JOURNAL OF Applied Polymer SCIENCE

Ring Opening Metathesis Copolymerization of Norbornene with Norbornadiene from Solutions with Different Mole Fractions of the Comonomers Catalyzed by Ru-Amine Complexes

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ABSTRACT: Copolymers from norbornene (NBE) with norbornadiene (NBD) were synthesized via ring opening metathesis copolymerization varying the mole fractions of the comonomers (0.8 : 0.2; 0.6 : 0.4; 0.4 : 0.6; 0.2 : 0.8) for a total monomer quantity of 5000 equivalents/[Ru]. The batch reactions were performed with [$RuCl_2(PPh_3)_2$(amine)] complex types as precatalysts, where amine is perhydroazepine (**1**) or piperidine (**2**), in $CHCl_3$ (2 mL) in the presence of ethyl diazoacetate (5 μL) for different intervals of times (5, 30, 60, and 120 min) at 40°C. The copolymers were characterized by ^{13}C NMR. Quantitative yields of isolated materials were obtained from solutions with NBD : NBE 0.8 : 0.2 mole fraction in the presence of **1,** decreasing to 70% for NBD : NBE 0.2 : 0.8 solutions. Concerning **2**, the yields were 70% at most. Polymeric materials obtained with **1** were less soluble in $CHCl_3$ than those synthesized with **2**. The dependence of the reaction yields and occurrence of crosslinking on the starting NBE : NBD proportion related to reactivity of the complexes **1** and **2** were discussed. A few differences in the amines such as ancillary ligands were sufficient to change the reactivity of the {$RuCl_2(PPh_3)$} moiety complex to provide copolymers with different compositions.

KEYWORDS: ROMP; copolymerization; organometallic catalysts; norbornene; norbornadiene

Received 4 July 2011; accepted 19 March 2012; published online 00 Month 2012
DOI: 10.1002/app.37741

INTRODUCTION

Ring opening metathesis (co)polymerization (ROMP or ROMCP) is a catalyzed reaction using a transition metal coordination complex for syntheses of polymers and copolymers from cyclic olefins in mild conditions.[1–3] An important feature in this kind of reaction is the control of the molecular weight and stereochemistry, with retention of the olefin unsaturation in the chain. Thus, diverse new polymeric materials including innovated mechanic and electronic properties have been invented.[4–6]

The success of the ROMP in various fields of science is mainly associated to the development of efficient coordination complexes from Mo, W, and Ru as catalysts.[7–11] The complexes present a carbene species of type [M(=CHR)L_n] in the complex coordination sphere. The key step in the reactivity of the catalysts is the formation of the metallacyclobutane intermediate in an intra-reaction of a carbene species with an incoming coordinated olefin monomer.[1–3]

Syntheses of copolymers via olefin metathesis depend on the reactivity of the catalyst to form the M1M2 and M2M1 dyads in the growing polymeric "P" chain.[11–13] The formation of the metallacyclobutane intermediate from the {M(=M2PCRH)} or {M(=M1PCRH)} moieties depends on the coordination and activation of the different comonomers (M1 or M2, respectively) to produce {M(=M1M2PCRH)} or {M(=M2M1PCRH)} species. Scheme 1 illustrates the ROMCP mechanism for the M2M1 dyad formation from norbornene (NBE) as the M1 species and norbornadiene (NBD) as the M2 species. NBE and NBD differ by a second double bond in NBD and this feature can result in a different reactivity if the catalyst presents ancillary ligands "L" with selected electronic and steric proprieties. Then, different reactivity from the respective homopolymerizations can occur when they are mixed to generate copolymers because of the difference in reactivity for each comonomer. For example, the saturated cyclic amine perhydroazepine (pep) and piperidine (pip) differ from one CH_2 unit in the ring and show some differences in the σ-donor characters and the steric hindrances (Figure 1). When present in [$RuCl_2(PPh_3)_2$L], L = pep (complex **1**) or pip (complex **2**), both complexes provided quantitative yields of polyNBE at room

Additional Supporting Information may be found in the online version of this article.

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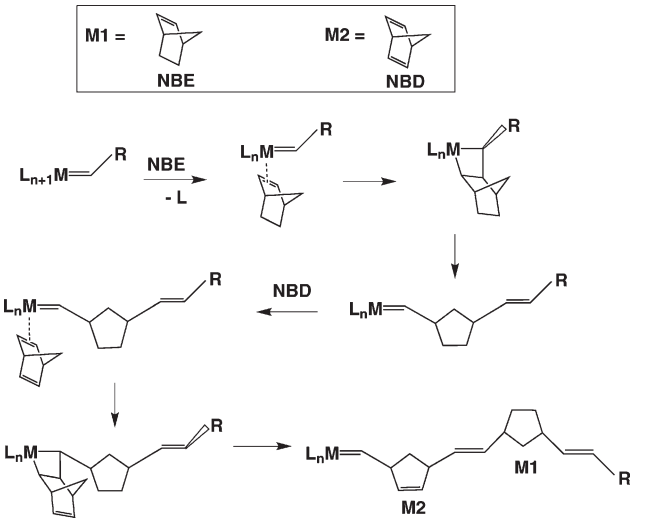

Scheme 1. Illustration of the ROMCP mechanism for the M2M1 dyad formation from NBE as the M1 species and NBD as the M2 species.

temperature for less than 1 min.[14,15] On the other hand, complex **1** provides a quantitative yield of polyNBD at room temperature,[14] whereas **2** produces only about 50% yield.[15] Thus, it has been discussed that the difference in the amines enabled the metal centers to undergo changes in the reactivities, resulting in changes in both the initiation and propagation steps for the ROMP of NBE and NBD. Moreover, it has been concluded that the presence and type of the amine in this type of complex provide fine tuning in the ROMP reactivity which differs from the complex $[RuCl_2(PPh_3)_3]$ which is practically inactive for the ROMP of NBE and NBD at room temperature.[14–18]

In this work, to verify the reactivity of the complexes **1** and **2** for syntheses of copolymeric materials of the type poly(NBE-*co*-NBD) via ROMCP, NBE and NBD were mixed in different mole fractions (NBE : NBD = 0.8 : 0.2, 0.6 : 0.4, 0.4 : 0.6, and 0.2 : 0.8). The dependence of the reaction yields and occurrence of crosslinking in the isolated materials in the NBE : NBD proportions were analyzed in function of the complex reactivities. The ^{13}C NMR spectra were used to analyze the microstructures, verifying the occurrence of copolymerization.

EXPERIMENTAL

General Remarks

All handling was performed in an argon atmosphere following standard air-less techniques. All the solvents used were high performed liquid chromatographic (HPLC) grade. $RuCl_3{\cdot}xH_2O$, NBE, NBD, pep, pip, PPh_3, and ethyl diazoacetate (EDA) from Sigma-Aldrich (St. Louis, MO, USA) were used as received. $[RuCl_2(PPh_3)_2pep]$ (complex **1**) and $[RuCl_2(PPh_3)_2pip]$ (complex **2**) were obtained following literature procedures and characterized by elemental analyses, FTIR, and $^{31}P\{^1H\}$ NMR spectroscopies.[14,15] Room temperature (RT) is (24 ± 1)°C.

Instrumentation

The NMR spectra were obtained in $CDCl_3$ at (25.0 ± 0.1)°C using a Bruker DRX-400 of 9.4 T. The chemical shifts are referenced to TMS. Gel permeation chromatography analyses were carried out on a Shimadzu Prominence LC system equipped with a LC-20AD pump, a DGU-20A5 degasser, a CBM-20A communication module, a CTO-20A oven at 40°C and a RID-10A detector, connected with three PL gel columns (5 m MIXED-C: 30 cm, Ø = 7.5 mm). The retention time was calibrated with standard monodispersed polystyrene using HPLC grade $CHCl_3$ as an eluent. Polydispersity Index (PDI) is M_w/M_n.

ROMCP Procedure

The reactions were carried out in 25 mL round bottom flasks. In a typical copolymerization experiment, NBE and NBD were dissolved in $CHCl_3$ (2 mL) so that it could result in a desired NBE : NBD mole fraction (0.8 : 0.2, 0.6 : 0.4, 0.4 : 0.6, or 0.2 : 0.8) with a total monomer concentration ratio of 5000 for 1 μmol of Ru ($[monomer]_{total}/[Ru]$ = 5000). The flask was brought rapidly to (40 ± 1)°C in a silicone oil bath. Then, the Ru complex (∼ 1.0 mg) was added, followed by adding 5.0 μL of EDA immediately to form the {Ru(=CHCOOEt)} metal carbene species.[14,15] The mixture was stirred for a specified period of time (5, 30, 60, or 120 min). At room temperature, 10 mL of methanol was added and the precipitated polymer was decanted, washed with methanol, and dried in a vacuum at 27°C before being weighed in an analytical balance. Each run was performed twice with an additional blank experiment.

RESULTS AND DISCUSSION

Yields and Solubility of the Polymeric Materials

All the batch reactions produced polymeric materials from the solutions with different mole fractions of the comonomers NBE and NBD, either using **1** or **2** as precatalysts. Figure 2 shows the results of yields from catalytic runs for 5, 30, 60, and 120 min at 40°C, with reproducibility better than 6% in most of the cases. A temperature of 40°C was chosen to avoid the solution being gelled immediately so that reliable results could be obtained for long-term experiments. No polymers were formed in the absence of a Ru complex for the same studied reaction times.

In general, the results can be described as curves with saturation profiles in both the catalyst cases, but with different behaviors for runs carried out for more than 5 min. In the case of **1**, quantitative yields for the NBE : NBD 0.2 : 0.8 solution were obtained, with a tendency of reducing the yield while the NBD quantity decreased. When using **2**, the yields show a tendency to be 60–80% in many experiments. The yields with **2** are lower than those observed in the experiments with **1** for solutions

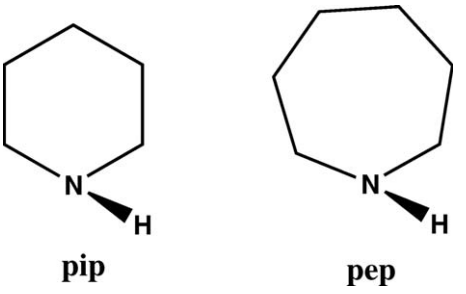

Figure 1. Chemical structures of the amine ligands.

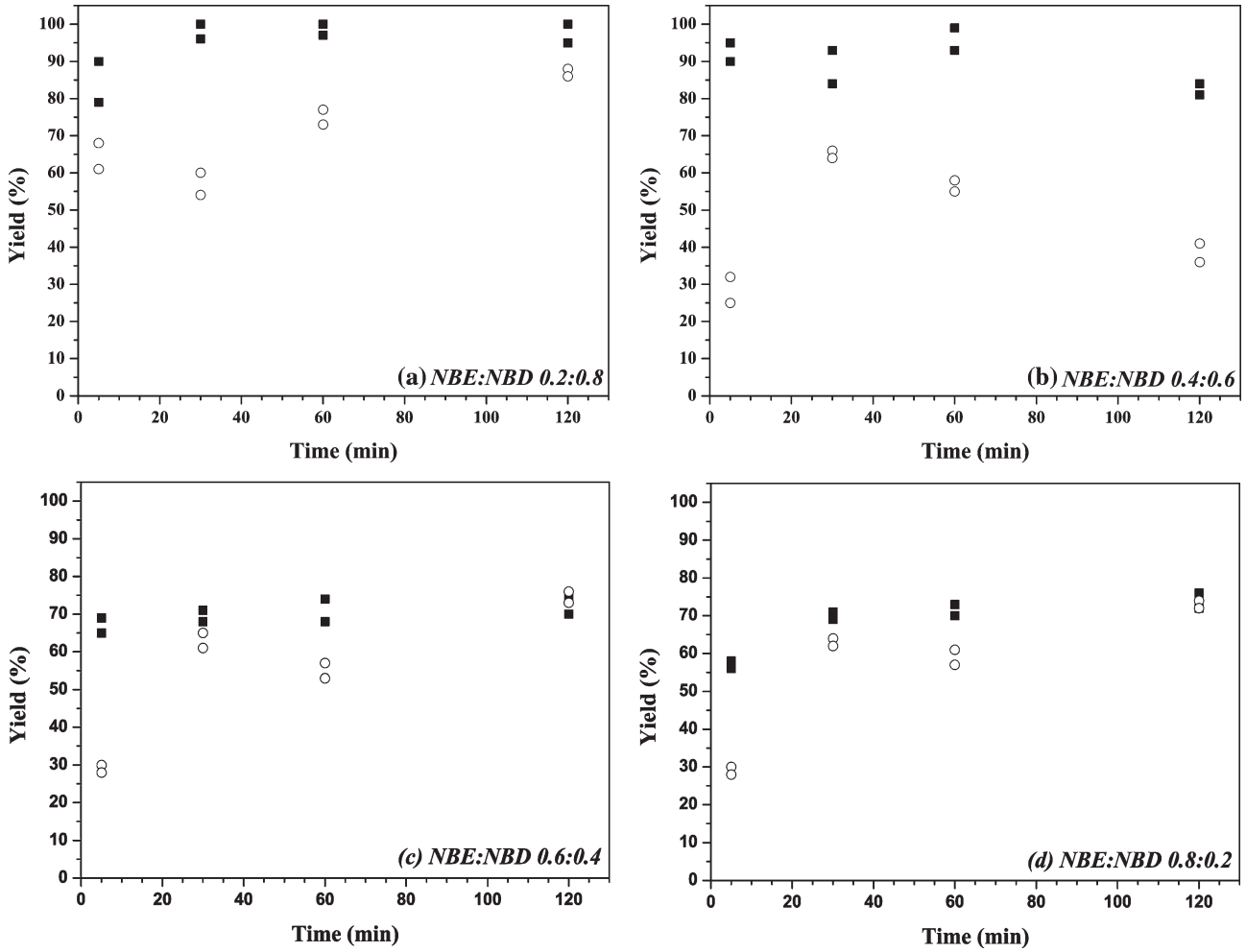

Figure 2. Dependence of the yield on the reaction time for the syntheses of copolymers from solutions with different NBE : NBD mole fractions (a, b, c, and d) in presence of **1** (solid symbol) or **2** (open symbol) at 40°C.

with a higher NBD content and they are similar with a higher NBE content.

Evaluating the homopolymerizations with **1** and **2** versus the copolymerization reactions, the tendency of each monomer to enter the polymer chain as a function of the Ru type complex can be observed.

PolyNBD and polyNBE were quantitatively obtained using **1** in similar conditions.[14] Here, when both monomers are present in the same solution, quantitative or semi-quantitative yields are obtained for solutions with high amounts of NBD (NBE : NBD proportions of 0.2 : 0.8 and 0.4 : 0.6). However, the yields are 70% at the most for solutions with reverse proportions (means, 60 or 80% of NBE). These results suggest priority reactions with NBD, while competitive reaction appears to occur when NBE is in a higher composition.

On the other hand, homopolymerizations of NBD with **2** at room temperature merely resulted in 48% yield,[15] whereas polyNBE was quantitatively obtained. Then, at least semi-quantitative yields for solutions with a high amount of NBE relative to NBD could be expected (equivalent to NBE : NBD proportion of 0.8 : 0.2 or 0.6 : 0.4), which was not obtained. Moreover, **2** does not show a clear tendency of results with solutions in the presence of a higher amount of NBD than NBE (Figure 2).

Partially, from the yield results, it can be concluded that **1** presents the best reactivity when NBD is present as the major component, and **2** presents improved regular reactivity when NBE is a large amount. Solutions with close mole fractions (0.4 : 0.6 or 0.6 : 0.4) of the comonomers show that the selections of the catalysts are very influenced by the presence of the respective comonomer.

A few differences in the electronic density in the amine→Ru→olefin synergism are essential to coordinate and activate the NBD. This feature has been discussed for syntheses of homopolymers of NBE and NBD with different amines.[14] The small σ-donor difference in favor of the pep ligand when compared to the pip ligand probably populated the π^* orbitals of the olefin more effectively to facilitate the ROMCP in the case of **1**. Furthermore, the difference between the results and behaviors observed with **1** and **2** can also be ascribed to a larger bulk of the pep ligand in **1** that facilitates the replacement of ligands

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in the catalyst coordination sphere, which is necessary for the ROM copolymerization to take place.[19–21]

Besides the electronic character and size of these amines determining the initiation and propagation steps, the monomer can also affect the reactions. In the present, NBD can be arranged in a chelating mode in agreement with the literature and this fact could affect the progress of the reaction.[22–26] ^{1}H NMR spectrum of NBD in the presence of complex **1** showed two double-doublets centered at 5.09 and 4.66 ppm, confirming that NBD is bound through the two double bonds, in addition to the signal of the mono-coordinate species centered at 4.43 ppm (Figure 3); the relative areas of the signals are 1 : 1 : 6.5. The two double-doublets represent the coupling between the H1/H4 atoms with the olefinic H2/H3 and H5/H6 atoms. COSY spectrum, presented in the Supporting Information, supports this fact confirming the double-coordination of NBD in the {$RuCl_2(PPh_3)$pep} moiety complex. Similar signals were observed with pip-Ru-complex, with relative areas of 1 : 1 : 2.5 (Figure 3). The values of the relative areas indicate that there is more NBD-mono-coordinated species in the case of **1** than in the case of complex **2**, suggesting that NBD is more able to do double-coordination in the case of **2** than in the case of **1**. The double-coordination can compete with the reaction with EDA to generate the metal-carbene species, hampering the ROMP to take place. However, as both complexes are active for ROMP of NBD, the chelated species can be labile enough to increase the concentration of NBD-mono-coordinated species to permit the occurrence of the ROMP. NBD-double-coordinated complexes were active for hydrogen transfer reaction with Ru-based catalysts and ROMP of NBD with W- and Mo-based catalysts.[27–30] Indeed, better yields were obtained for ROMP of NBD with the complex **1**, when observing the results from polyNBD with both **1** and **2** complexes,[14] whereas similar yields were obtained with polyNBE using either complex. Fewer amounts of the chelated

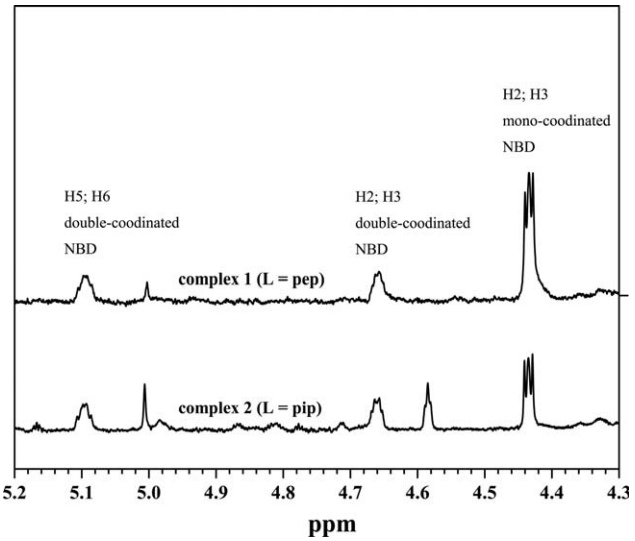
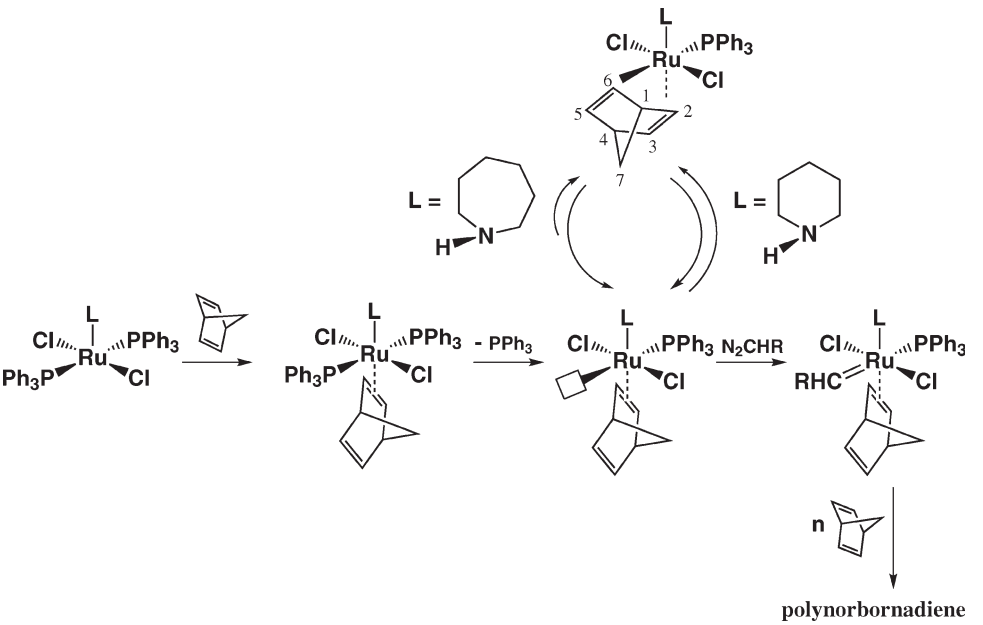


Figure 3. ^{1}H NMR spectra of NBD in $CDCl_3$ solution of **1** or **2** complex; hydrogen labels as show in Scheme 2.

species with complex **1** can be associated with the large bulk of the pep ligand. Thus, more species metal-carbene will be formed in the induction period to initiate the ROMP process. Scheme 2 illustrates these reactions. Similar behavior can be expected in the copolymerization experiments explaining the observed results in Figure 2, with better results with **2** and unclear tendency with **1** when in the presence of a higher amount of NBD than NBE, in addition to the different reactivity ratios for NBD/NBE.

Samples of the isolated polymers with **1** (c.a., 70 mg) from NBE : NBD solutions with 80, 60, and 40% of NBE swelled in 10 mL of $CHCl_3$ for 24 h at 25°C. The polymer from solution



Scheme 2. Probable sequence of ROMP reaction in presence of NBD.

Table I. GPC Data of Soluble Parts in $CHCl_3$ of Freshly Synthesized Copolymers at 40°C from Solutions with Different NBE : NBD Mole Fractions in Presence of **1** for 5 min or in Presence of **2** for 120 min

	Complex **1**		Complex **2**	
NBE : NBD mole fraction	M_w (10^4 g mol^{-1})	PDI	M_w (10^4 g mol^{-1})	PDI
0.2 : 0.8	3.6	2.8	0.71	1.9
0.4 : 0.6	4.3	2.8	0.75	1.9
0.6 : 0.4	2.5	2.8	1.9	1.9
0.8 : 0.2	6.0	2.3	4.0	2.2

with 80% of NBD (NBE : NBD mole fraction = 0.2 : 0.8) presented only a very small swelling. In the latter case, the polymer retained the weight after being decanted and dried in a vacuum. The other samples showed small decrease in the weights (8–15%). No evidence either of swelling or solubility in the case of the NBE : NBD 0.2 : 0.8 sample suggests the occurrence of a high crosslinking degree related to the other cases, where the polymeric chains are so strongly linked that it makes it difficult for the polymer to swell. Typical experiments of solubility for polymers synthesized with **2** showed that they were more soluble when compared to those obtained from **1**. The loss of weight was 30–35%; thus, a smaller swelling occurred than in the case of **1**.

Weight-average molecular weight (M_w) and PDI data for soluble portions of samples from freshly synthesized copolymers, after about 48 h stirring in $CHCl_3$, are shown in Table I. The order of magnitude in the M_w values is 10^4 in all the cases, besides the low solubility of the samples from solutions with 0.2 : 0.8 NBE : NBD mole fraction either in presence of **1** or **2** and 0.4 : 0.6 NBE : NBD mole fraction in presence of **1**. The PDI values are roughly the same in the case with **2**, whereas in the case of **1**, a tendency to decrease the values is observed when decreasing the NBD quantity. This can be associated to low occurrence of crosslinking when NBE quantity predominates in solution. Smaller PDI values are observed in the case with complex **2** than in the case with complex **1**. This can be associated to the larger reactivity of NBD with **1**, whereas **2** prefers NBE. These results are in agreement with the swelling studies where low solubility of the polymers was observed. It means, the molecular weighs data represent the soluble parts of the polymers which may be rich in small chains.

^{13}C NMR Spectra of the Polymeric Materials

A soluble portion of the polymers were analyzed by ^{13}C NMR to characterize the formation of copolymer. Figure 4 shows the spectrum of the synthesized material with **1** from NBE : NBD 0.8 : 0.2 solution for 5 min. The analyses show several signals that can be assigned to the copolymer of the type poly(NBE-*co*-NBD) as illustrated in Figure 5. Table II presents the assignments according to the literature.[1,28–31]

The *cis–trans* conformations in the olefin carbon region were not quantified due to the low resolution in the peaks once the polymers present low solubilities [Figure 4(b)]. The σ_c values

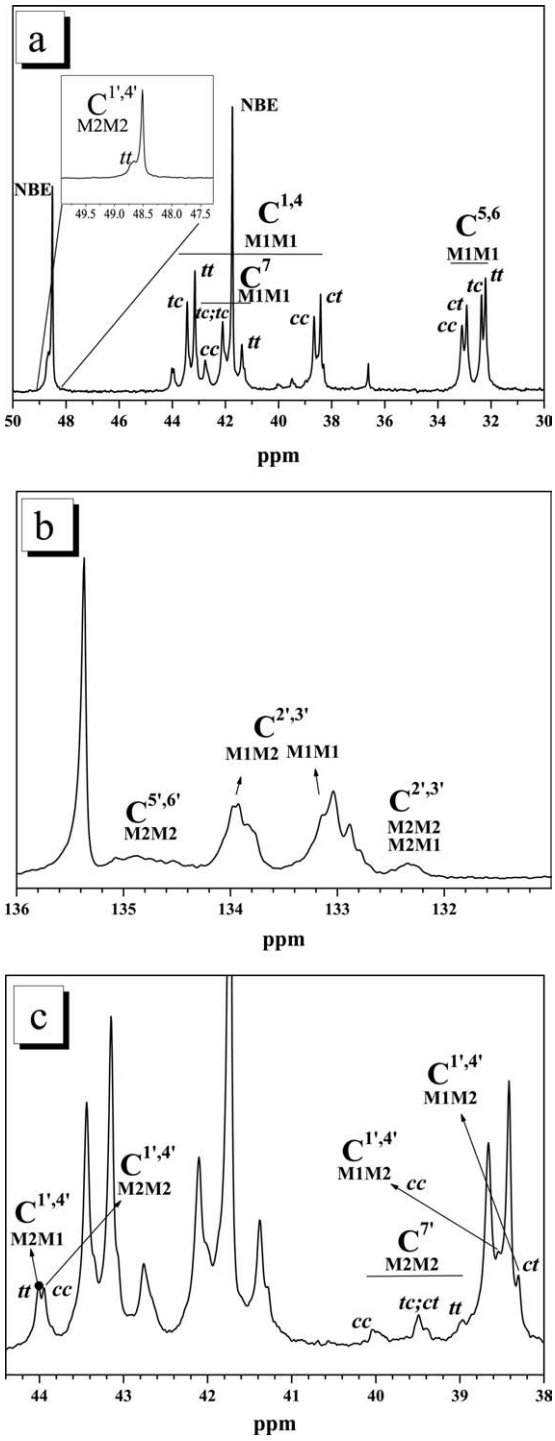


Figure 4. ^{13}C NMR spectrum of a copolymer synthesized from a solution with NBE : NBD 0.8 : 0.2 in presence of **1** for 5 min at 40°C. Frame **a** for the saturated carbon region; Frame **b** for the olefin carbon region; Frame **c** is an insert in the Frame **a**. The assignments are in accordance to the Table I.

for $C^{1,4}$, $C^{5,6}$, and C^7 in the M1M1 dyad are 0.44, 0.48, and 0.46, respectively. Unfortunately, the determinations of the σ_c for other dyads were not possible due to the positions and intensity of the peaks.

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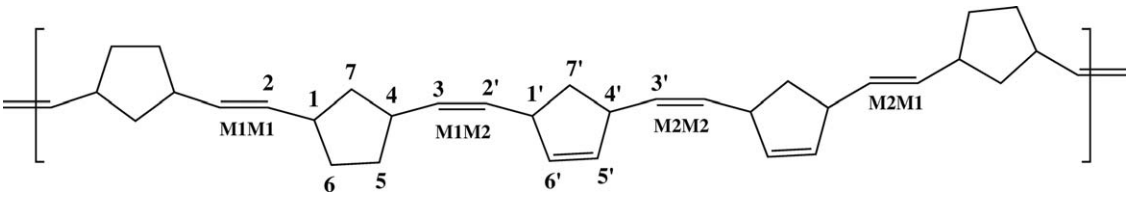

Figure 5. Chemical structure of a copolymer of type poly(NBE-*co*-NBD) to illustrate the M1M1, M1M2, M2M2, and M2M1 dyads.

From the spectra in the $C^{1',4'}$ and $C^{1,4}$ region of the copolymers when the NBD content increases in the NBE : NBD proportions from 0.8 : 0.2 to 0.4 : 0.6 (Figure 6; Table II), obtained from **1** for 5 min, some facts can be observed: (a) a higher increase in the intensity of the signs assigned to $C^{1',4'}$ at 43.93 and 43.85 ppm of the M2M2 dyad relative to the sign 44.01 ($C^{1',4'}$ in M2M1); (b) an increase in the intensity of the signs at 43.33 and 43.05 ppm assigned to the $C^{1,4}$ in the M1M2 dyad; (c) the intensities of the signs at 43.33 and 43.05 ppm increase in relation to the signs at 43.43 and 43.13 ppm, from the $C^{1',4'}$ in the dyad M1M2. Therefore, there is an increase in the NBD content in the copolymers, observed by an increase in the M2 content in the M2M2 and M1M2 dyads. These observations indicate that the different NBE : NBD mole fractions influence the microstructure of the copolymers formed.

Figure 7 shows the ^{13}C NMR spectra in the $C^{1',4'}$ and $C^{1,4}$ region of the copolymers obtained from solutions with different NBE : NBD mole fractions in the presence of **2** for 120 min. Contrary to the material obtained from solutions with the same mole fractions in the presence of **1** (Figure 6), the signs which refer to the $C^{1',4'}$ (Table III) of the dyad M2M2 and M2M1 for the NBE : NBD 0.8 : 0.2 sample are not well defined. However, as the NBD content increases, an increase in the intensity of these signs is observed. Furthermore, when the NBD content increases, an increase in the intensity of the signs at 43.33 and 43.05 ppm assigned to $C^{1,4}$ in the M1M2 dyad is also observed, as can be seen in the case of **1**.

It was not possible to calculate the r_1 and r_2 reactivity ratios for the comonomers NBE and NBD due to the difficultly in integrating the peaks relatives to the M1M2 and M2M1 dyads.

CONCLUSIONS

Copolymerizations of NBE with NBD proceeded successfully in an olefin metathesis polymerization mode using {Ru-amine}-based catalysts. The reaction took place with a high $[monomer]_{total}/[Ru]$ ratio, resulting in yields better than 60% of isolated material for 30 min. The ^{13}C NMR spectra showed the presence of both hetero- and homo-dyads, characterizing the copolymerizations.

The ancillary ligands pep and pip were responsible for the difference in the reactivity of the precatalysts. In spite of the small differences in the electronic and steric characteristics of these saturated cyclic amines, they are the possible features to explain the differences in the results.

This type of study is important to understand monomer distribution and identify appropriate reaction conditions to

Table II. Chemical Shift Assignments for the Peaks in the ^{13}C NMR Spectrum of a Copolymer Synthesized from a Solution with NBE : NBD 0.8 : 0.2 in Presence of **1** for 5 min at 40°C

Dyad	Assignment	Peak (ppm)
M1M1	$C^{1,4}$	43.43 (*tc*), 43.13 (*tt*), 38.66 (*cc*), 38.41 (*ct*)
	$C^{5,6}$	33.09 (*cc*), 32.91(*ct*), 32.35 (*tc*), 32.20 (*tt*)
	C^{7}	42.75 (*cc*), 42.09 (*tc,ct*), 41.37 (*tt*)
	$C^{2,3}$	133
M2M2	$C^{1',4'}$	48.65 (*tt*), 43.93 (*cc*)
	$C^{7'}$	40.02 (*cc*), 39.49 (*ct,tc*), 38.97 (*tt*)
	$C^{5',6'}$	135
M1M2	$C^{1',4'}$	38.54 (*cc*), 38.29 (*ct*)
	$C^{2,3}$	134
M2M1	$C^{1',4'}$	44.01 (*tt*)
M2M1/ M2M2	$C^{2',3'}$	132.4

t = *trans*; *c* = *cis*.

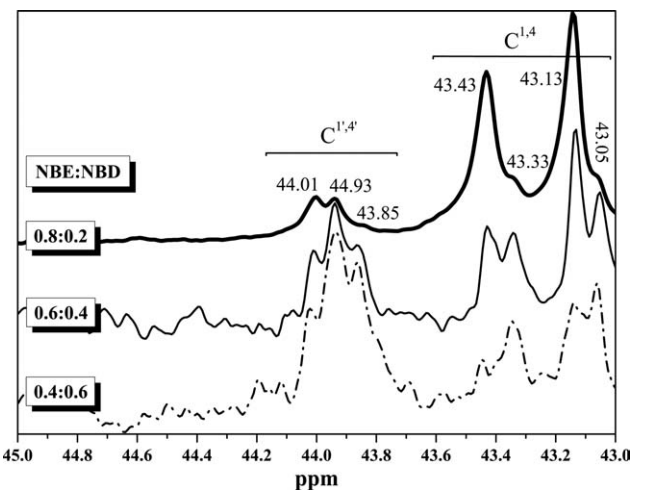

Figure 6. ^{13}C NMR spectra in the $C^{1',4'}$ and $C^{1,4}$ saturated carbon region of copolymers synthesized from solutions with different NBE : NBD mole fractions in presence of **1** for 5 min at 40°C. The assignments are in according to the Table II.

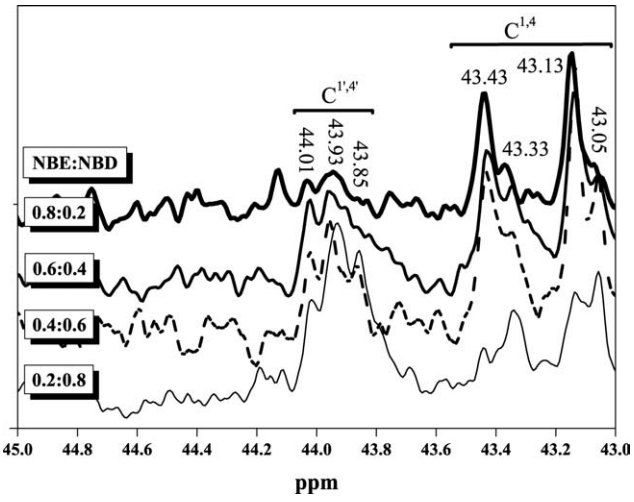

Figure 7. ^{13}C NMR spectra in the $C^{1',4'}$ and $C^{1,4}$ saturated carbon region of copolymers synthesized from solutions with different NBE : NBD mole fractions in presence of **2** for 120 min at 40°C. The assignments are in accordance to the Table II.

Table III. Chemical Shift Assignments for the Peaks in the $C^{1',4'}$ and $C^{1,4}$ Regions of ^{13}C NMR Spectra of Copolymers Synthesized from Solutions with Different NBE : NBD Mole Fractions in Presence of **1** or **2**

Dyad	Assignment	Peak (ppm)
M1M1	$C^{1,4}$	43.43 (*ct*), 43.13 (*tt*)
M2M2	$C^{1',4'}$	43.93 (*cc*), 43.85 (*ct*)
M1M2	$C^{1,4}$	43.33 (*tc*) 43.05 (*cc*)
M2M1	$C^{1',4'}$	44.01 (*tt*)

t = trans; c = cis.

manufacture copolymers with acceptable levels of compositional uniformity using alternative non-carbene precatalyst. Thus, it opens the doors for syntheses of the new NBE-based copolymers from NBE-derived or monomers with similar NBD strain characteristics. In addition, the above results were obtained from reactions with large amounts of monomers, different from those studies usually carried out in laboratory scales. This approach is partially aligned with the claim for catalysts to operate efficiently at industrial scales, as part of a continuous interests for the developments of robust, simple, and cheap initiators.[32–39] Highly efficient Ru-based catalysts have been developed for olefin metathesis polymerizations, but the challenge is to extend these approaches to a industrial reaction on a large scale, besides their high costs and difficult of reusing due to the low regeneration and reactivation possibilities.

ACKNOWLEDGMENTS

The authors are indebted to the financial support from FAPESP (Proc. 06/57577-4), CAPES and CNPq, and to Laís H. Vieira for carrying out some catalytic runs. The NRM measurements took place at the Departamento de Química of the Universidade Federal de São Carlos, Brazil.

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