

## Alkynol polymerization catalysed by Grubbs-type and Hoveyda-Grubbs ruthenium alkylidene complexes: a computational study.

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Density functional theory has been applied to study the mechanism of alkynol (3-butyn-2-ol) polymerization by the third generation Grubbs catalyst and the second generation Hoveyda–Grubbs catalyst. Besides typical linear products that can immediately undergo the next insertion step, cyclic products can be also formed, by oxygen-chelation to the ruthenium centre or as less stable rutenacyclobutene species. The initiation stage is predicted to be faster for the Grubbs-type catalyst, compared to the Hoveyda–Grubbs initiator. It is shown that  $\alpha$ -insertion is always kinetically preferred over the  $\beta$ -insertion path. On the other hand, the NMR calculations indicate that the experimentally observed  $^1\text{H}$  NMR signals can be assigned to alkylidene protons of ruthenium species formed in minor amounts by  $\beta$ -insertion. The choice of the DFT method affects significantly the theoretical values of the  $^1\text{H}$  NMR chemical shifts. The general conclusions about the kinetic preferences do not depend on the density functional used, although the calculated energy profiles are strongly influenced. The simulation of the solvent effect is less significant.

### Słowa kluczowe

ruthenium alkylidene, polymerization, alkynol, DFT calculation, Reaction mechanism, NMR

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