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Iron^{III} half salen catalysts for atom transfer radical and ring opening polymerizations

Eszter Fazekas,^a Gary S. Nichol,^a Jennifer A. Garden^{a*} and Michael P. Shaver^{a*}

^aEaStCHEM School of Chemistry, University of Edinburgh, Edinburgh, EH9 3FJ, UK.

E-mail: michael.shaver@ed.ac.uk, j.garden@ed.ac.uk

Abstract

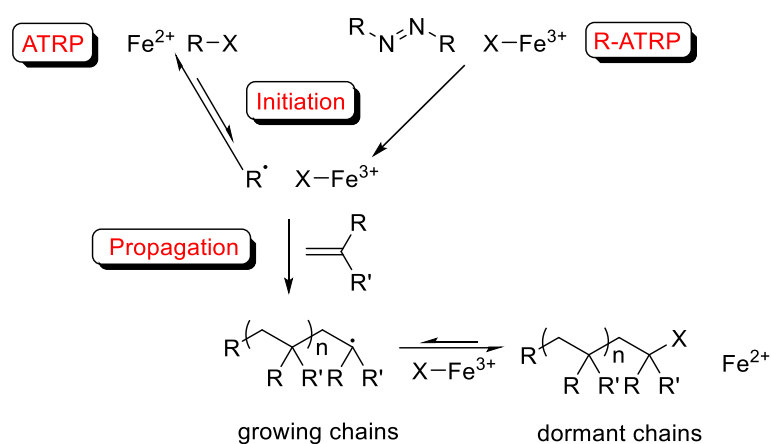
A series of monometallic pentacoordinate Fe^{III} chloride complexes has been prepared and characterized by high resolution mass spectrometry and elemental analysis. X-ray diffraction analysis showed that the pentacoordinate Fe^{III} complexes bear distorted trigonal bipyramidal geometries. The air- and moisture-stable Fe^{III} complexes were screened as mediators in the reverse atom transfer radical polymerization 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. While 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 a 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 Fe^{II} and Fe^{III} - 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

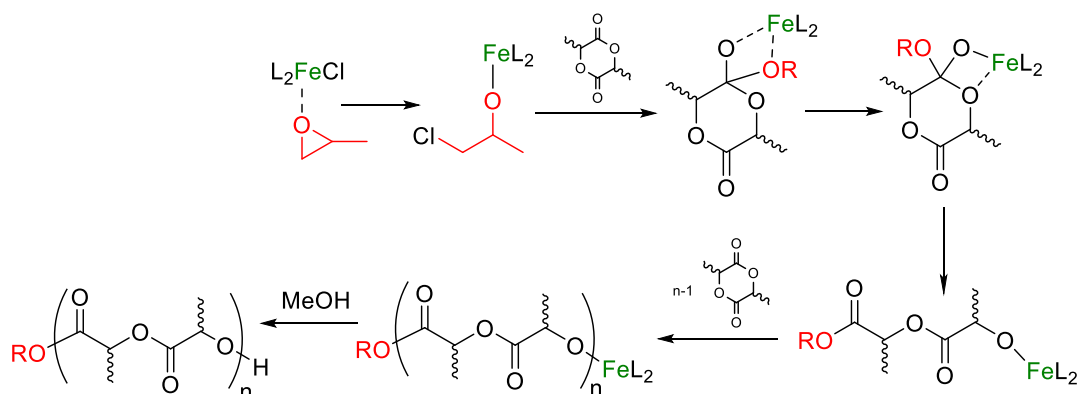
systems,¹⁰ the first Fe catalysts for ATRP were pioneered by the groups of Matyjaszewski and Sawamoto, originally using $\text{Fe}^{\text{II}}\text{X}_2(\text{PR}_3)_2$ ($\text{X} = \text{Cl}, \text{Br}$) type complexes.¹¹⁻¹² Since then, Fe salts and complexes with a variety of ligands (including phosphines, 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 Teyssié *et al.*,¹⁶ while amine bisphenolate complexes of both Fe^{II} and Fe^{III} showed good control in the RP of styrene and methyl methacrylate (MMA),¹⁷⁻²¹ through joint ATRP and organometallic mediated radical polymerization (OMRP) mechanisms.²²⁻²³



Scheme 1: Mechanism of Fe mediated ATRP and R-ATRP.

The ring opening polymerization (ROP) of cyclic esters - in particular the renewable cyclic diester lactide - is a burgeoning component of sustainable polymer development.²⁴ Industrially, poly(lactic acid) (PLA) is formed *via* the ROP of lactide catalysed by Sn-carboxylates. These catalysts require harsh reaction conditions, show limited control over the polymerization and can cause toxicity problems in biomedical applications. An intense effort to develop well defined, single site catalysts to achieve a better control over the dispersity and tacticity has led to a plethora of new catalysts for this reaction, including limited reports with some Cu complexes with relevance to ATRP.²⁵⁻²⁸ Iron catalysts are attractive alternatives due to their low cost and biocompatibility, but surprisingly few papers report efficient Fe ROP catalyst systems.²⁹⁻³⁶ Byers and co-workers developed a range of bis(imino)pyridine Fe alkoxide catalysts and showed that the polymerization was sensitive to both oxidation state and electron density of the Fe.^{9, 37} Salen complexes of Fe^{II} also supported the ROP of L-lactide, promoting isotacticity.³⁸ Following the recent trend of using propylene oxide (PO) triggered initiations,³⁹⁻⁴² Duan *et al.* reported on the *in situ* generation of salen-based Fe^{III} -alkoxide catalysts for the ROP of lactide and caprolactone.⁴³ The proposed mechanism suggests insertion of the PO into the Fe-Cl bond to form the catalytically active Fe-alkoxide (Scheme 2). Similar to Al-based

systems,³⁹ 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.



Scheme 2: Coordination-insertion mechanism of in situ Fe-alkoxide catalyzed lactide polymerization.

Complimentary to the well-studied tetradentate salen systems, tridentate derivatives of Schiff bases were also applied to support Fe^{III} as polymerization catalyst.⁴⁴ Considering the paucity of studies exploring Fe complexes with bidentate phenoxyimine ligands,^{45,46-47} we had recently developed a novel family of air-stable half salen Fe^{III} 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 application in R-ATRP (Scheme 1) and in ROP (Scheme 2) reactions. Half salen ligands offer the advantage of simple and modular synthesis to achieve stereoelectronically diverse properties (Figure 1). Aluminium complexes of these ligands have shown promising results in the ROP of cyclic esters,⁴⁹ including the application of monometallic Al-phenoxymimines 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

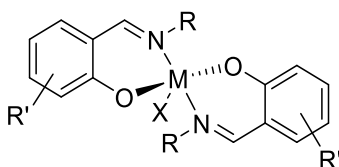
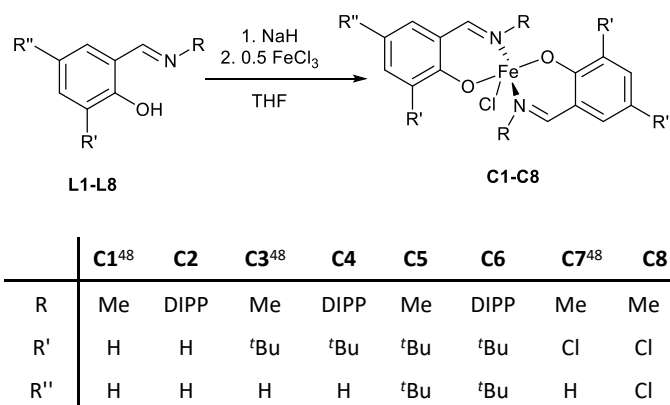


Figure 1: General structure of a bischelated half salen complex.

This work explores the synthesis of five bidentate phenoxyimine ligands, the corresponding novel Fe^{III} chloride complexes and their application in polymerization catalysis. Combined with the previously reported complexes, all eight Fe-phenoxymimines were screened as mediators in the reverse ATRP of styrene and MMA. Moreover, we explored the PO initiated ROP of *rac*-lactide, including understanding the limitations of this emerging initiation strategy.

Results and discussion

Synthesis and characterization



Scheme 3: Synthesis of Fe(III) complexes **C1-C8**.

A series of Fe^{III} 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 ^tBu 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 eq.) in THF solvent at ambient temperature gave an immediate colour change from yellow to dark purple, which indicated the formation of the desired L₂FeCl complexes (**C1-C8**). The resulting Fe complexes were isolated in moderate to high yields (45-89%) as dark purple-brown solids. As the paramagnetically shifted ¹H NMR spectra of the complexes provided limited information, the stoichiometry was confirmed with high resolution mass spectrometry and elemental analysis. All eight complexes were oxygen- and moisture stable, and single crystals of **C5**, **C6** and **C8** were obtained under air *via* the slow evaporation of DCM solvent. X-ray diffraction studies revealed that all three complexes display a mononuclear structure with distorted trigonal bipyramidal geometries ($\tau = 0.94, 0.87$ and 0.66 for **C5**, **C6** and **C8**, respectively) around the pentacoordinate Fe^{III} centre, using the τ factor developed by Addison *et al.* (where $\tau = 0$ for perfectly square pyramidal and $\tau = 1$ for perfectly trigonal bipyramidal geometries).⁵⁴ In line with the previously reported molecular structures of **C1**, **C3** and **C7**,⁴⁸ **C5** and **C8** both feature a N-Fe-N axis which is almost linear [**C5**, N(1)-Fe(1)-N(1'), 177.44(5)°; **C8**, N(1)-Fe(1)-N(2), 169.98(6)°], with one Cl and two phenoxy-O centres occupying the equatorial positions (Figures 2-3). In contrast, **C6** displays an O-Fe-O axis [O(1)-Fe(1)-O(2), 173.7(2)°]. This switch in axial and equatorial occupants may arise from the significant increase in steric bulk of the DIPP imine substituents. For **C5**, **C6** and **C8**, the bond metrics are comparable to previously reported Fe-half salen complexes,⁵⁵⁻⁵⁹ with Fe-N bond lengths ranging from 2.101(1) to 2.111(1) Å and Fe-O bond lengths of 1.8757(9)-1.911(1) Å. For all six structurally characterised complexes, the ancillary phenoxyimine ligands are arranged such that both nitrogen and both oxygen atoms are in mutually *trans* positions. These geometries differ

significantly from those observed with Fe^{III} salen and salalen complexes, which typically possess a square pyramidal geometry with mutually cis N and O ligands.^{41, 43} Upon the introduction of electronegative chloro substituents to the ligand scaffold, the Fe-Cl bond length is significantly shortened and strengthened, from 2.2713(5) Å for unsubstituted **C1**,⁴⁸ to 2.2517(6) Å for *mono*-chloro 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 μ_{eff} values of 4.6-5.5 B. M., which suggests high spin Fe^{III} complexes predominate.⁶⁰

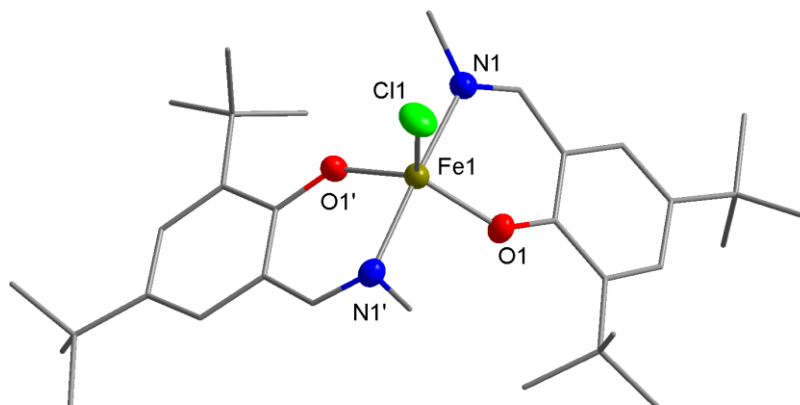


Figure 2: Molecular structure of **C5** with ellipsoids set at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Fe1 - Cl1 2.2713(5), Fe1 - O1 1.8758(9), Fe1 - N1 2.111(1). Selected bond angles (°): O1 - Fe1 - Cl1 119.50(3), O1' - Fe1 - O1 121.00(6), O1 - Fe1 - N1' 88.46(4), O1 - Fe1 - N1 90.28(4), N1 - Fe1 - Cl1 91.28(3), N1 - Fe1 - N1' 177.44(5).

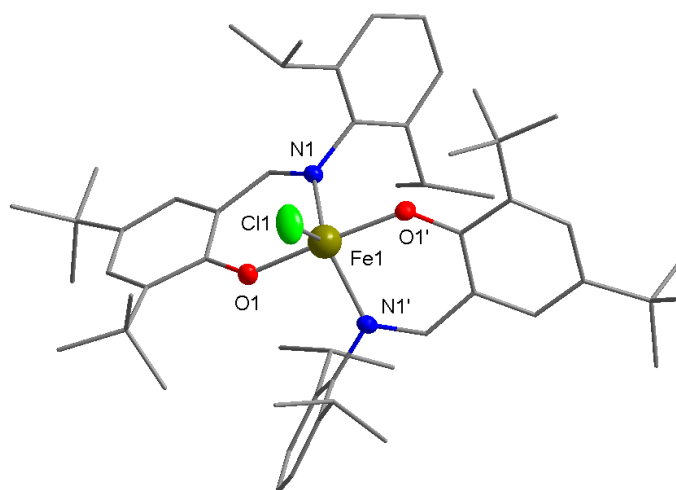


Figure 3: Molecular structure of **C6** with ellipsoids set at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Fe1 - Cl1 2.215(2), Fe1 - O1 1.921(3), Fe1 - N1 2.080(3). Selected bond angles (°): O1 - Fe1 - Cl1 93.2(1), O1 - Fe1 - O1' 173.7(2), O1 - Fe1 - N1 86.2(1), O1' - Fe1 - N1 90.7(1), N1 - Fe1 - Cl1 119.4(1), N1 - Fe1 - N1' 121.1(2).

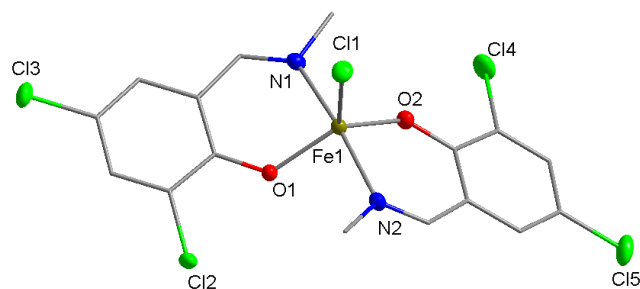


Figure 4: Molecular structure of **C8** with ellipsoids set at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Fe1 - Cl1 2.2271(5), Fe1 - O1 1.881(1), Fe1 - O2 1.911(1), Fe1 - N1 2.101(1), Fe1 - N2 2.104(2). Selected bond angles (°): O1 - Fe1 - Cl1 114.06(4), O1 - Fe1 - O2 130.30(5), O1 - Fe1 - N1 87.91(5), O1 - Fe1 - N2 90.12(5), O2 - Fe1 - Cl1 115.64(4), O2 - Fe1 - N1 87.02(5), O2 - Fe1 - N2 86.78(5), N1 - Fe1 - Cl1 96.19(4), N1 - Fe1 - N2 169.98(6), N2 - Fe1 - Cl1 93.58(4).

Atom Transfer Radical 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 a lower temperature of 75 °C (Table 1). As expected, the lower temperature of reaction used with V-70 lead 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 centre using AIBN and **C1**, **C7** and **C8** as mediators (entry 1, 13 and 15). Surprisingly, along providing one of the highest conversions (56%) **C8** also displayed good control over the dispersities, with \bar{D} values (1.2, entry 15 and 16) that are comparable with the best reported for Fe^{III} R-ATRP systems.^{19, 61} Of particular interest, catalyst **C6** was an excellent mediator using V-70, affording polystyrene with very narrow dispersity (\bar{D} = 1.05, entry 12) with matching theoretical and experimental molecular weights. This may suggest that the bulky ^tBu substituents can sterically stabilise the reduced Fe^{II} derivative during the R-ATRP process. The presence of these electron donating groups may possibly also decrease the Lewis acidity of the metal centre, and therefore limit the concentration of active chains. On the contrary, when **L6** was investigated by Gibson *et al.* in a monochelated FeLCl₂ type complex poor control was achieved, attributed to the relative instability of the reduced tricoordinate Fe^{II} species formed during polymerization.⁴⁴ Interestingly, **C5** with identical ^tBu 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 (\bar{D} = 1.4 to 1.5), while **C1**, **C2**, **C5** and **C7** were relatively poor mediators providing broad dispersities (\bar{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, 9-10), the number average molecular weights (M_n) were higher than the theoretical values ($M_{n,th}$), suggesting inefficient initiation.

Table 1 Screening of catalysts **C1-C8** in styrene R-ATRP.

| Entry | Complex | Init. | Conv. (%) | $M_{n,th}$ (Da) | M_n (Da) | \bar{D} |
|-------|-----------|-------------------|-----------|-----------------|------------|-----------|
| 1 | C1 | AIBN | 29 | 3000 | 3800 | 1.7 |
| 2 | | V-70 ^a | 18 | 1900 | 3600 | 1.4 |
| 3 | C2 | AIBN | 61 | 6400 | 11600 | 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 | 15500 | 2.2 |
| 10 | | V-70 | 33 | 6800 | 13800 | 1.8 |
| 11 | C6 | AIBN | 23 | 2400 | 4200 | 1.4 |
| 12 | | V-70 | 25 | 2600 | 2600 | 1.1 |
| 13 | C7 | AIBN | 45 | 4700 | 14200 | 1.6 |
| 14 | | V-70 | 23 | 2400 | 6000 | 1.4 |
| 15 | C8 | AIBN | 56 | 5800 | 10900 | 1.2 |
| 16 | | V-70 ^a | 14 | 1500 | 5700 | 1.2 |

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 hours. Conversion was determined using ¹H NMR spectra of crude reaction mixtures. $M_{n,th} = [\text{styrene}]_0 / [\text{Fe}] \times M(\text{styrene}) \times \text{conversion}$. ^a Insufficient polymer was precipitated after 2 hours to allow analysis, therefore a sample precipitated after 4 hours reaction time was used.

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 deviate from the expected first-order dependence on monomer concentration, which may be due to the presence of competing side-reactions (*vide infra*) (Figure 5).

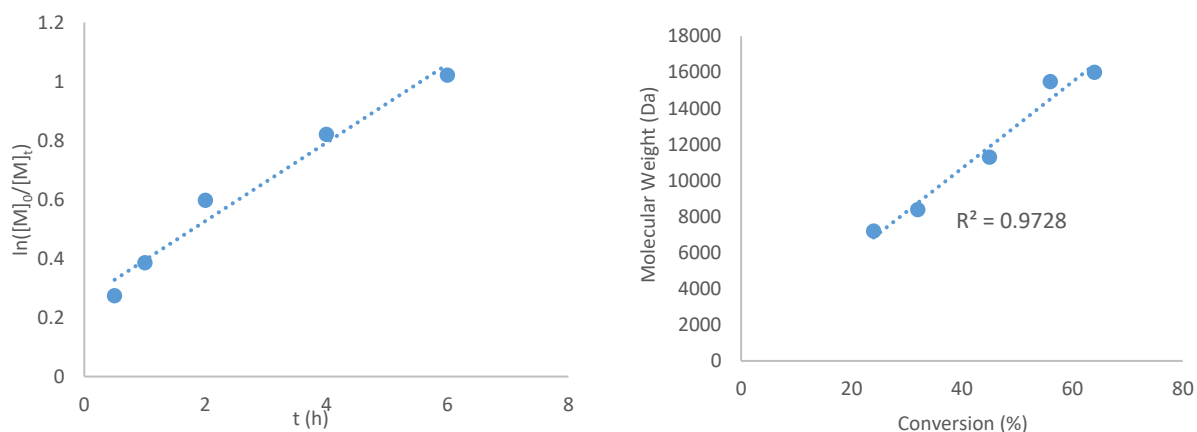


Figure 5: Kinetic plots for styrene polymerization: $\ln([M]_0/[M]_t)$ vs time (on left) and molecular weight vs conversion (right).

To provide insight into the nature of the polymer end groups, the purified polystyrene samples were investigated by ^1H NMR spectroscopy. Besides the expected halide capping group ($\text{ClCH}(\text{Ph})\text{CH}_2$ 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. These findings suggest that catalytic chain transfer (CCT) side reactions occur, which compete with the ATRP mechanism (Figure 6).¹⁸ However, molecular weights increased linearly with the conversion, as observed previously for intermediate spin α -diimine Fe complexes.⁶²⁻⁶³

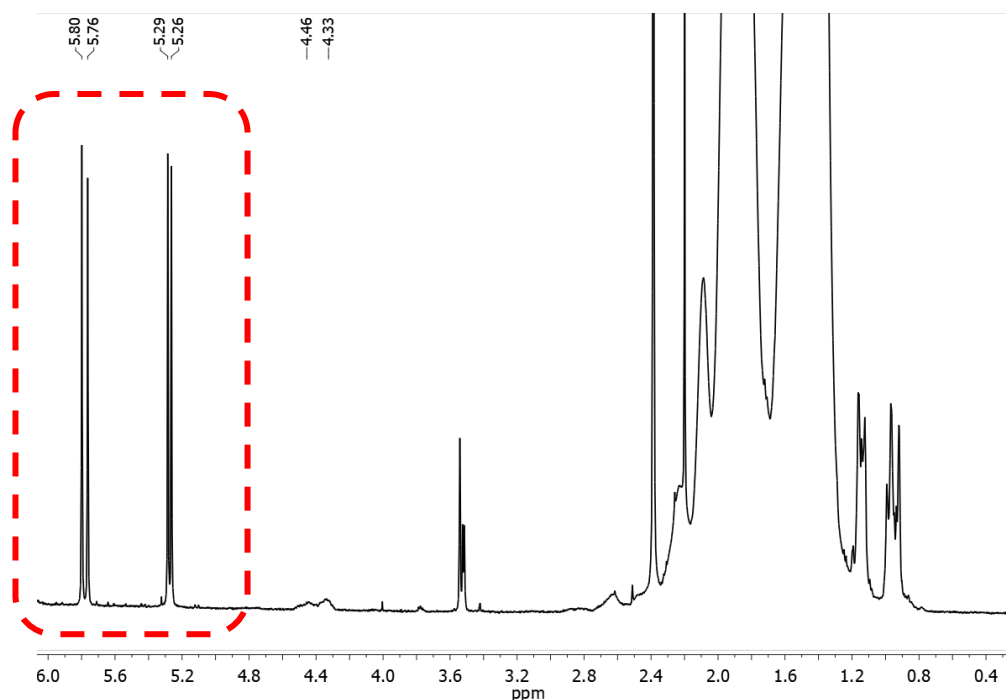
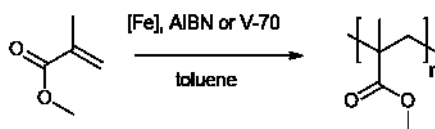


Figure 6: ^1H NMR spectrum (CDCl_3 , 20 °C) showing doublet peaks of olefin terminated polymer chains formed via CCT.

The R-ATRP of MMA using **C1-C8** as mediators afforded polymers with M_n significantly in excess of the theoretical values ($M_{n,\text{th}}$), which is a common phenomenon using this monomer with azo initiators (AIBN and V-70).¹⁷ Similarly to the styrene polymerizations, using **C1**, **C3** and **C5** as mediators the conversion increased with the presence of sterically bulky ^tBu substituents on the half salen ligand scaffold (Table 2, entry 1, and 9). The complexes were found to be moderate to poor mediators achieving relatively broad dispersities ($\mathcal{D} = 1.4\text{-}2.3$). The exception was unsubstituted complex **C1**, which achieved moderate activity (28-30% conversion) while exerting good control ($\mathcal{D} = 1.1$ 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.⁶⁴

Table 2 Screening of catalysts **C1-C8** in MMA R-ATRP.



| Entry | Complex | Init. | Conv. (%) | $M_{n,th}$ (Da) | M_n (Da) | \bar{D} |
|-------|---------|-------|-----------|--------------------|---------------|-----------|
| 1 | C1 | AIBN | 28 | 2800 | 8400 | 1.1 |
| 2 | | V-70 | 30 | 3000 | 13000 | 1.2 |
| 3 | C2 | AIBN | 76 | 7600 | 17000 | 1.8 |
| 4 | | V-70 | 66 | 6600 | 18900 | 2.3 |
| 5 | C3 | AIBN | 47 | 4700 | 12700 | 1.6 |
| 6 | | V-70 | 24 | 2400 | 18800 | 1.5 |
| 7 | C4 | AIBN | 85 | 8500 | 18400 | 1.4 |
| 8 | | V-70 | 68 | 6800 | 15700 | 1.4 |
| 9 | C5 | AIBN | 61 | 6100 | 16700 | 2.2 |
| 10 | | V-70 | 54 | 5400 | 16500 | 1.9 |
| 11 | C6 | AIBN | 65 | 6500 | 22800 | 1.4 |
| 12 | | V-70 | 62 | 6200 | 14900 | 1.4 |
| 13 | C7 | AIBN | 68 | 6800 | 18900 | 1.7 |
| 14 | | V-70 | 62 | 6200 | 19400 | 1.6 |
| 15 | C8 | AIBN | 64 | 6400 | 16100 | 1.8 |
| 16 | | V70 | 63 | 6300 | 16400 | 1.4 |

Conditions: $[MMA]:[Fe^{III}]:[I] = 100:1:0.6$, MMA : toluene = 1 : 1 (v/v), 120 °C for AIBN or 75 °C for V-70, 2 hours. Conversion was determined using 1H NMR spectra of crude reaction mixtures. $M_{n,th [Fe]} = [MMA]_0/[Fe] \times M(MMA) \times \text{conversion}$.

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 due to bimolecular termination side reactions.⁷ Similarly to the polystyrene samples, 1H NMR analysis revealed the presence of olefin terminated polymer chains (doublets at 5.50 and 6.23 ppm, Figure S14). However, the integrals of these peaks are relatively low compared to the polymer peaks, which suggests significantly less CCT than observed for styrene.

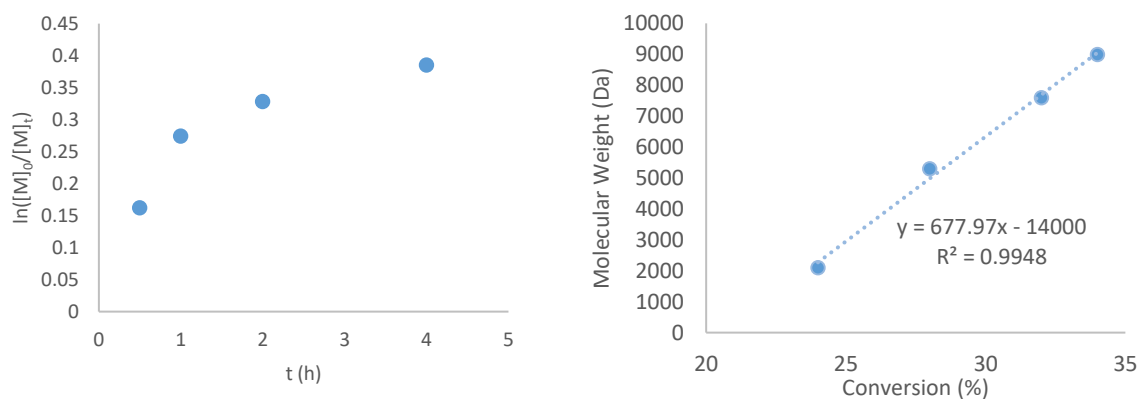


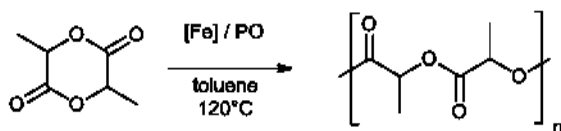
Figure 7: Kinetic plots for MMA polymerization with **C1**: $\ln([M]_0/[M]_t)$ vs time (left) and molecular weight vs conversion (right).

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 LA. Most catalysts for this reaction include a metal-alkoxide initiating group, which is typically formed from 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} and so we tested our Fe-Cl complexes for the ROP of *rac*-LA in the presence of propylene oxide as activator. Contrary to 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/lactide system due to 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 hours in toluene solvent. (Table S1, entry 1-4). This modification enabled the polymerizations to be performed in airtight 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, entry 1 and 2). Under the optimised conditions, **C1-C8** all achieved almost complete conversion of LA (>89%), although inconsistent molecular weights and broad dispersities indicated uncontrolled polymerizations (Table 3, entry 3-10). This was attributed to detrimental side-reactions, such as intramolecular and intermolecular transesterifications, which are commonly observed in ROP at high conversions.²⁵ The tacticity was investigated through homonuclear decoupled ¹H NMR experiments of the purified polymers, which revealed a lack of control over the tacticity with a P_i value of 0.52 indicating atactic enchainments (Figure S15). To reduce the rate of undesired side-reactions, the polymerization was tested under milder conditions (85 °C), affording only traces of PLA (Table S1, entry 5). Attempts to reduce the reaction time from 24 hours to 2 hours using **C1-C8** led to variable conversions (Table 3, Entry 11-18) with significant errors in reproducibility (Table S1, entry 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/CO₂ copolymerization reactions,⁶⁵⁻⁶⁷ but may have been overlooked in the *in situ* formation of metal-alkoxide catalysts for ROP. The higher average molecular weights observed after 2 hours of reaction time (compared to 24 h reactions) suggest the presence of extensive transesterification reactions that cleave longer polymer chains.²⁴ Efforts to minimize the reaction variability through the use of a PO stock solution or a higher-boiling activator (butylene oxide, b.p. 63 °C) were unsuccessful (Table S1, entry 6-12). The inefficient initiation observed after 2 hours of reaction time using **C2**, **C5**, **C7** and **C8** (Table 3, entry 12, 15, 17 and 18) 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). Screening of catalysts **C1-C8** in styrene R-ATRP. These results suggest that *in situ* initiation can lead to greater experimental variation in comparison to the

use of pre-formed metal-alkoxide complexes. Indeed, pre-forming the active Fe-alkoxide species by stirring the Fe^{III}-Cl species **C8** with excess PO for 16 hours, prior to the addition of LA, drastically increased the conversion from 1% (entry 18) to 90% (entry 19). Moreover, using the pre-formed 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 MALDI-ToF spectrum of the purified polymer showed a series of chains terminated by -OCH(Me)CH₂Cl and -OH groups (Figure S19-S20). Additional polymer series bearing -OCH(Me)CH₂OH 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 repeating 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 poly(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.

Table 3 ROP of *rac*-lactide catalysed by complexes **C1-C8** and propylene oxide.



| Entry | Complex | time (h) | Conv. (%) | M _{n, th} (Da) | M _n (Da) | Đ |
|-------------------|-----------|----------|-----------|-------------------------|---------------------|-----|
| 1 | - | 24 | 0 | - | - | - |
| 2 ^a | C8 | 24 | 0 | - | - | - |
| 3 | C1 | 24 | 95 | 13700 | 8800 | 1.4 |
| 4 | C2 | 24 | 95 | 13700 | 1500 | 1.7 |
| 5 | C3 | 24 | 95 | 13700 | 3300 | 1.4 |
| 6 | C4 | 24 | 95 | 13700 | 9000 | 1.6 |
| 7 | C5 | 24 | 93 | 13400 | 40600 | 1.6 |
| 8 | C6 | 24 | 95 | 13700 | 2100 | 4.0 |
| 9 | C7 | 24 | 93 | 13400 | 12600 | 1.8 |
| 10 | C8 | 24 | 89 | 12800 | 17200 | 1.5 |
| 11 ^b | C1 | 2 | 78 | - | - | - |
| 12 | C2 | 2 | 2 | - | - | - |
| 13 | C3 | 2 | 89 | 12900 | 5500 | 1.1 |
| 14 | C4 | 2 | 90 | 13000 | 45900 | 1.7 |
| 15 | C5 | 2 | 49 | 7100 | 50500 | 1.3 |
| 16 | C6 | 2 | 91 | 13100 | 42200 | 1.5 |
| 17 | C7 | 2 | 49 | 7100 | 22000 | 1.4 |
| 18 | C8 | 2 | 1 | - | - | - |
| 19 ^c | C8 | 2 | 90 | 13000 | 15900 | 2.1 |
| 20 ^{c,d} | C8 | 2 | 89 | 12800 | 17200 | 1.5 |

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. $M_{n,th}[\text{Fe}] = [\text{lactide}]_0/[\text{Fe}] \times M(\text{lactide}) \times \text{conversion}$. ^a Reaction was carried out without the addition of propylene oxide. ^b Efforts to recover polymer were unsuccessful, indicating the formation of shorter polymer chains. ^c The Fe complex was stirred for 16 hours in excess propylene oxide at room temperature prior to the addition of lactide. ^d The reaction was performed at 85 °C.

Conclusions

In summary, five new monometallic pentacoordinated Fe^{III} chloride complexes were prepared based on a half salen ligand scaffold. The new 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 bearing a range of ligand substituents have been tested as mediators in the reverse ATRP of styrene and methyl methacrylate, achieving good to moderate control over the polymerization. The complexes have been also applied in the ROP of *rac*-lactide, generally giving >95% conversion after 24 hours and showing that the *in situ* formation of Fe^{III}-alkoxide *via* epoxide opening is necessary for efficient initiation. While this method of initiation is currently gaining momentum within ROP, some of our Fe^{III} half salen catalysts give little or no conversion after two hours, 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^{III} half salen complexes, and show that this abundant, inexpensive, non-toxic metal can be a relevant alternative in polymerization catalysis.

Experimental

Materials and methods

All air- and/or moisture-sensitive experiments were performed under an 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 methyl methacrylate (MMA) were dried by stirring over calcium hydride, 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-Di-isopropylaniline was distilled under vacuum prior to use. N-Methylamine (40 m/m % in H₂O), salicylaldehyde, 3,5-dichlorosalicylaldehyde and 3,5-di-*tert*-butylsalicylaldehyde were used as received. Gel permeation chromatography (GPC) was carried out in 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)⁶⁸, 0.088 mL/g for poly(methyl methacrylate)⁶⁹ and 0.05 mL/g for poly(lactic acid).⁷⁰ NMR spectra were obtained a 500 MHz Bruker Avance III spectrometer.

Solution magnetic moments were determined *via* NMR spectroscopy using Evans' method.⁶⁰ EI 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 UltraflexExtreme MALDI-ToF spectrometer, samples were prepared dithranol ad 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.^{48, 53, 71-73} Characterization data for **L1**,⁴⁸ **L2**⁵², **L3**,⁴⁸ **L4**⁷³, **L5**⁷⁴, **L6**⁵² and **L7**⁴⁸ was 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 calculated [M]⁺ 202.9905. Elemental Analysis Calculated for C₈H₇Cl₂NO: C, 47.1; H, 3.5; N, 6.9. Found: C, 47.3; H, 3.35; N, 7.0.

General procedure for complexes **C2**, **C4-C6**, **C8**

To a solution of pro-ligand (**L1-8**) in THF solvent, 1.1 equivalents of NaH was gradually added and the mixture was stirred at ambient temperature for 1 hour. A solution of anhydrous FeCl₃ (0.5 equivalents) in THF was added dropwise to afford a dark colored mixture that was stirred for a further 16 hours at room temperature. Solvents were evaporated *in vacuo* and the crude product was taken up in toluene solvent. The NaCl by-product was removed by filtration through celite and the filtrate was dried *in vacuo*. The crude products were washed three times with hexane to afford dark purple-brown powders. Single crystals suitable for X-ray diffraction analysis were obtained *via* slow evaporation of DCM under air. Structures of **C5**, **C6** and **C8** can be found under CCDC numbers 1868412-1868414.

Data for C2 (1.1 g, 52%) HRMS (EI): *m/z* [M]⁺ 651.2441 calculated [M]⁺ 651.2441 Elemental Analysis Calculated for C₃₈H₄₄ClFeN₂O₂: C, 70.0; H, 6.8; N, 4.3. Found: C, 70.2; H, 6.8; N, 4.4.

Data for C4 (1.1 g, 49%) HRMS (EI): *m/z* [M]⁺ 763.3718 calculated [M]⁺ 763.3693 Elemental Analysis Calculated for C₄₆H₆₀ClFeN₂O₂: C, 72.3; H, 7.9; N, 3.7. Found: C, 70.1; H, 7.8; N, 4.0.

Data for C5 (1.4 g, 89%) HRMS (EI): *m/z* [M]⁺ 583.2790 calculated [M]⁺ 583.2754 Elemental Analysis Calculated for C₃₂H₄₈ClFeN₂O₂: C, 65.8; H, 8.3; N, 4.8. Found: C, 65.9; H, 8.4; N, 4.9.

Data for C6 (1.0 g, 49%) HRMS (EI): *m/z* [M]⁺ 875.5019 calculated [M]⁺ 875.4945 Elemental Analysis Calculated for C₅₄H₇₆ClFeN₂O₂: C, 74.0; H, 8.7; N, 3.2. Found: C, 74.1; H, 8.8; N, 3.2.

Data for C8 (0.6 g, 45%) HRMS (EI): m/z $[M]^+$ 494.8716 calculated $[M]^+$ 494.8691 Elemental Analysis Calculated for $C_{16}H_{12}Cl_5FeN_2O_2$: C, 38.6; H, 2.4; N, 5.6. Found: C, 38.8; H, 2.5; N, 5.6.

General procedure for the R-ATRP of styrene and methyl methacrylate

In a glovebox, the complex (**C1-C8**) (24.0 μ mol), monomer (100 equivalents, 2.40 mmol), toluene (toluene : monomer, 1 : 1, v/v) and initiator (AIBN or V-70) (0.6 equivalents, 14.4 μ mol) were sequentially added to an airtight screwcap vial equipped with a magnetic stirrer bar. The vial was removed from the glovebox and heated to 75 °C or 120 °C for 2 hours. The vial was subsequently cooled to room temperature, and an aliquot of the crude mixture was analysed *via* 1H NMR spectroscopy to determine the monomer conversion. The remainder of the reaction mixture was quenched with chloroform (approximately 1 mL) and the polymer was purified by precipitation in acidified methanol (MeOH : HCl(aq), approximately 75 ml : 1 ml). The polymer was isolated by filtration and was subsequently dried *in vacuo* until constant weight was achieved. Samples for GPC analysis were prepared in HPLC grade THF and filtered through a 0.20 μ m pore sized syringe filter.

General procedure for the ROP of *rac*-lactide

In a glovebox, complex (**C1-C8**) (10.0 μ mol), propylene oxide (50 equivalents, 0.5 mmol), *rac*-lactide (100 equivalents, 1.0 mmol) and toluene (1 ml) were added to an airtight screwcap vial equipped with a magnetic stirrer bar. The vial was transferred to the bench and heated to 120 °C in an oil bath for 24 hours. The vial was subsequently cooled to room temperature, the reaction mixture was quenched with hexane, and an aliquot of the crude mixture was analysed *via* 1H 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 ml : 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 μ m pore sized syringe filter prior to analysis.

Crystallography

Single crystal X-ray diffraction data were collected on an Rigaku Oxford Diffraction SuperNova diffractometer fitted with an Atlas CCD detector with Mo-K α radiation ($\lambda = 0.7107$ Å) or Cu-K α radiation ($\lambda = 1.5418$ 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 F^2 using SHELXL interfaced through Olex2.⁷⁵⁻⁷⁶ Molecular graphics for all structures were generated using Diamond.

Conflicts of interest

There are no conflicts of interest to declare.

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Author information

j.garden@ed.ac.uk, michael.shaver@ed.ac.uk, Eszter.Fazekas@ed.ac.uk, G.S.Nichol@ed.ac.uk

Supporting information

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

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