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Understanding Organometallic Mediated Radical Polymerization with an Iron(II) Amine-Bis(Phenolate)

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Supporting Information Placeholder

ABSTRACT: The organometallic mediated radical polymerization (OMRP) of methyl methacrylate (MMA), styrene and vinyl acetate, mediated by a novel *tert*-butyl substituted amine−*bis*(phenolate) iron(II) complex in the absence of a halide source, accesses an organometallic-only route to controlled radical polymerization. Using a low temperature radical initiator, V-70, detailed kinetic and end group studies were used to further understand the mechanism of control, and the relative rates of propagation and termination reactions. For the polymerization of MMA, propagation is favored at low conversions, with good control and reasonable dispersities achieved. Mechanistic studies suggest propagation proceeds through a RT-OMRP mechanism, while termination reactions become dominant at higher conversions. The polymerization temperature greatly affects the nature of termination, tuning whether bimolecular termination or catalytic chain transfer (CCT) dominates. With careful control of reaction conditions, the polymerization of styrene also shows good control, with dispersities as low as 1.27, and while not comparable to ATRP conditions, represents the most effective iron-mediated OMRP of styrene to date.

INTRODUCTION

Controlled radical polymerization (CRP) is a remarkably important development in the field of polymer chemistry, allowing for the synthesis of polymers with well-controlled properties including molecular weight, dispersity and architecture.[1,2] We, and others, have been particularly interested in using iron-based mediators to control radical reactivity, since they are highly earth abundant,[3] of low cost and low toxicity, and able to mediate a polymerization through both atom transfer radical polymerization (ATRP) and organometallic mediated radical polymerization (OMRP).[4–8] A variety of iron complexes have already been synthesized and used as polymerization mediators, especially for ATRP.[9–15] Of particular interest have been amine−*bis*(phenolate) iron complexes, which have been shown to effectively mediate the polymerization of substituted styrenes and methyl methacrylate (MMA), achieving rapid rates, low dispersities and predictable molecular weights.[5,6] Computational studies suggested control through a dual-mechanism of both ATRP and OMRP.[16] This was also verified experimentally, as synthesis of the iron(II) analogue allowed for separation of the ATRP and OMRP pathways, which showed that styrene polymerized solely through an ATRP mechanism, whereas MMA polymerized through an interplay of ATRP and OMRP.[7] However, controlling the polymerization of these monomers through an organometallic-only pathway was challenging, especially for styrene.

Depending on the reaction conditions and the properties of the metal center, an OMRP may be mediated through either reversible termination (RT-OMRP) or degenerative transfer (DT-OMRP) (Scheme 1).[17–21] The former is associated with rapid initiation and high temperatures, whereas the latter is promoted by prolonged initiator decomposition, due to low temperature and high initiator concentration. In addition to these reversible termination reactions, there are also irreversible termination events, which negatively affect a controlled radical polymerization. Bimolecular termination is ever-present in a radical polymerization, despite its suppression through the dormant species. However, this irreversible termination can also be catalyzed by the dormant species, termed catalyzed radical termination (CRT).[19] Catalytic chain transfer (CCT), occurring as a result of H-atom transfer, results in an olefin-terminated chain and a newly growing chain.[19] The presence of CCT gives shorter, olefin-terminated polymer chains with molecular weights independent of monomer conversion.

Whilst the interplay between ATRP and OMRP is now well-understood,[22] there has been little work to develop an iron-mediated OMRP-only mechanism for styrenes and (meth)acrylates. In this article, we consider the OMRP of MMA, styrene and vinyl acetate, accessing a deeper understanding of this system, including the balance between competing propagation and termination reactions. We also disclose conditions for Fe-mediated OMRP of both styrene and MMA.
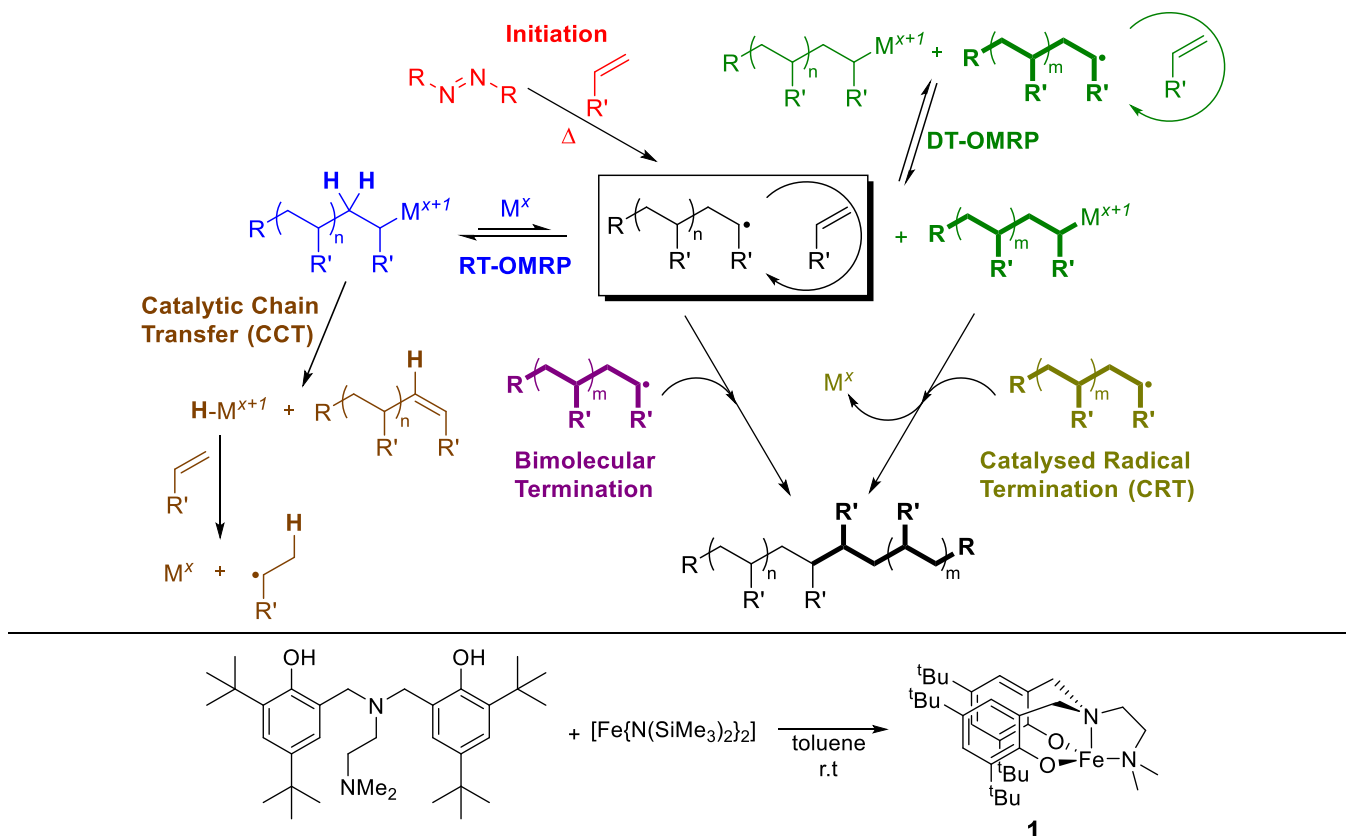
Scheme 1. Mechanisms involved in OMRP.

Figure 1. Synthesis of the iron(II) amine−*bis*(phenolate) complex 1.

RESULTS AND DISCUSSION

Complex Synthesis and Characterization. As the originally developed Cl-substituted Fe(II) complex lacked the requisite solubility needed for this study, a new Fe(II) mediator was developed (Figure 1). The amine *bis*(phenol) (ABP) ligand precursor chosen contains 2,4-*tert*-butyl substitution of the phenol rings (R = ^{t}Bu, Figure 1) due to the likely increased solubility of the resultant complex in common polymerization solvents like toluene or THF. Formation of the desired iron(II) complex (**1**) was achieved by reaction of equimolar amounts of the ligand precursor and [Fe(N(SiMe$_3$)$_2$)$_2$THF] (Fe(HMDS)$_2$THF)[23] in toluene. The highly air- and moisture-sensitive complex was isolated as a pale green amorphous solid in good yield. Characterization of **1** by ^{1}H NMR spectroscopy revealed a series of broad resonances between approximately 90 and -5 ppm. The total number of resonances in the ^{1}H NMR spectrum suggested desymmetrization of the ligand by formation of a (μ-OAr)$_2$-bridged dimer.[7] The solution magnetic moment of **1** (4.8 μB) was characteristic of a d^6 high-spin iron(II) complex. Despite our best efforts, it has thus far not been possible to obtain crystals of **1** suitable for single crystal x-ray diffraction analysis, possibly owing to its otherwise desirable high solubility in most common organic solvents. However, addition of an equimolar amount of 4-dimethylaminopyridine (DMAP) to **1** resulted in formation of **1·DMAP**, which could be recrystallized from

MeCN to afford pale yellow crystals (Figure 2). The structure of **1·DMAP** reveals a 5-coordinate iron(II) center bearing an N$_3$O$_2$-coordination sphere and, as anticipated, the iron(II) center is coordinated by the tetradentate ABP ligand and one molecule of DMAP. A more detailed analysis of the geometry about the metal using Addison and Reedijk's 5-coordinate structural parameter (τ_5)[24] reveals an iron(II) center with an intermediate geometry ($\tau_5 = 0.53$), which may result from steric imposition by the bulky ABP ligand. Metal-ligand bond lengths are comparable to those reported in the literature for similar complexes.[7,25]

OMRP of Methyl Methacrylate. The iron-carbon bond that moderates an OMRP process is necessarily weak; previous studies at high temperatures suggest this temperature disfavors Fe-C bond formation. The low temperature radical initiator V-70 permits radical formation at much lower temperatures than the traditional AIBN, so may permit the development of OMPR-only control. Initial kinetic studies on the OMRP of MMA using complex **1** as mediator at 75 °C would promote fast initiation of the V-70, thus establishing an RT-OMRP. The polymerization was controlled for a short period of time (Figure 3). However, even at moderate conversions, kinetics deviated from first-order behavior, slowing considerably. This was due to the onset of bimolecular termination, observed through the evolution of a high molecular weight shoulder in chromatography data (Figure S2) and a sharp increase in dispersity after a

gradual decrease during the controlled phase (Table S1). Furthermore, molecular weights were considerably greater than theoretical values, a trait commonly seen when using iron complexes in the OMRP of MMA.[7,8]
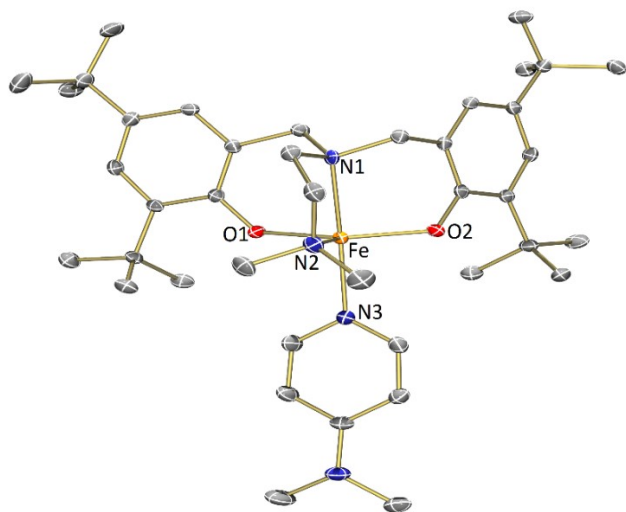

Figure 2. Molecular structure of **1·DMAP** with ellipsoids set at the 50% probability level. Hydrogen atoms and co-crystallized MeCN have been omitted for clarity. Selected bond lengths (Å) and angles (°): Fe-O1 1.9505(16), Fe-O2 1.9662(16), Fe-N1 2.2189(19), Fe-N2 2.243(2), Fe-N3 2.1814(19), N1-Fe-N3 173.82(7), O1-Fe-O2 142.06(7), N2-Fe-O1 104.58(7), N2-Fe-O2 112.51(7).
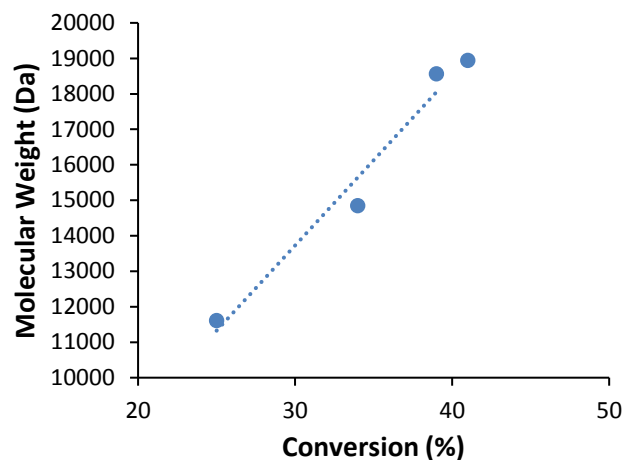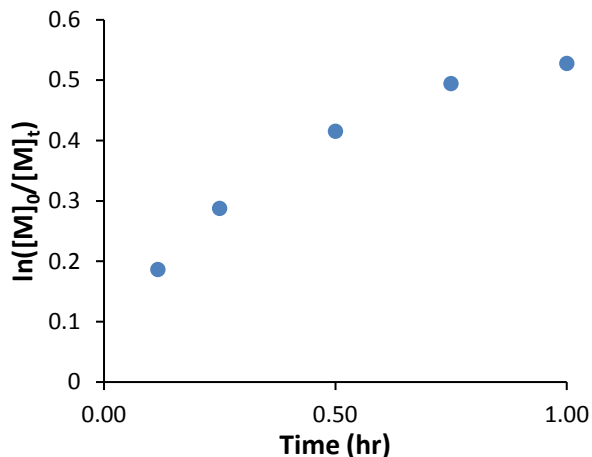

Figure 3. Plots of (top) $\ln([M]_0/[M]_t)$ vs time and (bottom) molecular weight vs conversion for MMA polymerization. [MMA]:[Fe^{II}]:[V-70] = 100:1.00:1.00, MMA:toluene = 1:1 (v/v), 75 °C. Dashed line is least-squares fit to data.

A variety of reaction conditions were explored to improve control over the polymerization (Table S2). Increasing the concentration of iron mediator had negligible effect on the polymerization. Molecular weights and dispersities were virtually unchanged as the concentration of mediator increased, suggesting that the iron complex had little influence over the efficiency of the initiation process. Conversely, increasing the concentration of initiator had a significant effect on the polymerization. Conversion increased whilst molecular weights decreased to nearer theoretical values, without any loss of control. These results, along with previous iron OMRP work,[7,8] suggest that the inherent poor initiation efficiency of azo-initiators, when used with MMA and iron complexes, is responsible for the high molecular weights. Interestingly, the negligible difference in control over the polymerization when using a coordinating solvent (THF) suggests that polymerization proceeds through a radical mechanism, as opposed to a coordination-insertion mechanism. This conclusion is further verified through ^{1}H NMR analysis of the tacticity of purified poly(methyl methacrylate) synthesized under these conditions.[26] The ratio of mm:rm:rr triads was found to be 4:35:61 (Figure S3). The ratio of mm:rm:rr triads in a typical free radical polymerization of MMA is 3:33:64,[26] and so suggests that, at 75 °C, the polymerization proceeds through a radical mechanism. Note that more coordinating solvents, such as pyridine, do inhibit the polymerization through the formation of [ABP]Fe(py)$_2$ complexes (see Supporting Information for X-ray structure).

Kinetic studies were performed to further explore the polymerization (Figure 4). Different concentrations of monomer were used to test this effect on the polymerization, whilst maintaining the overall concentration of mediator and initiator. As expected, increasing the concentration of monomer greatly increased the rate of propagation. However, in the case of both 100 and 200 equivalents, is it clear that the rate decreases over time, tending towards a maximum conversion. This is again showing the prevalence of bimolecular termination, reducing the number of growing chains over time. In the case of 300 equivalents, where no additional solvent is used, a linear increase in conversion, with respect to time, is exhibited. After 9 minutes the reaction mixture solidified, preventing the onset of bimolecular termination.

Molecular weight data for this 300-equivalent polymerization suggests that the system is not well-controlled, with variable molecular weights and broad dispersities observed. This is due to the use of a large excess of initiator, in order to keep molecular weights close to theoretical values, and the poor solubility of the initiator in the monomer. This issue can easily be addressed by reducing the concentration of initiator (Table S6), where control can then be regained with a dispersity of 1.47.

At 200 equivalents, despite the decrease in rate of propagation as the polymerization proceeds, molecular weights linearly increase with conversion (Figure 5). Dispersities decrease as molecular weights inc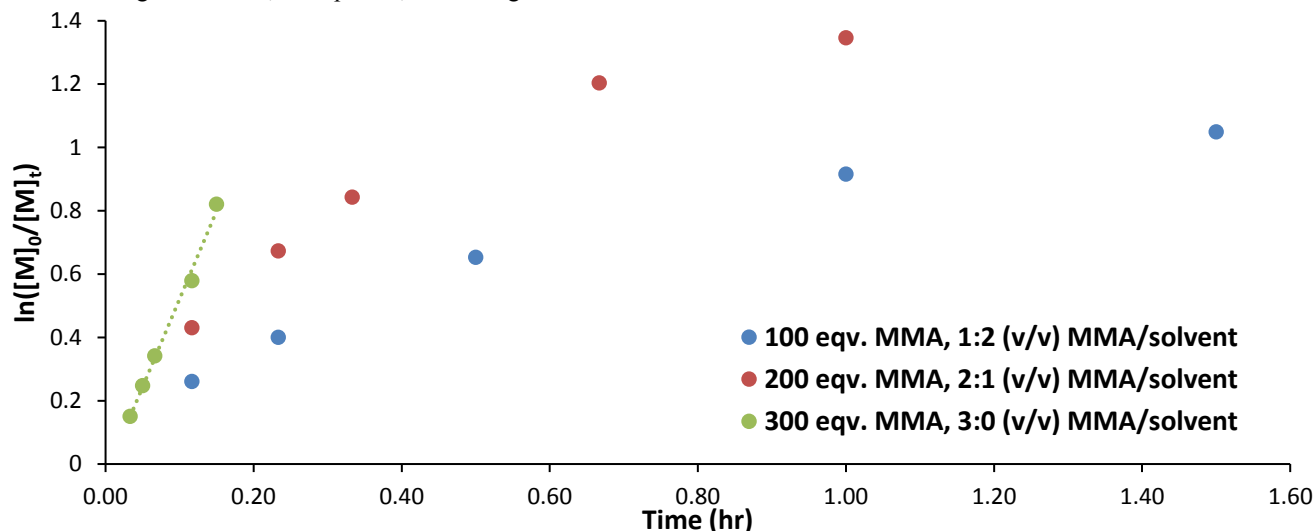rease, as expected, with a slight increase towards the end of the polymerization, as bimolecular termination begins to dominate. The lowest dispersities were achieved for lowest monomer concentration of 100 equivalents.

When considering the above polymerizations, examining an early time point in the reaction provides further mechanistic insight. A graph of $\ln([M]_0/[M]_t)$, after 7 minutes, against number of equivalents of MMA shows a linear relationship (Figure S4). This is due to an increase in radical concentration when more monomer is used, whilst both reaction time and propagation constant are unchanged. A larger monomer concentration allows for better radical trapping by the iron complex, resulting

Figure 4. Plot of $\ln([M]_0/[M]_t)$ vs time for MMA polymerizations at 75 °C. $[Fe^{II}]:[V\text{-}70] = 1.00:5.00$. Constant total volume. Dashed line is least-squares fit to data.
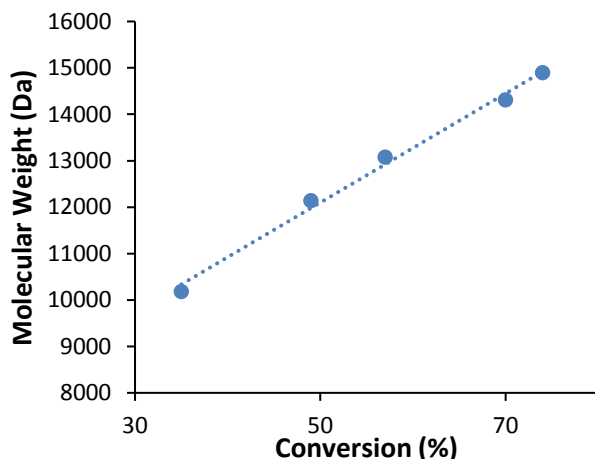

Figure 5. Plot of molecular weight vs conversion for MMA polymerization. $[MMA]:[Fe^{II}]:[V\text{-}70] = 200:1.00:5.00$, MMA:toluene = 2:1 (v/v), 75 °C. Dashed line is least-squares fit to data.

in an overall improved initiator efficiency. After loss of initiator radicals and polymerization for 7 minutes, there is no apparent significant termination. It is therefore possible, to a degree, to control the molecular weight by altering the monomer concentration and polymerizing for 7 minutes, to achieve a polymer chain with the desired molecular weight and minimal termination. It is worth noting that the chromatography data for these polymerizations do show a small high molecular weight shoulder, suggesting a minimum amount of early bimolecular termination, before the OMRP equilibrium is reached.

To demonstrate the chain-end fidelity of one of the "7 minute" polymers, a chain extension experiment was performed (Figure S5). An initial 100 equivalents of MMA were first polymerized for 7 minutes, before a second 100 equivalents were added and polymerized for another 7 minutes. The resultant polymer had a molecular weight of 13100 Da and a dispersity of 1.43. The increase in molecular weight, from the first to the second addition of monomer, and a low resultant dispersity suggests reasonable chain-end fidelity, although clearly not matching the more robust CRP methodologies.

The polymerization of MMA using **1** and V-70 was also explored at lower temperatures (Table 1). These conditions result in slow release of initiator radicals and thus often promote DT-OMRP, a mechanism favored by Co(acac)$_2$ OMRP of less active monomers (LAMs) such as vinyl acetate.[27,28] As expected, using a reaction temperature of 30 °C instead of 75 °C resulted in significantly slower propagation rates and therefore increased reaction times. Compared to polymerization at high temperature, conversions were greatly improved, and it was possible to access much higher conversions than at 75 °C. However, molecular weights persisted at approximately 23000 Da, irrespective of conversion. This behavior suggests that CCT is the predominant termination mechanism, rather than bimolecular termination. This mechanism has been previously observed for both β-ketiminate[8] and α-diimine[29,30] iron complexes under

ATRP and OMRP conditions. Indeed, ^{1}H NMR analysis of purified poly(methyl methacrylate) (PMMA) showed evidence of olefinic protons (Figure 6), confirming CCT is present as the favored termination mechanism. The tacticity of the synthesized PMMA was investigated, with the ratio of mm:rm:rr triads found to be 3:31:66, again suggesting a radical polymerization mechanism.

Table 1. Data for Polymerisation of MMA at Low Temperature.

#	Time (hr)	Conv. (%)	$M_{n,th}$ (Da)	M_n (Da)	Đ
1	6	31	3100	25900	1.44
2	18	60	6000	23000	1.44
3	24	70	7000	22800	1.47
4	42	80	8000	21500	1.50
5	48	83	8300	22600	1.44
6	72	88	8800	20800	1.50
7	94	92	9200	23800	1.40

Conditions: [MMA]:[Fe^{II}]:[V-70] = 100:1.00:1.00, MMA:toluene = 1:2 (v/v), 30 °C. Conversion determined by ^{1}H NMR spectroscopy. $M_{n,th}$ = [M]$_0$/[Fe] × M(monomer) × conversion.
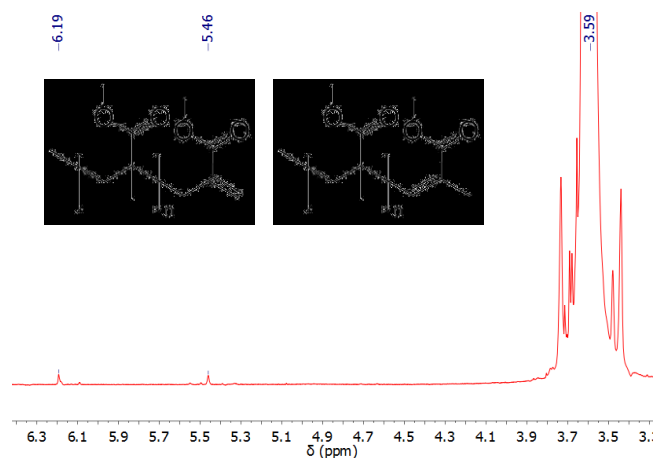

Figure 6. ^{1}H NMR spectrum of purified poly(methyl methacrylate), showing the presence of olefin protons (500 MHz, CDCl$_3$).

OMRP of Styrene. Styrene has proven to be a very difficult monomer to control using organometallic-only mechanisms. A system based on Cp$_2$TiCl$_2$/Zn has shown good control, proposed to operate through a radical polymerization mechanism.[31–36] Using complex **1** at high temperature gave poor control, with high molecular weights and a broad dispersity. This is consistent with the previous use of iron(II) ABP complexes and styrene under RT-OMRP conditions.[7] Interestingly, lowering the temperature, and thus slowing the rate of initiation and propagation, greatly improved control over the polymerization. Optimizing the reaction conditions by increasing the number of equivalents of initiator and volume of solvent improved control even further, achieving a dispersity of 1.30, offering exceptional control for styrene OMRP. As with the polymerization of MMA, there is little difference in the reaction when using THF or toluene, again suggesting radical polymerization as opposed to coordination-insertion polymerization.

Table 2. Effect of Temperature, Initiator Concentration, and Solvent on Styrene Polymerisation.

#	Temp (°C)	Equiv. V-70	Conv. (%)	$M_{n,th}$ (Da)	M_n (Da)	Đ
8	75	1	50	5200	13200	2.67
9	50	1	45	4700	7700	2.04
10	30	1	30	3100	7200	1.54
11	30^a	3.5	39	4100	3500	1.30
12	30^{a,b}	3.5	38	4000	4000	1.32

Conditions: [Sty]:[Fe^{II}]:[V-70] = 100:1.00:x, Sty:THF = 1:1 (v/v), 18 hr. Conversion determined by ^{1}H NMR spectroscopy. $M_{n,th}$ = [M]$_0$/[Fe] × M(monomer) × conversion. ^{a} Sty:THF = 1:3 (v/v). ^{b} performed in toluene.

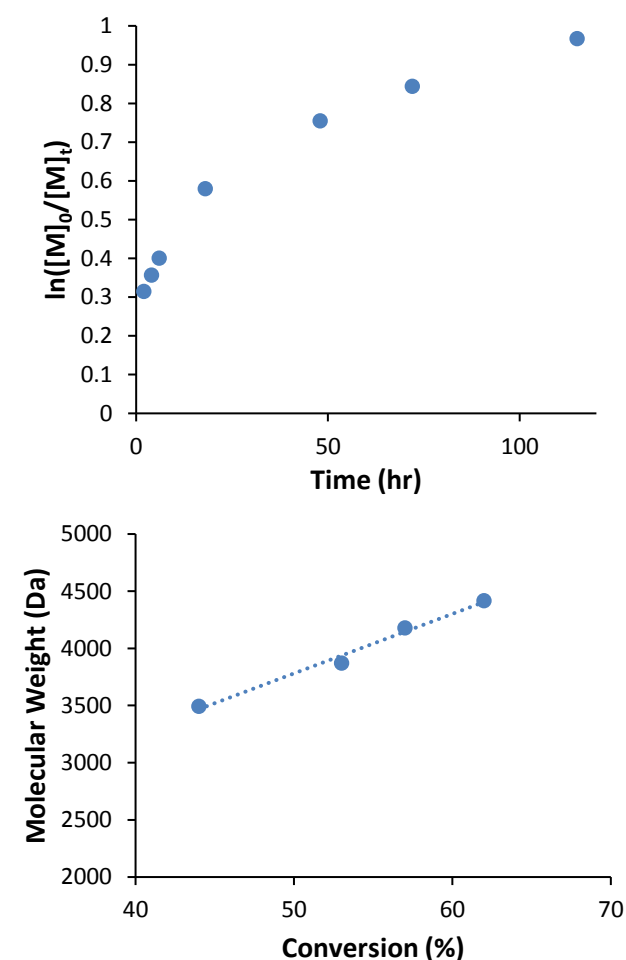**Figure 7.** Plots of (top) ln([M]$_0$/[M]$_t$) vs time and (bottom) molecular weight vs conversion for styrene polymerization. [Sty]:[Fe^{II}]:[V-70] = 100:1.00:3.50, Sty:THF = 1:3 (v/v), 30 °C.

Kinetic studies were performed on this system to further understand the mechanism of control (Figure 7 and Table S7). Conversion rapidly increased at the start of the polymerization,

before slowing considerably. After this initial rapid polymerization, conversion increases linearly with time. Molecular weights also linearly increase with conversion. These results, along with the low dispersities, show some evidence of a controlled polymerization. To the best of our knowledge, this is the most effective iron mediator of the OMRP of styrene, acknowledging that the Fe-mediated ATRP of styrene offers exceptionally better control. Molecular weights are considerably lower, and closer to theoretical values, with styrene than with MMA. This suggests the initiation efficiency is considerably greater with iron/V-70/styrene than with the MMA system. As a result, fewer equivalents of initiator are required to attain low molecular weights.

The rate of increase in molecular weight, with respect to conversion, is approximately half of the expected rate of increase. This, coupled with the rapid initial increase in conversion at early times, suggests that a number of dead chains are formed during initiation, before a controlled OMRP equilibrium is established. This makes it difficult to deconvolute the chromatography data, and is likely responsible for the slight increase in dispersity at the end of the polymerization.

OMRP of Vinyl Acetate. The polymerization of vinyl acetate, a less active monomer (LAM) compared to styrene and methyl methacrylate, has proven difficult through ATRP, although recent work suggests this might now be possible using copper.[37] This monomer has been successfully controlled through OMRP, particularly with cobalt complexes,[19,28,38] and iron complexes.[39–41] However, using complex **1** under OMRP-conditions yielded negligible poly(vinyl acetate), even under forcing conditions (Table S8). A distinct color change was observed, suggesting that initiation has taken place. We postulate that a highly stable deactive species quickly forms, from which no further polymerization can occur. This is likely to be an iron(III)-vinyl acetate species, stabilized by either a five- or six-membered chelate ring achieved through carbonyl donation from the monomer to the metal (Figure 8).
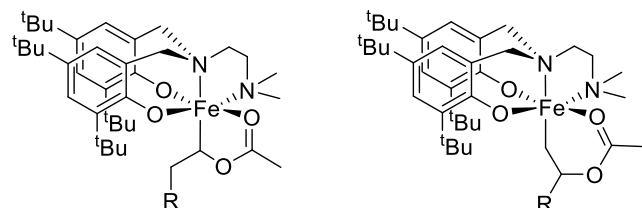

Figure 8. Putative iron(III)-vinyl acetate species, stabilized by a five-membered ring (left) or a six-membered ring (right).

Mechanistic Implications. This article began by highlighting the array of mechanisms active during OMRP, and how each mechanism interacts with each another; this work highlights this interplay. Previous mechanistic studies used temperatures in excess of 110 °C;[7] the temperature required for fast initiation and dictated by use of AIBN. The use of V-70 initiator in this work enabled fast initiation at moderate temperatures, allowing for a more stable Fe-C bond, and thus a deeper understanding of the OMRP process, and how the equilibria between propagation and termination varies at different temperatures.

The low dispersity at high conversions achieved during the OMRP of MMA at 110 °C, using AIBN as initiator,[7] is most likely due to CCT. Whilst well-controlled, molecular weights do not increase with conversion. Lowering the temperature to 75 °C (this work) separates out elements of control, particularly

under optimized conditions. Only moderate conversions were required for the equilibrium between propagation and termination to shift markedly towards bimolecular termination. Is it unclear whether this was in the form of bimolecular termination or CRT. Lowering the temperature even further, to 30 °C, saw very similar behavior to that of 110 °C. High monomer conversions, in excess of 90%, were achieved with reasonable control over dispersity. Again, the molecular weight is independent of conversion. However, it is likely possible to control the molecular weight by altering the monomer concentration at the start of the polymerization.

Using a range of temperatures also allowed for a range of rates of initiation, to explore whether the propagation mechanism is RT-OMRP or DT-OMRP. At high temperatures, the initiator decomposes rapidly, and therefore the only subsequent source of radicals in the polymerization is from the dormant organometallic species. Therefore, the polymerization of MMA at 75 °C is considerably more likely to proceed *via* RT-OMRP than DT-OMRP. Traditionally, low polymerization temperatures and slow rate of initiator decomposition promotes DT-OMRP, since it provides the required constant influx of radicals. A characteristic behavior of DT-OMRP is a "lag" period at the start of the polymerization, where no conversion is observed for a period of time, before a linear increase in conversion with time is established. In this work, neither the low temperature polymerization of MMA nor styrene showed any evidence of a "lag" period. In both cases an immediate increase in conversion with time is observed. This would again suggest that the low temperature polymerization of MMA and styrene proceeds through RT-OMRP and not DT-OMRP. Given that it is not possible to promote DT-OMRP control, this would suggest the amine-*bis*(phenolate) iron(II) complex is unable to undergo DT-OMRP at any temperature. This is likely due to a lack of a vacant coordination site on the metal, originating from the steric bulk of the *tert*-butyl substituents on the phenyl ring resulting in a coordinatively saturated complex.

For a successful well-controlled OMRP, it is imperative that the metal-alkyl bond in the dormant species is sufficiently labile for productive polymerization to occur, whilst also sufficiently strong for the propagation-reversible termination equilibrium to significantly favor the dormant species. Given the possibility of achieving reasonably well-controlled PMMA at all temperatures, ranging from 120 °C to 30 °C, this would suggest the bond strength between the ABP iron complex and the growing PMMA chain is ideal for productive OMRP at a wide range of temperatures. It is therefore unlikely that the tendency to undergo termination reactions, whether that is bimolecular or CCT, is dependent on the bond strength in the dormant species.

It is more interesting to consider the bond strengths in the case of styrene. Previous work, using Mössbauer studies,[7] suggested that the absence of an iron(III)-alkyl species during the polymerization of styrene is strong evidence for the inability of styrene to be polymerized through OMRP. At the high temperatures used in this study, the iron-alkyl bond is far too labile for OMRP-control. This work now shows that reducing the polymerization temperature to 30 °C greatly slows the rate of propagation, and decreases the lability of the metal-alkyl bond to the extent that a controlled OMRP can occur, supporting previous computational work which suggested Fe-mediated OMRP was feasible.[16]

CONCLUSION

In this work the OMRP of styrene, methyl methacrylate and vinyl acetate, mediated by an iron(II) ABP complex, have been thoroughly explored. Under certain conditions, the OMRP of MMA showed moderate control, with reasonable dispersities and some chain-end fidelity, demonstrated through chain extension. However, only moderate conversions are required before bimolecular termination becomes prevalent. At low temperatures, the OMRP of MMA is dominated by catalytic chain transfer, although high conversions and reasonable dispersities are achieved. The OMRP of styrene, at low temperature, represents the most effective Fe-mediated OMRP to date, with dispersities as low as 1.27. Even under these optimized conditions, the complex performance is significantly worse than under ATRP conditions. However, this understanding Fe-mediated OMRP does open up new opportunities. Future work will focus on using the controlled OMRP conditions achieved for both MMA and styrene, and exploring the range of block copolymers which are possible to synthesize due to the metal-capped polymer afforded by OMRP.

EXPERIMENTAL SECTION

Materials and Methods. All experiments involving moisture- and air-sensitive compounds were performed under a nitrogen atmosphere using an MBraun LABmaster sp glovebox system equipped with a −35 °C freezer and [H_2O] and [O_2] analyzers or using standard Schlenk techniques. Solvents used were obtained from a solvent purification system (Innovative Technologies) consisting of columns of alumina and copper catalyst and were further degassed by three freeze–pump–thaw cycles prior to use. Chloroform-d_1 was used as received. Styrene (Sty), methyl methacrylate (MMA) and vinyl acetate (VAc) were dried by stirring over calcium hydride for a minimum of 24 hours, before being vacuum transferred and stored at −35 °C. V-70 (Wako) was added to dry acetone at -10 °C, stirred for 30 minutes, filtered, dried under vacuum and stored at −35 °C. [$Fe(N(SiMe_3)_2)_2THF$] was synthesized using a modified literature procedure and stored under an inert atmosphere.[23] ^{t}Bu-ABP ligand was synthesized using a literature procedure.[42] Gel permeation chromatography (GPC) was carried out in THF at a flow rate of 1 mL min^{-1} 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 dn/dc values of 0.185 for poly(styrene),[43] 0.088 for poly(methyl methacrylate),[44] and 0.052 for poly(vinyl acetate).[43] NMR spectra were obtained on either a 400 MHz or 500 MHz Bruker Avance III spectrometer.

Synthesis of [^{t}Bu-ABP]Fe(II) (1). The ligand (0.31 g, 0.60 mmol) was taken up in anhydrous toluene (10 mL) in a glovebox. To this was added, with stirring, a solution of [$Fe(N(SiMe_3)_2)_2THF$] (0.27 g, 0.60 mmol) in toluene (5 mL). The resultant pale green solution was stirred vigorously at ambient temperature for 30 min. After this time, the extremely air-sensitive solid was isolated through removal of volatiles *in vacuo*. Yield: 0.28 g, 0.48 mmol, 81%. ^{1}H NMR (500 MHz, C_6D_6) δ: 88.11 (br s), 64.30 (br s), 43.45 (s), 39.39 (s), 26.58 (s), 20.83 (s), 8.03 (br s), 4.99 (s), 2.46 (s), -1.49 (br s). μ_{eff} = 4.8 μ_B. Anal. Calcd for $C_{34}H_{54}FeN_2O_2$: C, 70.57; H, 9.41; N, 4.84. Found: C, 70.51; H, 9.58; N, 4.88.

General Polymerisation Procedure. In a glovebox, a small ampoule was charged with iron(II) complex (24.0 μmol), monomer (2.40 mmol), toluene (monomer : toluene, 1 : 2, v/v) and V-70 (24.0 μmol). The ampoule was brought out of the glovebox and heated with a stir-rate of 500 rpm. After this time, the ampoule was cooled rapidly to ambient temperature, and an aliquot removed for analysis by ^{1}H NMR spectroscopy to determine monomer conversion. The remainder of the reaction mixture was taken-up in a small volume of THF (*ca*. 2 ml),

and the polymer precipitated by addition of the THF solution to acidified methanol (MeOH : HCl(aq), *ca*. 75 ml : 1 ml). The polymer was collected by filtration and dried *in vacuo*.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

NMR data, polymerization data, chromatographic data, and crystallographic data (PDF)

AUTHOR INFORMATION

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Notes
The authors declare no competing financial interest.

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