Abstract: Unsaturated copolyesters are of great interest in polymer science due to their broad potential applications and sustainability. Copolyesters were synthesized from the ring-opening metathesis copolymerization of ω-6-hexadecenlactone (HDL) and norbornene (NB) using ruthenium-alkylidene [Ru(Cl)2(=CHPh)(1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)(PCy3)] (Ru1), [Ru(Cl)2(=CHPh)(PCy3)2] (Ru2), and ruthenium-vinylidene [RuCl2(=C=CH(p-C6H4CF3))(PCy3)] (Ru3) catalysts, respectively, yielding HDL-NB copolymers with different ratios of the monomer HDL in the feed. The activity of N-heterocyclic-carbene (NHC) (Ru1) and phosphine (Ru2 and Ru3) ligands containing ruthenium-carbene catalysts were evaluated in the synthesis of copolymer HDL-NB. The catalysts Ru1 with an NHC ligand showed superior activity and stability over catalysts Ru2 and Ru3 bearing PCy3 ligands. The incorporation of the monomers in the copolymers determined by 1H-NMR spectroscopy was similar to that of the HDL-NB values in the feed. Experiments, at distinct monomer molar ratios, were carried out using the catalysts Ru1–Ru3 to determine the copolymerization reactivity constants by applying the Mayo–Lewis and Fineman–Ross methods. The copolymer distribution under equilibrium conditions was studied by the 13C NMR spectra, indicating that the copolymer HDL-NB is a gradient copolymer. The main factor determining the decrease in melting temperature is the inclusion of norbornene units, indicating that the PNHB units permeate through the HDL chains. The copolymers with different molar ratios [HDL]/[NB] have good thermal stability up to 411 °C in comparison with the homopolymer PHDL (384 °C). Further, the stress–strain measurements in tension for these copolymers depicted the appreciable increment in stress values as the NB content increases.

Keywords: ROMP; macrolactones; norbornene; copolyesters; ruthenium-carbene

1. Introduction

Aliphatic polyesters derived from renewable feedstock have drawn much attention for a long time due to their wide potential applications and sustainability. The macrolactones such as ambrettolide, ω-6-hexadecenlactone (6HDL), pentadecalactone (PDL), or ethylene brassylate (EB) can be isolated from plant oils [1], and they can also be obtained from the full fatty acid chain via self-metathesis [2,3]. A high versatility in the production of homopolymers and various block and random macrolactone-based copolymers with cyclic esters has been afforded by ring-opening polymerization (ROP) using aluminum salen complexes [4–8] and enzymatic catalysts [9–12]. Another method by which bio-based polyesters are obtained effectively is from ring-opening metathesis polymerization
The catalytic ROMP of unsaturated macrolactones to yield polymacro-
lactones using ruthenium-alkylidene (first- and second-generation Grubbs catalysts) and
ruthenium vinylidene catalysts has great potential since this route allows the formation of
high molecular weight products with excellent mechanical and thermal properties, which
has led to their use in a wide range of applications, from commodity-type to engineering
materials. For example, the synthesis of ω-6-hexadecenlactone to obtain unsaturated linear
poly(ω-6-hexadecenlactone) with remarkable thermal, mechanical, and biodegradability
properties was reported [13]. Other researchers studied the one-pot combination of en-
zymatic ring-opening polymerization (eROP) and ROMP to prepare block copolymers
from cyclooctadiene with lactones using Novozym 435 and Grubbs second-generation
catalysts [14]. Moreover, the combination of unsaturated macrolactone (i.e., ambrettolide
(Amb)) and the cycloolefin cis-cyclooctene (cCO) to yield aliphatic long-chain polyesters
was studied. The large number of methylene units in the backbone allows these polymers
to have a molecular structure similar to that of high-density polyethylene (HDPE) [18].

On the other hand, one of the attractive points of ROMP is the use of cycloolefins such
as norbornene and its functionalized derivatives (since norbornene is relatively cheap and
industrially available); in addition, most of the norbornene derivatives have exhibited high
activity towards ROMP, making them a point of study over the last two decades [19,20].
Besides the design, theoretical, and experimental studies of homopolymers obtained via
ROMP using norbornene derivatives, the copolymerization of these monomers has been
studied because this polymerization technique has a high tolerance towards many func-
tional groups and oxygen, and this method can proceed under mild reaction conditions at
high polymerization rates, especially with strained cyclic olefins [21]. Several studies have
focused on obtaining block copolymers via ROMP using those strained cycloolefins [22–25],
but there are only a few reports on the obtaining random precision copolymers, due to
the strict selection of the catalyst, and mostly because of the differences in reactivity in the
monomers used that impact the same incorporation of both fragments [26–29].

A limited example of this is the incorporation of a macrocycle fragment into a perfect
alternating copolymer architecture with a norbornene derivative fragment because two pa-
rameters could have difficulty with this incorporation; first, the symmetry of the macrocycle
to the vicinal carbons of the olefin brings several ways of accommodating the fragment, and
second, the polymerization and homogenous incorporation of the macrocycle fragment via
ROMP to the final material. For instance, based on the ROMP of cycloolefins, it has been re-
ported that the copolymerization of norbornene and cyclooctene by cross-metathesis of poly-
norbornene with polyoctenamer using first-generation Grubbs catalyst exhibits low activity
toward copolymerization of those monomers [30]. Even, the polymerization of macrorcycles
is a wide field of study, receiving a special name of entropy-driven ROMP (ED-ROMP) since
this polymerization is not based on the strain of the olefin monomer but only on the entropic
changes from cyclic to linear fragment [31–34]. With the homogenous incorporation of a
macrocycle though the copolymeric material, very interesting hydrolysable bonds could be
achieved for biodegradation and optimization of crystallinity, promising electro-optical
applications, among others [18,32,35]. In this context, and to the best of our knowledge,
we report for the first time on the copolymerization of ω-6-hexadecenlactone and polynor-
bornene using the ruthenium-alkylidene Ru(Cl2)(=CHPh)(1,3-bis(2,4,6-trimethylphenyl)-
2-imidazolidinylidene)(PCy3)] (Ru1), [Ru(Cl)2(=CHPh)(PCy3)2] (Ru2), and ruthenium-
vinyldiene [RuCl2(=C=CH(p-C6H4CF3))(PCy3)2] (Ru3) catalysts, respectively, yielding
HDL-NB copolymers with different ratios of the monomer HDL in the feed.

2. Results and Discussion

We have previously reported on the ring-opening metathesis polymerization (ROMP)
of homopolymer poly(ω-6-hexadecenlactone) (PHDL) from ω-6-hexadecenlactone (HDL),
an abundant compound in ambrette seed oil (Hibiscus abelmoschus L.) [21]. In order to obtain
unsaturated polyesters modified with cycloolefins, the ω-6-hexadecenlactone (HDL) was
copolymerized with norbornene (NB) via ROMP. The copolymerizations of HDL-NB were
accomplished at 50 °C using ruthenium-alkylidene Grubbs Ru(Cl)(=CHPh)(1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)(PCy3) ([Ru1]) and [Ru(Cl)(=CHPh)(PCy3)2] ([Ru2]), and at 80 °C with ruthenium-vinylidene [RuCl2(=C=CH(p-C6H4CF3))(PCy3)2] ([Ru3]) catalysts [36] (Scheme 1).

\[
\begin{align*}
\text{HDL} + \text{NB} & \rightarrow \text{HDL-NB Copolymer} \\
\text{Catalyst} & \\
\text{Ru1} & \text{Ru2} & \text{Ru3} \\
\text{Second generation Grubbs} & \text{First generation Grubbs} & \text{First generation Vinyldene} \\
\end{align*}
\]

Scheme 1. HDL copolymers with NB via ROMP.

At first, the homopolymerization of HDL and NB was performed, and subsequently, their copolymerization, in which the initial ratio of the two monomers was determined by molar ratio [HDL]/[NB] (Table 1). The maximum yield (96%) of poly(6-hexadecenlactone) (PHDL) was achieved in three hours using the Ru1 catalyst with a molecular weight around \( M_n = 109,600 \text{ g mol}^{-1} \) (entry 1). The homopolymerization of NB was completed in less than one hour using Ru1 catalyst to give poly(norbornene) (PNB) with molecular weight around 134,000 g mol\(^{-1}\) and yield of 99% (entry 2). Table 1 shows the results of the copolymerization HDL-NB that were synthesized using different ratios of the monomer HDL in the feed. In order to reach full conversion and thermodynamic equilibrium of the HDL-NB copolymers, the reactions were allowed to run for 20 h. The activity of N-heterocyclic-carbene (NHC) (Ru1) and phosphine (Ru2 and Ru3) ligands containing ruthenium-carbene catalysts were evaluated in the synthesis of copolymer HDL-NB. We can observe in Table 1 that the copolymers were successfully synthesized, with yields ranging from 96% to 98% and molecular weight around \( M_n = 1 \times 10^5 \text{ g mol}^{-1} \), when Ru1 catalyst is used (entries 7, 10–12, 15, and 16). The catalysts Ru1 with an NHC ligand showed superior activity upon catalysts Ru2 and Ru3 bearing PCy3 ligands. The copolymers HDL-NB using Ru2 and Ru3 catalysts had molecular weight values around \( M_n = 1 \times 10^8 \text{ g mol}^{-1} \), with yields ranging from 53% to 66% and from 42% to 57%, respectively (entries 8, 9, 13 and 14). It has been demonstrated that the free Gibbs activation energies of metathesis are consistently higher for catalyst Ru1 than for Ru2, with better transition state stabilization by the IMesH2 ligand compared with PCy3 [37].

The composition of HDL-NB copolymers with several molar ratios determined using \(^1\)H-NMR analysis is shown in Table 1. It can be seen that the composition of each copolymer obtained by \(^1\)H-NMR integration was similar according to the theoretical results (entries 7–16). Figure 1 shows \(^1\)H-NMR spectrum of copolymer HDL-NB using a ratio molar ([HDL]/[NB] = 2 and the catalyst Ru1 (Table 1, entry 12). The incorporation of HDL was obtained by integrating the area of the methylene ester groups region (\( \delta = 4.05 \text{ ppm} \), HDL) relative to the CH protons (\( \delta = 2.79 \text{ (cis), 2.44 (trans) ppm} \), NB). From the relative intensities of these signals, the ratio of HDL-NB copolymer was found to be 82/18%. The spectrum also shows the signals arising in the 5.35–5.12 ppm region, which correspond to the protons of the HDL-NB double bonds (=CH).
| Entry | Molar Ratio \[\text{HDL/NB}\] | [Ru] | \([\text{C=C]} / [\text{Ru}]\) | Time (h) | Temp (°C) | Yield (\%) | \(M_n\) (g mol\(^{-1}\)) | MWD | HDL/NB Expected wt. % | HDL/NB Measured wt. % |
|-------|------------------|------|-----------------|----------|-----------|------------|-----------------|------|-------------------|-------------------|
| 1     | 1:0              | Ru1  | 500             | 3        | 50        | 96         | 109,600         | 1.15 | -                 | -                 |
| 2     | 0:1              | Ru1  | 1000            | 40 min   | 25        | 99         | 134,000         | 1.10 | -                 | -                 |
| 3     | 1:1              | Ru1  | 500             | 4 min    | 50        | 22         | 78,876          | 2.80 | -                 | -                 |
| 4     | 1:1              | Ru1  | 500             | 30 min   | 50        | 36         | 81,500          | 2.90 | -                 | 42/58             |
| 5     | 1:1              | Ru1  | 500             | 3        | 50        | 49         | 88,677          | 2.78 | -                 | 57/43             |
| 6     | 1:1              | Ru1  | 500             | 8        | 50        | 72         | 91,981          | 2.84 | -                 | 61/39             |
| 7     | 1:1              | Ru1  | 500             | 20       | 50        | 97         | 104,424         | 2.10 | 74/26             | 72/28             |
| 8     | 1:1              | Ru2  | 250             | 20       | 50        | 66         | 94,210          | 2.00 | 74/26             | 70/30             |
| 9     | 1:1              | Ru3  | 250             | 80       | 57        | 92,005     | 2.09            | 74/26 | 69/31           |
| 10    | 1:5              | Ru1  | 500             | 20       | 50        | 96         | 110,500         | 2.20 | 35/65             | 32/68             |
| 11    | 1:10             | Ru1  | 500             | 20       | 50        | 96         | 118,080         | 2.00 | 20/80             | 17/83             |
| 12    | 2:1              | Ru1  | 500             | 20       | 50        | 98         | 114,600         | 2.10 | 84/16             | 82/18             |
| 13    | 2:1              | Ru2  | 250             | 20       | 50        | 53         | 90,600          | 2.10 | 84/16             | 79/21             |
| 14    | 2:1              | Ru3  | 250             | 20       | 80        | 42         | 88,500          | 2.38 | 84/16             | 77/23             |
| 15    | 3:1              | Ru1  | 500             | 20       | 50        | 97         | 115,000         | 2.10 | 89/11             | 87/13             |
| 16    | 10:1             | Ru1  | 500             | 20       | 50        | 98         | 113,790         | 2.00 | 91/9              | 89/11             |

\(a\) Initial HDL-NB monomers concentration \([M_0]\) = 1 mol/L. 1,2-Dichloroethane (entries 1–8, 10–13, 15 and 16) and chlorobenzene (entries 9 and 14) were used as solvents. \(b\) Molar ratio \([\text{HDL}]/[\text{NB}]\). \(c\) Molar ratio of \([\text{C=C}]\) to catalyst. \(d\) Isolated yield of products. \(e\) The number-average molecular weight \((M_n)\) and molecular weight distribution (MWD) of the polymers and copolymers were calculated by gel permeation chromatography (GPC) with THF as the eluent; values are reported relative to PS standards. \(f\) Determined by \(^1\)H NMR.
We can see from Table 1 that during copolymerization, NB monomer was polymerized to HDL-NB with a molecular weight $M_n \times 10^4$ g mol$^{-1}$. After 3 h, the HDL incorporation in NB was increased until the copolymerization reached equilibrium with a molecular weight $M_n \times 10^5$ g mol$^{-1}$ (entry 7).

On the other hand, the copolymerizations of HDL and NB via ROMP, for reactivity constants determination, were carried out at 50 °C and 80 °C using Ru1–Ru3 catalysts (Scheme 1). For each catalyst, the reactions were conducted at 50, 60, 67, 75, and 91 mol percentage of HDL in the feed and polymerized up to a conversion of max. 22.10 (Ru1), 19.50 (Ru2), and 15.70 (Ru3) weight percentage, respectively (Table 2). The molar ratio of C=C monomer to Ru1 was 500. Since at the conversion desired monomer HDL was not detected in the copolymer formed when the reactions were conducted at a molar ratio of [C=C]/[Ru2, Ru3] = 500, the experiments for reactivity constant determination were carried out at 250. The copolymer was separated from the residual monomer by precipitation, and the incorporation of HDL in the different copolymers synthesis was quantified by $^1$H-NMR (entries 1–15). Additionally, in Table 2 it can be seen that as the mol percentage of HDL in the feed increased for each catalyst, more reaction time was needed for copolymerization to take place until the conversion desired. The time required for incorporating HDL into the copolymer was relatively short when the catalyst Ru1 was used (entries 1–5), while for the presence of the catalysts Ru2 and Ru3, long periods from 2 to 7 h were required (entries 6–15).

![Figure 1. $^1$H-NMR (400 MHz, CDCl$_3$) spectrum of the copolymer HDL-NB (Table 1, entry 12).](image-url)
Table 2. Copolymerization conditions of HDL and NB monomers for reactivity constants determination.

| Entry | Mass of HDL in the Feed (g) | [HDL] a /[NB] | Mol % of HDL in the Feed b | Incorporation of HDL in Copolymer (c) | Time (h) | Yield d (%)
|-------|------------------------------|---------------|---------------------------|--------------------------------------|----------|----------------|
| 1     | 0.48                         | 1:1           | 50                        | 39.00                                | 4 min    | 22.10          |
| 2     | 0.48                         | 1.5:1         | 60                        | 48.00                                | 4 min    | 19.60          |
| 3     | 0.48                         | 2:1           | 67                        | 62.00                                | 6 min    | 16.50          |
| 4     | 0.48                         | 3:1           | 75                        | 74.00                                | 6 min    | 8.40           |
| 5     | 0.48                         | 10:1          | 91                        | 86.00                                | 10 min   | 5.30           |
| 6     | 0.48                         | 1:1           | 50                        | 35.40                                | 2        | 19.50          |
| 7     | 0.48                         | 1.5:1         | 60                        | 42.90                                | 2        | 15.40          |
| 8     | 0.48                         | 2:1           | 67                        | 48.00                                | 4        | 13.40          |
| 9     | 0.48                         | 3:1           | 75                        | 61.30                                | 4        | 10.20          |
| 10    | 0.48                         | 10:1          | 91                        | 78.90                                | 7        | 7.60           |
| 11    | 0.48                         | 1:1           | 50                        | 27.50                                | 2        | 15.70          |
| 12    | 0.48                         | 1.5:1         | 60                        | 43.40                                | 2        | 13.30          |
| 13    | 0.48                         | 2:1           | 67                        | 47.10                                | 4        | 12.30          |
| 14    | 0.48                         | 3:1           | 75                        | 59.40                                | 4        | 10.10          |
| 15    | 0.48                         | 10:1          | 91                        | 77.60                                | 7        | 7.20           |

a molar ratio [HDL]/[NB]. b Molar ratio of [C=\(\text{C}\)] to catalyst = 500, \(T = 50^\circ\text{C}\) (entries 1–5) and 250, \(T = 80^\circ\text{C}\) (entries 6–15), initial HDL-NB monomers concentration \([M_0]\) = 1 mol/L. c Determined by \(^1\text{H}-\text{NMR}\). d Methanol insoluble polymer.

On the basis of the results obtained from the copolymerization experiments, Mayo–Lewis \[38\] and Fineman–Ross \[39\] methods were applied to calculate the reactivity constants \(r_{\text{HDL}}\) and \(r_{\text{NB}}\) in the presence of Ru1–Ru3 catalysts, using the general copolymerization equation. Table 3 shows the reactivity constants \(r_{\text{HDL}}\) and \(r_{\text{NB}}\) obtained by the different methods. By applying the Mayo–Lewis method, the values obtained were similar to those values obtained for the Fineman—Ross method. It is important to note that the precision of experimentally determined monomer reactivity ratio depends on the experimental design and technique used to analyze the data \[40\]. It has been reported that the ring strain energy for norbornene is 27.2 kcal/mol, which is adequately high and therefore can be easily polymerized \[41\]. In contrast, large cyclic esters—for example, monomers containing 12 or more atoms—are lactones with unstrained rings \[42,43\]. In this context, the influence of the catalysts on the reactivity of the monomer is of great interest. For example, by applying the Mayo–Lewis method, the values obtained were \(r_{\text{HDL}} = 0.24\) and \(r_{\text{NB}} = 3.78\) when the second-generation Grubbs (Ru1) catalyst was used. The reactivity of HDL was changed considerably by alkylidene Ru2 or vinylidene Ru3 catalysts (Table 3).

The homopolymers distribution of copolymers was studied. The copolymerization HDL-NB was synthesized until reaching full conversion and thermodynamic equilibrium for 20 h. The \(^{13}\text{C}\) spectrum of copolymer HDL-NB (Figure 2) (Table 1, entry 7) shows several extra signals in the double-bound region at 135.05–134.77 ppm and 128.47–128.22 ppm; compared with both homopolymers, these signals may be due to the gradual change in composition from NB to HDL. A significant NB-NB homopolymer section was also observed. The spectrum shows signals at 43.43 and 38.41 ppm, which correspond the C-H of the norbornene. It suggests that the HDL-NB copolymer is a gradient copolymer. We can see that the spectra of the homopolymers have two similar signals observed at 130.40 ppm and 129.60 ppm for poly(\(\omega\)-6-hexadecenlactone (PHDL) and 132.84 ppm and 133.89 ppm for polynorbornene (PNB), which correspond to the double-bond trans and cis configuration, respectively (Figure 2).
Table 3. Monomer reactivity constants calculated by using Mayo–Lewis and Finemann–Ross methods.

| Catalyst | Mayo–Lewis Method | Finemann–Ross Method |
|----------|-------------------|----------------------|
| | $r_{\text{HDA}}$ | $r_{\text{NB}}$ | $r_{\text{HDA}}$ | $r_{\text{NB}}$ |
| | 0.10 | 5.60 | 0.12 | 5.81 |
| | 0.24 | 3.78 | 0.28 | 4.02 |
| | 0.06 | 4.47 | 0.07 | 4.30 |

Figure 2. $^{13}$C-NMR (100 MHz, CDCl$_3$) spectrum for the copolymer HDL-NB (Table 1, entry 7).

Differential scanning calorimetry (DSC) provides a tool for monitoring the HDL-NB copolymers' crystallinity. All thermal transition temperatures of the HDL-NB copolymers were determined using second heating scans from $-80 \, ^{\circ}\text{C}$ to $300 \, ^{\circ}\text{C}$ at $10 \, ^{\circ}\text{C}/\text{min}$. Figure 3A shows the DSC thermograms of pure PHDL and all HDL-NB copolymers except amorphous PNB. Table 4 contains the melting point $T_m$ and enthalpy of fusion $\Delta H_m$ parameters of the studied copolymers extracted from the DSC data; the glass transition temperature ($T_g$) was not detected in the scanned heating range. An endothermic peak was observed around $47.60 \, ^{\circ}\text{C}$, as was an enthalpy of fusion $\Delta H_m = 73 \, \text{J/g}$, which corresponds to the melting point of PHDL. It is possible to observe that the $T_m$ and $\Delta H_m$ decreased as the norbornene amount is increased, indicating that the PNB units permeate through the HDL chains.
Table 4. Thermal and mechanical properties of the copolymerization via ROMP of \( \omega \)-6-hexadecenlactone (HDL) with norbornene (NB).

| Entry | Molar Ratio a | Thermal Properties | Crystallinity X-ray e | Mechanical Properties f |
|-------|---------------|-------------------|----------------------|-------------------------|
|       | HDL:NB 1:0    | \( T_\text{m} \) b (°C) | \( T_\text{d} \) c (°C) | \( \Delta H_\text{m} \) d (J/g) | (%) | \( E \) (MPa) | \( \sigma \) (MPa) | \( \varepsilon \) (%) |
| 1     | 0 1 40.50 400 | 43.30 19.80 464 | 13.73 6.40 |                                  |
| 2     | 1 1 40.10 397 | 47.10 23.00 229 | 8.13 8.637 |                                  |
| 3     | 10 1 44.34 390 | 53.50 26.50 156 | 7.55 10.47 |                                  |
| 4     | 2 1 42.10 397 | 47.10 23.00 229 | 8.13 8.637 |                                  |
| 5     | 1 5 38.10 409 | 23.20 15.90 695 | 19.01 5.87 |                                  |
| 6     | 1 1 40.50 400 | 43.30 19.80 464 | 13.73 6.40 |                                  |
| 7     | 1 10 37.20 411 | 12.00 - - 775 | 26.33 4.55 |                                  |

a Molar ratio [HDL]/[NB], initial HDL-NB monomers concentration \([M_0]\) = 1 mol/L in 1,2-dichloroethane, and a molar ratio \([\text{C=C}]/[\text{Ru1}]\) = 500. b The peak of the melting exotherm in DSC. c Reported as the onset of 5% decomposition recorded by TGA at a heating rate of 20 °C/min in N₂. d Enthalpy of fusion determined by DSC. e Calculated from X-ray. f Mechanical properties under tension, elastic module \((E)\), stress \((\sigma)\), and strain \((\varepsilon)\).

The thermal stability of copolymers was also studied by thermogravimetric analysis (TGA) under N₂ (Table 4). TGA experiments show that copolymers with different molar ratios \([\text{HDL}]/[\text{NB}]\) have good thermal stability up to 411 °C, by comparison with the homopolymer PHDL (384 °C). As expected, the copolymers containing a greater percentage of HDL exhibit a little lower decomposition temperature. The latter is attributed to the lower norbornene content in the HDL-NB copolymers (entries 3–7). This result indicates that the norbornene segment in the copolymer improved its thermostability relatively.

Figure 3B shows the X-ray diffraction patterns of HDL-NB copolymers determined through X-ray diffraction analysis in the 2θ range of 2–50° (Table 4, entries 1–7). Whereas

![Figure 3](image-url)
PNB and the HDL-NB (1:10) copolymer are amorphous, the PHDL and the HDL-NB copolymers (10:1, 2:1, 1:1, and 1:5) are semicrystalline. The PHDL X-ray pattern presents a very strong crystalline peak at 2θ of 21° and three weak crystalline peaks at 2θ of 23°, 36°, and 41°. We can observe that the X-ray patterns of HDL-NB copolymers (10:1, 2:1, and 1:1) are similar to that of PHDL, except for the presence of the peaks at 2θ of 4.5°. PHDL displayed the highest crystallinity of 31%, followed by HDL-NB = 10:1 (26.5%), 2:1 (23.0%), and 1:1 (19.8%) copolymers, respectively (Table 4, entries 2–5). For HDL-NB (1:5), the copolymer shows crystalline peaks in 21° and 23° overlapped with a large amorphous halo centered at 2θ of 19°. The percentage crystallinity calculated was 15.9%. The PNB pattern presents one broad peak with a maximum 2θ value of 19.6°, while the pattern of HDL-NB (1:10) presents only a broad amorphous halo with one well-defined hump at 18.2°.

Stress–strain measurements using the tensile test for the films of the HDL-NB copolymers were studied (Table 4, entries 3–7). Figure 4 shows the tensile stress–strain curves depicting an appreciable increment in the stress values as the NB monomer content increases. Each curve was cut at the maximum stress and indicates that not only the stress (σ = 7.55 MPa to 26.33 MPa) but also the elastic modulus (E = 156 MPa to 775 MPa) for copolymers (Table 4, entries 3–7) are higher than those mechanical properties exhibited for PHDL (σ = 4.84 MPa and E = 119 MPa, respectively) (entry 2).

![Figure 4. Strain–stress curves of pure PNB, PHDL, and HDL-NB copolymers with several molar ratios [HDL]/[NB].](image)

### 3. Materials and Methods

#### 3.1. Materials and Characterization Techniques

[Ru(Cl2)(=CHPh)(1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)(PCy3)] (second-generation Grubbs catalyst) ([Ru1], [Ru(Cl2)(=CHPh)(PCy3)2]) (first-generation Grubbs catalyst) ([Ru2]), norbornene, ω-6-hexadecenlactone (≥98%, HDL), chlorobenzene anhydrous, and methanol were purchased from Aldrich Chemical Co. and used as received. Ru-vinylidene catalyst [RuCl2(=C=CH(p-C6H4CF3))(PCy3)2] ([Ru3]) was synthesized following the procedure described in our previous work [36]. 1,2-Dichloroethane was dried over anhydrous calcium chloride and distilled over CaH2.

Number-average molecular weight (Mn) and molecular weight distributions (MWD) were determined with reference to monodisperse polystyrene standards on a Waters 2695 ALLIANCE Separation Module GPC at 30 °C in tetrahydrofuran (THF) equipped with a universal column and with a flow rate of 0.3 mL/min. Nuclear magnetic resonance
(NMR) spectra were recorded at 298 K with a Bruker AVANCE 400 MHz spectrometer, at 400 MHz (\(1^1H\)) and 100 MHz (\(1^3C\)). The chemical shifts are provided in parts per million from SiMe\(_4\) (\(1^1H\) and \(1^3C\)) as internal reference. The samples (100 mg) were mixed in 3.30 mL of CDCl\(_3\). The melting point (\(T_m\)) and enthalpy of fusion (\(\Delta H_m\)) of the HDL-NB copolymers samples were measured by differential scanning calorimetry (DSC) analysis using a TA Instrument Q20 with a heat-rate of 10 °C/min under a nitrogen flow of 50 mL/min in the range of −80 °C to 300 °C. The decomposition onset temperature, \(T_d\), was determined using thermogravimetric analysis, TGA, using a heat rate of 10 °C/min under nitrogen atmosphere with a DuPont 2100 instrument. X-ray diffraction measurements of HDL-NB copolymers films were carried out in a Siemens D-5000 diffractometer between 2 and 50 degrees 2θ, at 35 KV 25 mA, using CuK\(_\alpha\) radiation (1.54 Å). Mechanical properties under tension, elastic modulus (\(E\)), stress (\(\sigma\)), and strain (\(\varepsilon\)) were measured in a Universal Mechanical Testing Machine Instron 1125–5500 R using a 50 Kg cell at a crosshead speed of 10 mm/min according to the method ASTM D1708 in film samples of 0.5 mm of thickness at room temperature.

3.2. General Monomer Polymerization

The ROMP reactions of NB and HDL to obtain their corresponding homopolymers and copolymers were carried out in glass vials under nitrogen atmosphere. The polymerizations were inhibited by adding a small amount of ethyl vinyl ether, and the resulting solution of the reaction was poured into an excess of methanol. The resulting homopolymers and copolymers were purified by solubilization in chloroform and further precipitation into methanol. The fibrous products were dried in a vacuum oven at 40 °C to constant weight.

3.2.1. Synthesis of Polynorbornene (PNB)

The general polymerization was followed, dissolving 1 g (10.62 mmol) of norbornene (NB) in 10.60 mL of 1,2-dichloroethane at room temperature. Then, 8.74 mg (0.0106 mmol) of Ru\(_2\) catalyst was added, and the mixture was stirred for 40 min. Yield = 99 %. \(1^1H\) NMR (400 MHz, CDCl\(_3\), ppm): \(\delta\) 5.35 (s, CH=CH \textit{trans}); \(\delta\) 5.21, 5.19 (d, CH=CH \textit{cis}); \(\delta\) 2.79 (bs, s, CH); \(\delta\) 2.44 (bs, \textit{trans}, CH\(_2\)); \(\delta\) 1.87–1.76 (m, CH\(_2\)); \(\delta\) 1.55 (s, CH\(_2\)); \(\delta\) 11.11–0.98 (m, CH\(_2\)). \(1^3C\) NMR (100 MHz, CDCl\(_3\), ppm): \(\delta\) 133.98 (d, C=C); \(\delta\) 41.34, 33.89, 32.18 (s, d, d, CH\(_2\)); \(\delta\) 43.13, 38.65 (d, d, C=CH\(_2\), \textit{trans}, cis).

3.2.2. Synthesis of Poly(\(\omega\)-Hexadecenlactone) (PHDL)

The general polymerization technique previously described was followed, dissolving 1 g (3.96 mmol) of \(\omega\)-hexadecenlactone (HDL) in 4.00 mL of 1,2-dichloroethane. Afterwards, 6.52 mg (0.008 mmol) of Ru\(_1\) catalyst was added. The reaction mixture was maintained at 50 °C for 3 h. Yield = 96 %. \(1^1H\) NMR (400 MHz, CDCl\(_3\), ppm): \(\delta\) 5.37, 5.21 (bs, \textit{trans}, CH=CH\(_2\)); \(\delta\) 4.05 (t, CH\(_2\)-O); \(\delta\) 2.26 (t, CH\(_2\)-CO\(_2\)); 1.94–1.98 (m, CH\(_2\)-C=); 1.60–1.56, 1.30–1.26 (m, CH\(_2\)). \(1^3C\) NMR (100 MHz, CDCl\(_3\), ppm): \(\delta\) 130.28, 129.83 (t, t, C=C); 64.36 (s, CH\(_2\)-O); \(\delta\) 34.57 (s, CH\(_2\)-CO); 32.54 (s, C=CH\(_2\)); 29.58–28.58, 25.77, 24.98 (m, –CH\(_2\)).

3.2.3. Synthesis of HDL-NB Copolymers

The synthesis route of the copolymer is shown in Scheme 1. The HDL-NB copolymerization was carried out in a glass vial under dry nitrogen atmosphere. \(\omega\)-Hexadecenlactone monomer (HDL) (2.00 g, 7.92 mmol) and norbornene monomer (NB) (0.75 g, 7.92 mmol) were initially dissolved in 1,2-dichloroethane (1 mol/L) at a ratio molar [HDL]/[NB] = 1. The HDL-NB copolymerizations were synthesized using a different ratio of the monomer HDL in the feed ([HDL]/[NB] = 1:1, 1:5, 1:10, 2:1, 3:1, and 10:1). Then, catalyst Ru\(_1\) (1.30 × 10\(^{-2}\) g, 1.58 × 10\(^{-2}\) mmol) was added, and the mixture was stirred at 50 °C. When the Ru\(_2\) catalyst was used, the reaction temperature was set at 80 °C. HDL-NB copolymer was synthesized using different molar ratios [HDL-NB]/[Ru1–Ru3] = 500, 250. After being inhibited by adding a small amount of ethyl vinyl ether (0.3 mL, 3.00 mmol), the solution was poured into an excess of methanol. The copolymer was purified by solubilization.
in chloroform containing a few drops of 1 N HCl and precipitation into methanol. The obtained polymer was dried in a vacuum oven at 40 °C to constant weight. 1H NMR (400 MHz, CDCl3, ppm): \( \delta \) 5.37, 5.21 (bs, CH=CH); \( \delta \) 4.05 (t, CH2-O); \( \delta \) 2.79 (bs, cis, CH2=C=, NB); \( \delta \) 2.44 (bs, trans, CH2=C=, NB); \( \delta \) 2.28 (t, CO-CH2); \( \delta \) 1.96 (bs, CH2-COO-); 1.94–1.77, 1.32, 1.11–0.98 (m, bs, m, CH2, NB); \( \delta \) 1.61, 1.32 (m, bs, -CH2, HDL); \( \delta \) 1.61 (m, -C=CH2, HDL).

13C NMR (100 MHz, CDCl3, ppm): \( \delta \) 173.93 (s, -C=O); \( \delta \) 135.34–128.05 (m, C=C); \( \delta \) 64.35 (s, CH2-O); \( \delta \) 43.13, 38.65 (d, d, C=CH2, trans, cis); \( \delta \) 34.37 (s, CH2-CO); \( \delta \) 41.34, 33.89, 32.18 (s, d, d, CH2=C=, NB); \( \delta \) 32.57, 27.19 (d, d = C-CH2, HDL, trans, cis); \( \delta \) 29.57–28.63, 25.80, 25.01 (m, s, s, -CH2, HDL).

4. Conclusions

The ruthenium-alkylidene (Ru1 and Ru2) and ruthenium-vinylidene (Ru3) catalysts showed high catalytic efficiency in the ring-opening of the \( \omega \)-hexadecen lactone and norbornene to obtain unsaturated copolyesters. The catalysts Ru1 with an NHC ligand showed superior activity and stability over catalysts Ru2 and Ru3 bearing PCy3 ligands. The HDL-NB copolymers were successfully synthesized with yields ranging from 96% to 98% and molecular weights around \( M_n = 1 \times 10^5 \) g mol\(^{-1}\) when Ru1 catalyst was used, while the presence of the catalysts Ru2 and Ru3 afforded molecular weight values around \( M_n = 1 \times 10^4 \) g mol\(^{-1}\), with yields ranging from 53% to 66% and from 42% to 57%, respectively. The incorporation of HDL in the NB chain was similar according to the theoretical results when these catalysts are used. The copolymer distribution under equilibrium conditions and considering the long reaction time indicated that the copolymer HDL-NB is a gradient copolymer. The monomer reactivity ratios using catalysts Ru1–Ru3 by applying the Mayo–Lewis and Fineman–Ross methods was studied. The values obtained by both methods were similar \( r_{\text{HDL}} = 0.24, 0.28 \) and \( r_{\text{NB}} = 3.78, 4.02 \) when the second-generation Grubbs (Ru1) catalyst was used, respectively. The reactivity of HDL was considerably affected by the alkylidene Ru2 or vinylidene Ru3 catalysts. The thermal stability of HDL-NB copolymers with different molar ratios was found to be up to 411 °C by comparison with the homopolymer PHDL, and it was observed that the \( T_m \) and \( \Delta H_m \) decreased as the norbornene amount was increased, indicating that the PNB units permeate through the HDL chains, showing a distribution of the amorphous and crystalline region. The HDL-NB copolymers obtained by Ru1–Ru3 catalysts showed improved mechanical properties.

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