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Controlled Radical Polymerization Mediated by Amine-bis(phenolate) Iron(III) Complexes**

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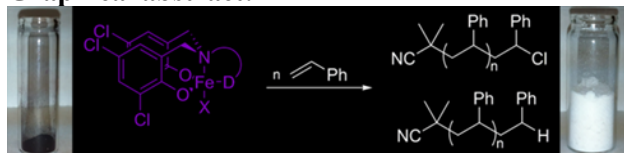
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Synopsis:

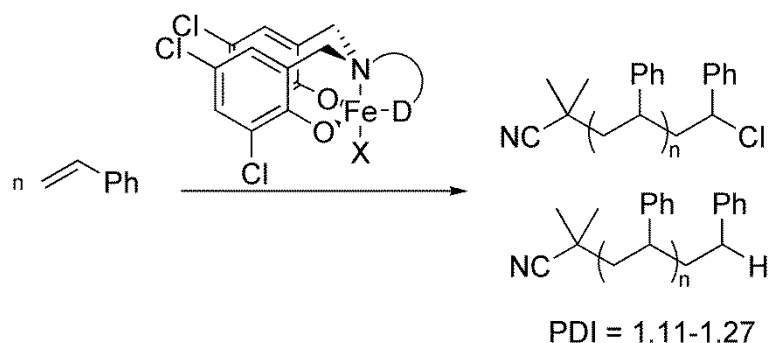
Facile recovery of white polymers is essential for the commercialization of controlled radical polymerization. A new family of highly active, benign iron catalysts, believed to operate through a unique dual control mechanism, is reported. Despite the deep purple color of the complexes and polymerization media, simple precipitation yields pure white polymers with polydispersities as low as 1.1.

Keywords:

atom transfer radical polymerization (ATRP); controlled radical polymerization; iron; polymethylmethacrylate (PMMA); polystyrene (PS)

Abstract

Tetradentate amine-bis(phenolate) iron(III) halide complexes containing chloro substituents on the aromatic ring are extremely efficient catalysts for controlled radical polymerization. Molecular weights are in good agreement with theoretical values and PDIs are as low as 1.11 for styrene and MMA polymerizations. Complexes containing alkyl substituents on the aromatic ring are less efficient. Kinetic data reveal activity for styrene polymerization among the fastest reported to date and initial studies implicate a multi-mechanism system. Despite the highly-coloured polymerization media, simple work-up procedures yield pure white polymers.



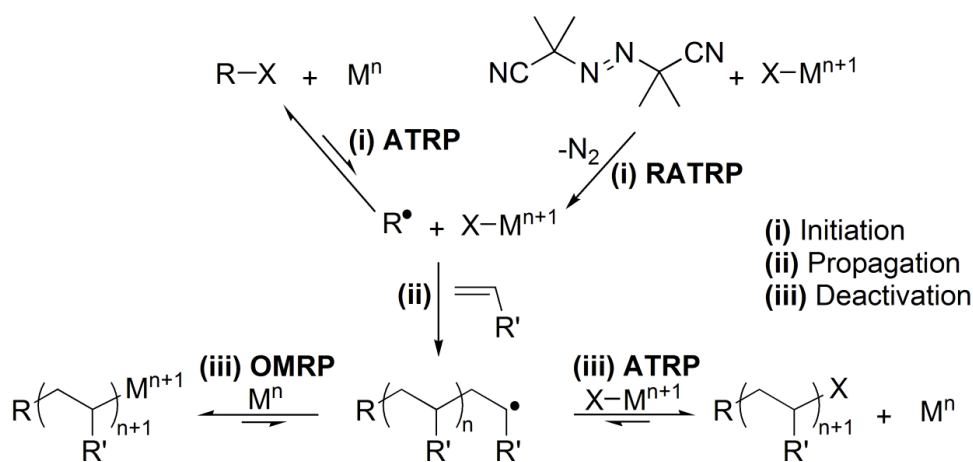
Introduction

Controlled radical polymerization (CRP) offers polymer chemists and engineers the ability to alter polymer macrostructure and create a unique array of materials with high functional group tolerance and defined molecular weights. Metal-mediated methods are especially important as tuning the supporting ligand framework in a metal complex can expand the monomer scope and open up new applications.^[1]

Unfortunately, commercialization of these methods has been challenging,^[2] particularly due to the residual color of the polymeric material and concerns over copper remaining in the final product. While important progress has been made to improve existing systems,^[3] the need for new systems that can address these challenges remains. This work highlights the development of a new family of non-toxic iron catalysts that control the radical polymerization of styrene and methyl methacrylate to form the desired white polymers with minimal purification, through a unique dual-control mechanism.

Atom transfer radical polymerization (ATRP) utilizes a redox-active transition metal catalyst, typically in conjunction with an alkyl halide initiator (**Scheme 1**).^[4] Metal-mediated halogen exchange between the oxidized metal complex and the propagating radical is used to control the equilibrium between active and dormant species. Halogen-terminated polymer chains with controlled molecular weights and narrow polydispersities are obtained. Reverse atom transfer radical polymerization (RATRP) operates using the same equilibrium as ATRP, but the metal complex is introduced in its higher oxidation state and used with a

conventional radical initiator (e.g. AIBN, see Scheme 1).^[5] These polymers are α -functionalized by nitrile groups and ω -functionalized by halides, and so can be used as the initiating species in subsequent ATRP to form block copolymers and other macromolecular structures. First reported in the mid 1990s,^[6] ATRP has been successful with a wide variety of transition metal catalysts including Mo, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd and Cu.^[4,7] More recently, interest in organometallic mediated radical polymerization (OMRP) has been growing.^[4,8] OMRP is based on the reversible homolytic cleavage of the weak bond between an alkyl group and a transition metal complex, which acts as a reversible spin-trap. Polymerization can be initiated by using a radical initiator with a redox-active metal compound, or by utilizing a complex containing a pre-formed metal-carbon bond.

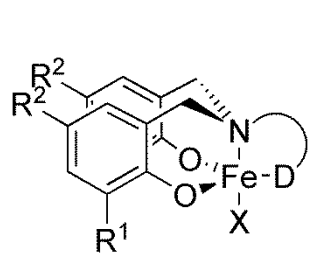


Scheme 1. Exchange equilibria used in ATRP, RATRP and OMRP.

Iron is an attractive metal to target for use in CRP, as it is of low toxicity and high abundance, and thus economically viable. Much work has been devoted to the development of iron catalysts in (R)ATRP, with multidentate amines,^[9] imines,^[10] phosphines,^[11] thiocarbamates,^[12] carbenes^[13] and organic acids^[14] all used as ligands for iron(II) or iron(III) halides. Simple systems comprising iron halides and ammonium, phosphonium, imidazolium or phosphazanium salts have also been studied.^[15] Of particular relevance to this work are the α -diimine iron complexes,^[16] which are reported to operate through both ATRP and catalytic chain transfer regimes, the latter via organometallic intermediates.

Results and Discussion

The iron(III) amine-bis(phenolate) complexes shown in **Figure 1** have previously been reported as active catalysts for the cross-coupling of aryl Grignard reagents with alkyl halides.^[17] We were interested in whether they could facilitate controlled radical polymerization and initially investigated the system for RATRP.



	R ¹	R ²	D	X
1	^t Bu	Me	CH ₂ Furf	Cl
2	^t Bu	Me	CH ₂ Furf	Br
3	^t Bu	^t Bu	CH ₂ Furf	Br
4	^t Bu	^t Bu	(CH ₂) ₂ OMe	Br
5	Cl	Cl	(CH ₂) ₂ NMe ₂	Cl
6	Cl	Cl	(CH ₂) ₂ NMe ₂	Br
7	Cl	Cl	CH ₂ Furf	Cl
8	Cl	Cl	CH ₂ Py	Cl
9	Cl	Cl	CH ₂ Py	Br
10	Cl	Cl	(CH ₂) ₂ OMe	Br

Furf = tetrahydro-2-furanyl
Py = 2-pyridinyl

Figure 1. Amine-bis(phenolate) iron(III) complexes.

Screening data for reactions carried out using complexes **1-10** with 100 equivalents of styrene are reported in **Table 1**. Complexes **1-4**, containing electron-donating alkyl substituents on the aromatic ring, were poor mediators of the polymerization. Although high conversions were achieved after 1 hour at 120°C, molecular weights were significantly higher than theoretical values and PDIs were broad, indicating a lack of control. Complexes **5-10**, containing electron-withdrawing chlorine substituents on the aromatic rings, were exceptional catalysts for the polymerization of styrene. Molecular weights were generally in good agreement with theoretical values and PDIs as low as 1.11 illustrate the excellent control over the polymerization. For comparable complexes, the iron chlorides were faster catalysts than the analogous iron bromides (e.g. complexes **1** and **2**, **5** and **6**, **8** and **9**), while the iron bromide complexes generally gave the best control over PDI. Similar trends were observed when 200 equivalents of styrene were used, with chloro-substituted complexes **5-10** imparting good control over the polymerizations (Table S1, supporting information). Molecular weights were in good agreement with the theoretical values and PDIs were only slightly broader than the values obtained at the lower styrene ratio, at 1.15-1.35.

To further investigate the efficacy of **1-10**, reactions to probe monomer scope were carried out. Chloro-substituted complexes **5-10** (Table 1), plus representative alkyl-substituted complexes **2** and **4** were screened for MMA polymerization. Reactions proceeded extremely rapidly in bulk, achieving complete conversion within the 1 h timeframe. Complexes **2** and **4** showed only moderate control over the polymerization, with molecular weights which were significantly higher than the theoretical values and PDIs of ca 1.5. However, complexes **5-10** showed excellent control over both molecular weights and PDIs, with PMMA molecular weight distributions of 1.14-1.36. To reduce the rate of polymerization and allow accurate conversions to be determined, the screening reactions were repeated using a 1:1 solution of MMA in toluene (Table S2, supporting information). Polymerizations using **5-10** were still well-controlled, with little deviation between the PDIs of polymers obtained from bulk reactions versus solution reactions. However, molecular weights were noticeably higher than the theoretical values, potentially due to the presence of longer-lived propagating

radicals in the more dilute solution polymerization. Attempts to polymerize vinyl acetate using **5** were unsuccessful, as only a trace of polymer was isolated after 6 hours at 120°C. The broad PDI and high molecular weight indicated that this was most likely a thermal polymerization and that the iron complex could not reactivate the chloro-capped vinyl acetate radicals. Complex **5** was more successful in mediating the polymerization of methyl acrylate, although a loss of control resulted in a bimodal distribution. Polymer samples contained both a high molecular weight component with a broad PDI and a moderate molecular weight component (close to the theoretical values calculated from the conversion) with low PDI, suggesting further investigations into this monomer are warranted.

Table 1. Monomer scope screening using iron(III) complexes **1-10**.

Complex	Monomer	% conv.	M _n	M _{n,th}	PDI
1	Styrene	79	12900	6900	2.01
2	Styrene	48	10500	4166	1.47
3	Styrene	86	13900	7433	2.44
4	Styrene	50	11500	4340	1.64
5	Styrene	63	6100	5445	1.19
6	Styrene	46	5600	3992	1.12
7	Styrene	54	7800	4687	1.27
8	Styrene	60	8500	5208	1.11
9	Styrene	37	4600	3298	1.16
10	Styrene	47	4900	4079	1.14
2	MMA	>99	14000	8378	1.53
4	MMA	>99	12800	8378	1.50
5	MMA	>99	8300	8378	1.22
6	MMA	>99	10500	8378	1.21
7	MMA	>99	8800	8378	1.36
8	MMA	>99	10200	8378	1.33
9	MMA	>99	8400	8378	1.19
10	MMA	>99	7500	8378	1.14
5	VAc)	10	54400b)	746	2.43
5	MA	>99	603200 8900c)	7174	1.81 1.29

Bulk polymerizations, initiated with AIBN at 120°C for 1 h with a complex:initiator:monomer ratio of 1:0.6:100. $M_{n,th} = [M]/2[I] \times MW(\text{monomer}) \times \text{conv.}$ ^{a)} VAc polymerization run for 6 h. ^{b)} M_n corrected using VAc correction factor. ^{c)} Bimodal distribution.

To investigate the mechanism of polymerization, kinetic studies were undertaken with a representative iron(III) amine-bis(phenolate) complex. A first-order rate constant of 0.41 h⁻¹ was obtained for styrene polymerization using the efficient chloro-substituted catalyst **5**, making it one of the most active iron catalysts for styrene polymerization to date.^[10b,16d,16e] **Figure 2a** shows the semilogarithmic plot of $\ln([M]_0/[M]_t)$ versus time, which is linear after the first 20 minutes, indicating that radical concentrations are constant during the

polymerization. Molecular weights are in excellent agreement with the theoretical values, as shown in **Figure 3**. Although the PDIs are narrow throughout the polymerization (Figure 3), they decrease significantly as the reaction progresses, from 1.32 initially to 1.16 at 90% conversion. This is indicative of a slow rate of activation relative to the rate of propagation,^[8a] which also explains the non-linearity of the polymerization rate during the first 20 minutes.

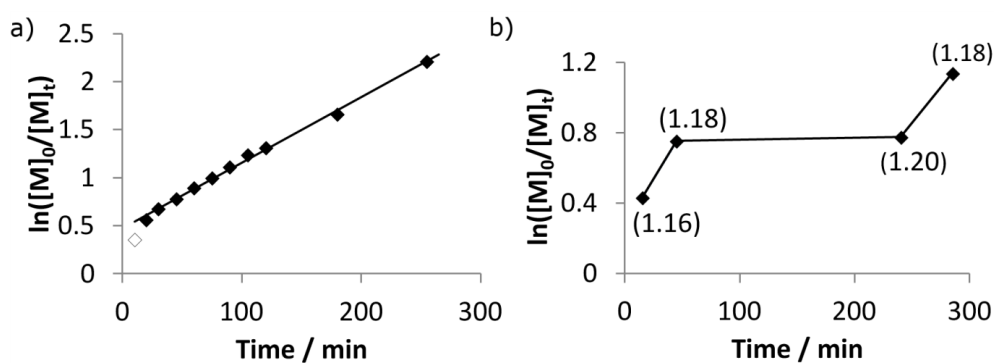


Figure 2. a) Plot of $\ln([M]_0/[M]_t)$ versus time for bulk styrene polymerization at 120°C using **5**. Solid data points used in calculating least-squares fit. b) Start-stop experiment for the bulk polymerization of styrene using **5**. Temp = 120°C/0°C/120°C. PDI values given in parentheses.

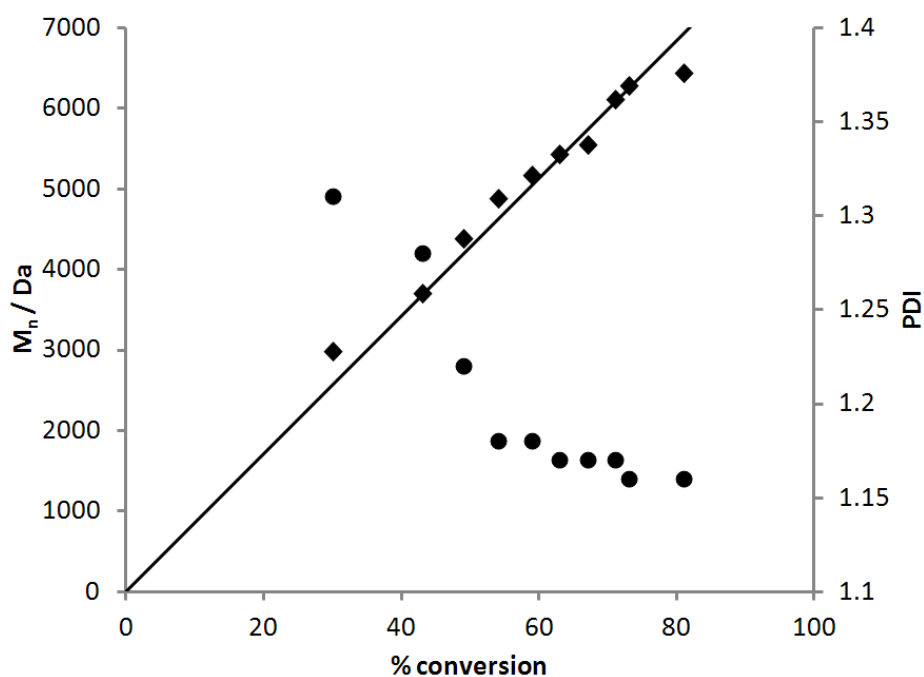


Figure 3. Plot of molecular weight (\blacklozenge) and PDI (\bullet) versus conversion for bulk styrene polymerization at 120°C using **5**. Solid line represents theoretical molecular weights.

The presence of chlorine end-groups, identified by the broad resonance at $\delta = 4.1\text{-}4.5$ ppm in the ^1H NMR spectra of low molecular weight crude polymer samples (e.g. $M_n = 3900$, PDI = 1.16), supports the RATRP mechanism. However, integration of this resonance with respect to the poly(styrene) signals suggests that other mechanisms may also be operating, as not all of the chains are chlorine-terminated. This is particularly evident when the integrations of the methine proton of the chlorine ω -end-group and the methyl protons from AIBN,^[18] present at the α -chain end, are compared. Instead of the expected 1:6 ratio, the spectra show that only 30-35% of the chains are chlorine-terminated. This may suggest that OMRP also occurs, with synergistic interplay between the mechanisms acting to control the polymerization. Dual trapping methods, whereby propagating radicals may react to abstract a halogen and form chlorine-terminated chains, or react directly with the metal complex, forming metal-terminated chains, would explain the low percentage of halogen-terminated polymer. Interplay between ATRP and OMRP has been previously reported for several other complexes, based on molybdenum,^[19] iron,^[16a-d,16f] chromium^[20] and osmium,^[21] but these systems displayed a significantly lower degree of control in comparison to the amine-bis(phenolate) iron(III) complexes. PDIs in these systems were generally broad (1.21-3.19), with molecular weights which were significantly higher than the theoretical values. To assess the ability of our system to reinitiate, a start-stop experiment was carried out. The polymerization was halted by lowering the temperature and restarted by raising the temperature back to 120°C, with the reaction resuming at the same rate (**Figure 2b**). The lack of increase in PDI indicates that all chains reinitiated successfully and the control over the polymerization remains excellent, supporting the theory that the other polymerization pathway also operates through a controlled radical mechanism rather than a competing reaction, such as catalytic chain transfer.

The effect of AIBN concentration on styrene polymerization using **5** was also investigated, to assess the optimum polymerization conditions and to see whether this offered any mechanistic elucidation (Table S4, Figure S1, supporting information). The use of 1.5 equivalents of AIBN resulted in only a slight loss of control, with PDIs broadening to 1.29 and molecular weights which were higher than theoretical values. As the catalyst still imparts reasonable control over the polymerization, this suggests that multiple trapping routes are available to the propagating chains and that very fast chain exchange occurs. With 0.3 equivalents of AIBN, half the standard amount, the catalyst is in excess and deactivation of the propagating radicals is favoured. The polymerization is significantly slower and this results in excellent PDIs of 1.11.

Of particular importance for industrial applications is the production of white polymers. Despite the highly coloured polymerization media, simple work-up procedures yield white polymers which can be easily isolated (Figure S2, supporting information). ICP-MS revealed that the residual iron content in poly(styrene) samples was 576 ppm, a significantly lower value than those obtained for similarly simple polymer work-ups after copper-mediated CRP.

Conclusion

In summary, a new family of highly efficient iron(III) catalysts for controlled radical polymerization has been reported. Polymerization utilizing chloro-substituted amine-bis(phenolate) iron(III) chlorides and bromides proceeds rapidly for both styrene and MMA, affording excellent control over both molecular weights and PDIs. Kinetic studies illustrate the controlled nature of the polymerization and polymer end-group analysis suggests that control is imparted by cooperation between ATRP and OMRP mechanisms. Current work is focused on further kinetic studies, monomer scope and mechanistic elucidation, as well as the design of optimized catalysts.

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