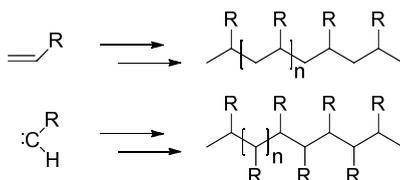


Summary

Polymerization of C=C bond containing substrates is currently the most important method to prepare polymeric materials, exemplified by the many large-scale industrial plants producing polyethylene, polypropylene, polystyrene, poly(vinyl chloride), poly(methyl methacrylate) and a variety of other polymers from vinylic substrates (C2 polymerization, see Scheme 1).



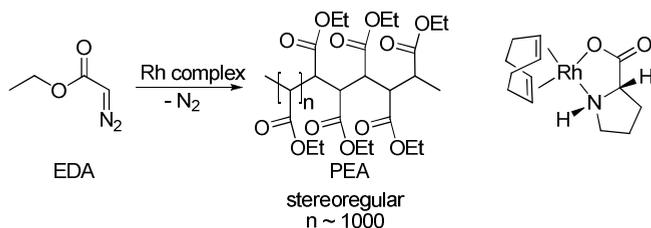
Scheme 1. Polymerization of C2 and C1 monomers.

A major challenge in *transition metal mediated* (migratory) olefin insertion polymerization is the *catalytic* synthesis of stereoregular polymers from polar functionalized monomers. To our best knowledge, there are currently no polymerization catalysts that allow the formation of stereoregular carbon-chain polymers that are functionalized at every carbon atom (from 1,2-disubstituted vinyl monomers). C1 polymerization methodologies offer interesting possibilities to prepare such *stereoregular* polymers with a densely functionalized main-chain structure.

In the introductory Chapter 1, C1 polymerization methodologies reported in the literature are reviewed. These include Lewis acid and transition metal mediated polymerization of carbenes from for example diazo compounds or sulfur ylides. Although C1 polymerization is a very promising research area, the mechanistic understanding and the developments and applications of most of the reported C1 polymerization methodologies showed to be still far from mature. For many of the reported C1 polymerization catalysts it proved difficult to obtain high molecular weight polymers, and control over the polymer tacticity was often poor.

This thesis describes the development of Rh-mediated carbene polymerization methodologies for the preparation of unprecedented stereoregular and highly functionalized polymers. In Chapter 2 the reaction of simple rhodium complexes with ethyl diazoacetate (EDA) is described, leading to highly *stereoregular* and high molecular weight polymers with an ester group on *every* carbon of the carbon-chain (Scheme 2). The stereocontrol in the formation of poly(ethyl 2-ylideneacetate) (PEA) most likely involves propagation under chain-end control.

Summary

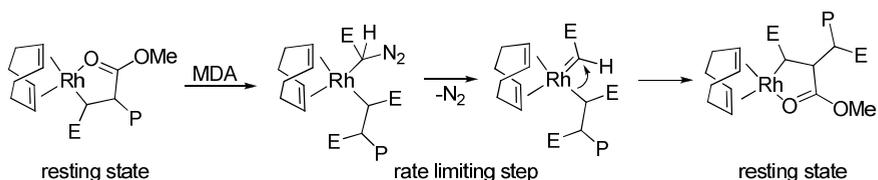


Scheme 2. Stereoregular polymerization of ethyl diazoacetate.

On the basis of a comparison of the ^{13}C NMR spectroscopy data with those obtained for isotactic enriched polyfumarates, the polymers obtained with Rh and EDA were found to be *syndiotactic*. This assignment was supported by solid state NMR spectroscopy experiments and molecular mechanics calculations. Diazoacetates containing other ester functionalities could also be polymerized, affording polymers containing polar functional side groups at each carbon of the carbon-chain backbone.

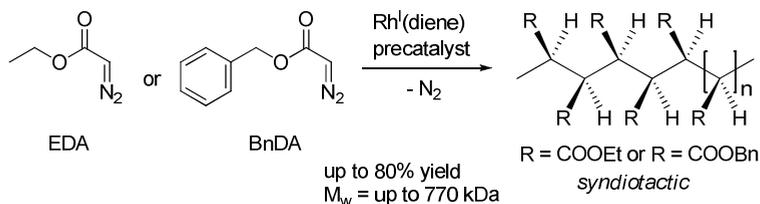
In the third Chapter the attempted use of supramolecular ligands to steer and control the carbene polymerization reaction is described. Supramolecular assemblies of $[(\text{cod})(\text{NHC})\text{Rh}]$ complexes with Zn^{II} -templates were reacted with EDA. Higher molecular weight polymers were obtained with these catalysts, but the effect of the Zn^{II} -templates is general; without the formation of the assemblies the same results were observed. The ‘true’ active species are probably based on $[\text{Rh}(\text{cod})]^+$ (or its derivatives) formed when the NHC ligand has dissociated from the metal, which is more clear from the results described in Chapter 4 and 6.

A study into the reaction mechanism is discussed in Chapter 4. Ligand variation in combination with the results described in Chapters 2 and 3 led to the conclusion that the active species for the polymerization is stabilized by the diene ligand. Kinetic experiments show a low initiation efficiency for the Rh(diene)-catalyst systems described in this Chapter (1-5% of the added pre-catalyst becomes active in the polymerization). DFT calculations suggested a chain-growth pathway involving consecutive migratory insertion steps of carbene fragments, formed from the carbon-bound diazo substrate by rate-limiting dinitrogen loss, into the Rh–C bond of the growing chain (Scheme 3). The computational results readily explain the formation of syndiotactic polymers *via* a chain-end control mechanism.



Scheme 3. Proposed mechanism of propagation steps of the Rh-mediated polymerization of polar functionalized carbenes (P = growing polymer chain, E = COOMe).

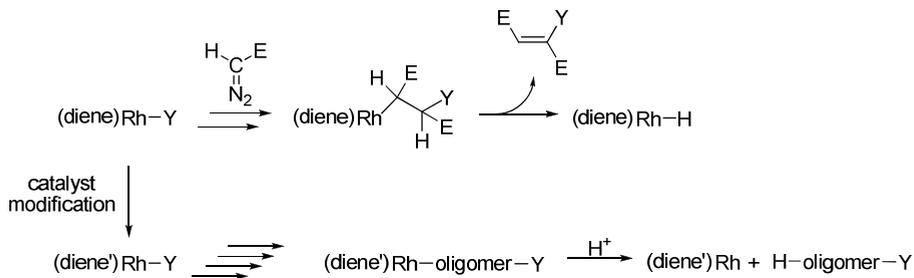
Chapter 5 describes an approach to decrease side product formation. The use of Me_2cod -based Rh precursors led to very high molecular weight polymers (Scheme 4). Remarkably, excellent polymer yields were obtained upon ‘aging’ the catalysts for prolonged times in air.



Scheme 4. Formation of stereoregular and high molecular weight polymers from ethyl or benzyl diazoacetate in high yield.

The results described in Chapter 6 provide valuable information about catalysts activation, initiation, termination and chain-transfer processes occurring during Rh-mediated carbene polymerization reactions. The use of well defined (diene) Rh^{I} -alkyl/aryl complexes did not lead to better initiation efficiencies, and hence catalyst activation under the applied reaction condition seems to be an important factor for the formation of high molecular-weight and stereoregular polycarbenes. Several species turned out to be active in Rh-mediated carbene transformations, explaining the formation of dimers, oligomers and polymers in the beginning of the reaction. This adds to the complexity of these reactions.

It seems that the chains start to grow from (diene) Rh -Y species (Y = anionic nucleophile or nucleophilic ligand), which undergo rapid β -hydrogen elimination in their non-modified forms, thus effectively leading to dimerization activity (Scheme 5). Modification of these (diene) Rh -Y and (diene) Rh -H species under the applied reaction conditions leads to species for which β -hydrogen elimination is absent or suppressed, thus leading to the formation of atactic oligomers. Further catalyst modification then allows for the formation of stereoregular polymers.



Scheme 5. Proposed product formation in reaction of the Rh-catalyst precursor with EDA (Y = nucleophilic donor ligand, anionic donor or H).

MALDI-ToF mass spectrometry analysis of the oligomers revealed the presence of saturated $\text{H}-(\text{CHCOOEt})_n-\text{H}$ and $\text{Y}-(\text{CHCOOEt})_n-\text{H}$ chains, suggesting that termination involves protonolysis in all cases. Chain-transfer takes place under the influence of alcohols (when added in high concentrations). Under such chain-transfer conditions, $\text{RO}-(\text{CHCOOEt})_n-\text{H}$ chains ($\text{R} = \text{Me}, \text{Et}, \text{Bu}$) are formed exclusively. The presence of the DEF and DEM dimeric side products negatively influences the polymerization reaction, and leads to lower polymer yields when they are added deliberately.

In the last Chapter the synthesis and characterization of syndiotactic copolymers of different diazoesters is described. The homopolymers from ethyl and benzyl diazoacetate were analyzed by polarizing optical microscopy and revealed thermotropic and lyotropic liquid crystallinity (nematic phases), which is remarkable for sp^3 -based carbon chain polymers. Furthermore, these homopolymers have relatively high storage moduli up to temperatures well above their T_g .

The formation of random and block copolymers from the different diazoesters (Figure 1) was confirmed by different techniques; NMR spectroscopy, size-exclusion chromatography, thermal analysis and 2D liquid chromatography. The thermal and mechanical material properties of the homo- and copolymers, investigated by several techniques (thermo gravimetric analysis, differential scanning calorimetry, polarizing optical microscopy, dynamic mechanical thermal analysis), are also included in this Chapter.

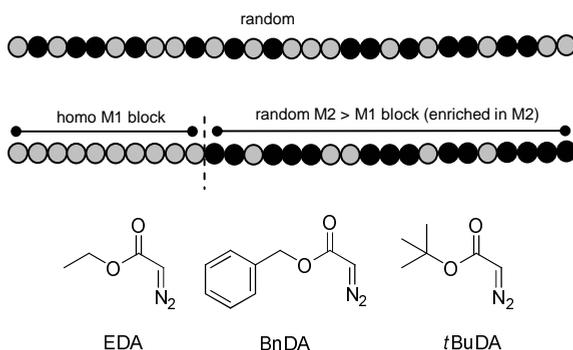


Figure 1. Schematic representation of random and poly($\{\text{M1}\}_b\text{-}\{\text{M2-}i\text{ran-M1}\}_b$) block copolymers prepared from ethyl, benzyl and *t*-butyl diazoacetate.

In conclusion, polymerization of carbenes from diazoesters by Rh^{I} pre-catalysts provides a valuable new method to obtain high molecular weight and stereoregular (co)polymers with a polar side group at every backbone carbon atom. The polymers reveal interesting material properties, can be obtained in high yields and the scope of this method can easily be extended by using different diazo compounds.

Perspective

It should be noted here that carbene polymerization can never compete commercially with traditional olefin polymerization methods. Diazoester monomers (C1-monomers) are intrinsically more expensive than olefins (C2-monomers). Any future applications of the new carbene polymerization techniques developed in this thesis should therefore be sought in the Performance Polymers / Engineering Plastics market, taking advantage of their special properties (*e.g.* using their densely packed polar functionalities for energy transfer purposes, LC behavior, retained modulus at elevated temperatures, or high thermal stability). Future investigations should therefore focus on unraveling even more special material properties of these new and unusual polymers, hopefully leading to commercial applications in a specialty-polymer market.

There are also some remaining synthetic challenges associated with the carbene polymerization methodologies described in this thesis. The initiation efficiencies are generally rather low, and in absence of chain transfer this requires the use of rather high Rh catalyst loadings (2 mol%) to obtain decent polymer yields. The high Rh price therefore contributes considerably to the production costs of these new polymers. Future research should therefore focus on raising the initiation efficiencies and achieving chain transfer in a controlled fashion (*i.e.* without producing too short polymers). These are likely solvable problems. Evidence for chain transfer pathways and improved initiation efficiencies in the presence of alcohols (as described in Chapter 6) are promising leads for future investigations in this direction, and should eventually make these reactions more efficient and truly 'catalytic'. The intriguing structures of the new highly stereoregular ester functionalized sp^3 -carbon chain (co)polymers (with high M_w) and their unusual material properties make such future investigations more than worthwhile, both from a commercial and an academic point of view.