# Investigations into Apopinene as a Biorenewable Monomer for Ring-Opening Metathesis Polymerization

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**S** *Supporting Information*

**ABSTRACT:** The ring-opening metathesis polymerization (ROMP) of apopinene is reported. We find that apopinene reacts with Ru-based metathesis catalysts to provide an all *trans*-polymer with a polydispersity index (PDI) as low as 1.6 and molecular weights in the 1100 to 15 600 g·mol$^{-1}$ range (9−127 monomer units). Because apopinene is readily prepared in one-step from myrtenal or two-steps from $\alpha$-pinene, both of which are commercially available and naturally abundant, these studies indicate that apopinene might find future use as a new biorenewable precursor for the sustainable production of ROMP-based materials.



**KEYWORDS:** *Biomass, Terpenes, Polymerization, Metathesis, Catalysis*
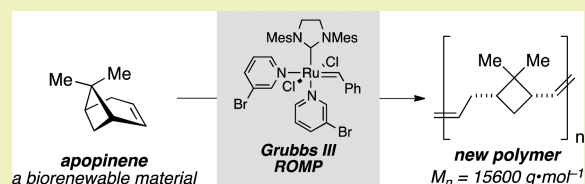
## INTRODUCTION

$\alpha$-Pinene (**1**) is the most abundant monoterpene present in nature and plays crucial roles in many biological, atmospheric, and industrial processes. Similar to many other readily accessed and biorenewable terpenes, $\alpha$-pinene is widely used in both the fine chemical and polymer industries.[1] More specifically, the Lewis acid-catalyzed polymerization of $\alpha$-pinene (**1**), which generates polymer **2** (Scheme 1), has found a variety of uses in a plethora of industrial applications such as adhesives, plastics, and rubbers.[1,2]

## Scheme 1. Polymerization of $\alpha$-Pinene (1)
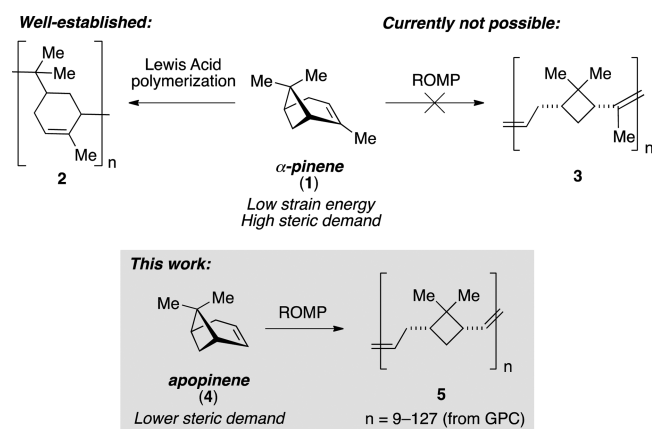


The high abundance, low cost, and biorenewability of $\alpha$-pinene make its incorporation into additional novel materials highly desirable from the standpoint of sustainability. One avenue that has sparked some theoretical interest is the ring-opening metathesis polymerization (ROMP) of $\alpha$-pinene (**1**).[3] Unfortunately, to our knowledge, there have been no reports of

$\alpha$-pinene (**1**) participating in ROMP and therefore no polymers of this type (i.e., **3**) are known. One factor contributing to the inability of $\alpha$-pinene (**1**) to engage in ROMP is its highly congested trisubstituted olefin that likely hampers initiation (and propagation).[4] We considered that a potentially practical way to circumvent this problem would be to alter the substrate by deleting the vinylic methyl substituent, resulting in the less sterically congested precursor, apopinene (**4**). Our hypothesis was that the reduced steric hindrance within **4** would facilitate initiation and polymerization with ROMP catalysts, provided that moderate strain energy was not a factor.

## RESULTS AND DISCUSSION

Fomine and Tlenkopatchev reported that $\alpha$-pinene (**1**) has a calculated strain enthalpy of 5.81 kcal·mol$^{-1}$,[3] which is

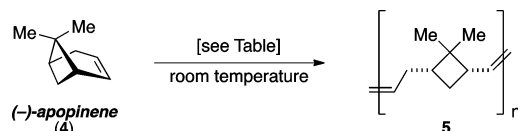## Scheme 2. Synthesis of Apopinene (4) from Biorenewable Precursors
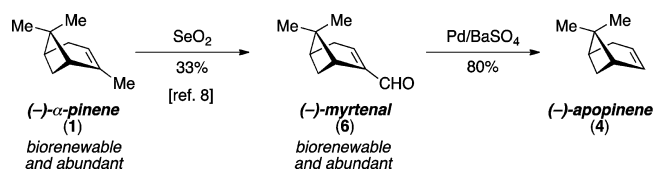


significantly lower than that of the mainstay for ROMP, norbornene (23.9 kcal·mol$^{-1}$),[5] providing another reason for its lack of ROMP activity. We conducted a similar calculation[6] for the homodesmotic reaction of apopinene (**4**) with ethylene and found a strain enthalpy of 8.1 kcal·mol$^{-1}$ ($\alpha$-pinene (**1**)
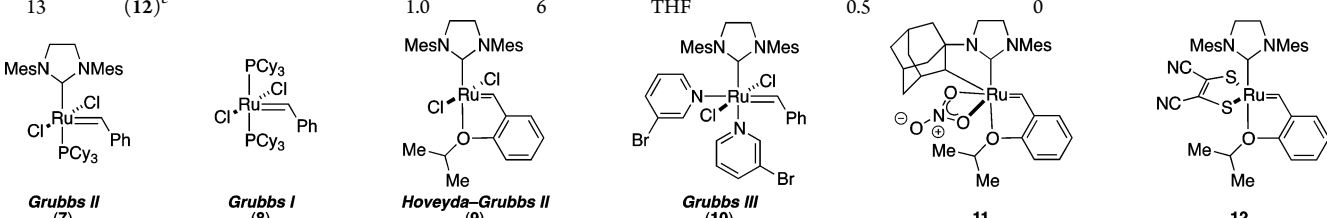
## Table 1. Ring-Opening Metathesis Polymerization of Apopinene (4)



| entry | catalyst | mol % | time (h) | solvent | concentration (M) | yield (%)[a] | PDI[b] | Mn[b] |
|---|---|---|---|---|---|---|---|---|
| 1 | Grubbs II (7) | 1.0 | 1.0 | DCM | 0.5 | 71 | 2.4 | 2500 |
| 2 | Grubbs II (7) | 1.0 | 1.0 | benzene | 0.5 | quant. | 2.7 | 1200 |
| 3 | Grubbs II (7) | 1.0 | 1.0 | THF | 0.5 | quant. | 1.6 | 1400 |
| 4 | Grubbs II (7) | 1.0 | 1.0 | THF | 1.0 | 97 | 2.3 | 1400 |
| 5 | Grubbs I (8) | 1.0 | 1.0 | THF | 1.0 | trace | | |
| 6 | Hoveyda−Grubbs II (9) | 1.0 | 1.0 | THF | 1.0 | 94 | 2.7 | 1100 |
| 7 | Grubbs II (7) | 0.5 | 18 | THF | 0.25 | 80 | 1.9 | 1400 |
| 8 | Grubbs I (8) | 0.5 | 18 | THF | 0.25 | 62 | 3.5 | 2300 |
| 9 | Hoveyda−Grubbs II (9) | 0.5 | 18 | THF | 0.25 | 54 | 4.5 | 1400 |
| 10 | Grubbs III (10) | 1.0 | 1.0 | DCM | 0.5 | 57 | 1.6 | 15600 |
| 11 | Grubbs III (10) | 1.0 | 1.0 | THF | 0.5 | 94 | 2.1 | 15600 |
| 12 | (11)[c] | 0.5 | 6 | DCM | 0.5 | 0 | | |
| 13 | (12)[c] | 1.0 | 6 | THF | 0.5 | 0 | | |



[a]Isolated yields. [b]Determined by gel permeation chromatography (GPC). [c]Reactions were also repeated at reflux.

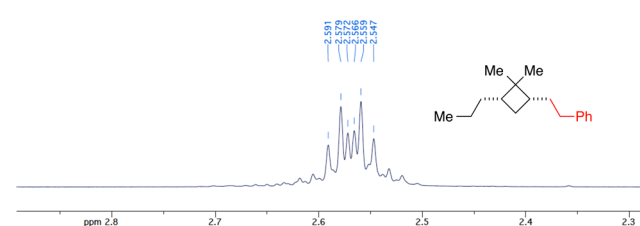## Scheme 3. Ring-Opening Cross Metathesis of Apopinene (4)



**A. 16 standard**



**B. Cross metathesis mixture**



**C. 17 standard**
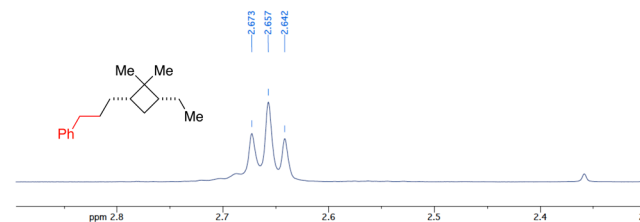


**Figure 1.** ^{1}H NMR spectrum of the benzylic protons of the cross metathesis reduction product (B) compared to the individual ^{1}H NMR spectra of synthesized cross metathesis standards (A and C).

afforded a value of 4.6 kcal·mol$^{-1}$ under the same conditions, in good agreement with Fomine and Tlenkopatchev[3]).
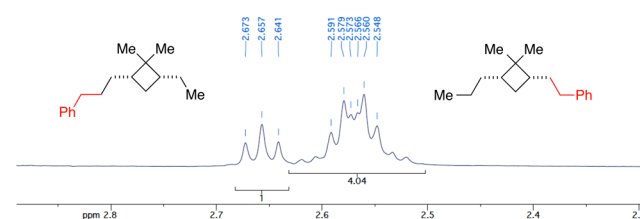
Apopinene (4) can be accessed from naturally abundant and inexpensive[7] $\alpha$-pinene (1) by an initial allylic oxidation of 1 to myrtenal (6) using selenium dioxide,[8] followed by a palladium-catalyzed decarbonylation (Scheme 2).[9] Myrtenal (6) itself is also a naturally occurring and sustainable feedstock chemical,[7] and so for our studies we chose to utilize commercially available (−)-myrtenal (6) as a more convenient direct precursor to (−)-apopinene (4).[10] Thus, apopinene (4) represents a potentially useful monomer for incorporation into sustainable polymers.[11]

Contrary to norbornene, the ROMP of apopinene is complicated by its asymmetry, leading to the potential for different head−tail combinations within the formed polymer (see Figure S1 in the Supporting Information). Although significant effort has been put toward developing catalysts that provide high tacticity and stereoregular polymers within other systems,[12] it was unclear at the outset how apopinene would behave in this regard. For the purposes of this study, we focused on the readily available ruthenium-based catalysts,

## Scheme 4. Proposed Catalytic Cycle
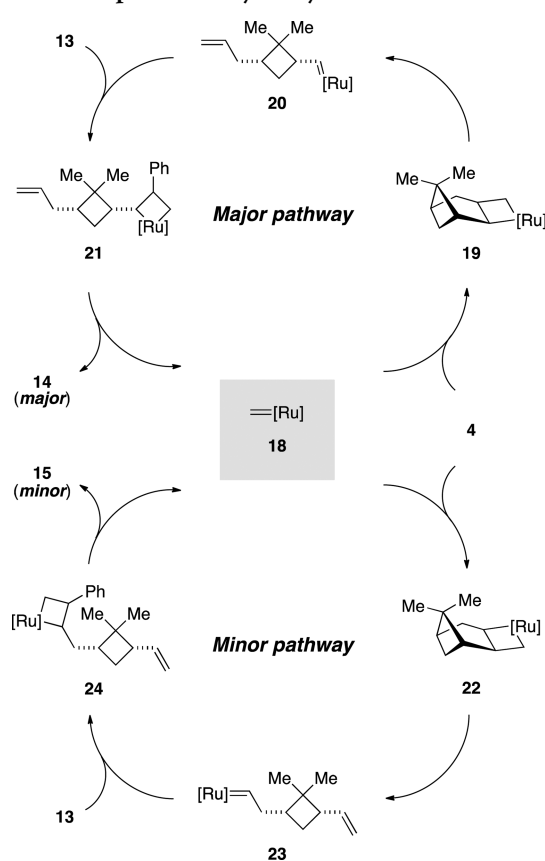


which maintain high reactivity rates and exhibit low air sensitivity. Initial attempts to polymerize apopinene (**4**) using noble metals, such as RuCl$_3$ and ReCl$_5$,[13] showed no signs of initiation at room temperature, whereas heating of these mixtures led to intractable mixtures. Switching to Grubbs-type catalysts, however, produced the desired ROMP-based polymer with varying yields (Table 1). The resulting polymers were broad and monomodal, but contained high variability in connectivity patterns due to head−tail asymmetry, as determined by ^{13}C NMR spectroscopy. Unfortunately, the predominantly *trans* metathesis polymers (determined by IR spectroscopy)[14] generated from Grubbs II (**7**), Grubbs I (**8**), and Hoveyda−Grubbs II (**9**) had low molecular weights (ranging from 1100 to 2500 g·mol⁻¹) and high polydispersity indices (PDIs), indicating that propagation occurs more rapidly than initiation (Table 1). ^{1}H NMR spectra of all these polymers indicated only trace signals derived from terminal end-group alkenes, indicating that backbiting to form cyclic polymers was likely occurring to a significant degree.[14] Grubbs II (**7**) consistently produced solid, film-like polymers with the lowest PDIs (Table 1, entries 1−4), whereas polymers formed from both Grubbs I (**8**) and Hoveyda−Grubbs II (**9**) maintained a gelatinous consistency with higher PDIs (Table 1, entries 5 and 6). Extending reaction times from 1 to 18 h led to no improvement (Table 1, entries 8−9). All three of these catalysts produced polymers roughly 9−20 units in length as determined by GPC,[15] with the second-generation catalysts being generally more active and well-behaved.

A significant improvement in polymerization was found when the fast initiating third-generation Grubbs III catalyst **10** was utilized (Table 1, entries 10 and 11).[16,17] Although

conversion after 1 h in DCM was modest, the resulting polymer had a molecular weight of 15 600 g·mol⁻¹ and a PDI of 1.6 (Table 1, entry 10). Changing solvents to THF led to an improved 94% isolated yield of polymer without sacrificing molecular weight, although the PDI increased to 2.1 (Table 1, entry 11). Similar to the results obtained using Grubbs II (**7**), the polymer generated using Grubbs III (**10**) contained only *trans*-alkenes and showed only trace signs of terminal alkenes.[14] In an attempt to generate a predominantly *cis* configured polymer, Z-selective olefin metathesis catalysts **11** and **12** were employed (Table 1, entries 12 and 13).[18,19] These catalysts, although viable for the polymerization of norbornene, failed to initiate with less strained apopinene (**4**), even at elevated temperatures (reflux in DCM or THF). Ultimately, the results outlined in Table 1 show that a high molecular weight all *trans*-polymer consisting of approximately 127 monomer units can be rapidly generated in high yield from apopinene (**4**) using the Grubbs III catalyst **10**, establishing apopinene (**4**) as a potentially viable sustainable monomer for polymer synthesis. In contrast, treatment of α-pinene (**1**) with Grubbs III (**10**) led to no productive polymer formation.

Because polymer **5** consists of only *trans*-olefins, the multiple olefinic signals in the ^{13}C NMR spectrum are most likely a result of incomplete head-to-tail selectivity during initiation and subsequent propagation steps. Unfortunately, these peaks occur at similar chemical shifts, making it challenging to assign or integrate them effectively. To help determine the selectivity of initiation, and to gain insight into the inherent regioselectivity that **4** displays toward Ru−carbene complexes, we performed a ring-opening cross metathesis experiment (Scheme 3) between apopinene (**4**) and styrene (**13**).

Treatment of apopinene (**4**) with Hoveyda−Grubbs II (**9**) in the presence of excess styrene (**13**) could potentially produce a mixture of regio- and stereoisomers. In the event, ring-opening cross metathesis of **4** gave rise to a mixture of alkene products in 32% yield whose composition was initially difficult to interpret, although the major isomers appeared to be *trans* configured.[20] Reduction of this mixture with palladium on carbon, however, produced a mixture of two major products with a simplified ^{1}H NMR spectrum (Figure 1B). Comparison of this spectrum to those of independently synthesized standards of **16** and **17** (Figure 1A and C, respectively)[21] showed clearly that **16** and **17** were produced in a 4:1 ratio through the ring-opening cross metathesis route (i.e., Scheme 3). Thus, we established that the initial products of this ring-opening cross metathesis were alkenes **14** (major) and **15** (minor).

Taken together, these results indicate that initiation of metathesis with active catalyst **18** places the ruthenium metal center on the carbon adjacent to the cyclobutane within **4** to give metallocyclobutanes **19** and **22** in a 4:1 ratio, respectively (Scheme 4). Ring opening then leads to carbene **20** (from **19**) or to carbene **23** (from **22**). Reaction of each of these species with styrene (**13**) then leads to the two products **14** and **15**, as described above.

## ■ CONCLUSIONS

Fomine and Tlenkopatchev reported computational studies of the ROMP of α-pinene (**1**) that predict that the metal center prefers to initiate at the more sterically hindered position, resulting in the disubstituted metallacarbene analogous to monosubstituted metallacarbene **20** (Scheme 4).[3,22] Despite their structural and electronic differences, our experimental

results for apopinene (**4**) show that initiation displays the same regioselectivity as that predicted for α-pinene (**1**).

Although the selectivity observed in this cross metathesis experiment provides some insight into the initiation step of this ROMP process, it is more difficult to provide information regarding the propagation steps. We assume that the regioselectivity of addition of carbenes **20** and **23** to apopinene (**4**) during polymer chain growth also proceeds with the same intrinsic selectivity, thus leading to the complex mixture of polymers we observe.[23] Despite the modest characteristics exhibited by these polymers, we have shown for the first time that apopinene (**4**) can act as a monomer for pinene-derived ROMP processes to yield polymers with molecular weights up to 15 600 g·mol⁻¹. Thus, our studies act as a beginning point for future efforts in the area using more reactive and selective metathesis catalysts. Such catalysts could provide a more syndiotactic polymer with higher molecular weights, ultimately leading to a potentially useful biorenewable polymer for the sustainable production of new materials.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Experimental procedures and characterization data (NMR, MS, IR, and GPC) for all new compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00255.

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### Notes
The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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(20) The low yield is a result of quenching the reaction early to avoid further cross metathesis reactions.

(21) For the synthesis of standards **16** and **17**, see the Supporting Information.

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(23) For additional discussion regarding the nature of the polymer formed from apopinene, see the Supporting Information.