Polymerization of acrylate monomers with MAO activated iron(II) and cobalt(II) complexes bearing tri- and tetradentate nitrogen ligands

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Abstract

Octahedral iron(II) and cobalt(II) based complexes, \([N,N'-\text{di}(\text{quinoline-2-methylene})-1,2-\text{phenylenediimine}]\text{MCl}_2\), and \([N,N'-\text{di}(\text{quinoline-2-methylene})\text{diiminocyclohexane}]\text{MCl}_2\) (M = Co and Fe), bearing tetradentate diimino nitrogen ligands were prepared and used in tert-butylacrylate (t-BA) polymerization after activation with methylaluminoxane (MAO). In general, polyacrylates with high molar mass and narrow molar mass distribution (MMD ≈ 2) were obtained. In order to understand the influence of the ligand on the polymerization process, polymerization behaviour of the hexacoordinated complexes was compared to pentacoordinated iron(II) and cobalt(II) complexes, 2,6-bis[1-(cyclohexylimido)ethyl]pyridine \(\text{MCl}_2\) (M = Co and Fe), bearing tridentate diimine nitrogen ligands as well as to free iron(II) chloride. The ability of the MAO activated hexacoordinated complexes to polymerize methylacrylate (MA) and methyl methacrylate (MMA) was also considered, but reduced activities as well as lower molar mass polymers were obtained than in the experiments with t-BA.

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1. Introduction

Highly active late transition metal catalysts for ethene polymerization were introduced almost a decade ago [1–7]. Essential to the catalyst development was the application of ligand frameworks containing unsaturated imino donor functionalities and the most successful examples include \(\pi\)-diimines (Ni,Pd) [8,9], bis(imino)pyridines (Fe,Co) [1,2] and phenolate–imines (Ni) [10,11]. Depending on the chosen catalyst precursor, the produced polyethylene materials vary from linear \(\pi\)-olefins [12] to high molar mass polymers [13], which microstructure can range from linear to highly branched...
For the polymerization of linear polyethylene after activation of the imine position give highly active catalysts [2,6-bis(imino)pyridyl ligands with bulky aryl substituents.](8,9,14,15). The lower oxophilicity and presumed better tolerance towards functional groups of these late transition metal catalysts compared to early transition metal ones make them attractive candidates when metal complex assisted polymerization of polar monomers is looked for.

Polymerization of acrylates is classically carried out using either anionic [16,17], radical [18–21] or group transfer polymerization (GTP) [22,23], but recently late transition metal complex based polymerization methods, including ATRP (atom transfer radical polymerization) [18,19] and MAO activated metal complexes, have been also developed, for example, for acrylates [24–27]. Although the actual mechanism for MAO activated late transition metal complex assisted polymerization of acrylate monomers is still unclear (ionic, coordination or radical), the advantage of those systems is that they function under mild polymerization conditions with low metal complex concentrations, and the produced polymers exhibit substantial high molar masses (above 1000 kg/mol) with controlled molar mass distributions (MMD ≈ 2). As an augmentation to previously studied palladium(II) [28], iron(II) and cobalt(II) [29] complexes bearing tetradentate nitrogen ligands, we report herein a series of octahedral iron(II) and cobalt(II) complexes. After MAO activation, the complexes were examined in the polymerization of tert-butylacrylate (t-BA) as well as in the polymerization of methylacrylate (MA) and methyl methacrylate (MMA). In order to understand the ligand influence, the polymerization properties of the above mentioned MAO activated iron(II) and cobalt(II) complexes were compared to the pentacoordinated iron(II) and cobalt(II) complexes bearing tridentate nitrogen ligands as well as to free iron(II) chloride.

2. Experimental section

2.1. General

All syntheses and experiments were performed under argon atmosphere using standard Schlenk techniques. Solvents (HPLC grade) were dried over sodium flakes and distilled before use. t-BA, MA and MMA were purchased from Fluka and used without further purification. MAO (30% in toluene) was received from Borealis Polymers and MAO (10% in toluene) was supplied from Eurecene. Other reagents were purchased from commercial sources with high purity grade and used as received. Anhydrous iron(II) chloride (FeCl₂) and cobalt(II) chloride (CoCl₂) were stored under argon atmosphere.

NMR spectra were recorded in CDCl₃ at 25 °C on a Varian Gemini 200 spectrometer operating at 200 MHz (¹H NMR) and 50 MHz (¹³C NMR). The ¹³C NMR of the polymers were collected in CDCl₃, at room temperature or at 60 °C with a Varian 300 NMR spectrometer at 75 MHz with 10 mm probe. The chemical shifts of ¹H NMR spectra were referenced to the residual proton signal of the solvent (δ = 7.27 ppm for CDCl₃); the carbon resonances in ¹³C NMR spectra were referred to the solvent signal (δ = 77.23 ppm for CDCl₃).

Mass spectra of ligand a was recorded with a JEOL JMS-SX102 EI⁺ instrument, using direct inlet system and electron impact ionization (70 eV). Mass spectra of complexes 2–4 were recorded with a Mariner electrospray ionization MS (ESI-MS). Mass spectra of complex 1 was measured with a Bruker Micro TOF esquire 3000Plus and FAB analysis of complex 6 was performed on a Finnigan MAT TSQ 7000 at University of Ulm, Germany. Elemental analyses were performed with EA 1110 CHNS-O CE instrument.

Monomer conversion was determined by gas chromatography (GC) using decane as the internal standard. Molar masses and molar mass distributions were determined with a Waters 515 HPLC pumpGPC with Styrage columns HR2, HR4 and HR6 having a UV detector Waters 2487 and a refractive index detector Waters 2410, in THF at 35 °C using polystyrene standards. DSC measurements were performed on a Mettler Toledo Star system at a heating rate 25 °C/min under nitrogen atmosphere. After the first heating up to 100 °C to eliminate thermal history, a sample was cooled to the starting temperature –10 °C and the second heating was run immediately. The midpoint of the heat capacity transition of the second heating was taken as Tg.

2.2. Synthesis of ligands

The synthesis of (1R,2R)-(−)-N,N’-di(quinoline-2-methylene)diiminocyclohexane for complexes 3 and 4 [30] and 2,6-bis[1-(cyclohexylimino)ethyl]pyridine for complexes 5 and 6 has been reported earlier by us [24].

2.2.1. N,N’-Di(quinoline-2-methylene)-1,2-phenylenediamine (a)

To a solution of 2-quinolinocarboxaldehyde (2.56 g, 16.3 mmol) in EtOH was added a solution of 1,2-phenylene diamine (0.84 g, 7.8 mmol) in EtOH and stirred for 1 1/2 h. The raw product was then filtered off and washed with EtOH and petroleum ether. After recrystallization from EtOH the product was dissolved in toluene and refluxed for 2 h. The solvent was evaporated and the resulting yellow product was dried in vacuum at 90 °C. Yield: 1.58 g, 53%; EI-MS: M(C₂₆H₁₈N₄)= 386, M⁺.
2.3. Synthesis of complexes

All the complexes were prepared in an analogous manner. When iron(II) or cobalt(II) chloride was added to a solution of ligand a rapid color change indicated the occurrence of a reaction. Stirring was continued at least for 24 h after which solids were filtered off, washed and dried in vacuum. 2,6-Bis[1-(cyclohexylimino)ethyl]pyridine iron(II) dichloride has been prepared earlier by us [24].

2.3.1. Dichloro{N,N’-di(quinoline-2-methylene)-1,2-phenylenediamine}iron(II) (1)

To a stirred solution of ligand a (0.60 g, 1.55 mmol) in CH₂Cl₂ (40 mL) was added a solution of iron(II) chloride (0.188 g, 1.45 mmol) in EtOH (20 mL). Stirring was continued for 48 h at room temperature. The solvent was evaporated and CH₂Cl₂ (30 mL) was added. The green product was filtered off and washed first with CH₂Cl₂ and then with Et₂O and dried in vacuum. Yield: 0.20 g, 28%; EA: Found: C, 60.74%; H, 3.48%; N, 11.24%; Calculated: C, 60.85%; H, 3.53%; N, 11.01%; Micro-TOF MS: 477 [M⁺] Cl, 14%; 387 [M⁺] Cl⁻ FeCl₂ 100%, [M⁺]⁻ C₁₀H₇NFeCl₂ 10%.

2.3.2. Dichloro{N,N’-di(quinoline-2-methylene)-1,2-phenylenediamine}cobalt(II) (2)

To a stirred solution of ligand a (0.60 g, 1.55 mmol) in CH₂Cl₂ (20 mL) was added a solution of cobalt(II) chloride (0.18 g, 1.40 mmol) in EtOH (20 mL). Stirring was continued for 24 h at room temperature. The brown product was filtered off and washed first with CH₂Cl₂ and then with Et₂O and dried in vacuum. Yield: 0.68 g, 95%; EA: Found: C, 59.98%; H, 4.01%; N, 10.35%; Calculated: C, 60.49%; H, 3.51%; N, 10.85%; ESI-MS: 517 [M⁺] Cl, 98%; 389 [M⁺] Cl⁻ Cl⁻ 100%, [M⁺]⁻ C₁₇₆NFeCl₂ 80%.

2.3.3. Dichloro{N,N’-di(quinoline-2-methylene)dianiminocyclohexane}iron(II) (3)

Solid iron(II) chloride (0.146 g, 1.2 mmol) was added to a stirred solution of (1R,2R)(−)-N,N’-di(quinoline-2-methylene)dianiminocyclohexane [30] (0.544 g, 1.4 mmol) in THF (30 mL). Stirring was continued for 48 h. The resulting dark green product was filtered off and washed first with THF and then with Et₂O, then dried in vacuum. Yield: 0.54 g, 87%; EA: Found: C, 59.98%; H, 5.15%; N, 10.62%; Calculated: C, 60.14%; H, 4.66%; N, 10.79%; ESI-MS: 520 [M⁺] H, 88%; [M⁺]⁻ Cl⁻ 18%; [M⁺]⁻ FeCl₂, 100%.

2.3.4. Dichloro{N,N’-di(quinoline-2-methylene)dianiminocyclohexane}cobalt(II) (4)

To a stirred solution of cobalt(II) chloride (0.156 g, 1.2 mmol) in EtOH (30 mL) was added a solution of (1R,2R)(−)-N,N’-di(quinoline-2-methylene)dianiminocyclohexane [30] (0.544 g, 1.4 mmol) in EtOH (20 mL). Stirring was continued for 24 h. The product was filtered off, washed first with EtOH and then with petroleum ether, then dried in vacuum. 10 mL of CH₂Cl₂ was added to dissolve the impurities and the mixture was stirred for 10 min. The brown product was filtered and washed with Et₂O and dried in vacuum. Yield: 0.248 g, 40%; EA: Found: C, 59.39%; H, 4.54%; N, 10.30%; Calculated: C, 59.79%; H, 4.63%; N, 10.73%; ESI-MS: 523 [M⁺]Cl, 100%; [M⁺]⁻ Cl⁻ 95%; [M⁺]⁻ CoCl₂ 72%.

2.3.5. 2,6-Bis[1-(cyclohexylimido)ethyl]pyridine CoCl₂ (6)

Cobalt(II) dichloride (0.188 g, 1.45 mmol) was added to a stirred solution of 2,6-bis[1-(cyclohexylimido)ethyl]pyridine [24] (0.5 g, 1.50 mmol) in THF (20 mL). The stirring was continued for 24 h. Et₂O (30 mL) was added to precipitate the green complex, which was filtered off and washed with Et₂O, then dried in vacuum. Yield: 0.61 g, 91%; EA: Found: C, 54.71%; H, 6.74%; N, 9.05%; Calculated: C, 55.47%; H, 6.87%; N, 9.24%; FAB-MS: 454 [M⁺], 8%; [M⁺]⁻ Cl⁻ 98%; [M⁺]⁻ Cl⁻ CoCl₂ 15%, [M⁺]⁻ CoCl₂ 4%.

2.4. Polymerization experiments

In a typical polymerization experiment, 2.0 μmol of the complex was dissolved in toluene (1.6–5.5 mL) and MAO was added. In the bulk polymerization (6.4 M monomer concentration) no solvent was used. After a short initiation time monomer was added. The polymerization reaction was terminated by addition of hexane, methanol and 10% HCl. The polymer was then dissolved in THF. Water was added and organic solvents were evaporated under reduced pressure. Polymers were collected and placed in water for 24 h to remove the acid and dried at 65 °C until a constant weight was observed.

Monomer conversion was determined by gas chromatography (GC) using decane as the internal standard. Samples (0.1 mL) were taken from the reaction mixture with a syringe, diluted with 6 mL of THF and filtered through Al₂O₃ to remove MAO, metal complex and polymer.

3. Results and discussion

3.1. Ligands and complexes

N,N’-Di(quinoline-2-methylene)-1,2-phenylenediamine (a) was prepared from 2-quinolinecarboxaldehyde.
and 1,2-diphenylene diamine as presented in Scheme 1. Other ligands in the work, (1\(R\),2\(R\))-(−)-N,N′-bis(quinoline-2-methylene)-1,2-cyclohexane diamine \(^{[30]}\) and 2,6-bis[1-(cyclohexylimino)ethyl]pyridine \(^{[24]}\), were prepared according to the previously published synthetic routes.

Iron and cobalt complexes 1–4 and 6 were synthesized from the corresponding ligand and metal dichloride while the synthesis of 5 has been published before \(^{[24]}\). The complexes were prepared either in THF or EtOH by mixing a ligand and metal dichloride, after which the desired complex precipitated. Therefore, the complex syntheses were straightforward to carry out and the isolated yields were high. The isolated complexes were microcrystalline or powder-like material, but despite of our efforts single-crystals suitable for the X-ray structure determination were not obtained. Due to the paramagnetic nature of all the studied iron(II) and cobalt(II) complexes NMR characterization turned out to be ambiguous.

3.1.1. \(\text{t-BA}\) polymerization

After activation with MAO, complexes 1–6 revealed to be active in the polymerization of acrylates. The intention of this study was to find out how the ligand structure can influence on the complex capability to assist polymerization of acrylates. Therefore iron and cobalt complexes 1–4 with tetradentate, 5 and 6 with tridentate ligands were chosen for the polymerization experiments (Scheme 1). Monomer conversion was followed by gas chromatography (GC) during the first 2 h, after which gelification of the reaction medium complicated further GC analysis.

As shown in Fig. 1 polymerization proceeds very fast in the beginning of the polymerization, and ligands markedly affect the polymerization activity. Especially,
in the beginning of the polymerization complexes 5 and 6 bearing the tridentate ligand gave higher activity than those with tetradentate ligands. The observed variations in the initial polymerization activities can be related to the structure of the complexes; in solid state iron(II) complexes with tetradentate ligands prefer octahedral coordination sphere [29,31], while the structural fluctuation between a square pyramidal and trigonal bipyramidal geometries has been reported for the tridentate complexes [13]. After a certain polymerization time the differences in initial activities e.g. within iron complexes are equalized. This is presumably due to presence of similar dormant and active species, which equilibrium is actually determining the average polymerization activity.

Besides the ligand also the metal has an influence on the acrylate polymerization. MAO activated cobalt complexes had lower activity than corresponding iron complexes. The GPC analysis revealed that iron(II) complexes produce higher molar masses than corresponding cobalt(II) complexes. In all cases molar mass distribution was close to 2 (Table 1, entries 1–5). The available data does not facilitate an unambiguous explanation for the low activities of cobalt(II) complexes, but similar effect is known in the polymerization of olefins [1,2,14,15]. It is reasonable to assume that the different configuration of d-electrons or activation processes [32,33] of Co-complexes are accountable for the observed phenomenon.

The control polymerizations with FeCl₂ and CoCl₂ alone gave no polymer, while MAO activated iron(II) chloride was able to form an active combination but that showed a significantly lower activity than MAO activated complexes 1, 3 and 5 (Fig. 1). However, under the polymerization conditions used FeCl₂/MAO produced polymers with the highest molar mass. MAO alone is also able to polymerize t-BA [34] and in our study a relatively high initial activity, which decays dramatically during the first 20 min was observed. Under the applied conditions MAO produced low molar mass polymer with broad MMD clearly indicating multi-centre behaviour (Table 1, entry 6). To conclude, the presence of both MAO and metal complex is needed here for an efficient and controlled polymerization of t-BA.

Monomer concentration has an essential influence on the polymerization activity as well as on the molar mass of the polymers; the polymerization reaction is linearly enhanced with increasing monomer concentration (Table 2). When the monomer concentration was increased to 6.4 M (bulk) the highest molar masses produced were 1900 kg/mol while with low monomer concentration molar masses as low as 10 kg/mol were obtained.

Polymerizations with octahedral iron and cobalt based complexes 3 and 4 were carried out also at different temperatures. For the both complexes activity grew as the temperature increased but resulted in decreased molar mass at some point between 40 and 60 °C. This decrease in molar mass is induced by increase of the reaction temperature which, in turn, probably results in a decrease of the propagation/chain transfer ratio. As this rise of polymerization temperature had no effect on MMD, the decrease of molar mass is due to changes in chain termination rates rather than in thermal decomposition of the metal species.

Various stereospecific polymerizations using Ziegler–Natta [35], metalloocene [36], radical [37] or anionic polymerization [23,38,39] have been reported earlier and highly isotactic poly(t-BA) has been synthesized using a chiral zirconocene ([(m) diad 83%] [36] or with n-BuLi in the presence of LiOH ([(m) diad 85%] [40]. The highest syndiotactic diad value reported is \([r] = 63\%\) for poly(t-BA) prepared by radical polymerization at low temperature [41] and a triad syndiotacticity \([rr]\) of about 40% has been reported for anionic polymerization of t-BA with diphenylmethyllithium, -potassium or -cesium initiators [42]. Due to the \(\alpha\)-methyl group in MMA higher syndiotacticity values are reached than with t-BA [43,44]. For example, Yasuda has reported on the rare-earth-metal initiated living polymerization of MMA giving syndiotacticity over 95% and Chen et al. have published the polymerization of syndiotactic \([rr] = 82\%\) PMMA with titanium alkyl and enolate complexes [43,44].

Polymers prepared with 1–4/MAO were studied by \(^{13}\)C NMR spectroscopy and as a summary these polymers are syndiorich atactic material with \([r]\) around

### Table 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
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<th>Conversion (%)</th>
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Conditions: \(n_{(cat)} = 2\ \mu\text{mol}, \text{MAO:complex} = 250:1,\) in toluene at room temperature, polymerization time 130 min (entries 1–4, 6) 135 min (entry 5).
The $r$ value is not dependent on the monomer concentration and even the chiral ligand framework of complexes 3 and 4 had no influence on the polymer microstructure (Table 3). Furthermore, $^{13}$C NMR studies revealed that variation in the polymerization temperature had no significant influence on the microstructure of the poly($t$-BA) if the polymerizations were carried out above 0°C. But lowering the temperature to −78°C increased the $[rr]$ triads indicating the emergence of chain end control (Fig. 2). A similar effect was observed in the MAO activated iron dichloride mediated polymerization.

Glass transition temperatures ($T_g$) of the polymers ranged from 40 to 50°C, and a few low or high values were detected. Anyhow, no clear trend between the glass transition temperature and tacticity of poly($t$-BA) could be detected, because all obtained polymers had a similar tacticity but different $T_g$ [37].

The mechanism for these transition metal assisted polymerizations is ambiguous. Earlier the inhibition of polymerization by galvinoxyl was used as a diagnostic for radical polymerizations [45,46], but because of its high reactivity, it is possible that this radical scavenger reacts and deactivates metal based systems via coordination [47]. Recently, it was reported that in the presence of MAO, radical traps such as galvinoxyl may fail to inhibit radical reactions [48]. In our experiments the presence of galvinoxyl lowered considerably the yield and molar mass of the produced polymer. For example, complex 3 in the 3.0 M monomer concentration

### Table 2

Results of $t$-BA polymerization at different monomer concentrations

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<th>Entry</th>
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Conditions: $n$(cat) = 2 μmol, MAO:complex = 250:1, in toluene at room temperature, polymerization time 24 h.

### Table 3

Selected NMR results of poly($t$-BA)

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<td>RT</td>
<td>21</td>
<td>47</td>
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<td>FeCl₃</td>
<td>RT</td>
<td>38</td>
<td>42</td>
<td>20</td>
</tr>
</tbody>
</table>

Conditions: $n$(cat) = 2 μmol, MAO:complex = 250:1, in toluene, polymerization time 12 h.

*a Observed in $^{13}$C NMR spectra.

40%. The $[r]$ value is not dependent on the monomer concentration and even the chiral ligand framework of complexes 3 and 4 had no influence on the polymer microstructure (Table 3). Furthermore, $^{13}$C NMR studies revealed that variation in the polymerization temperature had no significant influence on the microstructure of the poly($t$-BA) if the polymerizations were carried out above 0°C. But lowering the temperature to −78°C increased the $[rr]$ triads indicating the emergence of chain end control (Fig. 2). A similar effect was observed in the MAO activated iron dichloride mediated polymerization.
Polymerization produced only 0.07 g (3%) polymer with molar mass 7 kg/mol and MMD 1.62 in presence of galvinoxyl. Complex 4 under the same conditions produced 0.28 g (11%) polymer with molar mass 14 kg/mol and MMD 1.92. The analogous polymerizations without galvinoxyl resulted in polymers with molar mass 362 kg/mol and MMD 2.28 (complex 3) and 224 kg/mol and 2.61 (complex 4).

3.2. MA and MMA

The polymerizations of MA and MMA were carried out with 1/MAO, 2/MAO and 3/MAO at room temperature. In all experiments conversions remained low (Table 4). The obtained molar masses of poly(MA) and poly(MMA) were substantially low, varying from 15 to 41 kg/mol and from 2 to 4 kg/mol, respectively, with rather narrow MMD from 1.30 to 3.20. Ethylbridged tetradeutate nitrogen ligands with iron(II) and cobalt(II) chloride have been studied earlier in ATRP experiments [49]. These complexes gave rather similar molar masses and molar mass distributions under ATRP conditions with methyl methacrylate as the MAO treated complexes in this study.

4. Conclusion

In the polymerization of t-BA the activity and the molar masses of polymers are clearly influenced by the...
ligand structure and the choice of the metal centre. It was also seen in the study that in the beginning of the polymerization iron(II) complex 5 bearing the tridentate ligand was the most active, but rapidly the activity was decreased and after an hour the activity reached a constant value. Iron complexes showed higher activities in the beginning of the polymerization than their cobalt analogues and five coordinated complexes were more active than six coordinated complexes within the same metal centre. When MAO activated iron dichloride was used in the polymerization on t-BA low but constant activity was observed. In addition, the iron(II) and cobalt(II) complexes bearing tetradentate nitrogen ligands are able to polymerize other acrylates, that is MA and MMA, besides t-BA.

Furthermore, it was shown that by changing the polymerization conditions different polymer material could be prepared. When a low monomer concentration was used, a low molar mass polymer was observed. An increase in the monomer concentration raised the molar mass of the polymer and the activity was increased, too. Raising the polymerization temperature above 40 °C the activity increased and the molar mass decreased, but molar mass distribution was centred on two in all experiments indicating the presence of uniform centres of the polymer growth. According to 13C NMR, all complexes produced similar polymer microstructure regardless of the chirality of the bridge. The only differences arose when the polymerization temperature was lowered to −78 °C or when iron(II) chloride was used. In these experiments r diad content was doubled indicating a possibility for a chain end control at the applied conditions.

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