Polymerization of Acrylate Monomers by Iron(II) Complexes Bearing Bis(imido)pyridyl or Phosphine Ligands

*Pascal M. Castro, Mikko P. Lankinen, Anne-Marja Uusitalo, Markku Leskelä, Timo Repo**

Department of Chemistry, Laboratory of Inorganic Chemistry, PO Box 55, FIN-00014, University of Helsinki, Finland
E-mail: timo.repo@helsinki.fi

Summary: Iron(II) complexes bearing bis(imido)pyridyl or phosphine ligand were used for the polymerization of *tert*-butylacrylate and other (meth)acrylates after activation with methylaluminoxane. Phosphine based catalysts turned to be more active than the bis(imido)pyridyl ones. *tert*-Butylacrylate was the best polymerized monomer, while methylmethacrylate was slowly converted to poly(methylmethacrylate) and no activity was observed in the polymerization of styrene. Influence of the MAO to complex ratio was investigated and kinetics studies were conducted. Based on these results, a schematic representation of the polymerization mechanism was proposed.

Keywords: acrylate monomers; bis(imido)pyridyl ligand; methylaluminoxane; organometallic catalysts; phosphine ligand; transition metal chemistry

Introduction

(Meth)Acrylate polymers are easily formed via anionic or radical polymerization. Nevertheless, control of the polymerization (*e.g.* molar mass or polydispersity) requires specific conditions, for instance low temperature (anionic)[1] or dioxygen-free atmosphere (controlled radical).[2] Therefore, an interesting challenge in acrylate polymerization is to introduce catalytic control as it is known for transition metal catalyzed olefin polymerization. This would facilitate the use of mild reaction conditions and the control of the polymerization in terms of molar mass, polydispersity or stereostructure.

The recent development of late transition metal catalysts[3] opens interesting possibilities for this purpose, since late transition metals are less oxophilic than early transition metals, and are therefore supposed to be more tolerant towards Lewis bases. A wide variety of late

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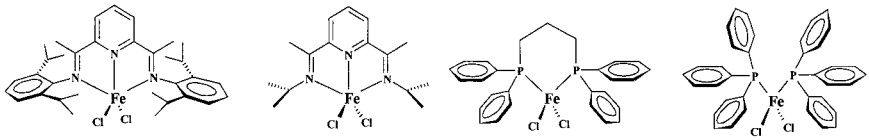
transition metal complexes are currently used for radical polymerization through atom transfer radical polymerization (ATRP),[4,5] and palladium(II) complexes[6] or organonickel/methylaluminoxane[7-9] systems are reported to homopolymerize methyl(meth)acrylate. Recently, iron(II) complexes bearing tridentate nitrogen ligands proved to be active for the polymerization of *tert*-butylacrylate after activation with methylaluminoxane (MAO). The activity of the catalyst and the molar mass of the polymer are clearly influenced by the ligand structure and the polymerization conditions.[10]

In the present work, polymerization kinetics of *tert*-butylacrylate and other (meth)acrylate monomers were investigated with the above mentioned iron(II) catalysts bearing bis(imido)pyridyl ligands, and a new polymerization system based on iron(II) complexes bearing phophine ligands (Figure 1). Phosphine based catalysts turned out to be more active for the polymerization of acrylates than the bis(imido)pyridyl ones, despite that the polymerization behaves similarly in both cases.



1 2 3 4

Figure 1. Complex chart.

Experimental

All the solvents were dried over sodium and purified by distillation prior to use. All other chemicals were used as received. MAO (30% in toluene) was received from Borealis Polymers Ltd. Polymerizations of *tert*-butylacrylate were carried out under argon atmosphere at room temperature in a Schlenk tube with standard Schlenk techniques, as described earlier in the literature.[10] Monomer conversion was determined by gas chromatography using *n*-decane as the internal standard. Molecular weights and molecular weight distributions were measured at 40°C in THF, by gel permeation chromatography relative to polystyrene standards using a Waters 515 HPLC pump GPC fitted with Styragel columns HR 2, HR 4, and HR 6, a UV-detector Waters 2487 and a RI-detector Waters 2410.

Four different complexes were used for this study. 2,6-bis[1-(2,6-bis(isopropyl)phenyl)imido)ethyl]pyridine iron dichloride (**1**)[10] and 2,6-bis[1-(isopropylimido)ethyl]pyridine iron dichloride (**2**)[11] complexes were synthesized according to published procedures. Bis(triphenylphosphine) iron dichloride (**3**) and 1,3-bis(diphenylphosphino)propane iron dichloride (**4**) were prepared via a straightforward synthesis.[12]

Results and Discussion

Activity

Batch polymerizations of *tert*-butylacrylate (tBA) were carried out with complexes **1**-**4** after activation with MAO, and monomer consumption was monitored by gas chromatography (Figure 2). The difference in activity observed between the bis(imido)pyridyl iron(II) catalysts **1**/MAO and **2**/MAO was attributed to the variation of steric hindrance around the metal, as bulky 2,6-bis(isopropyl)anilino substituents present on **1** prevent the access of tBA monomers to the reactive center.[10] Similarly, the difference between **3**/MAO and **4**/MAO can be explained by the distinct bridged (**3**) and unbridged (**4**) phosphine ligands: the 1,3-bis(diphenylphosphino)propane ligand markedly displays a more constrained coordination sphere than the unbridged bis(triphenylphosphine).[13] Anyhow, the definitive reason why **4**/MAO gives a higher activity than **3**/MAO remains open.

The phosphine based iron(II) catalysts **3**/MAO and **4**/MAO turned out to be more active than the bis(imido)pyridyl based ones, **1**/MAO and **2**/MAO. Firstly, one can ascribe these observations to the steric hindrance around the active center and to the rigidity of the ligand backbone, as discussed above. Secondly, the different influence from the bis(imido)pyridyl and the phosphine ligands on the electron density of the iron center have to be taken in account. Lastly, the distinct coordination sphere of complexes **1**-**2** and **3**-**4** can eventually affect the reactivity of iron towards tBA, as the four-coordinated complexes **3**-**4** would have a stronger tendency to expand their coordination number than the five-coordinated complexes **1**-**2**.

The time-conversion logarithmic plots presented in Figure 2/left show an apparent first-order kinetic for all the catalysts. Nevertheless, a deviation from linearity after a certain period of

time indicates that the amount of active species does not remain constant during the polymerization. The same data plotted as catalyst activity (kg of polymer / mol of catalyst / h) *vs.* time gives more information (Figure 2, right). It illustrates that the activation of the complexes is very fast without any induction period. High initial polymerization activities are measured, but then decline with time, reaching lower steady state values.

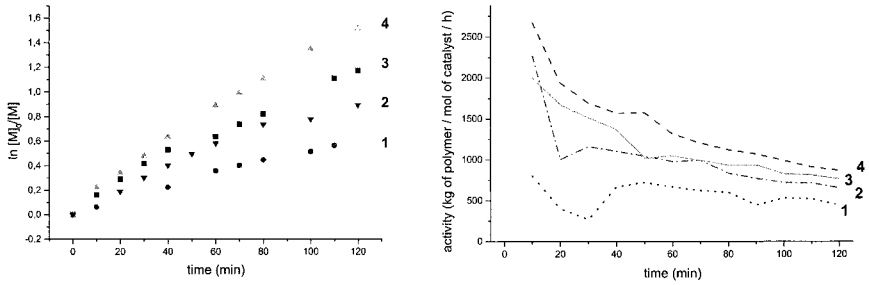


Figure 2. Time-conversion logarithmic plot (left) and activity dependence on time (right) for the polymerization of tBA with **1-4**/MAO. Conditions: [complex] = $6{,}33 \cdot 10^{-5}$ mol/L, [tBA] = 1,1 mol/L, MAO : complex = 250:1, in THF at room temperature.

We assume that the reason for this reduction of activity is twofold. As reported earlier, the activity of iron catalysts in tBA polymerization is depending on the monomer concentration,[10] and in batch polymerization, this monomer concentration gradually decreases. Since both the rate of declination and steady state value depend on the catalyst precursor (Figure 2, right), the observed changes can be related to the activation process itself. After fast activation the active species undergo a series of reversible and irreversible reactions involving e.g. condensation reactions with MAO and, at the steady state, the polymerization process is dominated by a sensitive equilibrium between active and dormant metal centers (i.e. catalytically inactive iron species), as described earlier for metallocene catalysts.[14, 15] A simple decay of the catalysts would rather show a slow death of the polymerization activities instead of the observed steady state polymerization kinetics.

Molar Mass

In order to verify the nature of the polymerization, the time dependence of molar mass was

investigated (Figure 3). Surprisingly, the higher M_n value was attained at the beginning of the polymerization (after only two minutes with **2**/MAO), and then it is gradually decreased. This is in agreement with previously published results where M_n dependence on monomer concentration was demonstrated.[10] Hence, the decrease of molar mass with time is due to the consumption of tBA, leading to a decrease of its concentration. Accordingly, it means that each polymer chain is formed instantaneously, and that every catalyst molecule produces several ones. This is corroborated by the calculation of the catalyst efficiency after two hours ($f = M_{n(obs)}/M_{n(calc)}$) which gives $f_{(2/MAO)}$= 0,0126 and $f_{(4/MAO)}$= 0,0085. In other words, it signifies that every single molecule of **2**/MAO and **4**/MAO produces 79 and 117 poly(tBA) chains, respectively. In addition, the polydispersity index (PDI) remained constant in each case. These facts definitely rule out any sort of living character for the studied system.

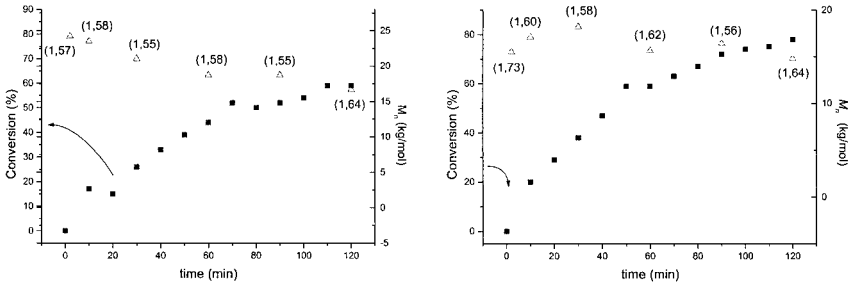


Figure 3. M_n and Conversion (%) *vs.* time for the polymerization of tBA with **2**/MAO (left) and **4**/MAO (right). The polydispersity index is given between the brackets. Conditions: [complex] = $6{,}33 \cdot 10^{-5}$ mol/L, [tBA] = 1,1 mol/L, MAO : complex = 250:1, in THF at room temperature.

Influence of MAO

The cocatalyst MAO is an important component of the catalytic system as it converts the iron dichloride precursor into a cationic species presumably responsible for the catalytic activity.[16, 17] The concentration of cocatalyst, and furthermore its ratio to the complex, will necessarily have an influence on the polymerization behavior like any other component of the polymerization system. The polymerization of tBA with **2** and different amount of MAO revealed a linear relationship between the MAO to complex ratio and both the molar mass of

the obtained poly(tBA) and the activity of the catalyst (Figure 4). The rise of activity is to be related to the augmentation of the presence of alkylaluminum species in the media, which is able to re-activate the dormant centers and shift the equilibrium towards active iron species, thus accelerating the polymerization of tBA. The decrease of the molar mass indicates the presence of chain transfer to aluminum as a chain termination mechanism. Similar results were reported for ethylene polymerization with **1**/MAO.[11]

It is important to notice that, due to its Lewis acidic nature, MAO has a strong tendency to coordinate to polar monomers like acrylates. In the polymerizations presented here, a high monomer to MAO ratio (typically 70 to 1) guarantees the presence of free monomers in solution, and that MAO does not have a significant role as a protecting group.

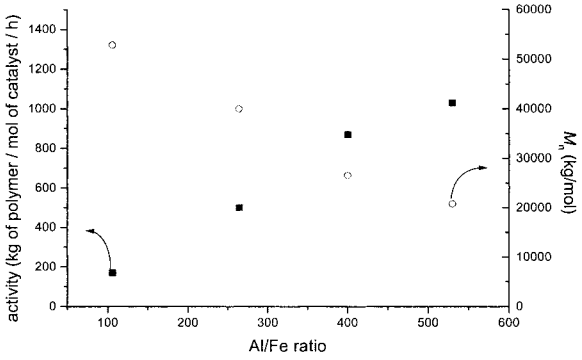


Figure 4. Activity and M_n dependence on the MAO to complex ratio for the polymerization of tBA with **2**/MAO. Conditions: [complex] = $6{,}33 \cdot 10^{-5}$ mol/L, [tBA] = 2,3 mol/L, in THF at room temperature.

Polymerization of different monomers with complex 4

The polymerization of methylacrylate (MA), *n*-butylacrylate (nBA), methyl methacrylate (MMA) and styrene (St) was carried out using **4**/MAO and compared with tBA polymerization (Figure 5). The highest activity is achieved with the bulky tBA, while MA and nBA are polymerized both with a similar conversion rate, and MMA bearing a methyl group at its α –position, is slowly converted to poly(MMA) by **4**/MAO. Nevertheless, this latter result has to be examined in relation to a recently published study by Carlini *et al.* about the

polymerization of MMA with MAO activated nickel(II) complexes.[9] The best activity obtained was 155 kg of PMMA / (mol of catalyst x h) with 32% conversion, while **4**/MAO gives 86,8 kg of PMMA / (mol of catalyst x h) after two hours. In the case of tBA, 29% of monomer consumption corresponds to an activity of 1937 kg of tBA / (mol of catalyst x h) (Figure 2, right). No activity was observed when styrene was employed as the monomer. Similar results were obtained with **2**/MAO.[18]

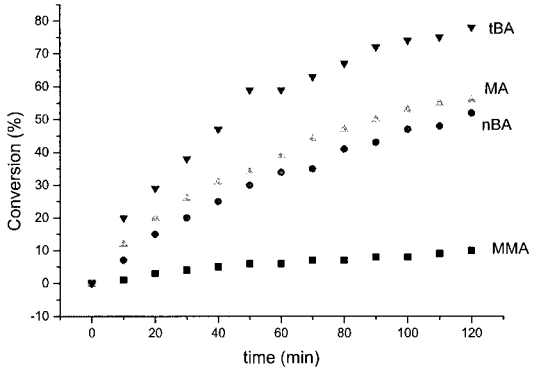
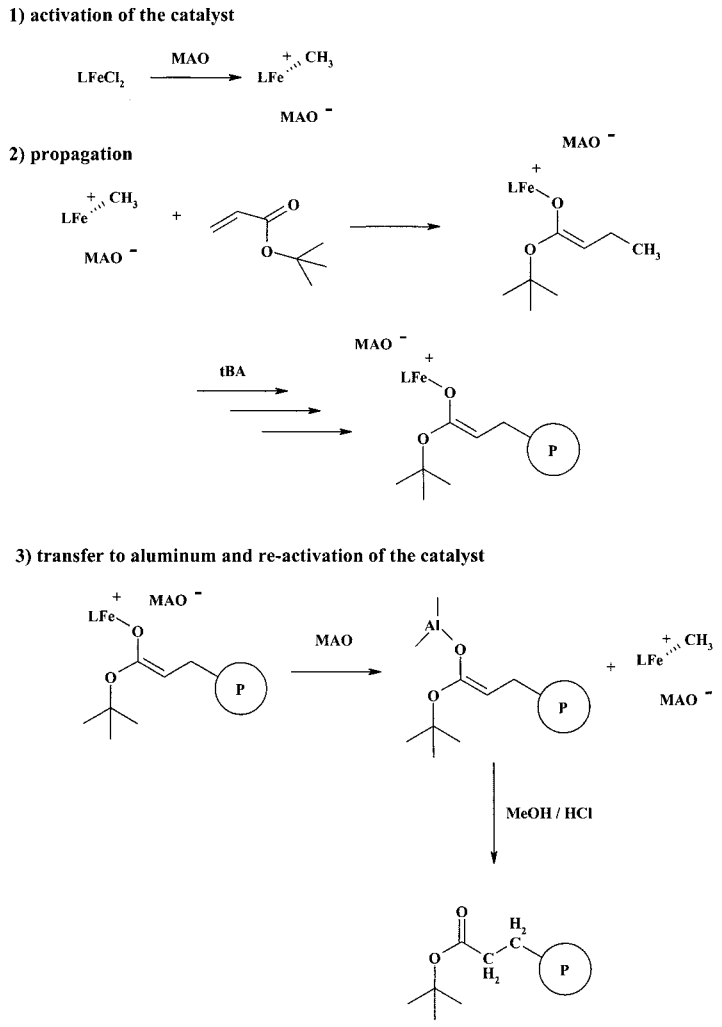


Figure 5. Conversion (%) *vs.* time for the polymerization of various (meth)acrylates with **2**/MAO. Conditions: [complex] = $6{,}33 \cdot 10^{-5}$ mol/L, [monomer] = 1,1 mol/L, MAO : complex = 250:1, in THF at room temperature.

Schematic Representation of the Mechanism

The presence of activated iron complexes is required for an efficient polymerization of acrylates, as both iron(II) complexes and MAO alone do not promote the polymerization of tBA.[10] Similar observations were also reported about nickel(II) complexes for MMA polymerization.[7, 9] MAO reacts with bis(imido)pyridyl iron(II) complexes to form a cationic Fe^{+}-Me species,[16, 17] and consequently, these cationic species are responsible for the polymerization (Scheme 1, step 1). This assertion is supported by Figure 3 which shows that the activity increases with the amount of aluminum present in the reaction mixture.

The propagation mechanism is not clarified yet. Radical polymerization was ruled out for both iron(II)[10] and nickel(II)[9] systems. After activation of the iron complex, two different



Scheme 1. Schematic representation of the polymerization mechanism. L represents the different ligands for complexes **1-4**.

phenomena can occur: methyl transfer from iron to monomer at the β –position (anionic like polymerization), or coordination of tBA to the iron followed by 2,1-insertion into the iron-methyl bond (coordination-insertion mechanism) (Scheme 1, step 2). Nevertheless, the moderate activity observed in the case of MMA polymerization and the absence of activity

for styrene polymerization, which is easily polymerized by both radical or ionic pathway, strengthens the idea of a coordination-insertion mechanism. Molar mass is clearly influenced by the MAO to catalyst ratio (Figure 3), which suggests chain transfer to aluminum as the dominating termination process (Scheme 1, step 3). Furthermore, Figure 4 strongly suggests the instantaneous formation of polymer chains, followed by chain transfer to aluminum and reactivation of the iron catalyst into the cationic Fe^{+}-Me species able to start a new chain.
The mechanism proposed in Scheme 1 is only a schematic representation of how the polymerization occurs, as the intimate propagation mechanism (Scheme 1, step 2) remains unclear.

Conclusion

The polymerization of *tert*-butylacrylate (tBA) was carried out using different MAO activated iron(II) complexes and consumption of the monomer was followed as a function of time. After high initial activity the polymerization capability of the catalysts declines to lower steady state values. The phosphine based iron(II) catalysts turned out to be more active than the bis(imido)pyridyl iron(II) ones. Polymerization is more efficient with acrylates, among them tBA, than with methylmethacrylate, while styrene is not polymerized.
The fact that the molar mass does not increase with time indicates that each polymer chain is formed instantaneously, and that every catalyst molecule produces several chains. The decrease of the molar mass with increasing MAO concentration indicates the presence of chain transfer to aluminum as a chain termination mechanism. According to these results, a schematic representation of the polymerization pathway was proposed.

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