# Summary

Polymerization of functionalized C1 monomers is a powerful tool to obtain highly functionalized polymers. Such polymers are difficult to prepare by traditional olefin polymerization (C2 in scheme 1). Preparing these highly functionalized polymers with additional polar groups, in a stereocontrolled way, are an even bigger challenge. Polar functionalities in a polymer are essential to achieve important properties such as adhesion and paint/printability. Stereoregularity and control over the amount of polar functional groups are necessary to amplify these properties, but are a challenge to obtain. Rh-mediated carbene polymerization can offer a solution to prepare such desired polymers.
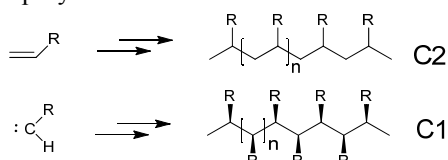

Scheme 1. Olefin (C2) and syndiotactic carbene polymerization (C1).

Carbene polymerization proceeds via migratory insertion steps of carbene units into the metal-carbon bond of the growing polymer chain. In Chapter 1 an overview is given of the different carbene insertion reactions to form a C–C bond. Both polymer forming reactions and reactions used in organic synthesis of smaller molecules are reviewed. Chapter 1 ends with a detailed overview of the current state-of-the-art in Rh-mediated stereoregular C1 polymerization reactions. In these reactions diazo esters are used as carbene monomer precursors, producing highly functionalized, syndiotactic polymers with a high M_w (see Scheme 2). Furthermore, the latest insights in the reaction mechanism of this polymerization reaction are reviewed. It is clear that at the start of this PhD project a detailed mechanistic picture of these Rh-mediated stereoregular carbene polymerization reactions was lacking, and our mechanistic understanding of many experimental observations was incomplete. therefore we aimed at gaining a deeper understanding of the reaction mechanism, and the obtained results are described in Chapter 2-5 of this Thesis. Important goals were to reveal the exact structure of the key polymer forming Rh species, the reason for the formation of high M_w polymers with rhodium (known to undergo rapid β-hydride elimination in many other systems), explaining the high syndio-tacticity of the reaction, and understanding the low initiation efficiency (IE < 5%) towards the active form of the catalyst. In this Thesis details about the propagation, termination and chain-transfer mechanisms are elucidated to provide answers to these important questions.
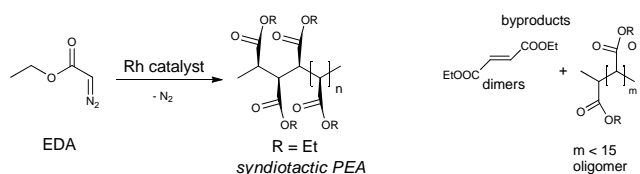
Scheme 2. Rh-mediated EDA polymerization with MeOH, showing syndiotactic poly(alkyl 2-ylidene-acetate) (PEA).

Chapter 2 describes the results obtained in experimental studies focusing on unraveling more details about the catalyst activation and the chain initiation, propagation and termination steps of the Rh-mediated carbene polymerization reaction. Through catalyst variation, end-group analysis, dilution-kinetic studies and polymerization reactions in the presence of alcohols many new insights were obtained. The use of well-defined $Rh^I(cod)$–alkyl, aryl and allyl complexes does not lead to better initiation efficiencies or higher polymer yields, thus pointing to a more complex catalyst activation processes under the applied reaction conditions. Indeed, dilution-kinetic studies reveal a complex, multistep catalyst activation process. Catalyst modification first leads to oligomerization activity with a suppressed tendency towards β-hydride elimination and accordingly a shift to saturated oligomeric chains that are generated by protonolysis. Further catalyst modifications lead to a shift from atactic oligomerization to stereoregular high molecular weight polymerization activity (Scheme 3).
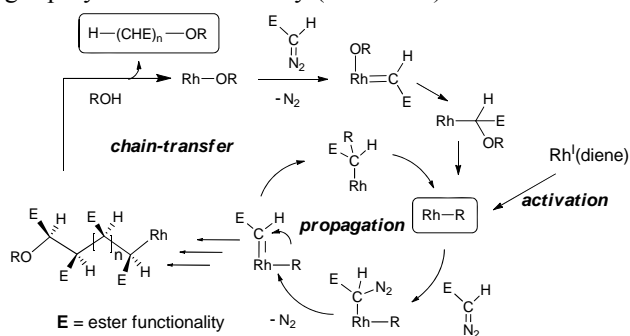
Scheme 3. Initiation, propagation and termination/chain-transfer processes occurring during Rh-mediated carbene polymerization reactions.

MALDI-ToF MS measurement provided important insights into the chain-initiation and chain-termination processes. Chain-termination takes place mainly by alcoholysis of the Rh–C bond of the growing chain. In the absence of alcohols, chain-initiation can occur by insertion of a preformed carbene into a Rh-ligand or Rh-hydride bond, but in the presence of alcohols (or water) the dominant chain-initiation process takes place by (internal or external) nucleophilic attack of the alcohol (or water) at a Rh-carbene moiety. When alcohol is present, chain-termination mainly involves nucleophilic alcoholysis (most likely σ-bond

metathesis type protonolysis), and leads to chain-transfer (Scheme 3). A remarkable feature of the alcohol-mediated chain-transfer process is a clear correlation between the chain-length of the polymer and the nucleophilic character of the alcohol. This points to an electrophilic polymer producing Rh-species, and thereby suggests that the active species has a higher oxidation state (most logically Rh^{III}) than the starting Rh^{I} precatalysts. In the absence of alcohols, chain-transfer is very slow compared to chain-propagation so that chain-growth can be observed in time and block-type copolymers can be prepared. Addition of (high concentrations of) alcohols accelerates the chain-transfer process. This is a significant finding that not only features a new control-factor to steer the polymer molecular weights, but also allows true catalytic turnover.

   More experimental investigations, aiming at gaining a deeper understanding of the (electronic) structure of the active Rh species responsible for polymer formation, are described in Chapter 3 and 4. In previous studies it was shown that exposing the solid catalyst $[(L\text{-}pro)Rh^{I}(Me_2cod)]$ to air for several days before use in the polymerization reaction, a much higher polymer yield (80% vs. 45%) was obtained compared to the non-oxidized form of the catalyst. Two hypotheses were explored, each of which in principle provides a plausible explanation for this behavior. The $[(L\text{-}pro)Rh^{I}(Me_2cod)]$ catalyst contains two chiral ligands (L-prolinate and 1,5-dimethylcyclooctadiene), and hence is formed as a mixture of two diastereomers. Aerobic oxidation of solid $[(L\text{-}pro)Rh^{I}(Me_2cod)]$ is slow and incomplete, and one of the diastereomers ("type-b") is oxidized faster than the other ("type-a"). In the first hypothesis explored (hypothesis I), we assume that the "type-a" diastereoisomer is the important precatalyst leading to formation of the active polymer forming species upon activation by EDA, while the "type-b" diastereoisomer would be responsible for the formation of unwanted side-products. Upon prolonged exposure to air, the undesirable activity of the "type-b" diastereoisomer could be suppressed by predominant oxidation of this species, leaving the desirable activity of "type-a" diastereoisomer in carbene polymerization. The second hypothesis (hypothesis II) is opposite, in which we speculate that oxidation of the Rh(diene) precatalysts plays a much more active role: Oxidation of the precatalyst could actually *activate* catalyst mixture towards polymerization. With the experiments described in Chapter 3 we the first hypothesis was explored. Several different (N,O-ligand)Rh(Me$_2$cod) precatalysts were synthesized and we followed different synthetic approaches to directly and indirectly influence the diastereomeric ratio of these (N,O-ligand)Rh(Me$_2$cod) complexes, thus aiming at influencing the catalytic performance. We also exposed these complexes and mixtures thereof for varying periods to air to investigate the effect on polymerization reaction. The main conclusion from all these experiments is that hypothesis I does not explain the results, while hypothesis II provides a much more

plausible explanation for all observations. Aerobic oxidation of the solid precatalyst must play a key role in the catalyst activation process. This was further investigated in Chapter 4.

A reaction mixture of the oxidized catalyst and EDA was investigated using a series of HR-ESI-MS experiments, allowing mass selection of the active polymer-forming species under the applied reaction conditions. The results obtained provided valuable new information about the reaction mechanism. The active species for the polymerization is, in fact, a cationic [(allyl-diene)Rh^{III}(polymeryl)]$^{+}$ species. Exposing the catalyst to oxygen, oxidizes Rh^{I} to Rh^{III} and the diene-ligand transforms into an (allyl-diene)-ligand (see Scheme 4).
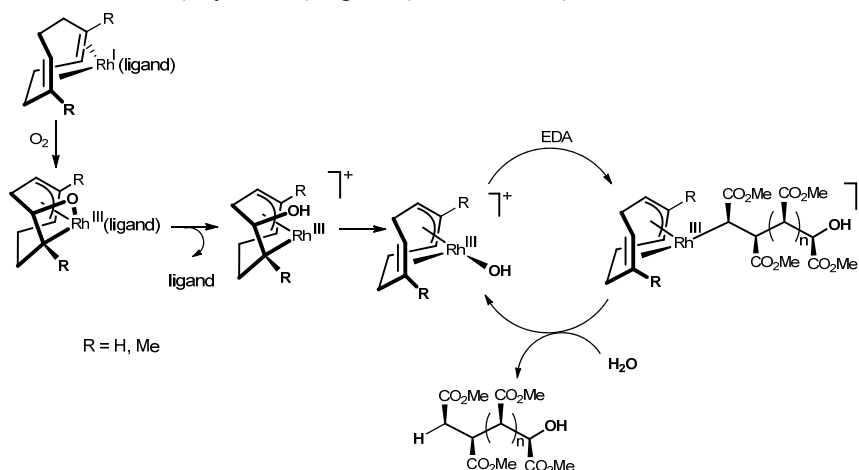
Scheme 4. Generalized reaction mechanism of catalyst activation by aerobic oxidation of the Rh^{I}(diene) precatalysts. The right part shows the water-mediated chain-transfer process as observed with HR-ESI-MS.

Oxidation of the Rh^{I}(diene) moiety proceeds van a 2-rhoda^{III}oxetane, which rearranges to an Rh^{III}(allyl-diene-OH) moiety. The latter undergoes β-hydroxy-elimination to form an (allyl-diene)Rh^{III}-OH species. The polymer in fact starts growing on the this formed Rh–OH moiety. Propagation involving carbene insertion steps is clearly indicated by the repetitive units in HR-ESI-MS spectra. In good agreement with the results obtained in Chapter 2, termination involves protonation by either water or an alcohol.

Further proof for the activation mechanism in Scheme 4 was obtained by using an isolated form of a precatalyst with an oxidized Rh(diene) moiety (see Figure 1). This species has a structure close to the final active species responsible for polymer formation, and only has to undergo β-hydroxy-elimination to become active. Indeed, this catalyst produced the polymer in high yields and much more rapidly than any other catalyst used thus far. Also the initiation efficiency of the catalyst was much higher than with Rh^{I}(diene) catalyst precursors.
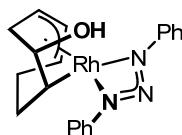
Figure 1. Complex $[(C_8H_{11}OH)Rh(N_3Ph_2)]$ containing an allyl-β-alkyl-hydroxide ligand, a catalyst precursor close to the active species responsible for polymer formation.

Further details of the reaction mechanism were studied using DFT calculations. The computational study focused primarily on the stereoselective propagation steps as well as two possible termination steps. The results are described in Chapter 5. Each propagation step in the carbene polymerization reaction involves binding of the diazo compound (I_d mechanism), followed by rate limiting carbene formation through loss of dinitrogen followed by migratory insertion of the carbene into the Rh–alkyl bond of the polymer chain (Schema 5).
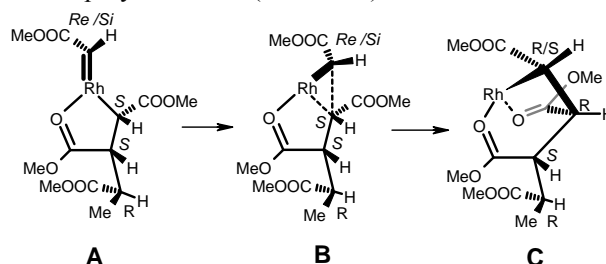
Schema 5. Insertion step in the polymerization reaction, which determines the tacticity of the polymer. *Re*-face or *Si*-face carbene insertion results in R or S configuration ((allyl-cod)-ligand is omitted for clarity). A) carbene formation, B) insertion step, C) extended polymer chain, where Rh is stabilized by coordination of two oxygen-carbonyls of the polymer chain and can coordinate the next monomer.

Steric factors affect the relative barriers for syndiotactic versus isotactic insertion steps; the tacticity of the polymerization reaction is chain-end controlled. In good agreement with the experimental results, the computations show a clear preference for syndiotactic insertion steps. When propagation is calculated from chain containing a stereo-error at the carbon stemming from the last inserted monomer-unit, the carbene intermediate is attacked by the ester carbonyl-moiety to form an oxygen-ylide (see Figure 2). This will substantially slow-down propagation. A similar effect may influence the initiation efficiency (IE) during the catalyst activation process, leading to intrinsically low activation efficiencies when starting from catalysts without a pre-formed syndiotactic chain fragment.
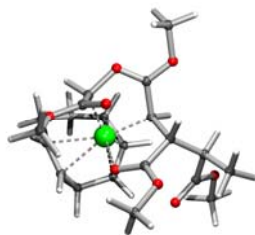
Figure 2. Catalyst with an oxygen ylide-structure, which slows down the polymerization reaction from non-syndiotactic chains.

Chain-transfer involving alcohol-mediated protonolysis is computed to be a more favorable pathway than β-hydride elimination. This explains the formation of saturated, alcohol-terminated RO–polymeryl–CH(COOR)–CH$_2$(COOR) chains rather than unsaturated (H–polymeryl–CH(COOR)=CH(COOR) chains. Furthermore, in good agreement with the experimental observations showing that the nucleophilicity of the alcohol plays a role (see Chapter 2), the calculated alcohol-mediated chain-transfer process proceeds via initial coordination of the alcohol moiety to the Rh-center. Protonolysis of the growing chain requires rearrangement of the Rh–polymeryl chain to an O-bound Rh-enolate, followed by rapid proton-transfer from the coordinated alcohol moiety to the enolate carbon-moiety. This process has a higher barrier than chain-propagation, but a lower barrier than β-hydride elimination. With these new computational insights, in combination with the experimental results described in Chapter 2-4, the mechanism of the polymerization reaction is largely clarified.

Chapter 6 deviates from the general mechanistic topic and describes the investigation into potential applications of the new, highly functionalized, stereoregular polymeric materials. One such potential application is to generate amphiphilic block copolymers by initiating the EDA polymerization on a preformed PEG polymeric chain containing an alcohol end-group, which are potentially of interest for application in micro-emulsion/micelle reactors in (catalytic) dual-phase reactions, as controlled-release drug carriers or as emulgators for mixtures of water and less polar solvents. Purification is a complication of this method to synthesize amphiphilic polymers A second potential application is to use poly-carbenes as conducting polymers, e.g. for applications in polymeric solar cells. For this reason several different benzylic diazo compounds were synthesized, substituted with different cyano- and fluoro-substituents, with the aim to influence the potential conducting properties of their (co)polymers through their electron-accepting side-chains. While these (co)polymers indeed have electron-accepting properties, application as polymeric solar cells is complicated by the fact that their electronic properties are not properly matched with those of other components in such devices. More research is necessary to optimally tune these new type of materials and/or to use different electron-donor materials in the device.