Published in "Materials Chemistry Frontiers 4(9): 2791–2796, 2020"
which should be cited to refer to this work.

Mono-telechelic Polymers by Catalytic Living Ring-Opening Metathesis Polymerization with Second-Generation Hoveyda–Grubbs Catalyst

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The second-generation Hoveyda–Grubbs (**HG2**) catalyst, which has a small initiation to propagation rate ratio (k_i/k_p) in ring-opening metathesis polymerization (ROMP), was successfully used in a recently developed catalytic living ROMP. This proved that slow-initiating catalysts can enable ROMP in a living fashion to produce polymers with narrow dispersity and controlled molecular weight. The molecular weight control experiments show a linear relationship between polymer molecular weight and monomer to chain-transfer agent (**CTA**) ratio. Different norbornene-derivatives can be utilized as monomers. Di-block copolymers and tri-block copolymers can be synthesized either using the first polymer block as macro-CTA or continuously adding different monomers sequentially. Mono-telechelic polymers, with functional end groups such as protected carboxylic acid, alcohol and amine can also be achieved. All polymers were fully characterized using NMR, GPC and MALDI-ToF analytical techniques. This procedure provides access to well-defined end-functional polymers at lower cost and with reduced rare metal residues that might be of interest for biomedical, materials, industrial and academic use.

Introduction

Living ring-opening metathesis polymerization (ROMP) has become a very powerful tool in the construction of macromolecular complexes[1]. This is because the absence of chain transfer and chain termination in living ROMP can result in good molecular weight control and narrow dispersity (Đ) which offer control over the microstructure and properties of polymers[2,3,4,5]. To achieve better control of living ROMP, many different catalysts[6,7,8,9,10] have been developed over the past decades. However, as these complexes act as polymerization initiators stoichiometric amounts with respect to the number of polymer chains are required. This results in a high catalyst loading and metal residue in the final polymer, especially when aiming at low molecular weight polymers. Therefore, many methods have been developed to decrease the loading of transition metal complexes, which are all examples of catalytic ROMP[11,12,13,14,15]. However, none of the reported catalytic ROMP methods are living as they typically rely on chain transfer events to occur. Block copolymers can therefore not be synthesized via these methods and the dispersity of the obtained polymer is typically broad. Recently, we developed a catalytic living ROMP method through a degenerative reversible chain-transfer mechanism, in which only a catalytic amount of transition metal complex is required for living ROMP[16,17]. Not only can this method be applied to the first and third generations Grubbs catalyst, also the

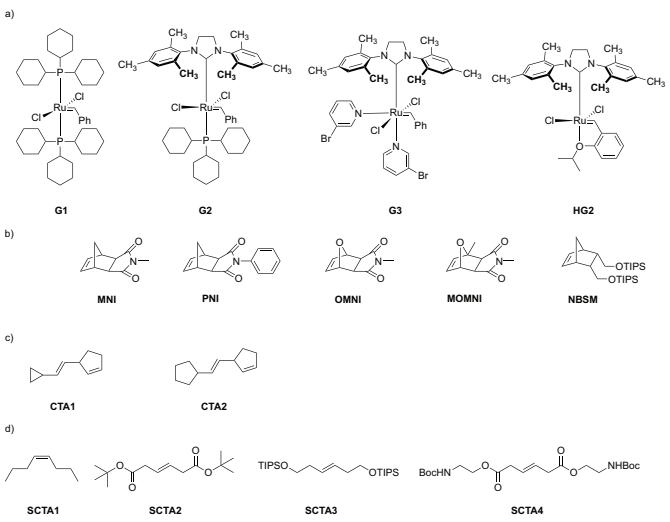

Fig. 1 Four commercially available metathesis catalysts. a) metathesis catalysts investigated b) monomer structures c) reversible chain transfer agents d) reagents for end-functionalization cross metathesis

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second-generation Grubbs catalyst can produce well-defined living polymers with narrow dispersity (Đ < 1.5).

On the other hand, the second-generation Hoveyda–Grubbs catalyst (**HG2**) is a very "user-friendly" catalyst due to its chemical and thermal stability, long-term stability in storage, recyclability and high catalytic activity[18,19,20]. However, similar to the second-generation Grubbs catalyst (**G2**), **HG2** is not a general catalyst for controlled living ROMP because the slow initiation and small k_i/k_p typically leads to a loss of molecular weight control[21,22]. Only few examples have been reported where the **HG2** complex could be used for controlled metathesis polymerizations giving well-defined polymers.[23,24]

An important characteristic of any living polymerization is a 'fast and complete initiation' typically achieved via a large k_i/k_p. Both the first-generation Grubbs catalyst (**G1**) and third-generation Grubbs catalyst (**G3**) can achieve living ROMP by coordination of the activated 14e⁻ catalyst species to ligands to form stable complexes with a 16e⁻ or 18e⁻ count. Such stabilization can slow down the propagation process, result in an increase of k_i/k_p and stabilize the catalyst species. Compared with these two generations of Grubbs catalysts, using the **HG2** catalyst in living ROMP is challenging as there is no ligand to stabilize the highly active 14e⁻ catalyst species once the propagation has started.

In 2004, Slugovc's group polymerized *endo*, *exo*-*bis*-ketone or -diester norbornene monomers with **HG1** and **HG2** catalysts in a controlled manner through coordination of the *endo*-carbonyl group of the monomer to the catalyst in order to slow down the propagation rate and stabilize the catalyst[25]. Four years later, Mingotaud's group reported controlled ROMP using the **HG2** catalyst in water[26]. Later, Choi's group reported a controlled living ROMP of tricyclo[4.2.2.0^{2,5}]deca-3,9-diene[27] and cyclopolymerization of 1,8-nonadiynes[28] with **G2** and **HG2** by coordinating the catalyst to the olefin in the monomer to increase k_i/k_p and stabilize the catalyst. They also isolated the propagating species during polymerization and confirmed their olefin-chelated structures[29]. Recently, we succeeded using the second-generation Grubbs catalyst (**G2**) in catalytic living ROMP by adding the monomers slowly in order to slow down the rate of propagation. To our knowledge, no report on catalytic living ROMP with **HG2** catalyst has been published. Here, we show that the highly stable **HG2** catalysts can be used in catalytic living ROMP yielding narrow dispersity polymers.

Results and discussion

Different from the three generations of Grubbs catalysts, the Hoveyda derivatives have no ligand to re-coordinate to the 14e⁻ ruthenium complex once the catalyst has initiated in ROMP. However, there are reports showing that heteroatoms such as N, O or S and olefins in the monomer structure can co-ordinate to the ruthenium complexes to affect the reactivity of the propagating carbene[24,30,31]. In order to follow the intermediates formed during our catalytic living ROMP using **HG2**, time-resolved ^{1}H NMR reactions were carried out. The **HG2** catalyst was dissolved in CD_2Cl_2 under argon with 10 equiv of the chain-transfer agent (*E*)-3-(2-cyclopropylvinyl)cyclopent-1-ene (**CTA**). A ^{1}H NMR spectrum was recorded, however, no new carbene peaks, differing from the pure **HG2** complex, appeared even after 1 h.

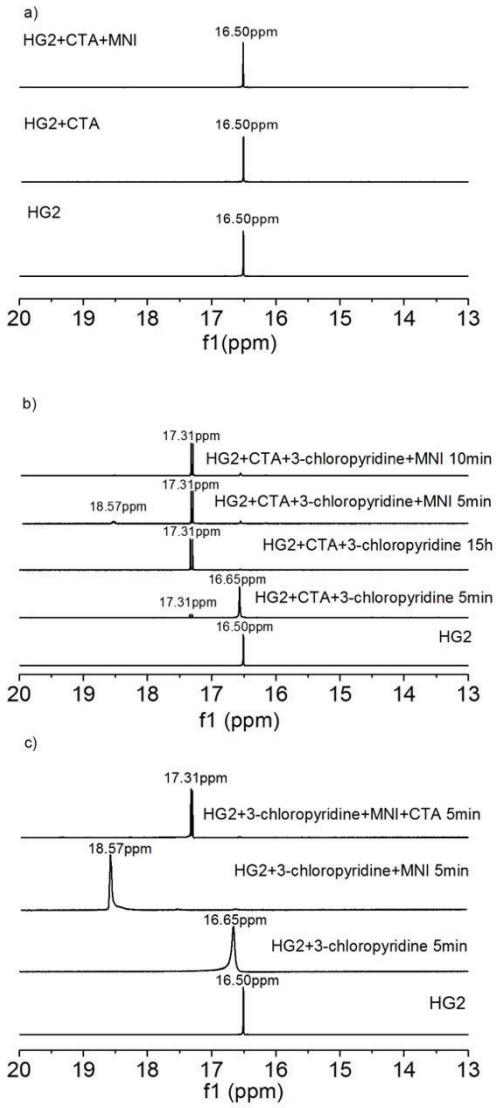

Fig. 2 ^{1}H NMR spectroscopic comparison of the reaction between **HG2** (3.2 mg, 1.0 equiv), **CTA** (6.7 mg, 10 equiv), **MNI** (50 mg, 56 equiv) and 3-chloropyridine (5.6 mg, 10 equiv). All reactions were carried out in 0.75 ml degassed CD_2Cl_2 under Ar. a) **CTA** was added to **HG2**, then **MNI** was added after 1 h. b) **CTA** and 3-chloropyridine were added to **HG2** together, then **MNI** was added after 15 h. c) 3-Chloropyridine was added to **HG2** first, next **MNI** was added after 10 min, **CTA** was added after another 10 min.

Then, 56 equiv *exo*-*N*-methyl norbornene imide (**MNI**) was added to this NMR tube and the ^{1}H NMR spectrum was measured immediately. We observed that all **MNI** monomer was polymerized by the time the NMR spectrum was recorded (in less than 5 min), however, the propagating carbene proton could still not be detected (Figure 2a). This confirmed that the heteroatoms present in our monomer and the olefin in our **CTA** do not appear to coordinate to the **HG2** ruthenium complexes to produce 16e$^-$ or 18e$^-$ detectable ruthenium complexes during the polymerization. The **HG2** ruthenium complexes most likely retains the activated 14e$^-$ form during the whole polymerization process. This makes controlled living ROMP using the **HG2** catalyst even more challenging because the unstabilized 14e$^-$ ruthenium complexes are highly reactive, easily decompose and can undergo side reactions. As far as we know, this is the first report of a controlled living ROMP using the **HG2** catalyst in a 14e$^-$ form without any additive to stabilize the activated catalyst species.

To further understand the reaction rate of the **HG2** catalyst with the **CTA** and monomer during catalytic living ROMP, 3-chloropyridine was added to the next ^{1}H NMR reaction to coordinate to the reacted ruthenium complex. After mixing **HG2** with 10 equiv of **CTA** and 3-chloropyridine, we detected the appearance of cyclopropyl methylidene species at 17.31 ppm even after 5 min. of reaction time (Figure 2b)[17]. However, the reaction rate was very slow. It took more than 15 h to completely convert the original **HG2** carbene signal to a cyclopropyl carbene. Once all of the **HG2** benzylidene signal had disappeared, 56 equiv of **MNI** was added to the NMR tube. Both propagating carbene peaks and cyclopropyl carbene peaks were detected within 5 min. after monomer addition (Figure 2b). The propagating carbene peaks, however, disappeared within 10 min (Figure 2b) and only the cyclopropyl carbene signals remained. This could be explained by assuming that only a small amount of cyclopropyl carbene complexes initiated the propagation. This small amount of propagating carbene complex then converted to a cyclopropyl carbene once again by reacting with the CTA after all monomer had been consumed. Alternatively, all cyclopropyl carbene complexes initiated the propagation but most of the propagating carbene complexes had already converted back to the cyclopropyl carbene complex before the first ^{1}H NMR was measured. To obtain further information with regard to the intermediates formed in this reaction a third ^{1}H NMR experiment was carried out. The **HG2** catalyst was first mixed with 10 equiv of 3-chloropyridine. We found that the **HG2** benzylidene peak shifted from 16.50 ppm to 16.65 ppm in less than 5 min (Figure 2c). This shift is caused by the coordination of 3-chloropyridine to the **HG2** catalyst carbene complex[24]. All coordinated **HG2** catalyst carbene complexes initiated the polymerization immediately after 56 equiv of **MNI** was added to the NMR tube. These propagating carbene complexes (18.57 ppm) converted to cyclopropyl carbene complexes (17.31 ppm) following the addition of 10 equiv **CTA** in less than 5 min (Figure 2c). These results confirmed that a) the heteroatoms and the olefin in **MNI** and the **CTA** do not coordinate to the **HG2** carbene complex, b) the **HG2** benzylidene complex reacts with the **CTA** at a very slow rate, c) the propagating carbene complex of **HG2** reacts with **CTA** in a very fast fashion.

With this information in mind, we polymerized *exo*-*N*-methyl norbornene imide (**MNI**) with the **HG2** complex in a ratio of **MNI**:**HG2** = 300:1. We expected to get a polymer that had an average molar mass of 53100 g mol^{-1} if this polymerization took place in a living fashion. As expected, only an insoluble gel of very high molecular weight was obtained which shows that **HG2** cannot be employed in living ROMP using **MNI** directly. Next, we tried the catalytic living ROMP method using the **HG2** complex in a ratio of **HG2**:**CTA**:**MNI** = 1:10:300. We first dissolved **HG2** (3.2 mg, 0.005 mmol) and (*E*)-3-(2-cyclopropylvinyl)cyclopent-1-ene **CTA** (6.7 mg, 0.05 mmol) in 2 ml degassed methylene chloride (DCM). Then **MNI** (266 mg, 1.5 mmol in 20 ml degassed DCM, 0.075 mol/l) was added dropwise with a syringe pump at 5 ml/h. We obtained a polymer (polyMNI) with 9000 g mol^{-1} molar mass and Đ = 1.26. We were delighted to find that these results match the molecular weight and dispersity control similar to those observed in a recently reported catalytic living ROMP[17]. We would like to emphasize at this point that no 3-chloropyridine was added to the polymerization experiment. 3-Chloropyridine helped in observing the metathesis reaction in ^{1}H-NMR experiments (Figure 2), however, we observed in a previous study[17] that the degenerate chain transfer mechanism of catalytic

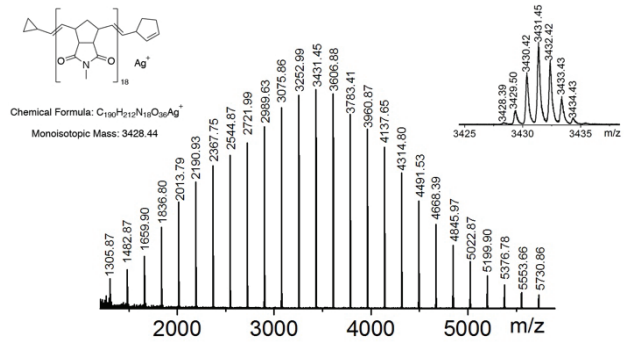

Fig. 3 MALDI-ToF mass distribution (DCTB, AgTFA) of **PolyMNI**. *Left*: Chemical structure of **PolyMNI** with calculated mono-isotopic mass. *Centre*: Mass distribution. *Right*: Most intense peak of the distribution, isotopically resolved.

living ROMP was insensitive to the carbene complex initiation rate. We therefore omitted 3-chloropyridine under catalytic living ROMP polymerization conditions.

Moreover, the MALDI-ToF mass spectrum of this polymer confirmed the assumed polymer structure with the end groups defined by the **CTA** (Figure 3). These results confirmed that the **HG2** catalyst can be employed in catalytic living ROMP to generate polymers with controlled molecular weight and dispersity.

Encouraged by these results, we further explored the molecular weight control by **HG2** for catalytic living ROMP. We previously reported that the polymer molecular weight was determined by the monomer:**CTA** ratio in catalytic living ROMP. Using **HG2**, we successfully synthesized different molecular weight polymers by changing the **MNI**:**CTA** ratio (polymers 3-7, see supporting information). The linear correlation between the molecular weight (Mn, $GPC_{chloroform}$) and the **MNI**:**CTA** ratio fulfils the characteristics of a living polymerization (Figure 4). A dispersity of the resulting polymers lower than 1.5 further confirmed the living character. Moreover, the **HG2**:**CTA** ratio shows the advantages of catalytic

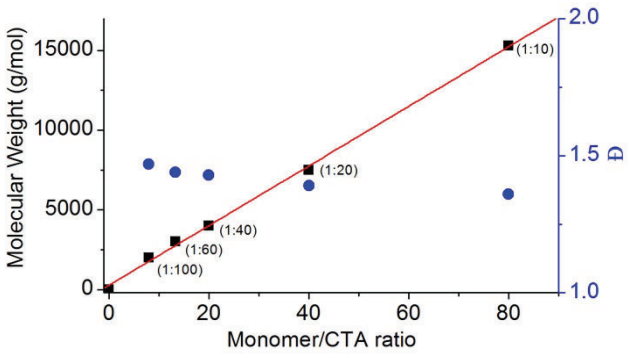

Fig. 4 Plot of the molecular weight (Mn, GPC (chloroform), black squares) and molecular weight dispersity (Đ, blue circles) versus the **MNI**/**CTA** ratio. The ratios reported in brackets denote the **HG2**/**CTA** ratio. (Polymers 3-7, see supporting information)

living ROMP in that the same molecular weight polymers can be synthesized using as much as 100 times less catalyst than used in the traditional living ROMP (Figure 4). The polymer structures were verified using MALDI-ToF mass spectrometry and NMR spectroscopy. They match the assumed structures with cyclopropyl and cyclopentenyl end groups (see supporting information).

Different types of monomers such as *exo*-*N*-phenyl norbornene imide (**PNI**), *exo*-*N*-methyl oxanorbornene imide (**OMNI**), *endo*-5-norbornene-2,3-bis(triisopropyl)silylmethanol (**NBSM**) and *exo*-*N*-methyl-7-oxabicyclo[2.2.1]hept-4-methyl-5-ene-2,3-dicarboximide (**MOMNI**) were explored in catalytic living ROMP using the **HG2** catalyst (see supporting information). Similar results were obtained for **MNI** and **PNI**. Larger dispersities were observed when **OMNI**, **NBSM** and **MOMNI** were applied in catalytic living ROMP with **HG2**. Even 10 equiv of 3-chloropyridine added to the reaction solution did not improve the dispersities. This can result from the co-ordination of oxygen in these functional monomers with the ruthenium in the **HG2** complex resulting in a slowing down of the chain-transfer rate while also slowing down the propagation rate[24,31]. In support of this assumption, we observed a coordinated carbene peak in the ^{1}H NMR reaction between **HG2** and **MOMNI** (see supporting information, Figure S1). However, the MALDI-ToF mass spectrum confirmed that all polymers had the expected end groups and repeat units (see supporting information, Polymer 8-12). It is worth mentioning that when the bulky and slowly propagating **MOMNI** was used as the monomer, the polymerization could be carried out in one pot rather than by slow addition using a syringe pump[17].

Block copolymers are very important owing to their ability to self-assemble in solution and in the solid state[32]. At the same time, they are also important structures to prove the living character of a polymerization technique. Linear ABC tri-block copolymers are more

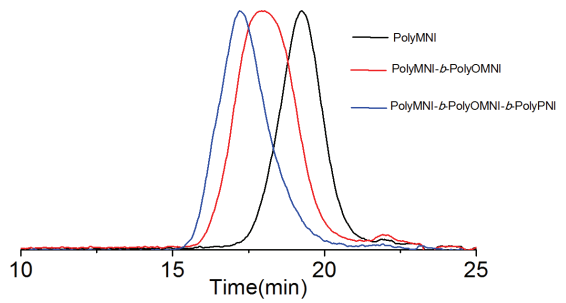

Fig. 5 Progressive GPC traces of the A-block, poly(MNI), the AB diblock copolymer poly(MNI)-b-poly(OMNI) and the ABC tri-block copolymer poly(MNI)-b-poly(OMIN)-b-poly(PNI).

challenging to synthesize than diblock copolymers and show more complex solution and solid state structures[33]. Therefore, we explored the ability of **HG2** in catalytic living ROMP to synthesize ABC tri-block copolymers. **MNI**, **OMNI** and **PNI** were added to the **HG2**:**CTA** (1:10) reaction solution sequentially. The GPC (chloroform) traces showed a monomodal molecular weight distribution and shift in molecular weight after each monomer addition which supported the formation of an ABC tri-block copolymer polyMNI-*b*-polyOMNI-*b*-polyPNI (Polymer 13, Figure 5). These results further proved the living character of the polymerization technique using **HG2**. Moreover, AB di-block copolymers were also synthesized by catalytic living ROMP with **HG2** using a macro-CTA

which is synthesized by catalytic living ROMP with the **HG2** catalyst. PolyMNI was first prepared by adding **MNI** to an **HG2**/**CTA** solution (**HG2**:**CTA**:**MNI** = 1:10:300) with a syringe pump at a speed of 0.83 ml/h. After precipitation, evaporation and analysis, polyMNI was used as macromolecular chain transfer agent for catalytic living ROMP of **PNI** and **HG2** to produce polyMNI-*b*-polyPNI (Polymer14). The shift of the monomodal GPC traces from polyMNI (Mn_{GPC} (chloroform) = 7300 g mol^{-1}, Đ = 1.33) to polyMNI-*b*-polyPNI (Mn_{GPC} (chloroform) = 21000 g mol^{-1}, Đ = 1.45) confirmed the synthesis of an AB di-block copolymer (See supporting information Figure S61).

Mono-end functional and telechelic polymers are important and industrially relevant materials[34,35]. To expand the applications of catalytic living ROMP, we investigated the possibility to synthesize telechelic polymers by catalytic living ROMP using **HG2**. We therefore polymerized **MNI**/**CTA**/**HG2** (300:10:1) in DCM by adding **MNI** into **CTA**/**HG2** mixture solution slowly. After all monomer had been consumed we added an excess (30 equiv with respect to **CTA**) of symmetrical *cis*-oct-4-ene to the reaction solution expecting a terminal cross-metathesis reaction with the cyclopentenyl end groups of polymer chains. To our surprise, no butenyl end-functionalized polymer could be detected in MALDI-ToF mass analysis. The only signal that was detected was the unreacted cyclopentenyl end-functionalized polymer. We assumed that the high dilution conditions of catalytic living ROMP were responsible for the low reactivity of the terminal cross metathesis reaction. In a second experiment, after addition of excess amounts of symmetrical *cis*-oct-4-ene, the reaction mixture was concentrated by evaporating the solvent and stirring overnight. After precipitation, the MALDI-ToF mass spectra and NMR analysis confirmed the successful exchange of the cyclopentenyl end group into a butenyl end-functionalized polymer (see supporting information Polymer 15).

Subsequently, *t*-butyl-protected *trans*-hex-3-enedioic acid, triisopropylsilyl (TIPS-) protected *trans*-hex-3-ene-1,6-diol and tert-butyloxycarbonyl (Boc-) protected amine were used as functional symmetrical chain-transfer agents (SCTA) to synthesize carboxylic acid-, hydroxyl- and amino-functionalized mono-telechelic polymers via catalytic living ROMP. The matched MALDI-ToF mass and NMR spectra demonstrated that the carboxylic acid-, hydroxyl- and amino-functionalized mono-telechelic polymers were synthesized successfully by catalytic living ROMP with **HG2** (see supporting information Polymer 16-18). These results also proved that not only the *cis*- symmetrical chain-transfer agents can be used in the cross metathesis of polymer end-groups, but also the *trans*- configuration. Moreover, these results once more confirmed that the polymer end groups remain reactive towards either propagation or cross metathesis reactions.

Conclusions

In conclusion, the user-friendly, stable and highly active second-generation Hoveyda–Grubbs (**HG2**) catalyst can be employed in catalytic living ROMP. The molecular weight can be controlled by changing the monomer:**CTA** ratio. Different substituted norbornene derivatives can be employed in this method. AB di-block copolymers and ABC tri-block copolymers can be synthesized using catalytic living ROMP either using a macromolecular-**CTA** or adding different monomers sequentially. Different end-group-functionalized mono-telechelic polymers are also accessible via a terminal cross metathesis reaction. These results will further expand the applications of catalytic living ROMP as a method for low cost polymers with low amounts of metal impurities. This can be particularly attractive for applications where low toxicity levels need to be achieved such as for biomedical functional polymeric materials.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

PL and AFMK thank the Swiss National Science Foundation for funding. ZD thanks the China Scholarship Council for financial support. We also thank Dr. Philip Scholten for the TGA and DSC measurements.

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Mono-telechelic polymers and triblock copolymers were synthesized by catalytic living ROMP with unstabilized 14e⁻ **HG2** catalyst.