

Ruthenium–indenylidene complexes in ring opening metathesis polymerization (ROMP) reactions

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Received 5 September 2007; received in revised form 27 November 2007; accepted 28 November 2007
Available online 14 December 2007

Abstract

The ring opening metathesis polymerization (ROMP) of cycloocta-1,5-diene (COD) is mediated by a series of six well-defined ruthenium-based indenylidene catalysts. The polymerization kinetics are monitored and compared with three generations of Grubbs' catalyst. Moderate control over the polymerizations was observed for both benzylidene and indenylidene-based catalysts.

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Keywords: Indenylidene; Ruthenium; Ring opening metathesis polymerization (ROMP)

1. Introduction

Metal catalyzed carbon–carbon bond forming reactions represent very powerful tools in organic and polymer chemistry [1]. The olefin metathesis reaction represents one such important C–C bond forming method. The versatility of the method, in its many incarnations: ring closing metathesis (RCM), cross metathesis (CM), ring opening polymerization metathesis (ROMP), or acyclic diene metathesis polymerization (ADMET) cannot be overstated. In 2005, Chauvin, Grubbs and Schrock received the Nobel Prize for their contributions to the development of this reaction and of the associated eponymous catalysts [2] (Scheme 1).

Developed in the early 1990s, the Schrock catalyst based on molybdenum was found extremely active [3]. But its use was limited by its air sensitive nature as well as by its low tolerance to functional groups [4]. In the mid-1990s, Grubbs et al. developed a series of active ruthenium alkylidene catalysts,

including **G-I**, with enhanced tolerance toward functionalized alkenes [5]. In the late 1990s, Hermann et al. [6] developed a new class of ruthenium catalyst, bearing two *N*-heterocyclic carbene (NHC) ligands. He was then followed a few months later by Nolan and Grubbs reporting separately some ruthenium catalysts, bearing some mixed phosphine/*N*-heterocyclic carbene ligands, with enhanced activity, stability and great tolerance toward functionalized olefins [7].

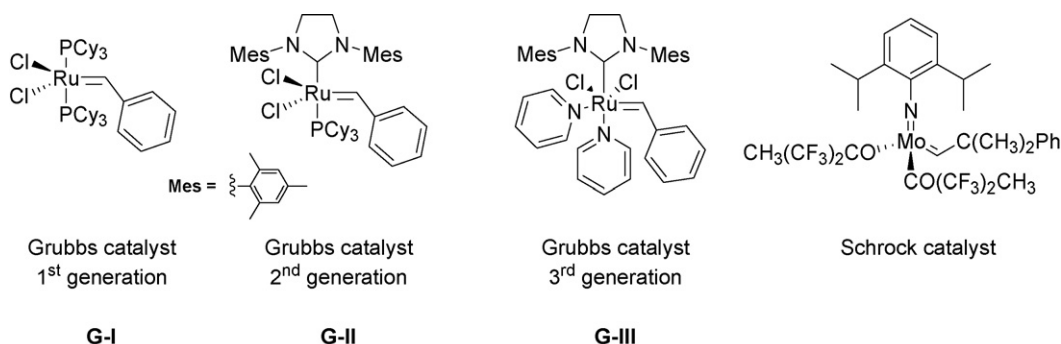
The metathesis reaction is comprised of an initiation and a propagation step with two distinct reaction intermediates [8]. Contrary to the RCM and CM reactions, the rate of initiation is a critical feature for controlled ROMP and the synthesis of well-defined polyolefins [9]. The controlled behavior of a catalyst depends on a subtle mix of its ability to provide good initiation and the stability of the generated propagating species. Tremendous efforts have been undertaken to rationalize the mechanism of the metathesis reaction and to design a most efficient catalyst [8b,10]. Among the numerous scaffolds available, we focused our study on the synthesis and application of the less investigated indenylidene ruthenium-based catalysts. This class of catalyst was synthesized initially by Hill in its phosphine-based version [11] and by Nolan [12] in its NHC-derived version. The second- and third-generation ruthenium NHC complexes were found more active in RCM and CM, and more thermally

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Scheme 1. Commercially available Grubbs and Schrock catalysts.

stable than Grubbs' catalysts bearing the benzylidene moiety [13].

The ROMP of strained *cyclo*-olefins is a very efficient route to access a wide range of unsaturated functionalized polymers with common polyisoprene or 1,4-polybutadiene backbones [9,14]. Suitable monomers for ROMP include, for example, norbornene, cyclopentadiene, cyclobutene, cyclooctene and cycloocta-1,5-diene (COD) [6,9b,15]. Due to its moderately strained cyclic structure, COD reacts smoothly in ROMP and is commonly used to benchmark new catalyst reactivity [16].

In the present paper, we report the evaluation in ROMP of six well-defined ruthenium–indenylidene-based catalysts (**1–6**) (Scheme 2) and a reactivity comparison with the three generations of Grubbs' catalyst (**G-I**, **G-II** and **G-III**) (Scheme 1). Reactions were monitored by ^1H NMR and size exclusion chromatography (SEC). These ruthenium–indenylidene catalysts were synthesized according to the literature procedures [13a,17] with the exception of (**3**) that was purchased from STREM Inc.

2. Experimental

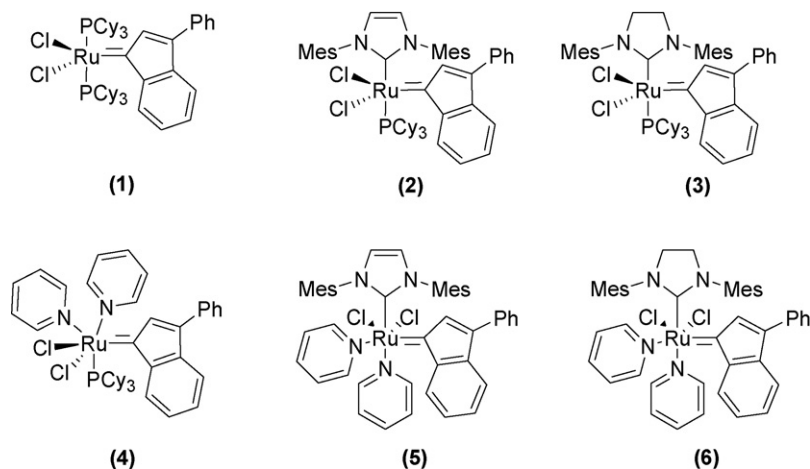
2.1. Materials

All solvents, the cycloocta-1,5-diene (COD) and the ethyl vinyl ether were purchased from ACROS. Deuterated chloroform (CDCl_3) was purchased from Cambridge Isotope

Laboratories, Inc. Chloroform was washed with distilled water, dried and distilled from CaCl_2 under argon. Acetone, COD, dibromomethane, dichloromethane (DCM) were dried and distilled according to standard procedures [19]. Catalysts **G-I** and **G-II** were purchased from Aldrich. Catalyst **3** was bought from STREM Inc. [18] while catalysts **1**, **2**, **4**, **5**, **6** and **G-III** were synthesized according to literature procedures [10c,13a,17]. All chemicals used for the kinetic studies were degassed under argon. Dibromomethane was used as the internal reference to follow the kinetics by ^1H NMR spectroscopy.

2.2. Measurements and spectroscopy

NMR spectra were recorded on a Bruker AC-400 spectrometer for ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz). Chemical shifts are reported in ppm relative to the tetramethylsilane (TMS) resonance. Number-average molecular weights (\overline{M}_n) and polydispersity indexes (PDI) were measured using size exclusion chromatography (SEC) on a system equipped with a SpectraSYSTEM AS 1000 autosampler, with a guard column (Polymer Laboratories, PL gel $5\ \mu\text{m}$ guard column, $50\ \text{mm} \times 7.5\ \text{mm}$) followed by two columns (Polymer Laboratories, 2 PL gel $5\ \mu\text{m}$ MIXED-D columns, $2\ \text{mm} \times 300\ \text{mm} \times 7.5\ \text{mm}$), with a SpectraSYSTEM RI-150. The eluent used was THF at a flow rate of $1\ \text{mL min}^{-1}$ at $35\ ^\circ\text{C}$.



Scheme 2. Indenylidene catalysts used to polymerize cycloocta-1,5-diene (COD).

Polystyrene standards ($580\text{--}483 \times 10^3 \text{ g mol}^{-1}$) were used to calibrate the SEC.

2.3. General procedure for monitoring ROMP reactions

Under argon, in deuterated chloroform, a stock solution of catalyst and a stock solution of COD containing CH_2Br_2 were prepared. In a NMR tube sealed with a septum, a desired volume of each solution was injected, in order to keep the monomer/initiator ratio $[M]/[I]$ near 50 and the final volume equal to $400 \mu\text{L}$ with a constant concentration of COD. At 20°C , the progress of the polymerization was monitored by ^1H NMR by following the disappearance of the characteristic signal associated with the unsaturation of the COD at 5.52 ppm [20].

2.4. General procedure for the kinetic studies of the ROMP

Under argon, using chloroform, a stock solution of catalyst and a stock solution of COD containing CH_2Br_2 were prepared. At 20°C , the catalyst solution was injected into the COD solution keeping the $[M]/[I]$ ratio and the COD concentration equal to 50 [20]. At the indicated time intervals, a $100 \mu\text{L}$ aliquot of the crude reaction mixture (roughly 10 mg of polymers) was sampled and injected in a NMR tube containing $10 \mu\text{L}$ of ethyl vinyl ether to quench the polymerization (30 equiv. compared to the COD present in the aliquot). The progress of the polymerization was monitored by ^1H NMR by following the disappearance of the characteristic signal associated to the COD unsaturation at 5.52 ppm . The solution contained in each tube, was then dried in vacuum and acetone was added to trigger the precipitation of the polybutadiene. The polymer was immobilized on a plug of silica gel, and the acetone solution was discarded. Rinsing the plug with DCM followed by its evaporation, gave clean polybutadiene as a white solid. This polymer sample was then dissolved in a 1:1000 solution of THF:toluene, then filtered and injected in the SEC column.

3. Results and discussion

At room temperature, all catalysts give nearly quantitative conversion of the COD, with the notable exception of **4** that requires much longer reaction times to reach high consumption of COD. Catalysts can be divided in two groups based on reaction time. The first group comprised of **1**, **2**, **3** and **G-I** allows

reactions to reach completion within 2 h (Fig. 1A), while the second group, made up of **5**, **6**, **G-II** and **G-III**, exhibits very high activity with reaction times shorter than 10 min (Fig. 1B).

As expected, **G-I** and its indenylidene analogue **1** exhibit similar kinetic behavior and represent the most sluggish reactions. Complex **2** exhibits higher activity than **1** and **G-I**, as a phosphine ligand has been replaced by *N,N'*-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes). Complex **3** gives the fastest ROMP activity, for the first group of catalysts. However this performance is unexpectedly slow compared to its benzylidene congener **G-II**. Interestingly, examination of the reaction profiles within this “slow group” shows that replacing a benzylidene by an indenylidene does not guarantee increased catalytic activity, as is reported for RCM reactions [13b].

Among the second group of catalysts, **5** is the least active and contrary to **6**, **G-II** and **G-III**, bears a saturated NHC, *N,N'*-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (SIMes). A closer look at the kinetic plots for **6**, **G-II** and **G-III** (Fig. 1B) shows that while all catalysts quantitatively polymerize the COD in less than 3 min, **6** and **G-III** initiates faster than **G-II**. This result emphasizes the fact that Ru–pyridine-based catalysts initiate very fast due to an easy dissociation of the pyridine from the Ru center leading the 14 electrons active species [10c]. This argument is of course also valid for ROMP. In contrast to **G-II**, the dissociation of the phosphine from the Ru center is not so rapid, resulting in slower initiation [10e]. The study of this second group of catalysts ultimately demonstrates that using the (NHC)-ligands SIMes and pyridine allows the formation of highly active catalytic species for ROMP. In view of its structure, we expected **4** to display reactivity between **5** and **G-I**. In fact, this catalyst shows poor conversion after extended reaction time. We believe that this atypical behavior is due to the instability of the propagating species, as postulated previously in RCM [17c].

While having high conversion for RCM and CM is acceptable, synthesizing polymers with well-defined structures by ROMP requires a living controlled polymerization. A living polymerization, where the concentration of propagating species remains constant without any termination, is a key step to control. If the polymerization is “living” [10a,21] the time dependence of the \ln concentration of the monomer disappearance ($\ln[M]_{t=0}/[M]_t$) should be linear, indicating first order kinetics for the monomer consumption. The plots for each catalyst are drawn in Fig. 2.

Catalysts **G-I** and **1** exhibit a nearly linear behavior indicating a lack of termination and a correct initiation. In contrast **2** and,

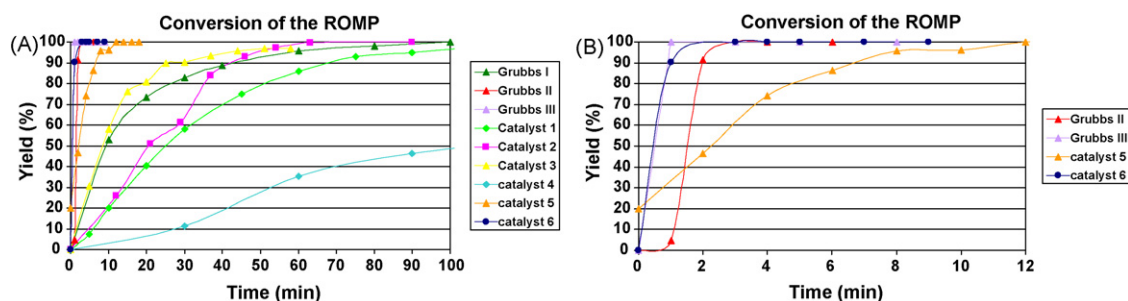


Fig. 1. Catalyst reactivity profile in ROMP as a function of time.

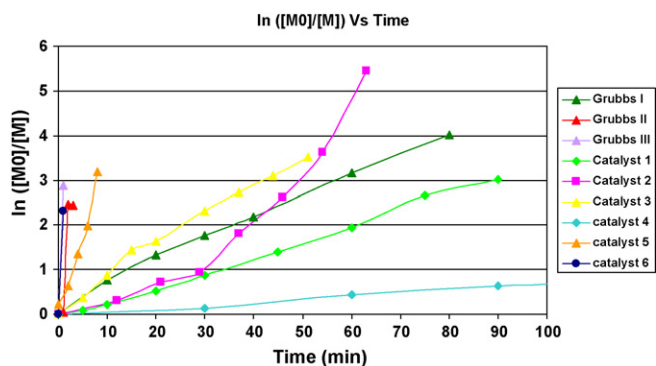


Fig. 2. Logarithmic representation of the COD concentration $[M]$ vs. time ($[M]_0 = [M]_{t=0}$) during ROMP of COD.

to a lesser extent **5**, exhibit a curved plot typical of a low rate of initiation compared to the propagation. Complex **3** exhibits some weak signs of early termination. Surprisingly, **4** does not exhibit any sign of early termination. This suggests that part of the catalyst decomposes during the initiation step. Depending on the propagation rate, a more significant amount of **4** might decompose to keep the overall rate of COD consumption small. Finally, **G-II** exhibits delayed initiation compared to **6** and **G-III**, but a similar rate of polymerization is observed for the three catalysts.

Very active ruthenium catalysts suffer from a lack of control in ROMP due to extensive transfers (or secondary metathesis reactions) between growing polymer chains. In 1998, Grubbs et al. stated that the ROMP of COD with first-generation catalyst gave kinetic data too complicated to be rationalized [15a]. Three years later, polybutadienes with high PDIs were still produced, but with partial control of the number-average molecular weight [22]. If the polymerization is living and transfer free, the number-average molecular weight of the polybutadiene should increase linearly with the conversion (or consumption of COD) and the PDI value should remain as low as 1.05. Surprisingly, we were not able to find any published examples of controlled ROMP of COD using a ruthenium catalyst.

For each catalyst, we followed by size exclusion chromatography the evolution of the polybutadiene number-average molecular weight (\overline{Mn}) and the PDI value, as the polymerization was proceeding (Fig. 3A and B, and Table 1). These values were corrected to account the difference between the hydrodynamic

Table 1
Catalyst efficiency and PDI of the polymers

Catalyst	Yield (%)	\overline{Mn}^a (SEC)	\overline{Mn}^b (theoric)	PDI ^a	f^b
1	98	8,700	5290	1.46	0.61
2	100	28,065	5400	3.88	0.19
3	97	22,005	5240	1.93	0.24
4	46	6,495	2485	1.25	0.38
5	100	8,075	5400	1.43	0.67
6	100	7,810	5400	1.47	0.69
G-I	100	8,480	5400	1.43	0.63
G-II	100	11,120	5400	1.70	0.49
G-III	100	13,400	5400	1.48	0.40

General conditions: ratio $[M]/[I] = 50$, $T = 20^\circ\text{C}$, $t_{\text{max}} = 100$ min (polymerization incomplete).

^a \overline{Mn} reported are corrected as the SEC column is calibrated with polystyrene.

^b Initiation efficiency: $f = \overline{Mn}_{\text{theoric}}/\overline{Mn}_{\text{SEC}}$ with $\overline{Mn}_{\text{theoric}} = \{[M]/[I]\}_{t=0} \times M_{\text{monomer}} \times (\text{yield}/100)$.

radius of the analyzed polybutadiene chains and the polystyrene chains used to calibrate the SEC column [23].

For all catalysts, the experimental data are characteristic of an uncontrolled polymerization with extensive chain transfer. At low conversion, the number-average molecular weight (\overline{Mn}) of all polybutadienes are very important and grow fast, compared to the theoretical \overline{Mn} calculated for a controlled polymerization. They highlight a partial initiation of the catalyst, generating very active propagating species. As transfers, to polymers, begin to compete with polymerization, the lengths of the polymers chains stop growing after 20% conversion for **1**, **4**, **G-II** and after 50% conversion for **2**, **3**, **5**, **G-I** while the PDI values keep increasing. The mass is statistically redistributed depending upon the location of chain transfer on the polymer backbone. At higher or quantitative conversion, the transfers become predominant as the COD becomes scarce, and the number-average molecular weight tends to slightly decrease. This is particularly the case for **6** and **G-III** which have to be quenched within seconds after the completion of the polymerization (Fig. 3B). All catalysts exhibit low initiation efficiency (f). Interestingly the best results come from the highly active catalysts **5** and **6**.

As a result of this strong tendency to catalyze cross metathesis (transfers), at 100% conversion, adding 100 equivalents of COD does not promote any significant chain growth. As the catalyst is still active, we observe even more transfers, with an associated increase in the PDI (Table 2). These results seem to indicate

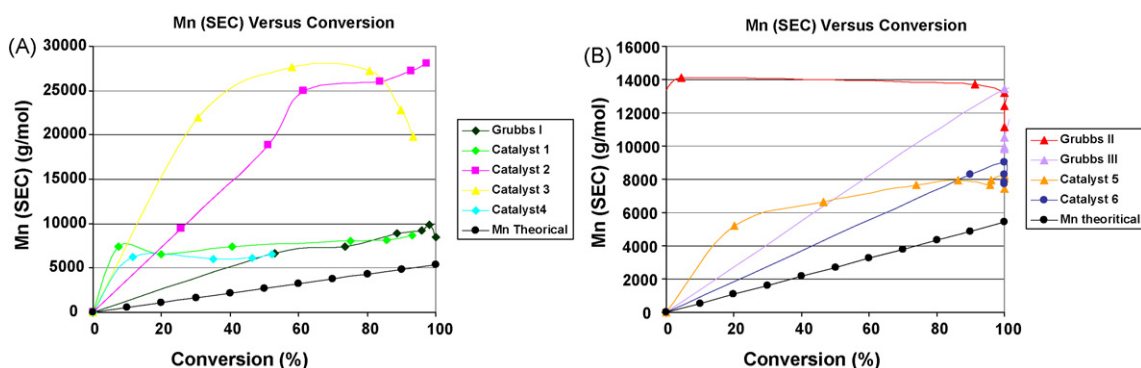


Fig. 3. (A and B) Evolution of the \overline{Mn} vs. conversion.

Table 2
Evolution of the \overline{Mn} and PDI of a polymerization in two steps

	1		5		6		G-II		G-III	
	\overline{Mn}	PDI	\overline{Mn}	PDI	\overline{Mn}	PDI	\overline{Mn}	PDI	\overline{Mn}	PDI
Block 1	9,470	1.46	8070	1.43	7,810	1.47	11,110	1.70	13,400	1.48
Block 2	10,700	1.62	6700	1.66	10,720	1.53	6,910	2.54	20,130	3.53

Table 3
Percentage (%) of *cis*- and *trans*- stereoisomers present in the ROMP product

	Catalyst					
	1	2	3	4	5	6
<i>cis</i>	17	51	24	60	22	18
<i>trans</i>	83	49	76	40	78	82

that surprisingly, after a limit size for the chains, only transfer reactions occur independently of the monomer concentration.

For low-strained cyclic monomers, benzylidene catalysts usually do not allow for control of the stereochemistry (*cis/trans*) of the polyolefins [9]. Nevertheless, a high proportion of chains transfer and/or secondary metathesis isomerization can increase the proportion of *trans*-stereoisomers up to 70–90% [9]. The stereochemistry of the polybutadienes synthesized with the indenylidene-based catalysts **1–6**, was determined by using a ^{13}C NMR INVERSE GATE sequence (Table 3). Complexes **2** and **4** gave polyolefin with a surprisingly low proportion of *trans*-stereoisomers. We are further investigating these anomalous results.

4. Conclusion

In this study, we have used the low-strained cycle COD as monomer to test nine well-defined ruthenium pre-catalysts including Grubbs first-, second- and third-generation complexes. We have observed that ligand/structural variations on the catalysts do have a profound effect on polymerization kinetic behavior. While all catalysts, with the exception of **4**, were highly active for the ROMP of COD, none performs the polymerization in a controlled manner due to important chain transfer behavior. This astonishing lack of control on an apparently very straightforward polymerization highlights the remaining challenge of catalyzing efficiently the ROMP of low-strained cycles without sacrificing the control of the polymeric architecture. The synthesis of new indenylidene ruthenium catalysts, more specifically dedicated to the controlled ROMP of low-strained monomers, is under investigation in our laboratories.

Acknowledgments

The ICIQ foundation, the Ministère de l'Enseignement supérieur et de la Recherche and the Ministerio de Educación y Ciencia are gratefully acknowledged for financial support of this work. We also thank Degussa and Umicore AG for their gen-

erous gift of materials. We also thank Martine Jean and Anita Loiseau at the Université du Maine for their technical assistance. SPN is an ICREA research professor.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2007.11.038.

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