IronIII Half Salen Catalysts for Atom Transfer Radical and Ring-Opening Polymerizations

Eszter Fazekas, Gary S. Nichol, Jennifer A. Garden,* and Michael P. Shaver*

EaStCHEM School of Chemistry, University of Edinburgh, Edinburgh EH9 3FJ, U.K.

ABSTRACT: A series of monometallic pentacoordinate FeIII chloride complexes have been prepared and characterized by high-resolution mass spectrometry and elemental analysis. X-ray diffraction analysis showed that the bis-chelated FeIII complexes bear distorted trigonal bipyramidal geometries. The air- and moisture-stable FeIII complexes were screened as mediators in the reverse atom transfer radical polymerization (ATRP) of styrene and methyl methacrylate. Moderate to excellent control was achieved with dispersities as low as 1.1 for both poly(methyl methacrylate) and polystyrene. Kinetic studies showed living characteristics, and end group analysis revealed the presence of olefin-terminated polymer chains, suggesting catalytic chain transfer as a competing polymerization mechanism. Although the catalysts are not the fastest Fe ATRP mediators, they are robust and flexible. Using propylene oxide as an initiator, the complexes were active catalysts for the ring-opening polymerization of rac-lactide with moderate control. While the addition of propylene oxide has been reported as an efficient method of converting a metal−halide bond to a metal−alkoxide bond in situ, we show herein that this initiation mechanism can limit polymerization reproducibility and introduce an induction period.

INTRODUCTION

Transition-metal complexes play an important role in the catalysis of polymerization reactions, from providing better control over the microstructure to tuning the properties of the obtained polymers.1 Non-toxic iron is an ideal candidate to be used for this purpose as the removal of catalyst residues from polymer products is still a major challenge for food or biomedical applications.2-4 Moreover, as Fe is the most abundant transition metal, it can maintain low costs even on industrial scales.5,6 With multiple active oxidation states, most commonly FeII and FeIII, to exploit in different catalytic processes, research in Fe-based catalysts has become an area of focus in polymer chemistry; complexes supported with a range of ligands have been characterized and applied in various types of polymerizations.1,7-9

Atom transfer radical polymerization (ATRP) is based on a dynamic equilibrium between the growing and the dormant polymer chains using a metal-mediated halogen-exchange process (Scheme 1). As an alternative to the typical Cu-based systems,10 the first Fe catalysts for ATRP were pioneered by the groups of Matyjaszewski and Sawamoto, originally using FeIIIX2(PR3)2 (X = Cl and Br)-type complexes.11,12 Since then, Fe salts and complexes with a variety of ligands (including phosphines, imines, and amines) have been explored in the ATRP of vinyl monomers,7,13,14 but interestingly the use of the ubiquitous salen ligand framework gave only limited control over the polymerization.15 Catalysts with Fe in its more stable oxidation state can have the additional benefit of air and moisture stability that enables simple, user-friendly synthesis and application. These systems traditionally feature an azo initiator (such as AIBN) and proceed via a reverse ATRP (R-ATRP) mechanism (Scheme 1). The first examples of Fe-mediated R-ATRP were reported by Teyssie et al.,16 whereas amine bisphenolate complexes of both FeII and FeIII showed good control in the RP of styrene and methyl methacrylate (MMA),17-21 through joint ATRP and organometallic-mediated radical polymerization mechanisms.22,23

The ring-opening polymerization (ROP) of cyclic esters, in particular the renewable cyclic diester lactide, is a burgeoning
complexes of these ligands have shown promising results in the R-ATRP (Scheme 1) and stereoelectronically diverse properties (Figure 1). Aluminum ROP (Scheme 2) reactions. Half salen ligands catalyzed the ROP of L-LA.38 Following the recent trend of alkoxide catalysts for the ROP of lactide and caprolactone.43 al. reported on the in situ generation of salen-based FeIII chloride catalysts that showed high activity in CO2/epoxide couplings.48 In these reactions, the conformational flexibility of the complexes proved to be an advantage over the standard salen scaffolds. The presence of the Fe–Cl bond in these catalysts opened up the possibility of their applications in R-ATRP (Scheme 1) and ROP (Scheme 2) reactions. Half salen ligands offer the advantage of simple and modular synthesis to achieve stereoelectronically diverse properties (Figure 1). Aluminum complexes of these ligands have shown promising results in the ROP of cyclic esters,49 including the application of monometallic Al–phenoxyimines in the ROP of γ-butyrolactone50 and the stereocontrolled ROP of lactide.51 Moreover, dimeric, oxygen-bridged Li, Na, and K phenoxyimine complexes were extremely active in the ROP of lactide; however, these systems exerted a lower control over molecular weights and tacticity.52

This work explores the synthesis of five bidentate phenoxyimine ligands, the corresponding novel FeIII chloride complexes, and their application in polymerization catalysis. Combined with the previously reported complexes, all eight Fe–phenoxyimines were screened as mediators in the R-ATRP of styrene and MMA. Moreover, we explored the PO-triggered ROP of rac-lactide, including understanding the limitations of this emerging initiation strategy.

RESULTS AND DISCUSSION

Synthesis and Characterization. A series of FeIII complexes were synthesized from half salen ligands, incorporating substituents with varying steric bulk [methyl or 2,6-diisopropylphenyl (DIPP)] at the imine position and peripheral Cl or ‘Bu substituents on the phenol moiety.52,53 Initially, the pro-ligands were deprotonated by NaH to form the corresponding Na–phenolates. Subsequent transmetalation with anhydrous FeCl3 (0.5 equiv) in tetrahydrofuran (THF) solvent at ambient temperature gave an immediate color change from yellow to dark purple, which indicated the formation of the desired L2FeCl complexes (Scheme 2). Similar to Al-based systems,54 the addition of a massive excess (2000 equivalents) of the carcinogenic PO was required to achieve good conversions, hence greatly reducing the atom efficiency and biocompatibility of this system.

Complimentary to the well-studied tetradequate salen systems, tridentate derivatives of Schiff bases were also applied to support FeIII as a polymerization catalyst.44 Considering the paucity of studies exploring Fe complexes with bidentate phenoxyimine ligands,55 we recently developed a novel family of air-stable half salen FeIII chloride catalysts that showed high activity in CO2/epoxide couplings.48 In these reactions, the conformational flexibility of the complexes proved to be an advantage over the standard salen scaffolds. The presence of the Fe–Cl bond in these catalysts opened up the possibility of their applications in R-ATRP (Scheme 1) and ROP (Scheme 2) reactions. Half salen ligands offer the advantage of simple and modular synthesis to achieve stereoelectronically diverse properties (Figure 1). Aluminum complexes of these ligands have shown promising results in the ROP of cyclic esters,49 including the application of monometallic Al–phenoxyimines in the ROP of γ-butyrolactone50 and the stereocontrolled ROP of lactide.51 Moreover, dimeric, oxygen-bridged Li, Na, and K phenoxyimine complexes were extremely active in the ROP of lactide; however, these systems exerted a lower control over molecular weights and tacticity.52

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observed with FeIII salen and salalen complexes, which typically possess a square pyramidal geometry with mutually cis N and O ligands. Upon the introduction of electronnegative chloro substituents to the ligand scaffold, the Fe–Cl bond length is significantly shortened and strengthened, from 2.2713(5) Å for unsubstituted C1, to 2.5217(6) Å for monochloro-substituted C7 and to 2.2271(5) Å for ortho, para-dichloro-substituted C8. The magnetic moments of all eight complexes were determined via the Evans method and displayed $\mu_{\text{eff}}$ values of 4.6–5.5 B. M., which suggests that high spin FeIII complexes predominate.

**Atom Transfer Radial Polymerization.** Complexes C1–C8 were screened as mediators in the R-ATRP of styrene using the standard AIBN initiator at 120 °C or an alternative azo-initiator (V-70) which ‘degrades quickly to radicals at 75 °C (Table 1). As expected, the lower temperature of reaction used with V-70 leads to lower conversions and slightly narrower molecular weight distributions. Following the Fe–Cl bond strengths, the conversion increased with the Lewis acidity of the Fe center using AIBN and C1, C7, and C8 as mediators (entries 1, 13, and 15). Surprisingly, along with providing one of the highest conversions (56%), C8 also displayed good control over the dispersities, with $D$ values (1.2, entries 15 and 16) that are comparable with the best reported for FeIII R-ATRP systems. Of particular interest, catalyst C6 was an excellent mediator using V-70, affording polystyrene with very narrow dispersity ($D = 1.05$, entry 12) by matching theoretical and experimental molecular weights. This may suggest that the bulky ‘Bu substituents can sterically stabilize the reduced FeII derivative during the R-ATRP process. The presence of these electron-donating groups may also decrease the Lewis acidity of the metal center and therefore limit the concentration of active chains. On the contrary, when L6 was investigated by Gibson et al. in a mono-chelated FeLCl2-type complex, poor control was achieved, attributed to the relative instability of the reduced tricoordinate FeII species formed during polymerization. Interestingly, C5 with identical ‘Bu substituents on the phenol moiety displayed significantly lower control, which can be linked to the lack of steric hindrance and thus protection of the coordination sphere by the DIPP group on the imine. Complexes C3 and C4 provided a moderate degree of control ($D = 1.4–1.5$), whereas C1, C2, C5, and C7 were relatively poor mediators providing broad dispersities ($D > 1.5$). These findings suggest that overall, the steric bulk at the imine position (Me or DIPP substituents) does not have a significant effect upon the degree of control. In some cases...
(e.g., entries 3 − 4 and 9 − 10), the number average molecular weights ($M_n$) were higher than the theoretical values ($M_{n,th}$), suggesting inefficient initiation.

Kinetic experiments were performed using complex C8, which exerted the highest control over dispersity using AIBN as the initiator. The molecular weights increased linearly with conversion, suggesting a controlled polymerization. The reaction kinetics deviated from the expected first-order dependence on monomer concentration, which may be due to the presence of competing side reactions (vide infra) (Figure 5).

To provide insight into the nature of the polymer end groups, the purified polystyrene samples were investigated by $^1$H NMR spectroscopy. Besides the expected halide capping group (ClCH(Ph)CH$_2$ at 4.4 ppm), the presence of olefin-terminated polymer chains was also observed, as indicated by diagnostic doublets at 5.27 and 5.78 ppm (Figure 6). These findings suggest that catalytic chain-transfer (CCT) side reactions occur, which compete with the ATRP mechanism. However, molecular weights increased linearly with the conversion, as observed previously for intermediate spin $\alpha$-diimine Fe complexes.

The R-ATRP of MMA using C1 − C8 as mediators afforded polymers with $M_n$ significantly in excess of the theoretical values ($M_{n,th}$), which is a common phenomenon using this monomer with azo initiators (AIBN and V-70). Similarly to the styrene polymerizations, using C1, C3, and C5 as mediators, the conversion increased with the presence of sterically bulky $t$Bu substituents on the half salen ligand scaffold (Table 2, entries 1, 5 and 9). The complexes were found to be moderate to poor mediators achieving relatively broad dispersities ($D = 1.4$ − $2.3$). The exception was the unsubstituted complex C1, which achieved moderate activities (28 − 30% conversion) while exerting good control ($D = 1.1$ and 1.2 using AIBN and V-70, respectively). This observation is consistent with the general principle in normal ATRP, where the mediator must be fine-tuned so that the polymerization rate is sufficiently rapid, but not so active that radical termination dominates the reaction.

Kinetic experiments using C1 showed that the polymerization was well controlled; the molecular weight increased linearly with conversion. However, the reaction slowed down considerably, reaching a plateau at moderate conversions (Figure 7), possibly because of bimolecular termination side reactions. Similarly to the polystyrene samples, $^1$H NMR analysis revealed the presence of olefin-terminated polymer

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### Table 1. Screening of Catalysts C1−C8 in Styrene R-ATRP

| entry | complex | init. | conv. (%) | $M_{n,th}$ (Da) | $M_n$ (Da) | $D$ |
|-------|---------|-------|-----------|-----------------|-----------|-----|
| 1     | C1      | AIBN  | 29        | 3000            | 3800      | 1.7 |
| 2     | V-70$^b$| 18    | 1900      | 3600            | 1.4       |
| 3     | C2      | AIBN  | 61        | 6400            | 11 600    | 1.7 |
| 4     | V-70    | 36    | 3800      | 6800            | 1.5       |
| 5     | C3      | AIBN  | 34        | 3500            | 4000      | 1.5 |
| 6     | V-70    | 24    | 2700      | 4000            | 1.5       |
| 7     | C4      | AIBN  | 40        | 4200            | 4200      | 1.4 |
| 8     | V-70    | 31    | 3200      | 3300            | 1.5       |
| 9     | C5      | AIBN  | 79        | 8200            | 15 500    | 2.2 |
| 10    | V-70    | 33    | 6800      | 13 800          | 1.8       |
| 11    | C6      | V-70  | 23        | 2400            | 4200      | 1.4 |
| 12    | V-70    | 25    | 2600      | 2600            | 1.1       |
| 13    | C7      | AIBN  | 45        | 4700            | 14 200    | 1.6 |
| 14    | V-70    | 23    | 2400      | 6000            | 1.4       |
| 15    | C8      | V-70  | 56        | 5800            | 10 900    | 1.2 |
| 16    | V-70$^b$| 14    | 1500      | 5700            | 1.2       |

$^a$Conditions: [styrene]/[Fe$^{III}$]/[I] = 100:1:0.6, styrene/toluene = 1:1 (v/v), 120 °C for AIBN or 75 °C for V-70, 2 h. Conversion was determined using $^1$H NMR spectra of crude reaction mixtures. $M_{n,th} = \frac{[\text{styrene}]_0/[\text{Fe}]}{[\text{Fe}]} \times M_{\text{styrene}} \times \text{conversion.}^b$Insufficient polymer was precipitated after 2 h to allow analysis; therefore, a sample precipitated after 4 h reaction time was used.

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Figure 5. Kinetic plots for styrene polymerization: ln($[M]_0/ [M]$) vs time (on left) and molecular weight vs conversion (right).

Figure 6. $^1$H NMR spectrum (CDCl$_3$, 20 °C) showing doublet peaks of olefin-terminated polymer chains formed via CCT.
in situ generation of metal excess of PO, which would compromise the benefits reported procedures,41,43 we aimed to avoid the use of a large addition of an epoxide to metal 2),41,43 thus we tested our Fe moment as an alternative initiation method (Scheme 2),41,43 and this was confirmed by the observed for styrene. polymer peaks, which suggested significantly less CCT than the integrals of these peaks were relatively low compared to the chains (doublets at 5.50 and 6.23 ppm, Figure S14). However, the integrals of these peaks were relatively low compared to the polymer peaks, which suggested significantly less CCT than that observed for styrene.

Ring-Opening Polymerization of rac-Lactide. Iron catalysts remain underexplored within ring-opening polymerization reactions, yet can offer benefits in terms of low cost, biocompatibility, and air stability. Complexes C1–C8 were therefore tested as catalysts for the ROP of lactide (LA). Most catalysts for this reaction include a metal–alkoxide initiating group, which is typically formed via the in situ conversion of a metal–alkyl group through deprotonation of an alcohol.25 The in situ generation of metal–alkoxide catalysts through the addition of an epoxide to metal–chlorides is currently gaining momentum as an alternative initiation method (Scheme 2),41,43 thus we tested our Fe–Cl complexes for the ROP of rac-LA in the presence of PO as an activator. On previously reported procedures,41,43 we aimed to avoid the use of a large excess of PO, which would compromise the benefits of the Fe/LA system because of the toxicity of this solvent. Initial optimization of the [Fe]/PO ratio with C8 showed that excellent conversions can be achieved with as low as 50 equivalents of PO when the reaction is carried out at 120 °C for 24 h in the toluene solvent (Table S1, entries 1–4). This modification enabled the polymerizations to be performed in air tight vials instead of autoclaves and significantly improved the overall atom efficiency. Control reactions without an Fe complex and without the addition of PO showed that both components are essential for the initiation (Table 3, entries 1 and 2). Under the optimized conditions, C1–C8 all achieved almost complete conversion of LA (>89%), although

| entry | complex | init. | conv. (%) | Mn,th (Da) | Mn (Da) | D |
|-------|---------|-------|------------|-------------|------------|---|
| 1     | C1      | AIBN  | 28         | 2800        | 8400       | 1.1 |
| 2     | V-70    | 30    | 3000       | 13 000      | 1.2 |
| 3     | C2      | AIBN  | 76         | 7600        | 17 000     | 1.8 |
| 4     | V-70    | 66    | 6600       | 18 900      | 2.3 |
| 5     | C3      | AIBN  | 47         | 4700        | 12 700     | 1.6 |
| 6     | V-70    | 24    | 2400       | 18 800      | 1.5 |
| 7     | C4      | AIBN  | 85         | 8500        | 18 400     | 1.4 |
| 8     | V-70    | 68    | 6800       | 15 700      | 1.4 |
| 9     | C5      | AIBN  | 61         | 6100        | 16 700     | 2.2 |
| 10    | V-70    | 54    | 5400       | 16 500      | 1.9 |
| 11    | C6      | AIBN  | 65         | 6500        | 22 800     | 1.4 |
| 12    | V-70    | 62    | 6200       | 14 900      | 1.4 |
| 13    | C7      | AIBN  | 68         | 6800        | 18 900     | 1.7 |
| 14    | V-70    | 62    | 6200       | 19 400      | 1.6 |
| 15    | C8      | AIBN  | 64         | 6400        | 16 100     | 1.8 |
| 16    | V70     | 63    | 6300       | 16 400      | 1.4 |

"Conditions: [MMA]/[Fe]/[I] = 100:1:0.6, MMA/toluene = 1:1 (v/v), 120 °C for AIBN or 75 °C for V-70, 2 h. Conversion was determined using 1H NMR spectra of crude reaction mixtures. Mn,th [Fe] = [MMA]/[Fe] × M(MMA) × conversion."

Table 3. ROP of rac-Lactide Catalyzed by Complexes C1–C8 and Propylene Oxide "Conditions: [lactide]/[Fe]/[PO] = 100:1:50, lactide concentration in toluene = 1 M, 120 °C. Conversion was determined using 1H NMR spectra of crude reaction mixtures. Mn,th [Fe] = [lactide]/[Fe] × M(lactide) × conversion. Reaction was carried out without the addition of PO. Efforts to recover polymer were unsuccessful, indicating the formation of shorter polymer chains. The Fe complex was stirred for 16 h in excess PO at room temperature prior to the addition of lactide. The reaction was performed at 85 °C.

| entry | complex | time (h) | conv. (%) | Mn,th (Da) | Mn (Da) | D |
|-------|---------|----------|------------|-------------|------------|---|
| 1     | C1      | 2        | 78         | 12 800      | 17 200     | 1.5 |
| 12    | C2      | 2        | 2          |             |            |   |
| 13    | C3      | 2        | 89         | 12 900      | 5500       | 1.1 |
| 14    | C4      | 2        | 90         | 13 000      | 45 900     | 1.7 |
| 15    | C5      | 2        | 49         | 7100        | 50 500     | 1.3 |
| 16    | C6      | 2        | 91         | 13 100      | 42 200     | 1.5 |
| 17    | C7      | 2        | 49         | 7100        | 22 000     | 1.4 |
| 18    | C8      | 2        | 1          |             |            |   |
| 19    | C8      | 2        | 90         | 13 000      | 15 900     | 2.1 |
| 20    | C8      | 2        | 89         | 12 800      | 17 200     | 1.5 |

Figure 7. Kinetic plots for MMA polymerization with C1: ln([M]₀/[M]) vs time (left) and molecular weight vs conversion (right).
inconsistent molecular weights and broad dispersities indicated uncontrolled polymerizations (Table 3, entries 3–10). This was attributed to detrimental side reactions, such as intra-molecular and intermolecular transesterifications, which are a commonly observed in ROP at high conversions. The tacticity was investigated via homonuclear decoupled $^1$H NMR experiments of the purified polymers, which revealed a lack of control over the tacticity with $P_i$ values around 0.52 indicating atactic enchainments (Figure S15). To reduce the rate of undesired side reactions, the polymerization was tested under milder conditions ($85 \, ^{\circ}\mathrm{C}$), affording only traces of PLA (Table S1, entry 5). Attempts to reduce the reaction time from 24 to 2 h using C1–C8 led to variable conversions (Table 3, entries 11–18) with significant errors in reproducibility (Table S1, entries 6–9), suggesting that the rate-limiting step is the in situ formation of the active Fe–alkoxide catalyst. It may also suggest the presence of an induction period for the epoxide ring opening by the metal–halide, a phenomenon that was previously often observed in epoxide/CO$_2$ copolymerization reactions, but may have been overlooked in the in situ formation of metal–alkoxide catalysts for ROP. The higher average molecular weights observed after 2 h of reaction time (compared to 24 h reactions) suggest the presence of extensive transesterification reactions that cleave longer polymer chains. Efforts to minimize the variability through the use of a PO stock solution or a higher boiling activator (butylene oxide, bp 63 °C) were unsuccessful (Table S1, entries 6–12). The inefficient initiation observed after 2 h of reaction time using C2, C5, C7, and C8 (Table 3, entries 12, 15, 17, and 18, respectively) may arise from the strength of the Fe–Cl bond. For example, the molecular structures of C1, C7, and C8 suggest that the presence of electronegative chloro-substituents shortens and strengthens the Fe–Cl bond (vide supra). This falls in line with the conversions obtained with C1 (78%, entry 11), C7 (49%, entry 17), and C8 (1%, entry 18). These results suggest that in situ initiation can lead to greater experimental variation in comparison to the use of isolated metal–alkoxide complexes. Indeed, preforming the active Fe–alkoxide species by stirring the Fe$^\text{III}$–Cl species C8 with excess PO for 16 h, prior to the addition of LA, drastically increased the conversion from 1% (entry 18) to 90% (entry 19). Moreover, using the preformed catalyst, the reaction temperature could be lowered to 85 °C while maintaining high activity (89%, Table 3, entry 20). In accordance with initiation via epoxide opening, the matrix-assisted laser desorption ionization time-of-flight (MALDI-ToF) spectrum of the purified polymer showed a series of chains terminated by –OCH(Me)CH$_2$Cl and –OH groups (Figures S19 and S20). Additional polymer series bearing –OCH(Me)CH$_2$OH end groups were also observed, suggesting that initiation also occurs through the opening of epoxide due to the presence of trace water. In addition to the expected lactide repeat units (144 Da), the spectra also showed equally intense repeating units corresponding to a half lactide unit (72 Da), which further corroborates the prevalence of transesterification reactions. It is worth noting that propylene oxide was absent from both the MALDI-ToF and the NMR spectra of the polymer products, suggesting that no polymerization of the epoxide occurred.

**CONCLUSIONS**

In summary, five new monometallic pentacoordinate Fe$^\text{III}$ chloride complexes were prepared based on a half salen ligand scaffold. The complexes were characterized through a combination of elemental analysis, high-resolution mass spectrometry, and in three cases, X-ray crystallography. Combined with three previously reported analogues, this series of eight complexes bears a range of ligand substituents has been tested as mediators in the R-ATRP of styrene and MMA, achieving good to moderate control over the polymerization. The complexes have also been applied in the ROP of rac-lactide, generally giving >95% conversion after 24 h and showing that the in situ formation of Fe$^\text{III}$–alkoxide via epoxide opening is necessary for efficient initiation. Although this method of initiation is currently gaining momentum within ROP, some of our Fe$^\text{III}$ halide complexes give little or no conversion after 2 h, suggesting that epoxide opening by a metal–halide may require an extreme excess of toxic epoxide (i.e., as a solvent) to achieve control. In general, these results demonstrate the versatility of simple, air-stable Fe$^\text{III}$ halide complexes and show that this abundant, inexpensive, and nontoxic metal can be a relevant alternative in polymerization catalysis.

**EXPERIMENTAL SECTION**

**Materials and Methods.** All air- and/or moisture-sensitive experiments were performed under argon atmosphere using an MBRAUN LABmaster glovebox and standard Schlenk techniques. Solvents were obtained from a solvent purification system (Innovative Technologies) consisting of columns of alumina and copper catalyst and were further degassed by freeze–pump–thaw cycles prior to use. Styrene and MMA were dried by stirring over calcium hydrxide, vacuum transferred, and stored at −35 °C. rac-Lactide was sublimed three times and stored at −35 °C. 2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) was washed with methanol, dried under vacuum, and stored at −35 °C. 2,2′-Azobis(2-methylpropionitrile) (AIBN) was recrystallized from methanol, dried under vacuum, and stored at −35 °C. 2,6-Diisopropylamine was distilled under vacuum prior to use. N-Methylamine (40 m/m % in H$_2$O), salicylaldehyde, 3,5-dichlorosalicylaldehyde, and 3,5-di-tert-butylsalicylaldehyde were used as received. Gel permeation chromatography (GPC) was carried out in the HPLC grade THF solvent at a flow rate of 1 mL/min at 35 °C on a Malvern Instruments Viscotek 270 GPC Max triple detection system with 2× mixed bed styrene/DVB columns (300 × 7.5 mm). Absolute molar masses were obtained using the refractive index increment ($dn/dc$ values) for this sample/solvent combination of 0.185 mL/g for poly(styrene), 0.088 mL/g for poly(methyl methacrylate), and 0.05 mL/g for PLA. NMR spectra were obtained on a 500 MHz Bruker AVANCE III spectrometer. Solution magnetic moments were determined via NMR spectroscopy using Evans’ method. El mass spectra were obtained on a Bruker DALTONICS micro TOF instrument operating in the positive ion electrospray mode. MALDI-ToF mass spectrometry was performed on a Bruker ultraflexXtreme MALDI-ToF spectrometer; samples were prepared with dithranol as matrix and sodium or potassium iodide as the ionization source. Elemental analyses were performed by Stephen Boyer at London Metropolitan University.

**Synthetic Procedures.** Pro-ligands L1–L8 and complexes C1, C3, and C7 were prepared according to previously reported literature methods. Characterization data for L1, L2, L3, L4, L5, L6, L7, and L8 were in agreement with reported values in the literature.
Data for L8. (2.90 g, 91%) 1H NMR (500 MHz CDCl3): δ 14.49 (s, 1H, OH), 8.23 (s, 1H, HC=−N), 7.39 (d, J = 2.5 Hz, 1H, ArH), 7.12 (d, J = 2.5 Hz, 1H, ArH), 3.51 (d, J = 1.5 Hz, 3H, CH3); 13C NMR (126 MHz CDCl3): δ 164.9 (C=−N), 157.8 (C=OH), 132.4, 128.9, 123.3, 122.2, 119.4 (Ar-C), 44.9 (CH3). HRMS (EI): m/z [M]+ 202.9906; calcd [M]+ 202.9905. Elemental Anal. Calcd for C8H4ClFeN2O2: C, 38.6; H, 2.4; N, 5.6. Found: C, 38.8; H, 2.3; N, 5.7. 2H NMR spectroscopy to determine monomer conversion. The remainder of the reaction mixture was dissolved in chloroform (approximately 1 mL), and the polymer was precipitated by the addition of the solution to cold (0 °C) acidified methanol (MeOH/HCl(aq), 75:1 mL). The polymer was then isolated by filtration and dried in vacuo until constant weight was achieved. Samples for GPC analysis were prepared in HPLC grade THF solvent and filtered through a 0.20 mm pore sized syringe filter prior to analysis.

Crystallography. Single-crystal X-ray diffraction data were collected on a Rigaku Oxford diffractometer fitted with an Atlas CCD detector with Mo Kα radiation (λ = 0.7107 Å) or Cu Kα radiation (λ = 1.5418 Å). Crystals were mounted under Paratone on MiTeGen loops. The structures were solved by direct methods using SHELXS or SHELXT and refined by full-matrix least-squares on F2 using SHELXL interfaced through Olex2. Molecular graphics for all structures were generated using Diamond.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02432.

GPC and HRMS data, 1H NMR and MALDI spectra, and single-crystal X-ray diffraction data (PDF)

AUTHOR INFORMATION

Corresponding Authors
*E-mail: j.garden@ed.ac.uk (J.A.G.).
*E-mail: michael.shaver@ed.ac.uk (M.P.S.).

ORCID

Michael P. Shaver: 0000-0002-7152-6750

Notes

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