Iron Complexes of Bis(oxazoline) Ligand as Novel Catalysts for Efficient Atom Transfer Radical Polymerization of Styrene

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Atom transfer radical polymerization has become a powerful tool for the synthesis of polymeric materials with well-defined architecture via controlled radical mechanism.[1] Matyjaszewski et al. investigated in great detail the chemistry of copper catalysts bearing a large variety of ligands.[2] Sawamoto et al.[3] and others extended this research to complexes of late and middle−late transition metals, e.g., ruthenium,[4] molybdenum,[5] iron,[6] nickel,[7] and rhodium.[8] Among these metals, iron is particularly attractive for biocompatibility, low cost, and easy accessibility to a wide number of metal complexes with different ligands.[6]

Trialkyl- and triarylphosphine complexes of iron(II) and iron(III) halides gave promising results in direct and reverse ATRP of styrene and methyl methacrylate.[9] The research was thus addressed toward less toxic ligands which similarly permit a fine-tuning of the steric and electronic properties at the metal center. Four-coordinate iron(II) complexes bearing α-diimine ligands with alkyl substituents were efficient catalysts for well-controlled ATRP of styrene.[10] However, the lowest value reached by the polydispersity index (PDI = M_w/M_n) for the polystyrenes by these catalysts is 1.27, which is greater than the value of 1.1 typically obtained with the copper-based catalysts[2] and iron(II) complexes of tridentate salicylaldiminato ligands.[11]

We are currently interested in the chemistry of readily accessible and derivatizable bis(oxazoline) ligands, which contain two strong Lewis basic imino nitrogen atoms. A huge library of these ligands is available, and the corresponding metal complexes are widely investigated in both homogeneous and asymmetric catalysis.[12] We hypothesized that properly sized ligands of this type could stabilize the pseudotetrahedral coordination environment of iron(II) complexes and tune the electronic properties of the metal center in order to produce efficient ATRP catalysts.

Herein we report the synthesis of the iron complexes Fe(box)Cl_2 and Fe(box)Cl_3 (box = 1,1′-bis(4,4-dimethyl-1,3-oxazolin-2-yl)ethane) (Scheme 1) and their performance in ATRP of styrene.

The complex Fe(box)Cl_2 was readily prepared by stirring a solution of $FeCl_2$ and the ligand in tetrahydrofuran at room temperature. The extraction of the reaction mixture with dichloromethane gave complex Fe(box)Cl_2 in good yield. Single crystals of Fe(box)Cl_2, suitable for X-ray analysis, were grown from THF/cyclohexane. The molecular structure of Fe(box)Cl_2 (see Figure 1) exhibits the iron atom in a distorted tetrahedral geometry. The chelated bis(oxazoline) ligand produces acute

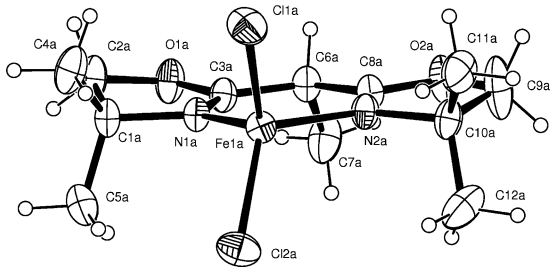
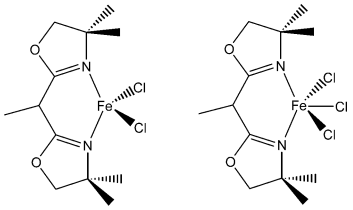


Figure 1. ORTEP view of complex Fe(box)Cl_2 with 30% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Fe−Cl1 = 2.245(1), Fe−Cl2 = 2.261(1), Fe1−N1 = 2.082(2), Fe1−N2 = 2.086(2). N1−C3 = 1.272(3), N2−C8 = 1.276(3), Cl1−Fe1−Cl2 = 113.38(3), Cl1−Fe1−N1 = 115.33(6), Cl1−Fe1−N2 = 110.15(6), Cl2−Fe1−N1 = 109.94(6), Cl2−Fe1−N2 = 117.58(6), N1−Fe1−N2 = 88.24(8).

Scheme 1. Iron Complexes Fe(box)Cl_2 and Fe(box)Cl_3 (box = 1,1′-Bis(4,4-dimethyl-1,3-oxazolin-2-yl)ethane)



N1−Fe1−N2 angles of 88.24(8)° and 87.77(8)° for the two independent molecules of the unit cell, which are compensated by more open Cl1−Fe1−Cl2 angles of 113.38(3)° and 117.67(4)°. The six-membered chelated rings are essentially planar with the Fe1 atom lying 0.1326(3) and 0.1568(4) Å out of the {N1, N2, C3, C8} planes. The Fe−N bond lengths, in the range 2.082(2)−2.091(2) Å, are comparable to that observed in the salicylaldiminato complex of iron(III)[11] but are shorter than those observed in the α-diimine complexes of iron(II),[10] suggesting an elevated coordination energy of this ligand to the metal center. Despite the wide use of iron complexes in catalysis, to the best of our knowledge there is only one precedent of single-crystal X-ray structure of pseudotetrahedral iron complexes bearing box type ligands, namely that of 2,2-bis[2-[4(S)-(CMe_3)-1,3-oxazolinyl]propaneFeX_2 (X = Cl; CH_2SiMe_3).[13]

Polymerizations of styrene catalyzed by Fe(box)Cl_2 using the 1-phenylethyl bromide (1-PEBr) initiator were carried out at 120 °C under an inert atmosphere. The number-averaged molecular weights (M_n) of the polystyrenes increase linearly from 3 to 26 kDa when plotted vs monomer-to-initiator ratio in the range 200−1000, as expected for living catalysts. However, the PDIs of the polymers are in the range 1.40−1.58, suggesting a modest control operated by Fe(box)Cl_2 during the polymerization process. Attempts to improve the PDI value by varying of the experimental conditions (temperature, monomer/initiator ratio, addition of solvent) were not fruitful.

Matyjaszewski et al.[14] evidenced a halogen effect in ATRP by copper halides catalysts. The replacement of copper bromide for copper chloride changes the equilibrium constant between the oxidized and reduced form of the catalyst by 1−2 orders of magnitude in favor of the former by varying of the ligand environment. Moreover, a significant difference in the initiation efficiency was also shown in favor of the bromide vs chloride derivative. In our case the replacement of $FeBr_2$ for $FeCl_2$ did not change significantly the

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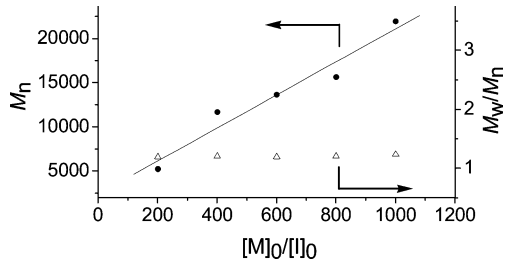

Figure 2. Plot of number-averaged molecular weights M_n (●) and polydispersity indexes M_w/M_n (△) vs monomer-to-initiator ratio $[M]_0/[I]_0$ for catalyst Fe(box)Cl_3 ($[TPED]_0$:$[FeCl_3]_0$:$[box]_0$:$[M]_0$ = 1:4:4:200, 400, 600, 800, 1000; styrene/toluene = 2/1; T = 120 °C; t = 20 h).

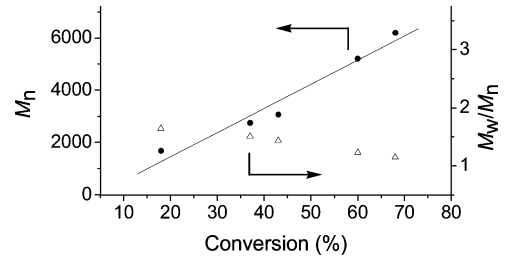

Figure 3. Plot of number-averaged molecular weights M_n (●) and polydispersity indexes M_w/M_n (△) vs conversion for catalyst Fe(box)Cl_3 ($[TPED]_0$:$[FeCl_3]_0$:$[box]_0$:$[M]_0$ = 1:4:4:200; styrene/toluene = 2/1; T = 120 °C).

molecular weight distribution of the polymers under different experimental conditions.

On the contrary, the iron(III) analogue Fe(box)Cl_3 furnished more interesting results in styrene polymerization under reverse ATRP protocol. The complex Fe(box)Cl_3 was prepared by reacting equimolar amounts of box and $FeCl_3$ in methanol at room temperature. Attempts to grow single crystals of Fe(box)Cl_3 under different conditions were unsuccessful. However, the rapid and quantitative formation of Fe(box)Cl_3 was confirmed by UV−vis measurements. The 1:1 stoichiometry was determined by Job's method,[15] also in the presence of excess ligands. The binding constant of $K_{ass} = (1.01 \pm 0.03) \times 10^4$ determined by Scatchard's method[15] confirmed the high coordination energy of the box ligand to the metal. To gain insight into the stability and reversibility of the redox couple, the redox potential ($E_{1/2}$) and the reversibility (ΔE) were evaluated by cyclic voltammetry (CV) for the in situ generated complexes. A reducing power of −636 mV (vs Ag/AgCl) and a ΔE value of 100 were determined for Fe(box)Cl_3, probing a good reversibility and reducing properties of the iron complex in the range expected for good performances in ATRP of styrene. Although Fe(box)Cl_3 can be readily synthesized, the ATRP runs were carried out using in situ generated catalyst, according to well-established literature procedures. The polymerization of styrene initiated by TPED in the presence of Fe(box)Cl_3 were carried out at 120 °C in toluene solution (styrene/toluene = 2/1 v/v) to ensure homogeneous conditions. M_n increases linearly with monomer-to-initiator ratio, and the PDI of the polystyrenes is about 1.20 (Figure 2). The semilogarithmic plot of $\ln([M]_0/[M]_t)$ vs time is linear and gives a pseudo-first-order rate constant k_{obs} of 0.058 ± 0.001 h^{-1} ($[TPED]_0$:$[FeCl_3]_0$:$[box]_0$:$[St]_0$ = 1:4:4:200), in agreement with a constant radical concentration throughout the polymerization process. The PDIs decreased to 1.15 when high monomer conversion (>70%) was reached (Figure 3).

The theoretical molecular weights $M_{n(th)}$ were calculated using the following equation:

$$M_{n(th)} = ([M]_0/2[TPED]_0) \times MW_{St} \times \text{conversion}$$

where $[M]_0$ and MW_{St} are the monomer concentration in feed and the molecular weight of styrene, respectively. These values are higher than the corresponding ones determined by gel permeation chromatography $M_{n(GPC)}$ over all data set. The apparent initiator efficiency f ($f = M_{n(th)}/M_{n(GPC)}$) is constant and slightly larger than one (1.26 as average value), probably as a result of the slow polymerization rate and parallel styrene polymerization by thermal self-initiation.

The ^{1}H NMR spectrum of the polystyrene by Fe(box)Cl_3 exhibited a broad signal at 4.4 ppm,[16] attributed to the chlorobenzylic proton of the ClC*H*(Ph)CH_2− end group of the polymer chain. This signal is expected for polymers resulting from a typical ATRP process in which the exchange of the chlorine atom between the growing radical polymeryl and the iron(III) complex leads to low concentrations of the radical species and assures the living condition. The average molecular weights were also calculated by integration of the ^{1}H signal of this end group and that of the aliphatic methine of styrene homosequences in the low molecular weight polystyrenes: the M_ns determined by the NMR method were found in fair agreement with those by GPC analysis.

In conclusion, the results reported herein strongly support that the polymerization of styrene mediated by the bis(oxazoline) iron complexes Fe(box)Cl_2 and Fe(box)Cl_3 proceeds throughout a classical ATRP mechanism. Complex Fe(box)Cl_3 is the first example of iron(III)-based catalytic systems showing an effective control in reverse ATRP styrene polymerization. The iron(II) species Fe(box)Cl_2 corresponding to the reduced form of the iron(II)/iron(III) redox couple has been fully characterized by X-ray diffraction; this supports the stability of the coordinative unsaturated iron complex in pseudo-tetrahedral coordination environment under monomeric form.

The reverse approach used with the title catalysts exhibits two main advantages: the radical initiator is generally less toxic and less expensive than alkyl halides used in the ATRP protocol, and the iron(III) catalyst precursor is more soluble, more stable thermally, and in air.

The wide versatility of the box framework and the tunable Lewis basicity of the nitrogen atom donors would permit further improvements of the electronic density at the iron center determining an enhancement of kinetic constant for the propagation rate of this novel class of ATRP catalysts. This study is in progress and will be reported elsewhere.

In the light of these results the scarce control operated by Fe(box)Cl_2 in the ATRP of styrene could be ascribed to the slow reaction between the initiator 1-PEBr and the iron complex.

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Supporting Information Available: Experimental preparations, polymerization procedures and ^{1}H NMR of complex Fe(box)Cl_2. Crystallographic data (CIF file) have been deposited at the Cambridge Crystallographic Data Centre and allocated deposition number CCDC 653091. This information is available free of charge via the Internet at http://pubs.acs.org.

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