Transition metal complexes of polymeric Schiff bases as catalyst precursors for the polymerization of ethylene

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Available online 8 August 2006

Dedicated to Prof. Bogdan Marciniecǐ 65th birthday.

Abstract

Coordination compounds derived from polymeric Schiff bases can be used as catalyst precursors for the polymerization of ethylene. After the activation with MAO, these systems are of heterogeneous nature and can prevent reactor fouling. The structure of the ligand backbone has strong influence on the polymerization activities and the properties of the resulting polyethylenes. Force field calculations using Allingers MM3 point out minimum energy structures, which help to explain the experimental results.
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Keywords: Polymeric Schiff bases; Iron; Catalysis; Polymerization; Ethylene; MM3

1. Introduction

Despite all the advantages the use of single site catalysts in olefin polymerization offers, the homogeneous nature of these systems causes a severe technical problem: the so-called reactor fouling [1]. This term describes the precipitation of the polymer on the walls of the reactor during the polymerization process. It is found in slurry as well as in gas phase reactors and makes a continuous reaction impossible. The growing layer of polymer inhibits reaction control and the reactors have to be cleaned from the precipitate time after time. In order to prevent reactor fouling, many methods have been developed in order to heterogenize the single site homogeneous catalysts. For instance, the approaches include the use of heterogeneous cocatalysts [2] fixing the catalyst precursors on particle surfaces [3], or the self-immobilization developed by Peifer and Alt [4]. In all cases the goal is to heterogenize the catalyst, so that the polymer produced precipitates at the active center and not on the reactor walls. Now the product can be removed easily from the reactor and a continuous process is possible.

In this paper, a new approach to prevent reactor fouling is described. With the use of polymeric Schiff bases as ligand framework, the catalyst precursors become insoluble in solvents commonly used for slurry polymerization reactions. Now these catalysts are heterogeneous and the polymer produced does not precipitate on the reactor walls.

2. Results and discussion

Small and Brookhart [5] and Gibson and co-workers [6] were the first who described the high activities of late transition metal catalysts bearing bis(imino)pyridine ligands. This class of compounds has been of large interest especially for ethylene polymerization [7–11]. The ligand precursors of these complexes are obtained by a double condensation reaction of 2,6-diacetylpyridine and substituted anilines [12]. The use of diamino reagents for this Schiff base analogous condensation reaction yields the ligand precursors described in this paper (Scheme 1).

The reaction of these ligand precursors with transition metal halides, e.g. iron(II) chloride, yields coordination compounds similar to the systems described by Marvel et al. [13] or by Goodwin and Bailar [14] (Scheme 2).
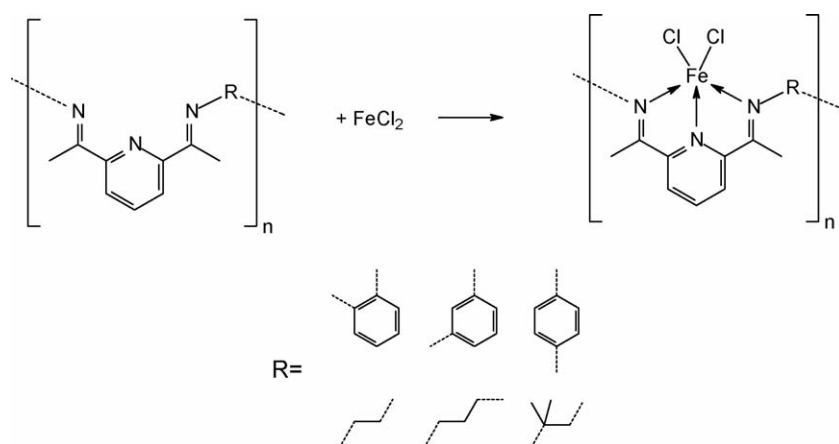
Elemental analyses of the resulting iron compounds reveal that different ratios of transition metal salt to coordination site
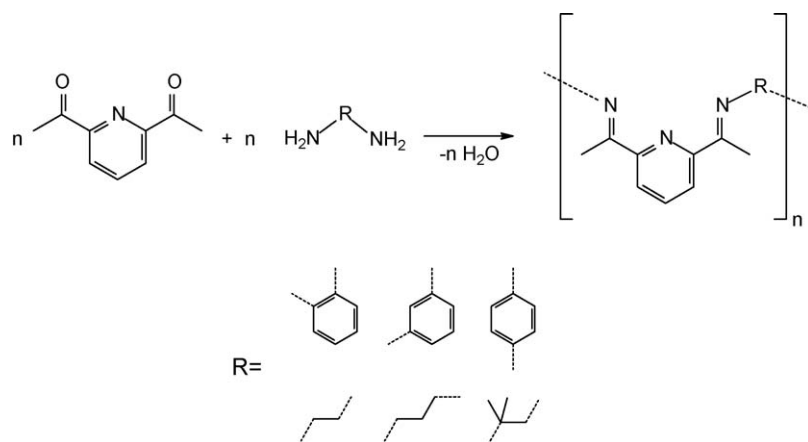

Scheme 1. Synthesis of the ligand precursors.

Scheme 2. Synthesis of the coordination compounds.

are found for different substituents R. The following picture shows the compositions of the three iron(II) chloride complexes with phenylene substituents in the bridge (Scheme 3).

With the alkyl substituents the metal to coordination site ratios are 1:2 for the ethylidene and the propylidene bridges and 1:3 for the isobutylidene bridges. The differences in the amount of coordination sites occupied by the transition metal can be explained by the geometries of the corresponding ligand precursors. In case of the compounds with aromatic bridges, the different conformers are obtained by changing the dihedral angle δ at the nitrogen aryl bonding (see Scheme 4).

Force field calculations with Allingers MM3 [15] were used to search for minimum energy structures. Therefore, the energies of approximately 300 conformers of each differently substituted
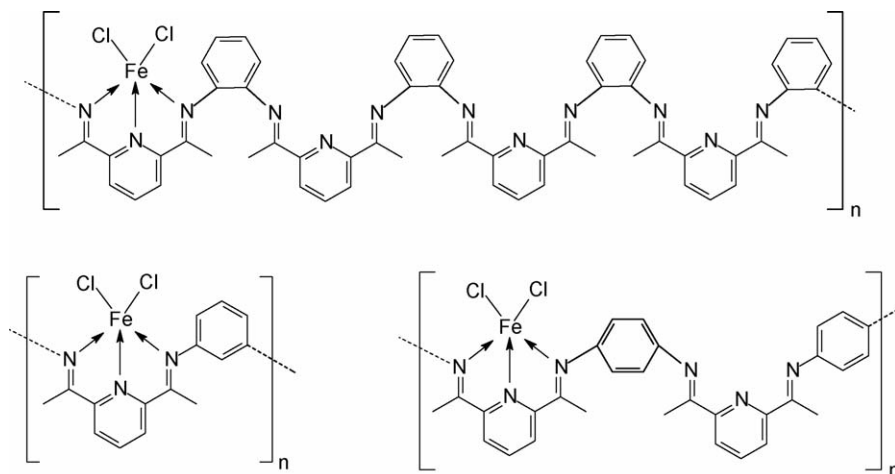
Scheme 3. Iron(II) chloride complexes with phenylene bridges.
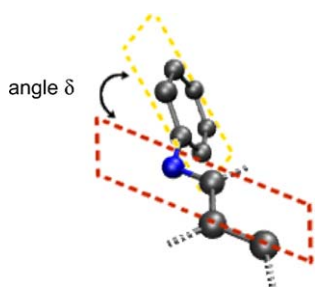
Scheme 4. Dihedral angle δ.

ligand precursor have been compared and the global minimum of the potential energy surface has been determined.

Scheme 5 shows the corresponding structures of the compounds with aromatic bridging groups.

It becomes obvious from the calculated structures that only in the case of the *meta*-substituted bridging group, the chain has a linear structure with good accessibility of the coordination sites. Therefore, this compound shows the highest occupation number, followed by the *para*-substituted derivative. The ligand precursor with *meta*-substituted bridges has the most intricate structure and therefore the coordination sites are less accessible for the transition metals resulting in the lowest occupation.

In case of the polymeric Schiff bases with aliphatic bridging groups, the energy differences between different conformers are too low to make any suggestions concerning the geometry. The lower occupation number of the compound with isobutylidene bridges compared to the ethylidene and propylidene derivatives can be explained by the higher steric demand of this substituent.

The coordination compounds have been used as catalyst precursors for the polymerization of ethylene. Therefore, the iron complexes have been activated with MAO. The resulting catalysts are insoluble in solvents commonly used for the polymerization of ethylene, e.g. pentane, hexane or toluene. Analogous to the corresponding bis(imino)pyridine complexes, the com-
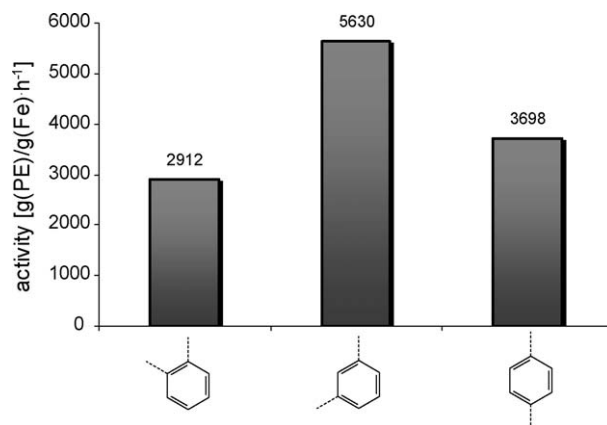
Scheme 6. Activities of the catalyst precursors; polymerization conditions: catalyst precursors in 500 ml pentane, activation with MAO (Al:Fe = 2500:1), 10 bar ethylene pressure, 60 °C, 1 h.

pounds with aliphatic substituents do not show any activity. Scheme 6 shows the results of the polymerization reactions using the derivatives with aromatic bridges.

The polymerization results indicate that the *meta*-substituted derivative shows the highest activity followed by the *para* substituted. The coordination compound with *ortho*-substituted bridging groups shows the lowest activity in the polymerization of ethylene. This behavior can be explained by the geometries of the ligand precursors calculated with MM3. With the *meta* substitution, the catalyst precursor shows an almost linear conformation. Therefore, the active sites are accessible more easily than in the case of *meta*- or *para*-substituted bridges. As a result this system shows the highest activities. All three catalysts do not show any reactor fouling. Due to the heterogeneous nature of the catalytic centers, the polymer formed precipitates at the catalyst particles and not on the reactor walls. Analyses of the resulting polymers reveal that the polydispersities are high ($D = 40.54$) and there are low average molecular weights ($M_n = 1100$, $M_w = 44,600$).
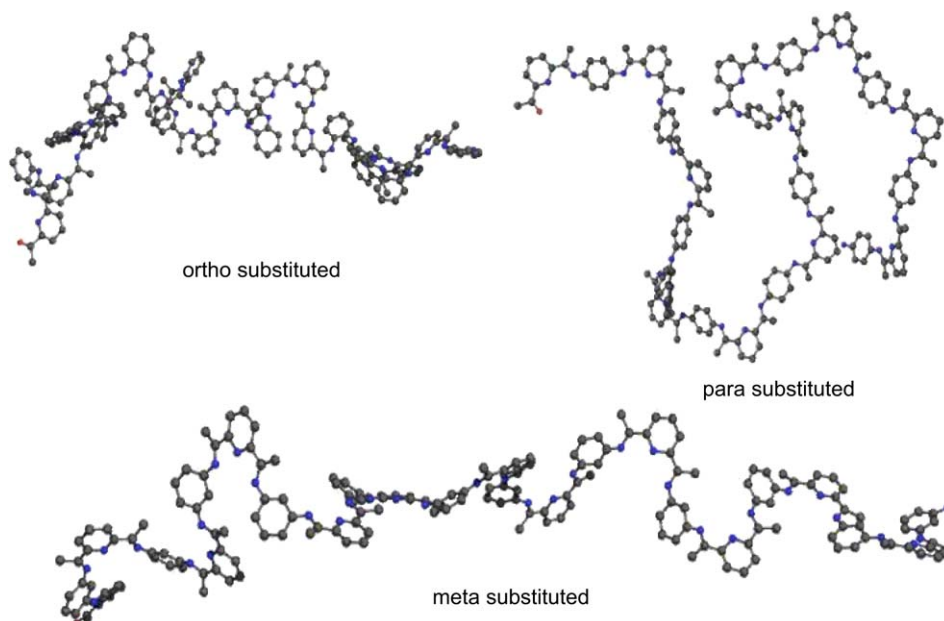
Scheme 5. Minimum energy structures of ligand precursors with aromatic bridging groups.

This is also a result of the geometry of the catalysts. Because of the variety of conformers there are many different active sites, producing various polyethylenes resulting a broad molecular weight distribution. Because the active sites are close to each other, there is no room for long chains, and chain termination reactions occur more frequently lowering the molecular weight.

3. Summary and conclusions

Transition metal complexes with polymeric Schiff bases as ligand framework are suitable catalysts for the polymerization of ethylene. Due to the heterogeneous nature of the active centers, these systems can prevent reactor fouling. The calculation of minimum energy structures with the MM3 force field shows that the geometry of the ligand framework depends on the bridging groups between the coordination sites. The conformation of the ligand backbone controls the degree of transition metal coordination. More linear structures as in case of the *meta*-substituted phenylene derivative allow higher occupation than intricate conformers as found with the *ortho*-substituted polymeric Schiff base. This rule can also be applied to polymerization activities. The accessibility of the active centers controls the polymerization kinetics and therefore the compound with the most linear structure shows the highest activity. Due to the sterically demanding vicinity of the catalytic centers the activities are lower than the activities of comparable mononuclear bis(imino)pyridine complexes by a factor of 140. As a result of the conformational freedom of the polymeric Schiff bases, many different active sites are present in these catalysts. Therefore, polyethylenes with broad molecular weight distributions are produced. Because of the sterically demanding ligand backbone and the close vicinity of the catalytic centers, chain termination becomes fast compared to chain propagation yielding low average molecular weights. Future investigations have to address these problems.

4. Experimental

4.1. General methods

All manipulations of air and water sensitive compounds were performed using standard Schlenk techniques. Therefore, argon was purified by passage over BTS catalyst and molecular sieves 4 Å. All solvents used were purchased in technical grade and purified by distillation over Na/K alloy under argon atmosphere. Methylaluminoxane (MAO) was supplied by Witco GmbH, Bergkamen, as 30% solution in toluene (average M_w 1100 g/mol, aluminum content: 13.1%, 3.5% as trimethylaluminum). All other chemicals were commercially available or were synthesized according to literature procedures.

IR spectra of the compounds were recorded after grinding with CsI as pressed disks at a *Perkin-Elmer Spectrum* 2000 *FT-IR* spectrometer using the *Spectrum for Windows* software application. Molecular weight determinations of the polyethylene samples were performed using a Millipore Waters 150 C HT-GPC with refractometric detection (RI Waters 401). The polymer samples were dissolved in 1,2,4-trichlorobenzene (flow rate 1 ml/min) and measured at 150 °C.

4.2. Synthesis of the polymeric Schiff bases

2,6-Diacetylpyridine (6.13 mmol) was dissolved in toluene. After the addition of approximately 10 mg of *p*-toluenesulfonic acid as catalyst, the solution was heated to reflux. The diamino compound (6.13 mmol) was dissolved in toluene and was added slowly to the boiling reaction mixture. The reaction was refluxed until no more water could be separated and the products precipitated as amorphous solids. After separation the polymeric Schiff bases were washed with toluene, diluted aqueous NaHCO$_3$ solution, water and acetone and were dried at room temperature.

Bridging group	Yield (%)	IR (cm^{-1})	Elemental analysis
o-Phenylene	63	1618	Measured: C, 75.28; H, 6.57; N, 19.15. Calculated: C, 76.70; H, 5.57; N, 17.86
m-Phenylene	81	1622	Measured: C, 76.17; H, 5.80; N, 18.03. Calculated: C, 76.70; H, 5.57; N, 17.86
p-Phenylene	77	1631	Measured: C, 75.68; H, 6.29; N, 18.03. Calculated: C, 76.70; H, 5.57; N, 17.86
Ethylidene	58	1639	Measured: C, 70.11; H, 7.57; N, 22.32. Calculated: C, 70.56; H, 7.00; N, 22.44
Propylidene	63	1627	Measured: C, 70.81; H, 7.76; N, 21.43. Calculated: C, 71.61; H, 7.51; N, 20.88
Isobutylidene	79	1636	Measured: C, 71.93; H, 7.76; N, 20.31. Calculated: C, 72.52; H, 7.96; N, 19.52

4.3. Synthesis of the coordination compounds

To a slurry of the polymeric Schiff bases (0.2–0.4 g) in toluene the amount of iron(II) chloride equivalent to the number of coordination sites was added. The mixture was kept at reflux for 8 h. Thereafter the hot suspension was filtrated and the residue was washed with pentane several times. After drying, the products were obtained as dark amorphous solids.

Bridging group	Yield (%)	IR (cm^{-1})	Elemental analysis
o-Phenylene	82	1629	Measured: C, 64.58; H, 4.35; N, 14.29. Calculated: C, 67.48; H, 4.91; N, 15.74
m-Phenylene	86	1633	Measured: C, 50.81; H, 4.92; N, 13.11. Calculated: C, 49.76; H, 3.62; N, 11.61
p-Phenylene	81	1633	Measured: C, 62.17; H, 6.09; N, 15.57. Calculated: C, 60.32; H, 4.39; N, 14.07
Ethylidene	75	1634	Measured: C, 47.91; H, 6.08; N, 16.93. Calculated: C, 49.23; H, 4.88; N, 15.66
Propylidene	77	1624	Measured: C, 53.86; H, 6.17; N, 15.68. Calculated: C, 54.46; H, 5.71; N, 15.88
Isobutylidene	71	1632	Measured: C, 58.07; H, 7.06; N, 16.37. Calculated: C, 57.97; H, 6.36; N, 15.60

4.4. Activation of the catalyst precursors

An amount of 10 mg of the corresponding complex was suspended in pentane and activated with an excess of MAO (Al/Fe = 2500/1). The activated catalyst was used for ethylene polymerization within 15 min.

4.5. Polymerization of ethylene

The activated complex was added to a 1l steel autoclave (Büchi), filled with 500 ml *n*-pentane. The polymerizations were performed with constant ethylene pressure of 10 bar (99.98% ethylene, dried over aluminum oxide) and at a temperature of 60 °C. After a period of 1 h, the autoclave was cooled to room temperature and the pressure was reduced. The polymerization mixture was filtered, the remaining polymer was washed with half concentrated hydrochloric acid, dried and weighed.

4.6. Conformational search with MM3

The search for minimum energy structures was performed with the software CaChe 6.1. The first step was the optimization of the monomeric building block. Here and in the following steps Allingers MM3 was used for the force field calculations. Four of the optimized units were connected via imino bonds. The dihedral angles at the newly formed bonds were changed continuously between $-180°$ and $180°$ in steps of $120°$ and every resulting structure was again optimized by MM3. Following this scheme, 256 structures were obtained and the minimum

energy structure was determined by comparison of the potential energies. Three building blocks with the minimum energy conformation were connected via imino bonds and the dihedral angles at these connections were changed between $-180°$ and $180°$ in five steps, $72°$ each. From the energies of the resulting 36 structures, the minimum energy conformer could be determined and was again optimized by MM3.

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