

Design of Highly Active Iron-Based Catalysts for Atom Transfer Radical Polymerization: Tridentate Salicylaldiminato Ligands Affording near Ideal Nernstian Behavior

Rachel K. O'Reilly, Vernon C. Gibson,* Andrew J. P. White, and David J. Williams

Department of Chemistry, Imperial College London, Exhibition Road, South Kensington, London, UK, SW7 2AZ

Received April 4, 2003; E-mail: v.gibson@imperial.ac.uk

Atom transfer radical polymerization (ATRP) has become established as a powerful method for the synthesis of materials via controlled radical polymerization.¹ Following the key reports by Matyjaszewski² and Sawamoto³ in the mid-1990s, of highly efficient ATRP catalysts based on copper and ruthenium, respectively, a number of different metal–ligand combinations have been investigated, including systems based on Pd,⁴ Rh,⁵ Ni,⁶ and Fe.⁷ There remains, however, a need to develop new low toxicity, highly active catalyst systems, especially for the synthesis of materials for in vivo biomedical applications. The natural capacity of the body to store and transport iron⁸ makes this metal particularly attractive for use as an ATRP catalyst.

There are several important criteria for the successful design of ATRP catalysts: (i) the metal must possess an accessible one-electron redox couple, (ii) the oxidation potential should be low, but optimal for reversible halogen atom transfer, (iii) there should be good reversibility between the reduced and oxidized forms of the catalyst—favored by ligands which minimize changes to the metal coordination sphere between the reduced and oxidized states, and (iv) the metal center must be sterically unencumbered in its reduced form to allow a halogen atom to be accommodated. The electrochemical parameters, $E_{1/2}$ and ΔE_p , accessible via cyclic voltammetry, provide a useful guide to evaluating (i–iii).

We were attracted to readily accessible and derivatizable salicylaldiminato ligands which in recent years have been successfully exploited in a range of olefin polymerization catalyst systems.⁹ The starting points for our studies were the bidentate salicylaldiminato complexes **1–3** which were prepared by treatment of the salicylaldimine with NaH, followed by FeCl₃ (Scheme 1). These were tested using reverse ATRP protocols¹⁰ but gave poor control using styrene and methyl methacrylate, an observation we attribute to the relative instability of the reduced three-coordinate Fe(II) species. We therefore decided to investigate the tridentate derivatives **4–6** where we envisaged the donor arm may afford the reduced species additional stability as well as lower its oxidation potential. **4–6** were isolated as dark red microcrystalline, paramagnetic solids in good yields according to Scheme 1.

Polymerizations of styrene (100 equiv, bulk) initiated by 1-phenylethyl bromide (1-PEBr) in the presence of **4–6** were monitored at 120 °C under inert atmosphere. The semilogarithmic plot of $\ln([M]_0/[M])$ vs time is linear in all cases with a pseudo-first-order rate constant (k_{obs}) of 0.39 h⁻¹ for **4**, 0.46 h⁻¹ for **5**, and 0.49 h⁻¹ for **6**, indicating that the radical concentration is constant throughout the polymerizations. Molecular weights (M_n) increase linearly with conversion (Figure 1) and with monomer-to-initiator ratio; a plot of M_n vs $[M]_0/[I]_0$ using **4** is shown in Figure 2. Polydispersities (M_w/M_n) are low, typically ca. 1.10, and decrease with monomer conversion. ¹H NMR spectra of the resultant polystyrene samples show the presence of the halide capping group (ClCH(Ph)CH₂— ≈ 4.4 ppm) which is also supported by halide microanalysis.¹¹ These

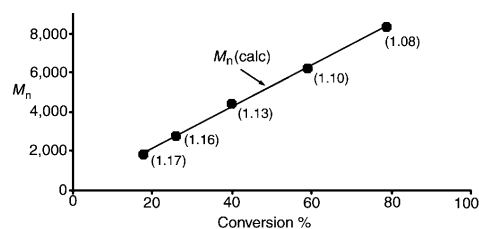


Figure 1. Plot of M_n vs conversion for **6** with M_w/M_n in parentheses. ($[6]_0$: [1-PEBr]₀: [St]₀ = 1:1:100).

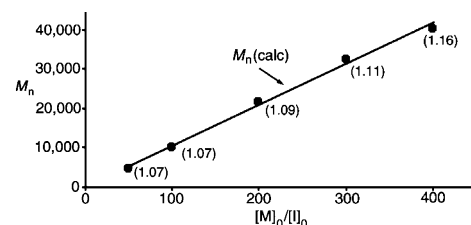
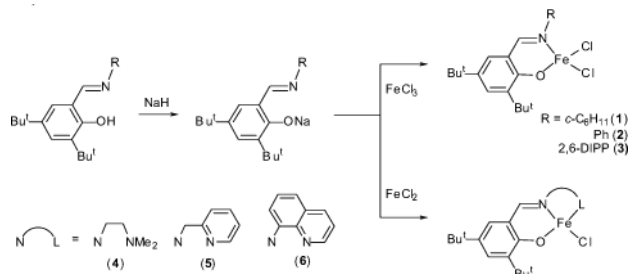


Figure 2. Plot of M_n vs $[M]_0/[I]_0$ for **4** with M_w/M_n in parentheses. ($[4]_0$: [1-PEBr]₀: [St]₀ = 1:1:50, 100, 200, 300, 400).

Scheme 1. Synthesis of Complexes **1–6**



results clearly indicate that polymerizations using complexes **4–6** exhibit all the characteristics of a well-controlled and extremely fast radical polymerization with rates comparable to those of copper-based systems¹² which are among the most active catalysts.

Encouraged by these observations, we investigated the polymerization of styrene in toluene solution at the lower reaction temperature of 85 °C. Similar results were obtained as found for the bulk polymerization except that the polymerizations were expectedly slower ($k_{\text{obs}}(\mathbf{4}) = 0.06 \text{ h}^{-1}$, $k_{\text{obs}}(\mathbf{5}) = 0.10 \text{ h}^{-1}$, $k_{\text{obs}}(\mathbf{6}) = 0.15 \text{ h}^{-1}$). However, no loss of control was observed, the polymerizations in bulk and solvent affording polystyrene with similar polydispersities and molecular weight control.

To obtain an understanding of the exceptional activities of these complexes, their redox potentials ($E_{1/2}$) and reversibility (ΔE_p) were probed by cyclic voltammetry. **4–6** were all found to possess accessible redox couples with their polymerization rates showing good correlation with the increasing reducing power of the iron

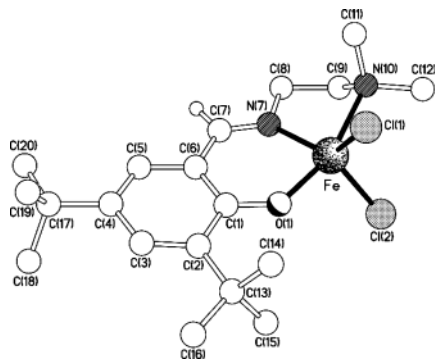


Figure 3. The molecular structure of **4a**.

centers [**6** ($E_{1/2} - 480$) > **5** ($E_{1/2} - 410$) > **4** ($E_{1/2} - 280$)]. Also, the peak potentials of all three complexes show relatively small differences (ΔE_p) (**6**, ΔE_p 65 < **5**, ΔE_p 70 < **4**, ΔE_p 75), with that for **6**, giving close to ideal Nernstian behavior ($\Delta E_p \approx 60$ mV). This is indicative of a small energy barrier between the reduced and oxidized species, most likely a result of the conformational rigidity of the attendant ligand.

With a view to obtaining a better understanding of the coordination environment around the iron centers, we attempted to grow suitable crystals of the Fe(II) species for an X-ray structure determination, but all attempts were unsuccessful. However, we were able to determine the crystal structure of the (oxidized) Fe(III) species **4a**; a view is shown in Figure 3. The geometry at iron is distorted trigonal bipyramidal with equatorial angles in the range 113.20(8)–128.8(2)°, the axial substituents, O(1) and N(10), subtending an angle of 160.8(2)° at the metal center.

The iron atom is displaced 0.125 Å out of the equatorial plane in the direction of O(1), a distortion similar to that observed in an Al(Me)₂ analogue where the deviation was 0.157 Å.¹³ The six-membered chelate ring has a folded (asymmetric boat) conformation with Fe and C(1) lying 0.381 and 0.040 Å out of (and on the same side of) the {C(1),O(1),C(7),N(7)} plane, which is coplanar to within 0.007 Å. The five-membered chelate ring has an envelope conformation with N(10) lying 0.809 Å out of the plane of the remaining atoms (which are coplanar to within 0.057 Å). A notable feature of the bonding to the iron center is that the bond to the amino nitrogen N(10) [2.250(4) Å] is substantially longer than that to the imino nitrogen [2.071(4) Å]. This difference in bond length was even more pronounced in the Al(Me)₂ analogue and was attributed to the weaker nature of the interaction with the axial amino nitrogen atom. A stronger interaction was found in pyridylmethyl and quinolyl aluminum derivatives which most probably accounts for their lower redox potentials here.

An important factor in the exceptional ATRP behavior of these complexes is likely to be the rigidity of the tridentate salicylaldiminato ligand, which is expected to increase from the aminoethyl donor arm of **4** to the less flexible pyridinemethyl arm of **5**, to the highly constrained quinolyl arm of **6**, and correlates well with the trend toward Nernstian behavior for the more rigid ligand. When combined with ample space to accommodate a halogen atom in

the plane orthogonal to the ligand backbone, these factors combine to optimize efficient halogen atom transfer. A similar correlation of ATRP performance with ligand rigidity has recently been noted in copper catalysts bearing tetradentate nitrogen donor ligands.¹⁴ The results of the present study suggest this may be a general effect and an important design characteristic for ATRP catalysts.

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Supporting Information Available: Crystallographic data (CIF) and experimental preparations, polymerization procedures and CV data (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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