

SYNTHESIS OF RENEWABLE TELECHELIC OLIGOMERS VIA SELF-METATHESIS FROM ALLYL HEXANOATE. FEASIBILITY STUDY

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Allyl hexanoate (HA) is an interesting asymmetric olefin that can be obtained from renewable sources such as pineapple waste. Previous research has shown that this olefin can act as a chain transfer agent (CTA) in metathesis depolymerization reactions. In particular, it has been successfully used in the synthesis of telechelic oligomers by metathesis depolymerization of natural rubber (*Hevea brasiliensis*). However, during depolymerization, HA was observed to participate in self-metathesis reactions (Scheme 1), which were thermodynamically favored by its terminal double bond [1-2]. In general, degradation reactions are better controlled if the CTA used is symmetric [3] because side reactions are reduced due to the catalyst's preference for the olefin's terminal double bond ($\text{CH}_2=\text{CH-R}$). with respect to the internal double bond in a symmetrical olefin (R-CH=CHR') or the trisubstituted double bond in natural rubber $\{\text{R-C}(\text{CH}_3)=\text{CH-R}\}$.

To understand the role of HA in self-metathesis reactions and even evaluate the feasibility of obtaining renewable telechelic bis-acyloxy oligomers, this research focused on the synthesis of the symmetrical olefin 1,4-dihexanoate-2-butene (DHA) via self-metathesis, using the second-generation Grubbs catalyst (G2). Variables such as pressure and reaction times were considered for the study, as well as the proximity of the carbonyl group to the double bond in HA (a methylene spacer $-\text{CH}_2-$), and its comparison with other α -olefins with an acyloxy group.

Scheme 1. Self-metathesis reaction of allyl hexanoate (HA) (a) to obtain the renewable telechelic oligomer: 1,4-dihexanoate-2-butene (DHA) (b).

a. Study of self-metathesis of the olefin allyl hexanoate under different pressure conditions

According to Scheme 1, during the self-metathesis reaction of HA, the symmetrical olefin (DHA) and ethylene were formed as a byproduct. However, to shift the equilibrium and favor the formation of DHA, the reaction was carried out under different pressure conditions. The reaction ranged from a closed system (N_2 atmosphere, atmospheric pressure, and 24 h) to reduced pressures of 0.66 kPa and 0.33 kPa, with times of 3, 6, and 12 h. All reactions were carried out with an olefin/G2 molar ratio of 1000:1 and characterized by FT-IR, $^1\text{H-NMR}$, and GC-MS. According to the calculated conversions, it was found that lower reduced pressures result in higher conversions in the same time. Pressures of 0.33 kPa and 0.66 kPa yielded DHA conversion rates of 82% and 60%, respectively, in 6 h of reaction.

b. Self-metathesis study of the olefin allyl hexanoate by varying the reaction time.

Derived from the conversion rate results, an absolute pressure of 0.66 kPa was chosen for the following study: to establish the time at which the reaction reaches equilibrium. Samples were taken

at reaction times of 30 min, 1, 2, 4, and 6 h. The products were characterized by GC-MS and $^1\text{H-NMR}$. According to the conversions, equilibrium was reached after 6 h.

c. Self-metathesis study of α -olefins with acyloxy groups: catalyst loading optimization.

Under the conditions found (reaction time and vacuum pressure) the last part of the study was carried out, which consisted of observing how the reaction behaves with different catalyst loadings depending on the position of the acyloxy group, in a series of α -olefins composed of HA, methyl 10-undecenoate (UM), 5-hexenyl acetate (A5H), and 1-octene (OC); using G2 and second generation Hoveyda-Grubbs catalysts (HG2), with $[\text{Ru}]/[\text{olefin}]$ molar ratios of 100:1, 500:1, 1000:1 and 2000:1. The results showed that high catalyst loadings yielded excellent conversions, even with a separation between the double bond and the functional group of only one methylene spacer, as was the case with HA at a catalyst ratio of 100:1, achieving a conversion of 82% (for G2) and >99% (for HG2). Contrarily, at the lowest molar ratio of 2000:1, for both olefins (HA and UM), only the corresponding symmetrical product was formed with 40% conversion.

d. Synthesis of oligomers via cross-metathesis by depolymerization of natural rubber from Oaxaca (NR).

Based on the previous study, conditions of 500:1 olefin/G2, with an absolute pressure of 0.66 kPa, were selected for the synthesis of the dimer (DHA) via self-metathesis. The product was subsequently used as CTA in a 1:1 $[\text{NR}]/[\text{CTA}]$ molar ratio and a 1000:1 $[\text{NR}]/[\text{G2}]$ ratio to obtain oligomers with two acyloxy terminal units. Under these conditions, NR was depolymerized with a molecular weight of 1.7×10^6 g/mol ($\bar{D} = 1.35$) to renewable telechelic bis-acyloxy oligomers with a molecular weight of 440.4 g/mol ($m = 2$).

References

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