



Electronic synergism in $[\text{RuCl}_2(\text{PPh}_3)_2(\text{amine})]$ complexes differing the reactivity for ROMP of norbornene and norbornadiene

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ABSTRACT

The reactivity of the new complex $[\text{RuCl}_2(\text{PPh}_3)_2(3,5\text{-Me}_2\text{piperidine})]$, complex **1**, was investigated for ring opening metathesis polymerization (ROMP) of norbornene (NBE) and norbornadiene (NBD) in the presence of ethyl diazoacetate (EDA) in CHCl_3 . The aim is to observe the combination of PPh_3 and an amine as ancillary ligands concerning the steric hindrance and the electronic perturbation in the properties of the N-bound site when replacing the amines. Thus, the results with **1** were compared to the results obtained when the amine is piperidine (complex **2**). Reaction with **1** provides 70% yield of isolated polyNBE ($M_n = 8.3 \times 10^4$ g/mol; PDI = 2.03), whereas **2** provides quantitative reaction ($M_n = 1.2 \times 10^5$ g/mol; PDI = 1.90) with $[\text{NBE}]/[\text{Ru}] = 5000$, $[\text{EDA}]/[\text{Ru}] = 48$ and $1.1 \mu\text{mol}$ of Ru for 5 min at 25°C . The resulting polymers showed *c.a.* 62% of *trans*-polyNBE, determined by $^1\text{H NMR}$, and $T_g = 32^\circ\text{C}$, determined by DSC and DMTA. For ROMP of NBD, **1** showed quantitative yield with PDI = 2.62 when $[\text{NBD}]/[\text{Ru}] = 5000$ for 20 min at 25°C , whereas the reaction with **2** reached 55% with PDI = 2.16 in the same conditions. It is concluded that the presence of the two methyl groups in the piperidine ring provides an increase in the induction period to produce the Ru-carbene species justifying better polyNBE results with **2**, and a greater amine $\overset{\sigma}{\text{Ru}} \rightarrow \overset{\pi}{\text{monomer}}$ synergism which contributed to the best activation of less tensioned olefin as NBD.

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1. Introduction

Ring opening metathesis polymerization (ROMP) of cycloolefins promoted by transition metal catalysts produces polymer containing unsaturated chains, as illustrated in Scheme 1 [1–16].

Successful ROMP depends on careful selection of the catalyst system where a carbene-transition metal is the active species. Thus, many researchers have been involved with the fascinating art of discovering transition metal catalysts for ROMP of cyclic olefins [1–7]. The studies focus on tuning the electronic and steric features of ancillary ligands into the metal coordination sphere in an attempt to achieve desired optimal catalyst results. This includes the reaction conditions (for example, time, temperature, concentration of the reactants and presence of additives), the produced polymer characteristics (for example, yield, molecular weights, polydispersity index, cross linking degree, glass transition temperature, rheology and mechanical properties), and the catalyst characteristics (for example, price, storing and handling, turnover frequency, reactivity in presence of air, initiating and propagating

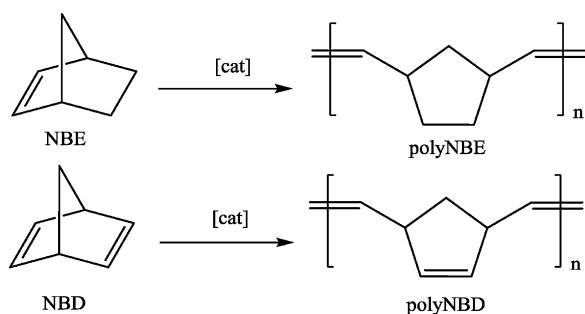
species, initiation and propagation rates, selectivity, latency and metal recovering).

Much success has been obtained using the Ru-based catalysts, denominated Grubbs type catalysts, to initiate the ROMP of different monomers [1–7]. With these catalysts, ROMP has been very helpful to obtain unsaturated and functionalized polymers for many fields of science [1–15].

Besides the success with the Grubbs type catalysts, many industrial process use simple salts in presence of co-catalysts as the case of the Norsorex[®] (polynorbornene) [1,14] and there is a claim for more robust catalyst for large application [6,17,14]. With this in mind, we have developed complexes of type $\{\text{Ru}^{\text{II}}\text{Cl}_2(\text{phosphine})(\text{amine})\}$ motivated by the fact that the isolated compounds, and when in solution, are fairly non-sensitive to the air, moisture, light and warm, which are appropriated conditions for large practical applications, at least. In general, we have observed that a combination between phosphines and amines on the starting non-carbene Ru^{II} coordination sphere can provide polymers with reasonable results of yield, molecular weights and PDI [18–23], where the carbene-Ru active species are generated *in situ* from reaction with ethyl diazoacetate (EDA).

In a continuous effort to modulate the reactivity of the $\{\text{Ru}^{\text{II}}\text{Cl}_2(\text{phosphine})(\text{amine})\}$ backbone for ROMP, this study investigates the combination of PPh_3 and 3,5-dimethylpiperidine

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Scheme 1. Illustration for ROMP of NBE and NBD.

(3,5-Me₂pip; complex **1**) to observe the steric hindrance of the two methyl groups and the perturbation in the electronic properties of the N-bound site in the piperidine compared with the combination of PPh₃ and piperidine (pip; complex **2**) (Fig. 1). Indeed, the complex **2** was already studied for ROMP [18], and we have observed that saturated amines such as piperidine (pK_a = 11.2; $\theta = 121^\circ$), peridiazepine and acyclic amines are good ancillary ligands [18,20–22]. Thus, it is important to introduce a few changes in these ligands to observe the further behavior. Therefore, the ROMP of norbornene (NBE) was investigated with **1** and the ROMP of norbornadiene (NBD) was investigated with **1** and **2** as function of monomer and EDA concentration, temperature and reaction time. The effects of these variables on the reaction yields, M_n and PDI values are discussed, besides characteristic results from NMR and thermal analyses (TGA, DSC and DMTA), in order to compare the behavior of the two parent complexes.

This study was partially motivated because the 3,5-Me₂pip is much less toxic than pip and it is a non-flammable and non-corrosive liquid, contrary to pip, that are favorable properties for transporting, storing and handling.

2. Experimental

2.1. General remarks

All manipulations were performed under argon atmosphere. HPLC-grade CHCl₃ was used throughout. Other solvents were analytical grade and were distilled from the appropriate drying agents immediately prior to use. Other commercially available reagents were purified by standard procedure or used without further purification. RuCl₃·xH₂O, norbornene (NBE), norbornadiene (NBD), 3,5-dimethylpiperidine (3,5-Me₂pip), piperidine (pip) and ethyl diazoacetate (EDA) from Aldrich were used as acquired. The [RuCl₂(PPh₃)₃] complex was prepared following the literature and its purity was checked by satisfactory elemental analysis and spectroscopic examination (³¹P{¹H} and ¹H NMR and FTIR) [24–26]. The room temperature (RT) was 24 ± 1 °C. Slush bath at –41 °C was prepared from acetonitrile/N₂ [27].

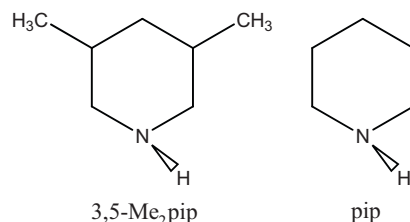


Fig. 1. 3,5-Me₂pip and pip chemical structures.

2.2. Synthesis of [RuCl₂(PPh₃)₂(3,5-Me₂pip)] (**1**)

3,5-Me₂pip (0.34 mmol; 0.028 g) was added to a solution of [RuCl₂(PPh₃)₃] (0.26 mmol; 0.25 g) in acetone (40 mL) and the resulting dark green solution was stirred for 2 h at RT. A green precipitate was then filtered and washed with methanol and ethyl ether and then dried in a vacuum. Yield: 72%. Analytical data for RuCl₂P₂NC₄₃H₄₅ were 63.91 C, 5.75 H and 1.82% N; Calcd. 63.78 C, 5.60 H and 1.73% N. FTIR in CsI: 320 cm⁻¹ [ν (Ru–Cl)] was found; 3251 cm⁻¹ [ν (3,5-Me₂pip N–H)]. ESR: no signal was observed.

2.3. Instrumentation

Elemental analyses were performed using an EA1110 CHNS-O Carlo Erba Instrument. ESR was carried out at 77 K using a Bruker ESR 300C apparatus (X-band) equipped with a TE102 cavity and HP 52152A frequency counter. The IR spectra were obtained in CsI pellets on a Bomem FTIR MB 102. NMR (¹H; ¹³C{¹H}; ³¹P{¹H}) spectra were obtained in CDCl₃ at 25.0 ± 0.1 °C using a Bruker AC-200 or in CD₂Cl₂ at –45.0 °C using a Bruker DRX500 spectrometer. The obtained chemical shifts were reported in ppm relative to the high frequency of TMS or 85% H₃PO₄. GPC analyses were obtained in a Shimadzu 7725.1 spectrometer system equipped oven and PL gel column (5 m MIXED-C: 30 cm, $\phi = 7.5$ mm). The retention times were calibrated with standard monodispersed polystyrene using HPLC-grade CHCl₃ as eluent. PDI is M_w/M_n . TGA analyses were carried out in a TGA-50.0 Shimadzu equipment heating the sample at 20 °C/min from 25 to 700 °C with a N₂ flow of 20 cm³/min. DSC measurements were performed using a DSC Q100 differential scanning calorimeter from TA Instruments. Samples were heated from 0 to 150 °C at a heating rate of 10 °C/min in N₂ atmosphere. DMTA measurements were performed with a RSA3 (TA Instruments) working in the tensile mode. The tests were performed under isochronal conditions at 1 Hz and the temperature was varied between –100 and 200 °C at a heating rate of 5 °C/min.

2.4. Polymerization reactions

In a typical ROMP experiment, 1.1 μ mol of catalyst (**1** or **2**) was dissolved in 2 mL of CHCl₃ and a certain amount of monomer (NBE or NBD) and EDA were added. The solution gelled for 1–2 min, but the reaction mixture was left under stirring for different periods of time at various temperatures in a silicon oil bath (± 1 °C). The [EDA]/[Ru] and [NBE]/[Ru] molar ratios were also varied. At RT, 5 mL of methanol was added and the polymer was filtered, washed with methanol and dried at RT before being weighted. All catalytic runs were made at least three times. The reported yield results are average values with 10% error at most. The GPC data for NBE with **1** are from isolated polymers dissolved in 2 mL of CHCl₃. The GPC data for NBD with **1** and **2** were obtained from diluted aliquots in CHCl₃ of the reaction solution.

3. Results and discussion

3.1. Characterization of the complex **1** and an insight into the reactivity for ROMP

The new complex **1** was synthesized via a phosphine exchange with 3,5-Me₂pip from [RuCl₂(PPh₃)₃] with a good yield. The isolated complex does not show signal in the ESR spectrum, suggesting that the ruthenium center presents a low spin d⁶ configuration in the 2+ oxidation state. This agrees with the proposed formulation from the CHN elemental analysis, ensuring the five-coordinated complex. Typical vibration bands in the FTIR spectrum confirm the presence of Cl⁻ ions and 3,5-Me₂pip in the isolated complex.

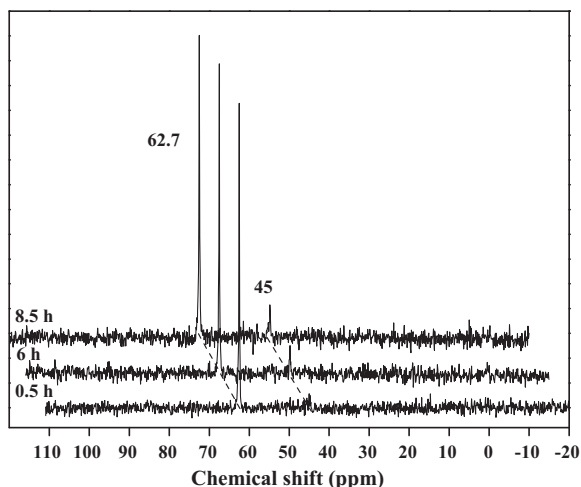


Fig. 2. ^{31}P NMR spectra of **1** in CDCl_3 recorded after 0.5, 6 and 8.5 h.

One $\nu(\text{Ru}-\text{Cl})$ band suggests that the two Cl^- ligands are *trans*-positioned to each other in the solid state [21,22,28].

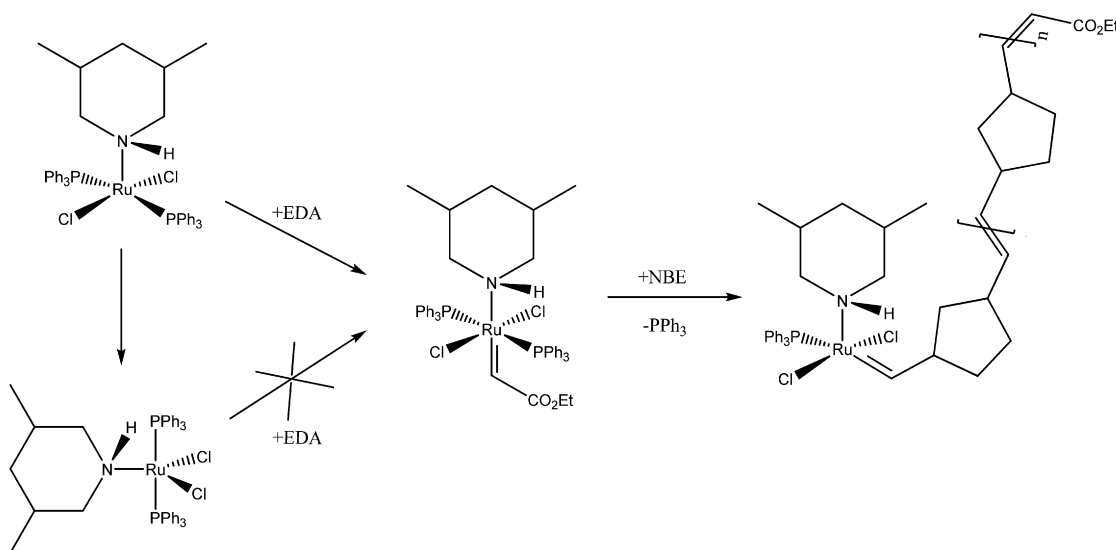
The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **1** in the CDCl_3 at 25°C shows a singlet at 62.7 ppm suggesting that the two PPh_3 ligands are equivalently located in the complex (Fig. 2). Correlating this result with the IR spectrum, which suggested that the two Cl^- ligands are *trans*-positioned, a square pyramid geometric configuration is concluded for the complex with the 3,5- Me_2pip at the apical position (Scheme 2). Further, the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum shows the appearance of another singlet at 45 ppm as a function of time (Fig. 2), suggesting the presence of a geometric isomer in the solution with the PPh_3 ligands also equivalent on the Ru^{II} center, such as a trigonal bipyramidal structure [25]. It is important to observe the absence of signals associated to a binuclear species in the solution as promptly occurs when dissolving $[\text{RuCl}_2(\text{PPh}_3)_3]$ in CHCl_3 with a loss of one PPh_3 molecule [18,21,22,24–26]; free PPh_3 appears at -4.9 ppm which is not observed in the present case, even for 8.5 h. Thus, the presence of the amine 3,5- Me_2pip in the complex avoids a similar dimerization process as have been observed with other phosphine-amine Ru-complexes [18–22]. The complex **1** does not undergo additional rearrangements for 8.5 h at RT (Fig. 2). Similar behavior was observed when studying the pip derivative complex

(**2**): absence of dimerization and presence of a second singlet signal at 45 ppm in the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum as a function of time [18]. However, in the latter case, the lower field signal (62.5 ppm) practically disappeared for 5.5 h, whereas, in the present study, that process is slower as can be deduced from the spectrum for 8.5 h (Fig. 2). This difference can be attributed to the presence of the two methyl groups in 3,5- Me_2pip that makes difficult geometrical twist because space restriction.

We were unable to isolate a carbene-ruthenium complex for several attempts even at low temperature, although the solution changed from green to a brown-yellow color upon addition of EDA. On the other hand, the evidence of the metalcarbene formation was observed by ^1H NMR measurements at -45°C when performing a reaction of **1** with 5 equivalents of EDA in CD_2Cl_2 at -41°C . It was observed a triplet signal at 17.4 ppm ($^3J_{\text{HP}} = 11.5$ Hz) in the ^1H NMR spectrum, that suggests the presence of two PPh_3 molecules in the complex [29], such as six-coordinated $[\text{RuCl}_2(\text{PPh}_3)_2(3,5\text{-Me}_2\text{pip})(=\text{CHCO}_2\text{Et})]$ species. This is in agreement with the fact that **1** is an unsaturated 16 electrons species, able to promptly react with EDA to give the corresponding 18-electron derivative complex without PPh_3 displacement. Similar results were observed with **2** ($\delta_{\text{H}} 17.5$ ppm; $^3J_{\text{HP}} = 10.0$ Hz).

The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum with **1** obtained from the experiment at -41°C showed the disappearance of the peak at 62.7 ppm while new peaks arised, without the appearance of the signal at 45 ppm: a peak at 32.4 ppm assigned to carbene complex $[\text{RuCl}_2(\text{PPh}_3)_2(3,5\text{-Me}_2\text{pip})(=\text{CHCO}_2\text{Et})]$, a signal at 22.6 ppm assigned to phosphazine (EDA/ PPh_3 adduct), a signal at 21.7 ppm and a peak at 18.1 ppm, which corresponds to the phosphorus ylide [30,31]. The adduct signal is confirmed by mixing PPh_3 with EDA (5 equivalents) in absence of the metal complex.

The signal at 21.7 ppm was associated to an uncharacterized ruthenium complex. It was also observed in the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of the complex **1** in the presence of EDA at RT. In this case, the signal at 62.7 ppm disappeared as observed at low temperature, but the signal at 45 ppm associated to the five-coordinated isomer remained, showing that this species does not react with EDA because its geometric structure with two phosphine molecules in the z axis (PPh_3 cone angle of 145°). An additional signal at 29.8 ppm was also observed which was attributed to the free OPPh_3 produced in the solution after discoordination of the PPh_3 from the Ru-complex and then, it reacts with residual O_2 upon addition of EDA to the solution [18–22]. This is a clear indication



Scheme 2. Possible reaction routes for ROMP of NBE with **1**.

that the PPh_3 leaves the complex to produce a five-coordinated carbene-Ru species via an associative type mechanism. A resulting six-coordinated carbene-species at RT is ruled out because the presence of free PPh_3 (or OPPh_3).

Thus, from the low temperature and RT experiments, it is possible to propose that the six-coordinated species observed at -45°C is an intermediate to generate the five-coordinated catalytic species.

In order to confirm this proposal, two flasks with solutions of NBE in CH_2Cl_2 were cooled to -41°C and complex **1** was added, followed by the addition of EDA to each flask (as a similar experiment for $[\text{NBE}]/[\text{Ru}] = 5000$ and $[\text{EDA}]/[\text{Ru}] = 48$). The mixtures were stirred for 5 min, without formation of gel as occurred at RT. To one of the flasks, methanol was added and it was not observed precipitation of polymer. The second flask was allowed to warm to RT for 5 min into a water bath. At the meantime, the solution was completely gelled and polyNBE was then precipitated by the addition of methanol. These procedures confirm that the ROMP reaction did not occur at -41°C , although the carbene complex formation took place. The ROMP will only occur when the PPh_3 molecule undergoes discoordination from the metal center (Scheme 2). This is supported by polymerization experiment carried out with **1** at RT in the presence of PPh_3 excess, where formation of polymer for 5 min was not observed.

From an *in situ* polymerization experiment monitored by ^1H NMR and carried out with $[\text{NBE}]/[\text{Ru}] = 500$ and $[\text{EDA}]/[\text{Ru}] = 48$, the presence of the hydrogen atom signals from the coordinated 3,5-Me₂pip molecule was observed in the spectrum [3.21–2.75 ppm (*ortho*); 2.62 ppm (*N-H*); 2.54–2.49 ppm (*meta*); 1.80–1.69 ppm (*para*); 0.84 ppm (CH_3)]. No signal of free amine in the solution was observed. The signals assigned to free OPPh_3 [7.93–7.89 (*meta*); 7.79–7.75 (*ortho* and *para*)] and PPh_3 coordinated [7.7–7.65 (*meta*); 7.57–7.44 (*ortho* and *para*)] in the spectrum agrees with the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum analysis [25,26]. Thus, an amine and a phosphine are coordinated in the course of the ROMP reaction, working as ancillary ligands through a combination of electronic and steric features, as well as the Cl^- ions. The presence of typical signals of amine and phosphine in the NMR spectra indicates a mechanism reaction via coordination of an olefin in the open position of the five-coordinated carbene species. The behavior is similar to the observed with the complex with pip [18].

3.2. Studies with NBE obtained with **1**

The catalytic activity showed to be sensitive to the $[\text{EDA}]/[\text{Ru}]$ molar ratio (Fig. 3), with an abrupt increase in the yield up to $[\text{EDA}]/[\text{Ru}] = 48$, followed by a drop for $[\text{EDA}]/[\text{Ru}] > 48$, when using $[\text{NBE}]/[\text{Ru}] = 5000$ for 5 min at 25°C ; no reaction was observed in the absence of EDA. The M_n values follow the same curve profile as observed for the yield results, whereas the PDI values show a concomitant opposite result (Fig. 3). This can be attributed to a metal complex reacting via an associative type mechanism that supports the ROMP reaction to take place [2], according to Scheme 2; consequently, increasing M_n and decreasing PDI. However, with very excessive amount of EDA ($[\text{EDA}]/[\text{Ru}] > 48$), the divergent effect for both yields and molecular weights can be associated to secondary reactions, such as competition between NBE and EDA for the Ru metal center [18,19], alkene cyclopropanation [32,33] and decomposition of EDA to form diethyl maleate or diethyl fumarate [30,31]. Consequently, the large amount of EDA interferes in the dynamic of the ROMP reaction (initiation and propagation) and as a result, low yield and broad PDI are obtained.

The effect of the $[\text{NBE}]/[\text{Ru}]$ ratio on the yield of the isolated polymers follows a saturation curve profile (Fig. 4), when using $[\text{EDA}]/[\text{Ru}] = 48$ for 5 min at 25°C . This fact is associated to the formation of gel in the beginning of the reaction, as already observed

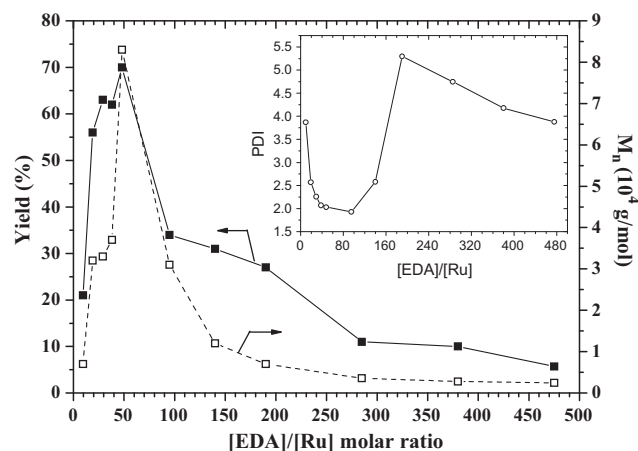


Fig. 3. Dependence of yield and M_n on the $[\text{EDA}]/[\text{Ru}]$ molar ratio for ROMP of NBE with **1**; $[\text{NBE}]/[\text{Ru}] = 5000$ with $1.1 \mu\text{mol}$ of **1** in CHCl_3 at 25°C for 5 min. Insert: Dependence of PDI on the $[\text{EDA}]/[\text{Ru}]$ molar ratio.

in the literature [34,35]. In Fig. 4, the yield rises up to 60–70% when the $[\text{NBE}]/[\text{Ru}]$ ratio was increased from 1000 up to 4000–5000. The PDI values are roughly constant over the studied range, whereas the M_n values raise from 2.0×10^4 up to 8.0×10^4 g/mol when the $[\text{NBE}]/[\text{Ru}]$ ratio was increased from 2000 up to 10,000. With $[\text{NBE}]/[\text{Ru}] = 1000$, the isolated polyNBE showed a bimodal molecular weight distribution (3.3×10^4 and 0.2×10^4 g/mol) probably due to the fact that high Ru concentration with regard to the low monomer concentration can produce small chains with different sizes [1]. On the other hand, the fact that the PDI practically does not change when the amount of NBE is increased in the reaction over 2000–10,000, with monomodal molecular weight distribution, suggests that the relationship between the initiation and propagation steps is maintained throughout the investigated range of $[\text{NBE}]/[\text{Ru}]$. This different behavior for the ratio of 1000 and higher than 2000 can be certified by the fact that the most favorable conditions for a successful ROMP are to use the highest monomer concentration at the lowest temperature possible [1,3]. An increase in the monomer concentration contributes entropically to the reaction, decreasing the entropic term ($-T\Delta S$) in the Gibbs free energy equation which is always positive ($S_f < S_i$). This entropic consequence is compensated by the enthalpic contribution (ΔH) which is associated to the release of ring-strain, finally favoring the $\Delta G_{\text{polymerization}}$ [1,3]. Then, this fact is observed in the present study

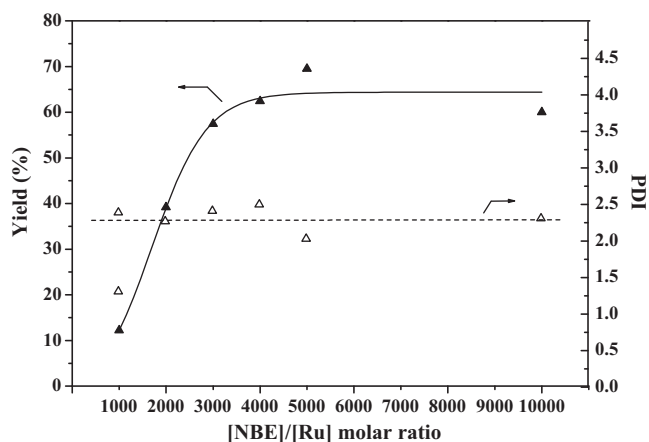


Fig. 4. Dependence of yield and PDI on the $[\text{NBE}]/[\text{Ru}]$ molar ratio for ROMP of NBE with **1**; $[\text{EDA}]/[\text{Ru}] = 48$ with $1.1 \mu\text{mol}$ of **1** in CHCl_3 at 25°C for 5 min.

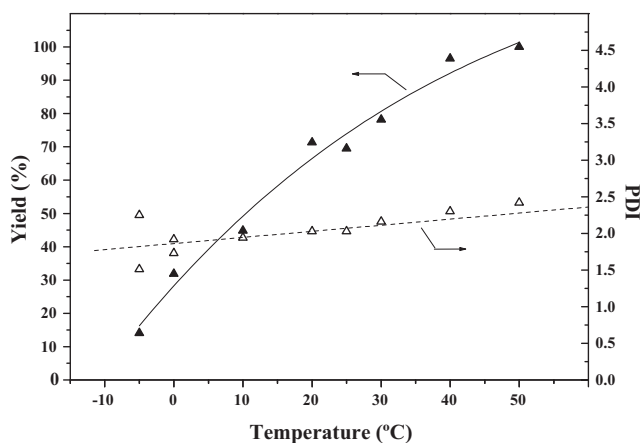


Fig. 5. Dependence of yield and PDI on the temperature for ROMP of NBE with **1**; [NBE]/[Ru] = 5000 and [EDA]/[Ru] = 48 with 1.1 μmol of **1** in CHCl_3 for 5 min.

with an increase in the polymer chain when the [NBE]/[Ru] ratio increases.

Quantitative yields were reached when the temperature was increased from -5 up to 50°C (Fig. 5), using [NBE]/[Ru] = 5000 and [EDA]/[Ru] = 48 for 5 min. This behavior can be associated with an improvement in dis Coordinating the PPh_3 from the Ru metal center, essential to produce the *in situ* catalyst and then, the ROMP initiation step occurs (Scheme 2). At elevated temperature, the solution is less viscous which provides better development of the reaction with quantitative yield. At the lowest studied temperatures (-5 and 10°C), bimodal molecular weight distributions are observed (Fig. 5). This bimodal result is associated to a slower reaction rate at low temperatures for the replacement of a PPh_3 molecule with the carbene in the induction period. Fig. 5 also illustrates that a smooth increasing in the PDI values occurs as increasing the temperature. This can be due to the occurrence of a disordered polymer growth once elevated temperature inhibits the ROMP reaction itself [1].

Besides the occurrence of gel for 1–2 min, the polymers were only isolated at different time intervals (3–60 min) when methanol was added, for reactions with [NBE]/[Ru] = 5000 and [EDA]/[Ru] = 48 at 25°C . Plotting the isolated polymer yields as a function of time (Fig. 6), it is first observed an increase in the range of 3–10 min, and then, a roughly constant result (80–83% yield) for 10–50 min. The M_n values plotted as a function of time (Fig. 6) suggest some increase in the sizes of the polymer chains up to 10 min (8.5×10^4 to 9.0×10^4 g/mol), and then, there is a drop up

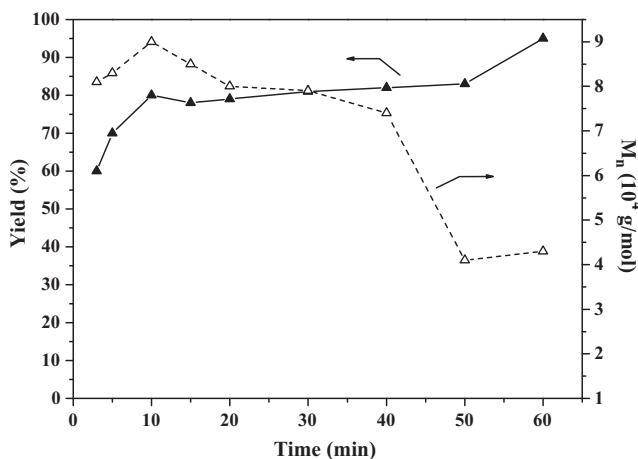


Fig. 6. Dependence of yield and M_n on the reaction time for ROMP of NBE with **1**; [NBE]/[Ru] = 5000 and [EDA]/[Ru] = 48 with 1.1 μmol of **1** in CHCl_3 at 25°C .

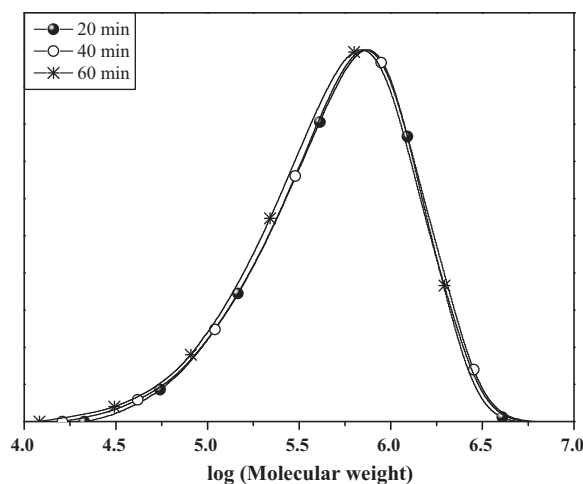
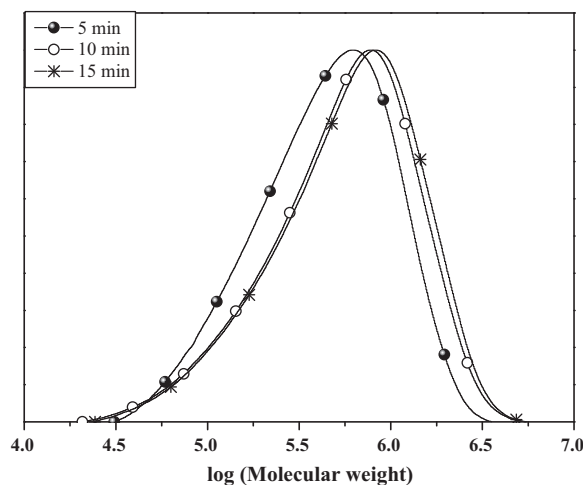


Fig. 7. GPC traces as a function of time for ROMP of NBE with **1**; [NBE]/[Ru] = 500 and [EDA]/[Ru] = 48 with 1.1 μmol of **1** in CHCl_3 at 25°C . Top: for 5, 10 and 15 min. Bottom: for 20, 40 and 60 min.

to 4×10^4 g/mol with 50–60 min of reaction. Significant random results in the PDI values (from 2 up to 4) were obtained. It is concluded that there is a continual reaction when leaving the reaction to occur up to 60 min, increasing the production of polymer, but borrow the PDI.

The GPC traces of diluted aliquots removed for different times from a batch polymerization run show an increase in the molecular weight for 5 up to 15 min of reaction (Fig. 7). From 15 up to 60 min, a reduction of the molecular weight of polyNBE can be observed. This can confirm the intermolecular chain-transfer or backbiting with the decreasing M_n when the reaction time is increased [1–3].

The resulting polymer obtained with [NBE]/[Ru] = 5000, [EDA]/[Ru] = 48 and 1.1 μmol of Ru for 5 min at 25°C in CHCl_3 was characterized by NMR (^1H ; ^{13}C) spectroscopy. The $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum in CDCl_3 showed the singlet at 133.1 ppm assigned to the carbon atoms of the double bond of the polymer, in agreement with the literature data [36]. ^1H NMR spectrum showed a multiplet centered at 5.32 ppm assigned to the *trans*-positioned olefin-protons. A predominant formation of the *trans*-polyNBE (62%) was concluded.

Fig. 8 shows a typical TGA curve of a polyNBE obtained with **1**, where a continuous loss of weight up to 840°C is observed. First, the curve reveals a slight weight loss (c.a. 1.5%) at temperature range between 45 and 70°C attributed to the loss of CHCl_3 soaked up in the polymer, becoming flat at 70 – 90°C (Fig. 8, insert). Then, the

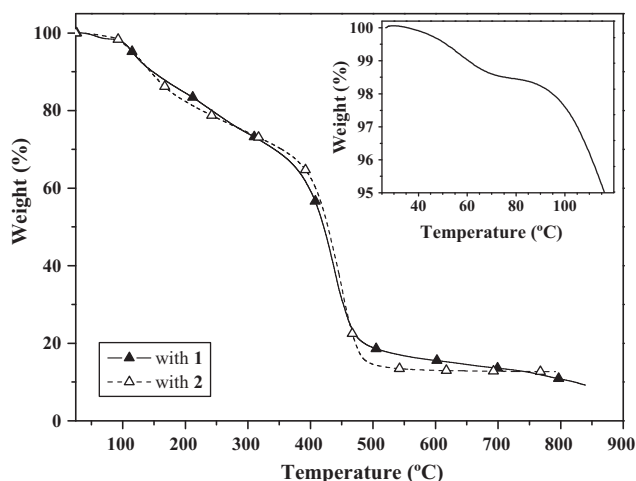


Fig. 8. TGA curves of polyNBE samples obtained with $[NBE]/[Ru]=5000$, $[EDA]/[Ru]=48$ and $1.1 \mu\text{mol}$ of **1** (\blacktriangle) or **2** (\triangle) in CHCl_3 at 25°C for 5 min. *Insert:* Curve of polyNBE from **1** at temperature range $25\text{--}120^\circ\text{C}$.

polymer started to decompose. A weight loss (*c.a.* 20%) between 100 and 360°C can be attributed to a decomposition of small polymer chains. At 400°C , the curve shows a sharp drop in the weight loss indicating a rapid degradation of the polyNBE backbone which is consistent with the literature [37]. A similar TGA curve profile is observed for a polyNBE obtained with **2** (Fig. 8).

The DSC curve of a polyNBE obtained with **1** shows a change in the baseline between 20 and 40°C in a first run of the sample (Fig. 9), which can be associated with the temperature range within the glass transition temperature (T_g) in accordance with the literature [36,37]. This assignment was confirmed by DMTA of a solution-cast film with loss modulus maximum (E'') at 32°C . Further, in the DSC curve, an exothermic peak at 92°C is observed probably due to the sorption of N_2 in the cavities of the polymer, after loss of solvent, which is not observed in the second run (Fig. 9). Similar behavior has been reported in the literature [36,37]. The DSC curve for the polyNBE obtained with **2** also showed the exothermic peak, but at 85°C . In this case, the T_g was 38°C from E' .

Table 1 summarizes the data for the polyNBEs obtained with **1** and **2** for a selected reaction conditions. It is observed that the results for yields are different with some agreement for M_n and

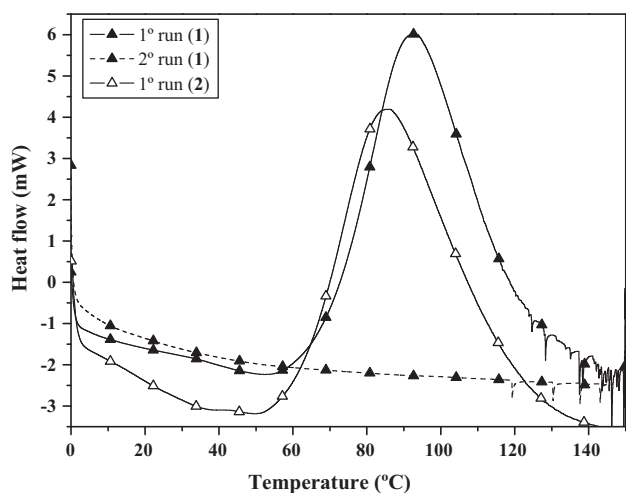


Fig. 9. DSC curves of polyNBE samples obtained with $[NBE]/[Ru]=5000$, $[EDA]/[Ru]=48$ and $1.1 \mu\text{mol}$ of Ru in CHCl_3 at 25°C for 5 min. Solid lines: first run for polyNBE from **1** (\blacktriangle) or **2** (\triangle). Dashed line: second run for the same sample from **1**.

Table 1

Results for polyNBE obtained with **1** and **2**; $[NBE]/[Ru]=5000$ and $[EDA]/[Ru]=48$ with $1.1 \mu\text{mol}$ of Ru in CHCl_3 for 5 min at 25°C .

Complex	Yield (%)	M_n (g/mol)	PDI	% <i>trans</i>
1	70	8.3×10^4	2.03	62
2^a	99	1.2×10^5	1.90	59

^a Ref. [18].

PDI. This can suggest that the behavior of both species are similar, perhaps differing in monomer time-consuming, as can be deduced when comparing the $^31\text{P}\{^1\text{H}\}$ -NMR spectra of **1** (Fig. 2) and **2** obtained from RT experiments [18]. In both cases, it was shown the presence of two species in solution as a function of time. In the case of **2**, the process is faster which it is almost completely converted for 5 h, whereas **1** remains almost invariable for more than 8 h. It suggests that **2** is more dynamic in solution than **1**, since the isomerization process occurred more quickly. Thus, it is possible to affirm that the induction period for formation of the active species with **1** is longer than in the case of **2**. Consequently, the ROMP of NBE is more favorable with **2** considering that NBE is a rather strained monomer and can be easily polymerized either with **1** or **2**.

In ROMP of NBE with **1** and **2**, the solutions became very viscous for 1–2 min. This indicates that the propagation is fast in both cases [38], differing perhaps in the initiation steps. It is well known that more complete is the initiation, narrower PDI is obtained [1]. Therefore, the slower formation of the Ru-carbene in the induction period can justify the lower yields displayed by **1** in relation with **2**.

3.3. Studies with NBD obtained with **1** and **2**

The effects of $[NBD]/[Ru]$ molar ratio in the range of 5000 up to 25,000 on the yields and PDI values of polyNBD obtained in the presence of $5 \mu\text{L}$ of EDA for 5 min at 25°C are shown in Fig. 10. The yields increase using either **1** or **2**, achieving semi-quantitative yields in the case of **1** and *c.a.* 80% with **2**. These raise in the yields are followed by a decreasing in the PDI values using any complexes, with broader polymers with **1**.

The GPC traces clearly indicate that the molecular weights increased when increasing the $[NBD]/[Ru]$ molar ratio, as shown in Fig. 11. The M_n values increased from 1.1×10^4 to 3.9×10^4 g/mol with **1** and 1.9×10^4 to 4.9×10^4 g/mol with **2**.

Investigating the polymerization yield as a function of time up to 60 min (Fig. 12), with $[NBD]/[Ru]$ ratio of 5000, the monomer

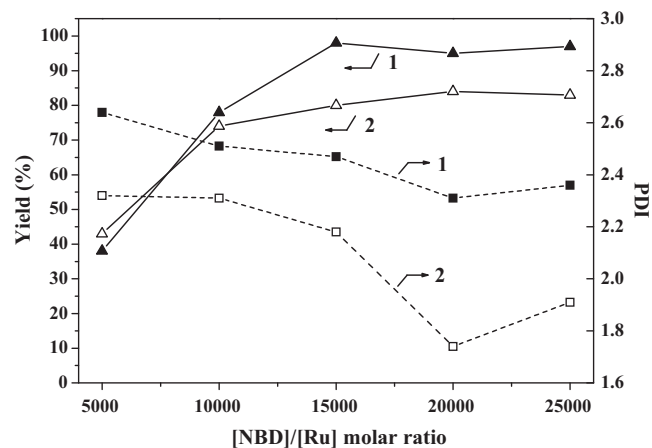


Fig. 10. Dependence of yield (solid lines: \blacktriangle to **1** and \triangle to **2**) and PDI (dashed lines: \blacksquare to **1** and \square to **2**) on the $[NBD]/[Ru]$ molar ratio for polyNBD; $[EDA]/[Ru]=48$ with $1.1 \mu\text{mol}$ of Ru in CHCl_3 at 25°C for 5 min.

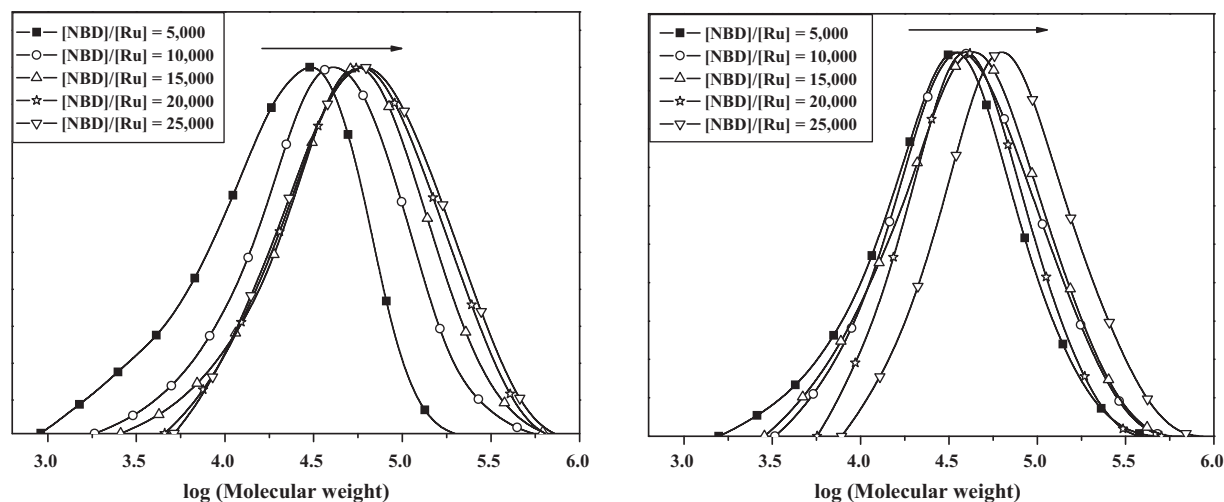


Fig. 11. GPC traces as function of [NBD]/[Ru] molar ratio for ROMP of NBD with **1** (left) and **2** (right); [NBE]/[Ru] = 5000 and [EDA]/[Ru] = 48 with 1.1 μ mol of Ru in CHCl_3 at 25 °C for 5 min.

conversion with **1** was semi-quantitative for 20 min with PDI *c.a.* 2.6. In the case of **2**, a linear relationship between yield and time is observed, reaching 80% for 50 min (PDI = 2.36). Further, the behavior of these compounds also differs considering the results of M_n and PDI. In the case of **1**, the M_n values were roughly constant (1.0×10^4 to 1.4×10^4 g/mol) with a decreasing PDI values (2.9–2.1). In the case of **2**, the M_n value increased from 0.5×10^4 to 1.2×10^5 g/mol for 30 min with decreasing PDI (2.5 up to 2.0), and then decrease up to 1.4×10^4 g/mol for 60 min with PDI = 2.67. These different trends in the results can be associated with the reactivity of the complexes in solution. **1** provides faster quantitative yields, whereas **2** provides a slower linear increase of yield with time.

Evaluating the catalytic reactivity of **1** and **2** based on the results for ROMP of NBD, it was verified that **1** shows higher yields than **2** over all conditions examined [18]. This can be predominantly associated with the electronic features in the 3,5-Me₂pip ligand. For ROMP of NBE, a high catalytic efficiency is not required since the ring opening is facilitated by the ring strain. On the other hand, ROMP of NBD, which is less strained than NBE, is strongly favored by the greater σ -donor contribution from the 3,5-Me₂pip amine compared to pip. More efficient is the amine $\xrightarrow{\sigma} \text{Ru} \xrightarrow{\pi}$ monomer

electronic synergism, highest is the activation of the olefin, highlighting the importance of the amine as ancillary ligand.

4. Conclusion

PolyNBE and polyNBD were obtained with complexes using the amines 3,5-Me₂piperidine (**1**) and piperidine (**2**) as ancillary ligands. It was inferred that both complexes present the same catalytic behavior when solution, but at different monomer time-consuming. First, a difference could be ascribed to a longer induction period for **1** against **2** in the formation of the Ru-carbene due to a greater steric hindrance for an expected associative type mechanism. This can be considered as a determinant factor to obtain better yields with **2** for polyNBE, considering that NBE is a monomer susceptible to undergo easy ROMP [1]. Further, a more efficiency in obtaining the Ru-carbene species affords a better initiation reaction [1], consequently, better PDI values were obtained with **2**. On the other hand, for ROMP of NBD, **1** provided better yields than **2**, even with worst PDI. This could be attributed to a greater amine $\xrightarrow{\sigma} \text{Ru} \xrightarrow{\pi}$ monomer electronic synergism when working with **1**, proper for a monomer in which higher catalyst efficiency for ROMP is required. Thus, the propagation reaction in this case is improved by the higher electronic population in the Ru metal center, affording the activation of a less tensioned cyclic olefin more efficiently [22]. The results under these circumstances suggest a fine tuning in the choice of the catalyst for ROMP reaction using accessible compounds when combining friendly and cheap ancillary ligands.

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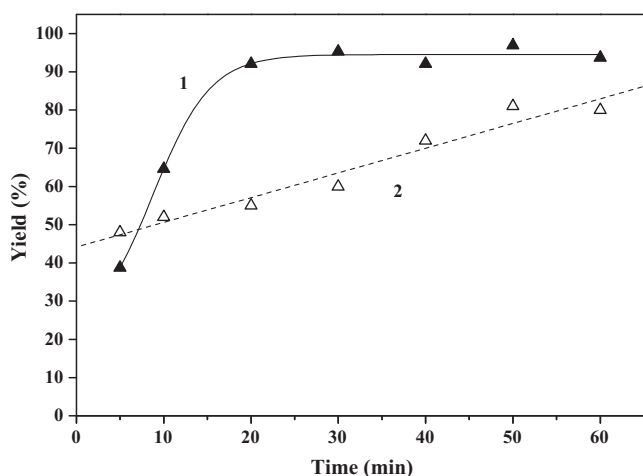


Fig. 12. Dependence of yield on the reaction time for ROMP of NBD with **1** (\blacktriangle) or **2** (\triangle); [NBE]/[Ru] = 5000 and [EDA]/[Ru] = 48 with 1.1 μ mol of Ru in CHCl_3 at 25 °C for 5 min.

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