempted on these new polymers—**P2**, **P3**, and **P6**. Although the lengths of the tethers on **P2** and **P3** were different (n = 1 for **P3**, n = 2 for **P1**, and n = 3 for **P2**), both contained the same pyrrolidine structure and olefins with the E/Z ratio of 6/4. These features were similar to those of **P1**, and not surprisingly, Diels–Alder reaction of **P2** and **P3** with tetracyanoethylene resulted in 60% conversion with the full conversion of the diene with *trans*-isomers only, while the remaining 40% of the dienes with *cis*-isomer did not react at all, just like in the case of **P1** (Table 2, entries 1 and 2). A minor difference in reactivity between **P2** and **P3** was that Diels–Alder reaction on **P3** was relatively slower than **P2**, presumably because of fewer number of methylene in the repeat unit. To resolve this congestion issue, the Diels–Alder reaction was conducted at 60 °C to achieve the same conversion as in **P2**

Table 2. Post-Functionalization of Polymers by Diels-Alder Reaction



entry	prepolymer (M_n/PDI)[a]	time	conv.[b]	final polymer (M_n/PDI)[a]
1	**P2** 12.3 k/1.21	48 h	60%[d]	**P2a** 14.3 k/1.28
2[c]	**P3** 12.0 k/1.56	16 h	60%[d]	**P3a** 14.0 k/1.64
3	**P6** 8.9 k/1.65	8 h	100%	**P6a** 11.0 k/1.69

[a]Determined by THF SEC calibrated using PS standards. [b]Conversion determined by crude ^{1}H NMR. [c]Reaction was done at 60 °C in 1,2-dichloroethane as a solvent due to low reactivity. [d]Only the *trans* diene underwent Diels–Alder reaction while all the *cis* diene remained.

(entry 2). However, **P6** with the six-membered ring structure showed a much higher reactivity toward the Diels–Alder post-modification with tetracyanoethylene, as all of the dienes regardless of E or Z isomers were converted to Diels–Alder adducts within just 8 h (entry 3). After all three Diels–Alder post-modifications, the SEC traces of polymers were shifted left to give new traces corresponding to higher-molecular-weight polymers while maintaining the PDIs constant. These results suggest that the post-modification did not alter the integrity of the polymers, and a small modification of the polymer structures significantly affected the reactivity of the polymers toward the Diels–Alder post-modification.

Since this relay-type tandem RO/RCM is unique and unprecedented, it would be worthwhile to investigate its mechanism in detail. There are three possible pathways: first, catalyst initiating from the alkyne selectively (pathway **A**: alkyne first); second, catalyst initiating from the cycloalkene selectively (pathway **B**: cycloalkene first); and last, random initiation of the catalyst on either alkyne or cycloalkene nonselectively (pathway **C**: alkyne–cycloalkene mixed) (Scheme 3). If the catalyst selectively initiated and propagated on a single functional group, such as in pathways **A** or **B**, the polymer unit structure would always have head-to-tail structure, and as a result, the polymer would have a regular microstructure. On the other hand, nonselective pathway **C** would produce polymers comprising mixture junctions of head-to-tail, head-to-head, and tail-to-tail, and the polymer structure would be completely random. In our previous study, we intentionally prepared **P1a** by ADMET polymerization of monomer **1a** (Scheme 3). By comparing ^{1}H NMR spectra of **P1** and **P1a**, we could easily rule out the pathway **C**, because NMR spectrum of **P1** vividly showed highly regular repeat units, while that of **P1a** showed random repeat units.[14] Therefore, the pathways **A** and

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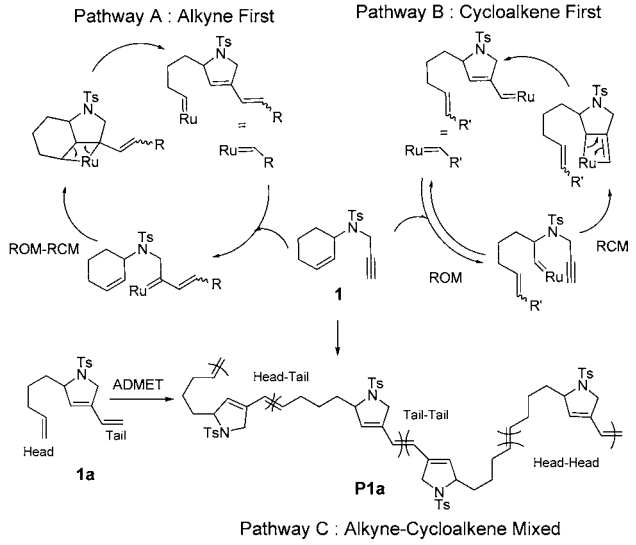
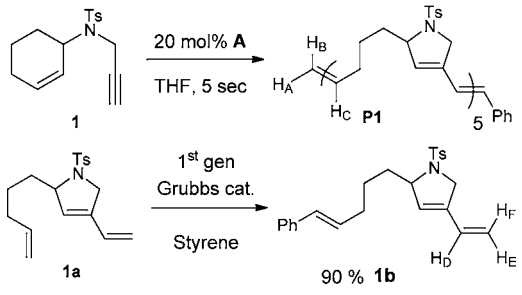
Scheme 3. Possible Mechanisms of Tandem Metathesis Polymerization



B were considered to be the possible pathways of the relay-type tandem RO/RCM. We have previously proposed the pathway **A** as the potentially correct mechanism for the tandem RO/RCM polymerization, because this pathway was more suitable for explaining the extremely fast polymerization.[14]

In order to confirm which mechanism was correct for the tandem polymerization, we performed mechanistic studies on monomers **1** and **2**. If the polymerization followed pathway **A**, the styryl group on the catalyst would be transferred onto the conjugated diene group and the chain-end group would be the terminal nonconjugated alkene obtained after quenching with ethyl vinyl ether. On the other hand, if the catalyst initiated on the cycloalkene first (pathway **B**), the styryl group would be transferred to the nonconjugated alkene and the chain-end group would be conjugated diene. Therefore, we could determine the actual mechanism for the tandem RO/RCM polymerization by conducting end-group analysis using ^{1}H NMR analysis. First, we prepared oligomeric **P1** by treating **1** with 20 mol % **A** and quenching the polymerization by adding ethyl vinyl ether so that its end-groups could be analyzed in detail. For a comparison study, **1b** was independently prepared by selective CM between styrene and the more reactive nonconjugated terminal alkene on **1a** (Scheme 4). When the ^{1}H NMR spectra of three substrates (**1a**, **1b**, and oligo-**P1**) were compared, peaks for all the terminal olefins could be unambiguously assigned (Figure 2a–c). From these data, we observed that oligo-**P1** vividly showed nonconjugated terminal alkene proton signals as H_A, H_B, and H_C, whereas the chemical

Scheme 4. Comparison between P1 and CM Product 1b



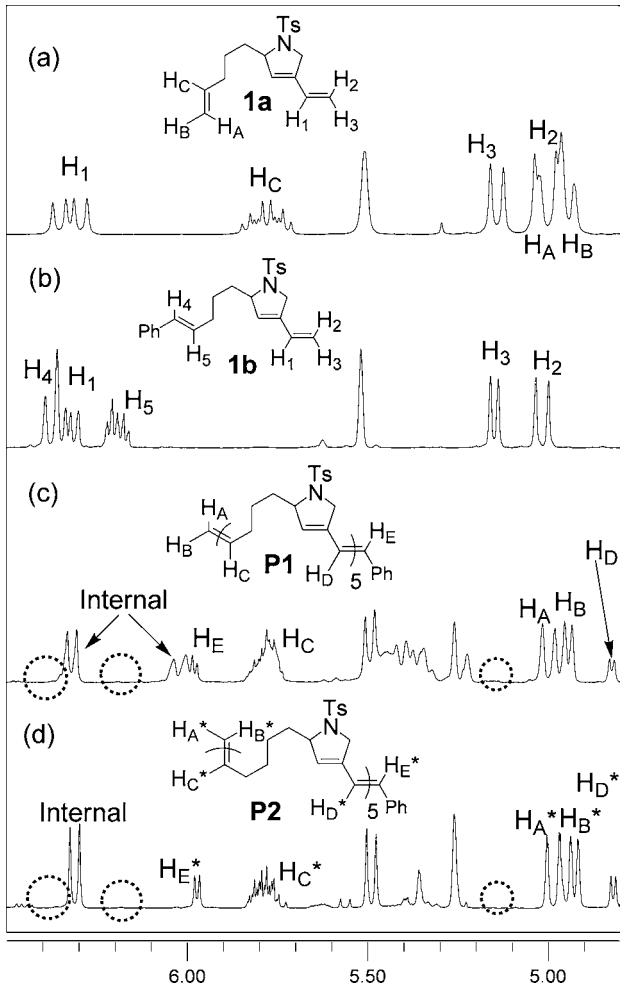


Figure 2. NMR spectra of (a) **1a**, (b) **1b**, (c) oligo-**P1**, and (d) oligo-**P2**.

shifts corresponding to H_{1-5} of **1b** were totally absent. This confirmed that the tandem RO/RCM polymerization of **1** followed the pathway **A** exclusively. We also conducted a similar mechanistic study on **2**, because the monomer containing cycloalkenes with higher ring strains might follow different pathway. Similar chemical shifts, H_A*, H_B*, and H_C* without H_{1-5}, were observed for the oligomeric **P2** as well, suggesting that the polymerization pathway was not altered by the ring strain of cycloalkenes (Figure 2d). All these observations proved that the mechanism of the tandem RO/RCM polymerization follows the pathway **A** exclusively.

One important question was what determined the vastly different reactivities of the various monomers (Scheme 5). As the tandem polymerization proceeded via pathway **A**, several structure–reactivity relationships were postulated. First, there was no clear relationship between the size of cycloalkenes and the reactivity, because a cyclopentene with a propargyl group (**3**) showed the lowest reactivity among the analogous monomers containing different cycloalkenes (**1** and **2**), while a cyclopentene with the homopropargyl group (**6**) was the only monomer promoting successful polymerization (no polymer obtained from **4** and **5**). Second, the reactivity dependence on the length of the alkynes (propargyl vs homopropargyl) was not direct, because **3** and **6**, which differed only by one carbon on the alkyne, showed very similar reactivities. However, other analogous monomers (**1** vs **4** and **2** vs **5**) showed completely

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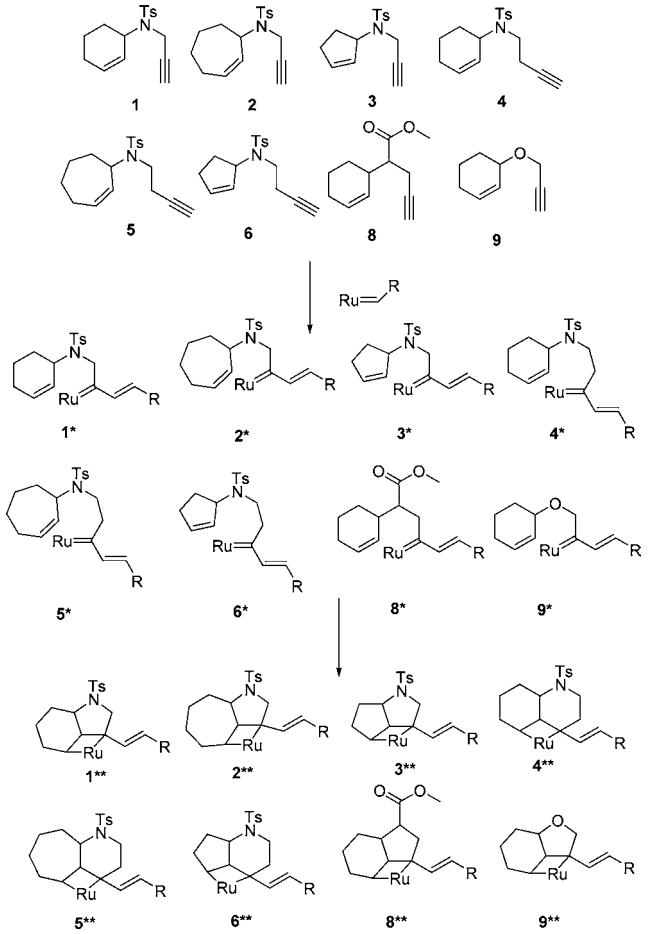
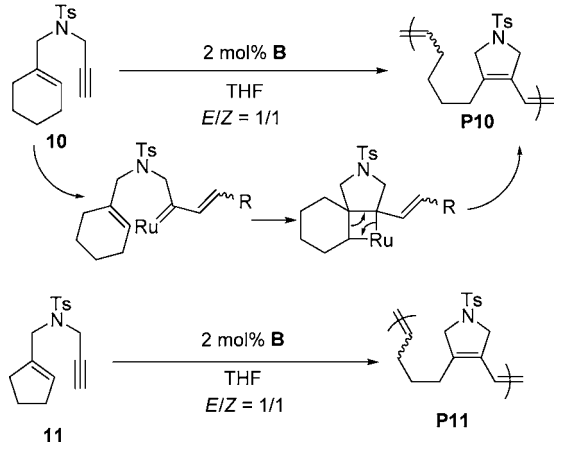
Scheme 5. Possible Intermediates of 1−9 during RO/RCM Reaction



different reactivities. Finally, we postulated that both the ring size and the alkyne length affected the reactivity. With the mechanism of pathway **A**, various metallocyclobutane intermediates from monomers having different cycloalkenes and linker alkynes (Scheme 5, **1******−9****) should be produced. The stability of these intermediates would be governed by the size of both the cycloalkenes and the linker alkynes; even changing the linker atoms from nitrogen (**1**) to carbon (**8**) or oxygen (**9**) greatly affected the polymerization because of different bond lengths and bond angles. In other words, the kinetics of RCM from the resulting alkylidenes, which were obtained by α-insertion, into the alkynes (Scheme 5, 1*−**9***) would be dramatically different because of the slight changes either in the distance or in the bond angle.

Up to now, sterically hindered trisubstituted cycloalkenes with low ring strain, such as 1-methylcyclopentene or 1-methylcyclohexene, have not been polymerized by ROMP.[18] However, we envisioned that utilizing the relay sequence of this efficient RO/RCM process, monomers containing extremely challenging trisubstituted cycloalkenes might undergo the tandem polymerization just as three-substituted cycloalkenes underwent efficient tadem RO/RCM polymerization. Initially, monomer **10** containing a trisubstituted cyclohexene and propargyl group was subjected to 2 mol % of catalyst **B** at room temperature, but no polymer was obtained because of severe steric hindrance of the trisubstituted olefin (Table 3, entry 1). In order to enhance the reactivity, reaction

Table 3. Tandem Metathesis Polymerization of Monomers with Trisubstituted Cycloalkenes

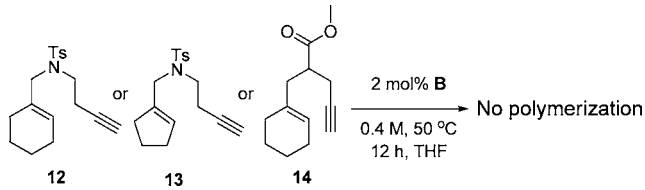


entry	mono.	temp. (°C)	conc. (M)	time	conv.[a]	M_n (PDI)[b]
1	**10**	rt	0.4	3 h	0%	–
2	**10**	50	0.4	6 h	37%	4.4 k (1.61)
3	**10**	60	0.8	12 h	50%	3.9 k (1.25)
4	**11**	50	0.4	12 h	65%	8.0 k (1.93)
5	**11**	60	0.6	12 h	100%	6.0 k (1.57)

[a]Conversion determined by crude ^{1}H NMR. [b]Determined by THF SEC calibrated using PS standards.

temperature was increased to 50 °C to yield **P10** containing tetrasubstituted cyclopentene moiety in 37% conversion (entry 2) and further to 60 °C to achieve 50% conversion, with M_n of 3.9 k (entry 3). To our delight, monomer **11** containing trisubstituted cyclopentene showed 65% conversion at 50 °C and 100% conversion at 60 °C, implying that **11** was more reactive monomer than **10** at the same reaction condition (entries 4 and 5). These results were contrast to the previous results which showed that the monomer containing propargyl group and cyclohexene (**1**) was more reactive than its cyclopentene derivative (**3**). In both cases, E/Z ratio on the newly generated olefin was 1/1, similar to the previous results. On the other hand, monomers containing trisubstituted cycloalkenes and 1-butynyl moieties, **12** and **13**, were totally inactive for the tandem polymerization (Scheme 6). At least,

Scheme 6. Unsuccessful Tandem Metathesis Polymerization of Monomers Containing Carbon or Oxygen Linker



polymerization result of **13** was rather disappointing because its three-substituted cyclopentene derivative, **6**, showed good reactivity toward the tandem polymerization to give the polymer having a six-membered ring repeat unit (Table 1, entries 8 and 9). Also, **14** with carbon linker failed to give any polymer which was consistent with its three-substituted cyclohexene analogue **8** (Scheme 6). This suggested that the monomers with sterically hindered trisubstituted cycloalkenes were much more challenging to undergo the tandem polymerization compared to the disubstituted cycloalkene

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derivatives, and their reactivities were also sensitive to the monomer structures presumably because those slight structural changes had large influence on the stability of intermediates as postulated in Scheme 5.

CONCLUSION

In conclusion, we investigated the tandem RO/RCM polymerization for various monomers containing cycloalkenes and terminal alkynes. We observed that the reactivity was heavily influenced by not only the ring size of the cycloalkenes but also the length of the alkynes and the linker moieties. Monomers **1** and **2** were the most reactive so that even controlled polymerization was possible. However, small modifications of the monomer structure were subtle enough to totally shut down the catalysis completely. The post-modification reaction of the resulting polymers was successfully carried out by the addition of a dienophile that underwent Diels–Alder reaction with the diene moieties on the polymer backbone. This reaction was also influenced by the ring structure in the repeat unit of the polymers. Then, details of the mechanism for the tandem polymerization were studied by conducting end-group analysis using ^{1}H NMR, and it was concluded that the polymerization occurred by the alkyne-first pathway exclusively. With this mechanistic conclusion, we proposed that the stability of the metallocyclobutane intermediates or the accessibility of the newly generated alkylidenes toward the cycloalkenes caused the dramatic structure–reactivity relationship of the monomers for the tandem polymerization. Lastly, we successfully performed rather challenging RO/RCM polymerization of monomers containing trisubstituted cycloalkenes, even though they showed decreased reactivity because of the steric hindrance. In short, we demonstrated a powerful tandem polymerization of monomers containing functional groups that were otherwise sterically and thermodynamically inactive for the conventional ROMP.

ASSOCIATED CONTENT

Supporting Information

Experimental details, synthesis characterization data (^{1}H and ^{13}C NMR, MS, SEC traces, etc.), and spectra of the compounds are available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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