



Iron(III) complexes of bidentate nitrogen ligands as catalysts in reverse atom transfer radical polymerization of styrene

Rossella Ferro, Stefano Milione*, Tonino Caruso, Alfonso Grassi

Dipartimento di Chimica, Università di Salerno, via Ponte don Melillo, I-84084 Fisciano (SA), Italy

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ABSTRACT

Three iron(III) complexes of bidentate nitrogen ligands, namely 3,5-dimethyl-bispyrazolylmethane (bpzm), 2,2'-dipyridyl (bipy) and 1,1-bis(4,4-dimethyl-1,3-oxazolyn-2-yl)-ethane (box), have been tested in atom transfer radical polymerization (ATRP) of styrene at 120 °C using the 1,1,2,2-tetraphenyl-1,2-ethanediol (TPED) initiator under reverse protocol. Good control of the polymerization reaction and narrow average molecular weight distribution (PDI) have been found for the TPED/FeCl₃/box catalyst whereas TPED/FeCl₃/bpzm and TPED/FeCl₃/bipy produce linear dependence of M_n vs polymerization time but PDI values broader than that expected for a controlled mechanism.

Attempts to clarify the performances of these catalysts were carried out, evaluating the formation constants β^{III} and the electrochemical parameters $E_{1/2}$ of the FeCl₃/L adducts (L=bpzm; bipy; box) by means of UV–vis spectroscopy and cyclic voltammetry, respectively.

A regular increase of both β^{III} and $E_{1/2}$ values was observed as the Lewis basic properties of the ligands increase in the order bpzm < bipy < box. The best performances of the FeCl₃/box catalyst have been thus attributed to the highest formation constant that produce easy and reversible reduction of the iron(III) metal centre to the corresponding iron(II). Lower reducibility and reversibility were found for the iron(III)/iron(II) redox couple in FeCl₃/bipy and FeCl₃/bpzm in agreement with the modest performances in ATRP of styrene of these complexes.

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1. Introduction

Atom transfer radical polymerization (ATRP) is emerging in polymer science as a powerful synthetic methodology for the possibility of obtaining controlled radical polymerization of vinyl monomers by means of a fast and dynamic equilibrium between the radical polymer chain ending (P^{\bullet}) and a halogenated dormant species (P-X) resulting from the metal mediated halide exchange process shown in Scheme 1 [1]. When the ATRP equilibrium is shifted towards the dormant species, an extremely low radical concentration is thus obtained and the rate of the termination reactions characteristic of a radical process, e.g. disproportionation as well as the radical coupling, is dramatically reduced. The efficiency in the halide exchange ensures all polymer chains grow at the same rate and an excellent control over the radical polymerization is thus expected.

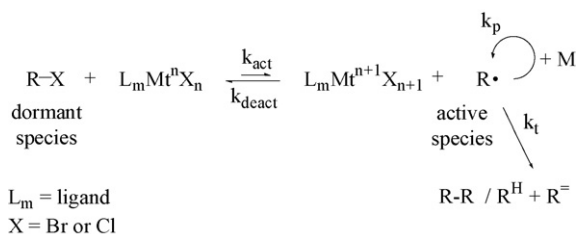
A different approach, leading to the same result, is the so called reverse ATRP [2]. This technique follows the same ATRP elementary steps of Scheme 1 but differs for the initiation reaction. A typical

radical initiator (e.g. 2,2'-azo-bisisobutyronitrile (AIBN), 1,1,2,2-tetraphenyl-1,2-ethanediol (TPED)) is left to react with monomer in the presence of the metal halide in higher oxidation state: after this step the polymerization proceeds in the classical fashion pictured in Scheme 1. Reverse ATRP displays two advantages: (i) the radical initiator is generally less toxic and less expensive than the organic halide used in direct ATRP; (ii) the metal catalyst is more soluble, thermally and air-stable because of the highest oxidation state.

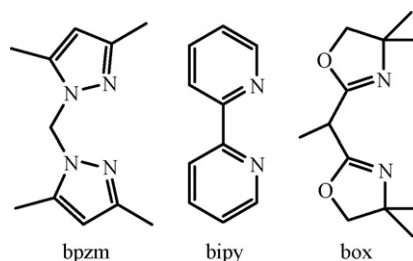
In recent years ATRP of styrenes, acrylates and methacrylates monomers has been described with copper based systems [3]. Metal complexes of Mo [4], Rh [5], Ru [6], Fe [7], Ni [8], Pd [9] with a variety of ligands have also been successfully employed but produce worse control of the polymerization process. Among these metals, iron is particularly attractive for the cheapness, low toxicity and easy accessibility to metal complexes with a variety of ligands. ATRP of styrene and methylmethacrylate has been obtained with different iron(II) complexes but only few examples appear to behave as real living system with remarkable activity. A mixture of FeCl₂ and PPh₃ (1:3 molar ratio) was first reported to produce controlled polymerization of methylmethacrylate: the polymer products exhibit polydispersity index ($PDI = M_w/M_n$) of 1.1–1.3 and M_n values in the range 6–12 kDa [10]. The increase of the Lewis basic properties of

* Corresponding author. Fax: +39 089 969603.

E-mail address: smilione@unisa.it (S. Milione).



Scheme 1.



Scheme 2.

the ligand, e.g. using the more basic tributylphosphine gives better results. In line with this trend, the 1:1 complex of FeCl_2 with imidazolylidene, a carbene ligand exhibiting strong electron releasing properties, is to date the best iron based catalyst in ATRP of styrene showing a pseudo-first-order rate constant (k_{obs}) of 0.12 h^{-1} and PDI of ca. 1.0 [11].

Gibson et al. studied a series of tetra-coordinate α -diimine complexes $[\text{N,N}]\text{FeCl}_2$ [12] and penta-coordinate $[\text{N,N,N}]\text{FeCl}_2$ triamine complexes [13] to assess the electronic and steric requirements of the metal centre leading to good performances in ATRP of styrene. Higher catalytic activity and lower PDI of the polymers were found with the tetra-coordinate iron(II) complexes because of the lower steric hindrance that would favour the oxidability or the accessibility of the halide to the metal. However the overall picture is not completely clear because the electronic factors seem to play a significant role. Among the α -diimine iron(II) complexes the alkyl substituted ligands yielded high propagation rate (k_{obs} of 0.27 h^{-1}) a good control during propagation ($M_w/M_n = 1.3$) whereas the aryl substituted ligands produced not linear plot of M_n vs polymerization time likely as a result of a different polymerization mechanism (e.g. Catalytic Chain Transfer (CCT) mechanism) [14]. This was attributed to a different halide affinity toward the metal centre due to the different electronic configuration of the iron(II), namely in d^6 high spin or low spin for the alkyl substituted and aryl substituted α -diimine complexes, respectively [15]. To shed further light on the electronic factors the authors tried to correlate the efficiency in ATRP and redox properties of the metal complexes by means of cyclic voltammetry studies. Indeed the alkyl substituted α -diimine complexes exhibited reversible one-electron redox peak with $\Delta E_p = 120\text{--}130 \text{ mV}$ whereas the aryl substituted α -diimine complexes gave less reversible redox peak with ΔE_p of $210\text{--}260 \text{ mV}$ [12].

The inverse ATRP protocol seems more attractive in view of the increased stability and availability of a variety of iron(III) complexes. The $\text{FeCl}_3/\text{PPh}_3$ system was successfully tested in ATRP of styrene [16] and methylmethacrylate [17]: however the inverse protocol furnished lower control and broader PDI values when compared to the direct ATRP protocol (M_w/M_n of ca. 1.3 vs 1.1).

We recently reported that the iron(III) complex of the 1,1-bis(4,4-dimethyl-1,3-oxazolyn-2-yl)-ethane (box) ligand shows an excellent control in styrene polymerization [18]. Actually polystyrenes with PDI of 1.1 were obtained at high monomer conversion. The planarity of the ligand and the Lewis basic properties of the imino nitrogen atoms assure elevated coordination energy, easy accessibility of the halogen atom to the metal and good reversibility between the oxidized and reduced states of the metal complex.

To enlarge the class of ligands containing “diimine”-like framework suitable in ATRP processes and to contribute towards the understanding of the electronic and steric factors determining the activity of the corresponding iron(III) complexes in reverse ATRP of styrene we investigated the coordinating ability of 3,5-dimethyl-bispyrazolylmethane (bpzm), 2,2'-dipyridyl (bipy) and 1,1-bis(4,4-dimethyl-1,3-oxazolyn-2-yl)-ethane (box) to iron(III): these ligands (Scheme 2) exhibit similar planar structure and tunable Lewis basic donor sets of nitrogen atoms.

2. Experimental part

2.1. Materials

All manipulations of air- and/or water-sensitive compounds were performed under nitrogen atmosphere using standard Schlenk techniques or an MBraun drybox. FeCl_3 (97%, Aldrich), TPED (99%, Aldrich), 2,2'-bipyridyl ($\geq 99\%$, Aldrich), and Bu_4NBF_4 (98%, Aldrich) were used as received. The ligands bipy [19] and bpzm [20] were synthesized according to the published procedure. Commercial grade toluene (Carlo Erba) was dried over calcium chloride, refluxed 48 h under nitrogen atmosphere over sodium and distilled before use. Styrene (Aldrich) and acetonitrile were purified by distillation over calcium hydride under reduced pressure.

2.2. UV-vis measurements

UV-vis spectra were recorded in the range 800–200 nm on a PerkinElmer Lambda EZ201 instrument, using 1 cm quartz cell and PESSW 1.2 Revision E software. Job plots [21] were performed measuring the absorbance dependence vs the molar concentration of FeCl_3 , keeping constant $[\text{FeCl}_3] + [\text{L}] = 1.0 \times 10^{-4} \text{ M}$.

Spectrophotometric titrations were carried out to evaluate the stability constants β^{III} of the FeCl_3 complexes with ligands L (L = bpzm, bipy and box) [22]. Ten acetonitrile solutions were prepared keeping constant the concentration of FeCl_3 ($4.0 \times 10^{-5} \text{ M}$) and varying the amount of L (0.8×10^{-5} to $8.0 \times 10^{-5} \text{ M}$). The UV-vis spectra of 5.0 mL aliquot of each solution were recorded. The absorbance was monitored at 224, 287 and 289 nm for $\text{FeCl}_3/\text{bpzm}$, $\text{FeCl}_3/\text{bipy}$ and FeCl_3/box , respectively.

2.3. Cyclic voltammetric measurements

Cyclic voltammetry was performed at room temperature with a Metrohm 757VA Computrace instrument. Experiments were carried out in acetonitrile (10 mL) under nitrogen in a three-electrode cell. The auxiliary electrode was a platinum rod, the reference electrode was a Pt quasireference electrode [23] and a platinum electrode of 0.5 mm diameter was used as working electrode. The molar concentrations of Bu_4NBF_4 , FeCl_3 and L were 0.1, 0.01 and 0.01 M, respectively. The scan rate was in the range $0.01\text{--}0.5 \text{ V s}^{-1}$. Under the conditions employed, the ferrocenium/ferrocene (Fc^+/Fc) redox couple exhibited redox potential ($E_{1/2}$) of 0.225 V and ΔE_p of 0.088 V.

2.4. Polymerization of styrene

Polymerizations were performed under nitrogen atmosphere. In a 5 mL glass ampoule fitted with a Teflon stopcock and equipped with a magnetic bar were introduced in the order TPED, FeCl_3 , toluene (if required), ligand and styrene in the appropriate molar ratios. The ampoule was evacuated by means of three freeze-pump-

thaw cycles and transferred to a preheated oil bath at 120 °C. The polymerization was stopped by adding 2 mL of THF. The polymer was precipitated with a plenty of methanol, filtered and dried in vacuum. The monomer conversion was determined gravimetrically.

2.5. Characterization of polystyrenes

¹H and ¹³C NMR spectra were recorded with Bruker ADVANCE 400 (400 MHz for ¹H and 100 MHz for ¹³C), Bruker AVANCE 300 (300 MHz for ¹H and 75 MHz for ¹³C) and Bruker AM 250 (250 MHz for ¹H and 63 MHz for ¹³C) spectrometers at 25 °C in CDCl₃ or CD₃CN solution. The ¹H NMR chemical shift were referred to tetramethylsilane as external standard using the residual protio impurities of the deuterated solvents as reference.

Molecular weights and molecular weight distributions of polystyrene samples were measured by gel permeation chromatography (GPC) using a Alliance 2695 Waters instrument equipped with a RI detector Waters 410. Data were processed with Millennium 32 300NT (Waters) software. The analysis were performed with PLgel MIXED-A LS (Polymer) columns at 40 °C, THF as eluent (1.0 mL/min). Polystyrene standards were used for the calibration.

3. Results and discussion

The FeCl₃/L (L = bpzm, bipy and box) complexes were tested in reverse ATRP of styrene using the *in situ* generated catalysts at 120 °C and 1,1,2,2-tetraphenyl-1,2-ethanediol (TPED) as radical initiator. Molar ratios TPED/FeCl₃/L of 1:2:2 and 1:4:4 were tentatively explored to find the conditions for a better control of styrene polymerization: the main results for the polymerization experiments carried out in bulk are summarized in Table 1. At molar ratios TPED/FeCl₃/L of 1:2:2 the control of the iron complexes was scarce as suggested by the broad average molecular weight distribution that in the case of polystyrenes by FeCl₃/bipy was bimodal. The number average molecular weights determined by gel permeation chromatography $M_{n(GPC)}$ were higher than the theoretical $M_{n(th)}$ values expected on the basis of the following Eq. (1):

$$M_{n(th)} = ([M]_0/2[TPED]_0) \cdot MW_{St} \cdot \text{conversion} \quad (1)$$

This indicates that a fraction of the radical polymer chains is irreversibly deactivated under the polymerization conditions.

At molar ratios TPED/FeCl₃/L of 1:4:4 the polymerization activities dramatically decreased but the average molecular weights of polystyrenes were lower and the PDI values narrower than the control experiment (entry 7) indicating that a partly controlled styrene polymerization has been thus obtained. Among the tested catalysts the FeCl₃/box resulted the most efficient combining good

Table 1
Polymerization of styrene in bulk initiated by TPED/FeCl₃/L (L = bpzm, bipy, box; TPED = 1,1,2,2-tetraphenyl-1,2-ethanediol).

Entry ^a	Ligand	TPED/FeCl ₃ /Lig	Convers. (%)	M_w/M_n^b	$M_n^b (\times 10^3)$
1	bpzm	1/2/2	88	1.8	28.7
2	bpzm	1/4/4	6	1.8	3.4
3	bipy	1/2/2	55	^c	15.8
4	bipy	1/4/4	20	2.2	3.2
5	box	1/2/2	77	2.0	22.1
6	box	1/4/4	64	1.3	3.6
7 ^d	–	–	100	2.6	38.0

^a Experimental conditions: [TPED]₀: [styrene]₀ = 1:200 (0.016 g of TPED 44 μmol, 1.0 mL of styrene). T = 120 °C; t = 18 h.

^b Determined by GPC analysis.

^c Bimodal.

^d Control radical polymerization initiated with TPED (0.016 g of TPED, 1.0 mL of styrene).

Table 2

Polymerization of styrene in toluene solution initiated by TPED/FeCl₃/L (L = bpzm, bipy, box; TPED = 1,1,2,2-tetraphenyl-1,2-ethanediol).

Entry ^a	Ligand	Styrene/TPED	Convers. (%)	M_w/M_n^b	$M_n^b (\times 10^3)$
8	bpzm	200	48	2.1	1.2
9	bpzm	600	12	1.5	2.4
10	bpzm	1000	4	2.6	3.1
11	bipy	200	44	3.6	2.1
12	bipy	600	5	1.4	2.3
13	bipy	1000	3	1.7	2.7
14	box	200	60	1.2	5.2
15	box	600	64	1.2	13.6
16	box	1000	57	1.2	21.9

^a Experimental conditions: TPED/FeCl₃/Lig = 1/4/4 (0.016 g of TPED 44 μmol; 28 mg of FeCl₃, 176 μmol) styrene (1, 2, 3, 4 and 5 mL, respectively). Styrene/toluene = 2/1; T = 120 °C; t = 20 h.

^b Determined by GPC analysis.

monomer conversion and low PDI value ($M_w/M_n = 1.3$, entry 6, Table 1). Despite the low solubility of the investigated iron complexes in styrene solution at 120 °C, the dependence of PDI and M_n from the initiator to metal ratio suggests that the synthesis *in situ* of the metal catalyst does not lead to complete precipitation and the excess of the iron complex at the beginning of the polymerization run is useful to the catalytic performances. We have previously shown that the addition of toluene to the FeCl₃/box catalyst (styrene/toluene = 2/1) exerts a beneficial effect on the PDI without affecting significantly the monomer conversion [18]. Thus we tried to further optimize the performances of the title catalysts under this condition at variance of the styrene/initiator ratios. Selected polymerization results are reported in Table 2. The FeCl₃/box still gave the best results in terms of monomer conversion and PDI. A detailed investigation of the performances of this catalyst showed a linear increase of M_n with monomer conversion and PDI of about 1.20 at TPED/FeCl₃/box/styrene molar ratios of 1:4:4:600 (see Fig. 1). The semilogarithmic plot of $\ln([M]_0/[M]_t)$ vs time is linear and gives a pseudo-first-order rate constant k_{obs} of $0.070 \pm 0.001 \text{ h}^{-1}$, in agreement with a constant radical concentration throughout the polymerization process. Under the same conditions the FeCl₃/bpzm and FeCl₃/bipy catalysts gave the narrower PDI values suggesting a moderate control in styrene polymerization (entries 9, 12, Table 2).

To definitively confirm that a ATRP mechanism is operative, the chemical structure of the polymer end groups was assessed by ¹H NMR spectroscopy. Actually the chlorobenzyl end group characterized by the ¹H signal at 4.2 ppm was found in agreement with the halide exchange equilibrium of Scheme 1 [24].

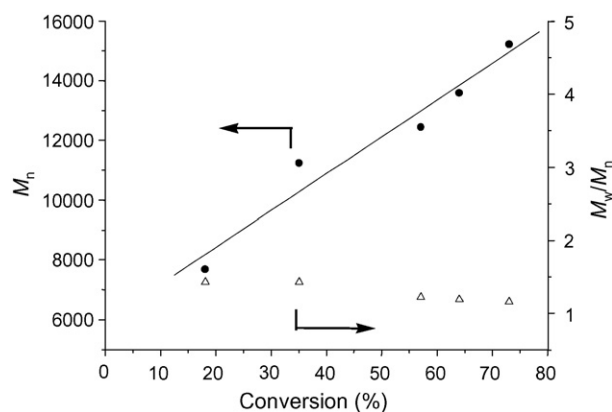


Fig. 1. Plot of number-averaged molecular weights M_n (●) and polydispersity indexes M_w/M_n (Δ) vs conversion for FeCl₃/box ([TPED]₀: [FeCl₃]₀: [box]₀: [M]₀ = 1:4:4:600; styrene/toluene = 2/1; T = 120 °C).

To justify the aforementioned behaviour of the bpzm, bipy and box ligands in reverse iron mediated ATRP of styrene, the structural and redox properties of the corresponding adducts with FeCl_3 were investigated in detail.

The UV–vis monitoring of the reaction of ligands L with FeCl_3 (Fe/L molar ratio = 1) evidenced a rapid and quantitative coordination of the ligand to the metal centre: characteristic UV bands were observed for the iron complexes of bpzm, bipy and box at 230, 280 and 290 nm, respectively. These spectroscopic signals were attributed to the spin-allowed $d\pi(\text{Fe}) \rightarrow \pi^*(\text{lig})$ metal-to ligand charge transfer (MLCT) transition. For FeCl_3/box the signal at 290 nm falls in a clean spectral region whereas a partial overlap of the UV signals of the ligand and complex was observed for the other two iron complexes.

The method of continuous variation was applied to evaluate the stoichiometry of the complexes. The Job's plot [21] shows for the FeCl_3/box system a maximum at $x_L = 0.5$ (x_L = ligand mole fraction), corresponding to the 1:1 Fe/L stoichiometry of the complex. Because of the partial overlap of the UV signals of the bpzm and bipy ligands with those of the iron complexes the absorbance of the latter needs to be corrected by subtracting the UV spectrum of the ligand solution in appropriate concentrations. Although the measurements at $x_L > 0.5$ are affected by error the Job's plots unequivocally show a maximum at $x_L = 0.5$ corresponding to the 1:1 stoichiometry for both (bpzm) FeCl_3 and (bipy) FeCl_3 .

There are few precedents of single crystal X-ray molecular structure of neutral iron complexes with chelated bidentate nitrogen ligands [25,26]. It was previously shown that the box ligand is κ^2 coordinated to FeCl_2 via the imino nitrogen atoms and produces a stable complex in pseudo-tetrahedral coordination geometry [18]. Just recently, a five-coordinate iron(III) complex bearing α -diimine ligand was characterized by single crystal X-ray diffraction and found in a trigonal bipyramidal coordination geometry [27]. By analogy we suggest in the following discussion a similar coordination of bpzm and bipy in the corresponding 1:1 iron(II) and iron(III) complexes.

Despite the wide use of metal catalysts in ATRP, limited attention has been paid to the formation constants β of the complexes that furnish a measurement of the Lewis basic–acidic interactions between the ligand and the metal and would permit to rationalize the redox potential separating the oxidized and reduced states of the metal involved in the ATRP process. We evaluated the β constants for $\text{FeCl}_3/\text{bpzm}$, $\text{FeCl}_3/\text{bipy}$ and FeCl_3/box using the Scatchard method [22]. Acetonitrile solutions of FeCl_3 were titrated with aliquots of acetonitrile solutions of the ligand L. The $(\Delta A)/[L]$ ratio is then plotted vs ΔA where ΔA (or $A - A_0$) is the absorbance difference of the solutions containing variable molar concentrations of the ligand (A_L) and a reference solution of FeCl_3 (A_0 ; $[L] = 0$) and $[L]$ is the molar concentration of the ligand in solution. The slope of the linear plot gives the formation constant β . The UV–vis spectra of FeCl_3/L at different molar ratios and the corresponding Scatchard plots are pictured in Fig. 2.

The $\text{p}K_b$ values [28–30] of the ligands L together with the determined formation constants β^{III} of the corresponding FeCl_3 adducts are listed in Table 3. The inspection of this table reveals that the β^{III} values increase at Lewis basic properties of the ligand increasing, as expected for a strong interaction with an acidic metal centre.

For a series of metal complexes with ligands showing similar structure, the catalytic activity in ATRP can be predicted on the basis of the redox potentials determined by cyclic voltammetry (CV) measurements [1]. The redox potential for the one electron reduction of the FeCl_3/L complexes was thus measured: the CV profiles are shown in Fig. 3 and the electrochemical parameters $E_{1/2}$ and ΔE are listed in Table 3.

The CV profile of $\text{FeCl}_3/\text{bpzm}$ exhibited three reduction waves at -0.790 , -0.978 and -1.200 V. However only the most intense

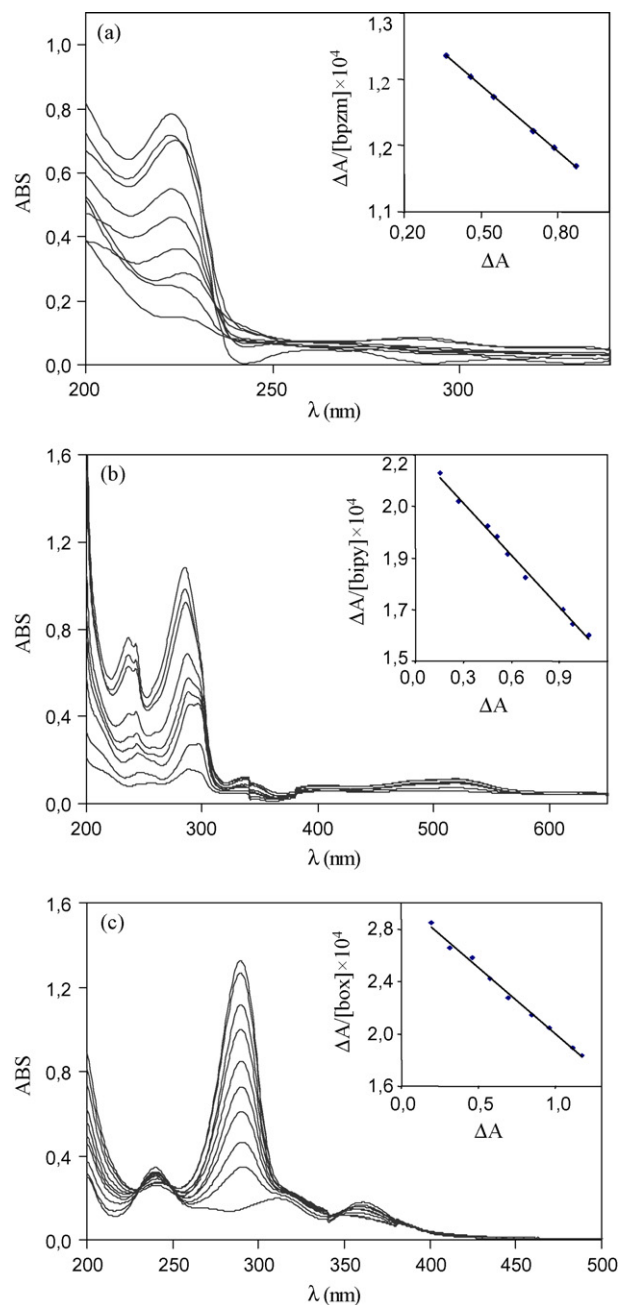


Fig. 2. UV–vis spectra resulting from the titration of FeCl_3 with bpzm (a), bipy (b) and box (c) in acetonitrile solution. The corresponding Scatchard plot at 224 ± 1 nm, 287 ± 2 nm and 289 ± 1 nm for bpzm, bipy and box are respectively displayed.

Table 3

Formation constants and electrochemical parameters for FeCl_3/L assumed with 1:1 Fe/L stoichiometry^a.

	$\text{p}K_b$	β^{IIIb} (FeCl_3) ($\times 10^3$)	β^{IIc} (ZnCl_2) ($\times 10^3$)	$E_{1/2}^{\text{d}}$ (V)	ΔE_{P} (V)
bpzm	11.8	1.98 ± 0.02	1.6 ± 0.5	-1.156	0.154
bipy	9.9	6.1 ± 0.2	11.0 ± 0.2	-0.780	0.236
box	8.7	10.1 ± 0.3	43 ± 5	-0.636	0.106

^a Evaluated by Job's method ($[\text{FeCl}_3] + [\text{ligand}] = 1 \times 10^{-4}$ M in acetonitrile, $T = 25^\circ\text{C}$).

^b Calculated by the Scatchard's method. ($[\text{FeCl}_3] = 4 \times 10^{-5}$ M in acetonitrile, $T = 25^\circ\text{C}$).

^c Determined by means of standard ^1H NMR titrations [22].

^d The redox potentials are referred to Fc^+/Fc redox couple.

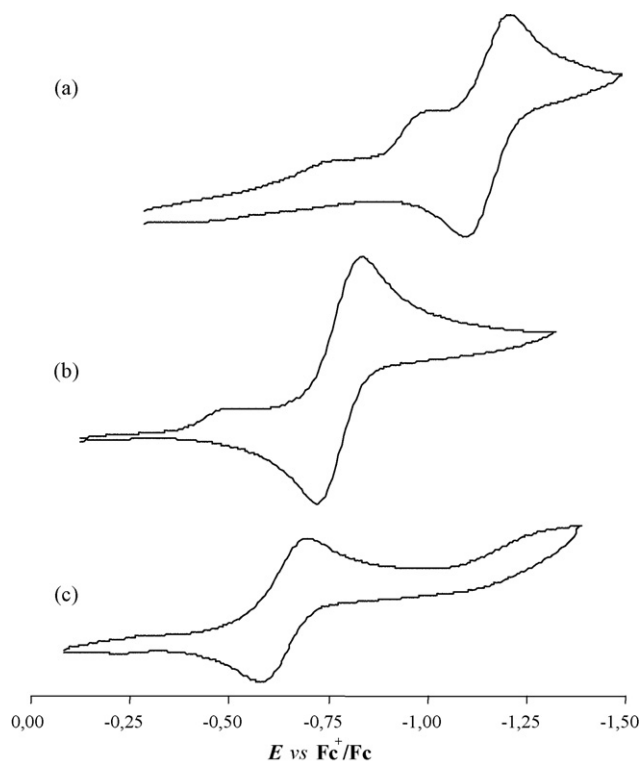


Fig. 3. Cyclic voltammograms of $\text{FeCl}_3/\text{bpzm}$ (a), $\text{FeCl}_3/\text{bipy}$ (b), FeCl_3/box (c) in acetonitrile solution (500 mV/s, 0.1 M $[\text{NBu}_4][\text{PF}_6]$). The redox potentials are referred to Fc^+/Fc redox couple.

peak observed at the lowest voltage was completely reversible and in the oxidation reaction only one signal at -1.112 V was observed. The two additional peaks were only observed in the first reduction wave and resulted unchanged at variance of different sweep rates (0.01 – 0.5 V s^{-1}) and initial voltages. Although we are currently unable to attribute these reduction waves, the corresponding species are expected to be inactive in the ATRP process because of their absence in the oxidation wave and in the repeated cyclic scans. In conclusion the one electron oxidation/reduction of iron(III) to iron(II) redox couple in $\text{FeCl}_3/\text{bpzm}$ was attributed to the reversible peak at -1.156 V.

The CV profile of $\text{FeCl}_3/\text{bipy}$ exhibited two reduction processes at less reducing potential, namely -0.855 and -0.518 V. The latter was still not reversible and thus the reversible peak at -0.780 V was attributed to iron(III) to iron(II) redox couple in $\text{FeCl}_3/\text{bipy}$ for the same reason above discussed.

Finally the CV of FeCl_3/box exhibited the one-electron chemically reversible reduction process at -0.636 V. In conclusion the $E_{1/2}$ values increased in the order $\text{bpzm} < \text{bipy} < \text{box}$ of about 500 mV. This trend is parallel to the increase of the basicity of the ligand ($\text{p}K_b$) and β^{III} of the iron complexes. Moreover the cathodic–anodic peak separation (ΔE_p) in the CV profiles indicates a good reversibility of the redox processes and the overall electrochemical processes behave as slow charge transfer.

In a series of complexes of the same metal with close stereochemistry, oxidation and spin states it is possible to predict the redox potential using a simple parameterization. Indeed the one electron redox potential of the complex depends on the relative stability of the higher and lower oxidation state in the presence of the ligand L, according to Eq. (2)

$$E \approx E^\circ + RT/F \ln[\text{Fe}^{\text{III}}]_{\text{tot}}/[\text{Fe}^{\text{II}}]_{\text{tot}} - RT/F \ln \beta^{\text{III}}/\beta^{\text{II}} \quad (2)$$

where β^{III} and β^{II} are the formation constants of the Fe^{III} and Fe^{II} complexes coordinating the ligand L. The redox potential of the

$\text{Fe}^{\text{III}}\text{L}/\text{Fe}^{\text{II}}\text{L}$ couple increases as the $\beta^{\text{III}}/\beta^{\text{II}}$ ratio decreases. Since β^{III} increases in the order bpzm , bipy and box , β^{II} must show a more pronounced increase in the same order. Unfortunately the insolubility of FeCl_2 in the most common solvents made unpractical the application of Scatchard method with spectroscopic methods. ZnCl_2 and the corresponding complexes of the L ligands are more soluble in organic solvents and the formation constants of the corresponding diamagnetic complexes were reported using ^1H NMR methods [31]. These values represent a rough estimation of the affinity of the ligands L to FeCl_2 and have been included in Table 3 for a comparison. In this case, greater increments of β^{II} were obtained in the series bpzm , bipy box in line with the trend of redox potential observed for the FeCl_3/L complexes.

Matyjaszewsky et al. concluded that in a series of copper(I) catalysts active in ATRP of styrene and methylmethacrylate the more reducing, or easy to be oxidized, Cu^{I} complexes are more active in ATRP catalysis determining low molar concentration of the propagating radical species and good control of the polymerization process [32].

Attempts to correlate electrochemical properties of the metal catalysts with polymerization activity in reverse ATRP have never been reported. In this case the metal complex in higher oxidation state, namely FeCl_3/L , must react with the propagating radical species to establish the ATRP equilibrium. It can be expected that oxidizing iron complexes shift the ATRP equilibrium towards a low concentration of radical species and lead to an efficient control in the radical polymerization. On the opposite complexes that are not prone to reduction would exhibit high propagation rate (high radical concentration) but poorer control.

Actually FeCl_3/box , that showed the lowest redox potential and the highest β^{III} , was found as the most efficient ATRP catalyst. The $\text{FeCl}_3/\text{bipy}$ and $\text{FeCl}_3/\text{bpzm}$ complexes, that are less prone to reduction, need a high metal to initiator ratio (namely TPED/ Fe of 1:4) to be efficient in controlling styrene polymerization but are irreversibly deactivated under this condition likely for their low thermal stability (lower β^{III} values).

In conclusion this work suggests for a preliminary screening of iron complexes potentially active in reverse ATRP of styrene, that the redox potential of -0.636 V (vs Fc^+/Fc) could be the lowest value for the one electron reduction of the metal centre suitable in this kind of polymerization catalysis.

4. Conclusions

The performances of $\text{FeCl}_3/\text{bpzm}$, $\text{FeCl}_3/\text{bipy}$ and FeCl_3/box in ATRP of styrene have been studied using TPED initiator under reverse ATRP protocol. Good control of the molecular weights and narrow PDI values were found with TPED/ FeCl_3/box at 1:4:4 molar ratios whereas the $\text{FeCl}_3/\text{bpzm}$ and $\text{FeCl}_3/\text{bipy}$ catalysts resulted less effective under the same experimental conditions.

In order to justify the polymerization activities, the spectroscopic and electrochemical properties of the iron(III) metal complexes were deeply investigated. The formation constants β^{III} , evaluated with the Scatchard method, increase in the order $\text{bpzm} < \text{bipy} < \text{box}$ as well as the $E_{1/2}$ values. The box ligand produced the most stable FeCl_3/box adduct which is reduced at higher potential than $\text{FeCl}_3/\text{bipy}$ and $\text{FeCl}_3/\text{bpzm}$: the latter complexes are less easily reduced and exhibit lower stability in agreement with the very modest performances in ATRP of styrene. The results reported in this study indicate that the strong stabilization of the metal centre by means of ligand coordination seems to be an essential requirement for the development of effective reverse ATRP catalysts and the redox potential of -0.636 V could be considered among the lowest redox potential suitable for iron(III) under reverse protocol.

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