

Organometallic Mediated Radical Polymerisation of Vinyl Monomers with Iron



Daniel L. Coward, Benjamin R. M. Lake, Michael P. Shaver

EaStCHEM, School of Chemistry, Joseph Black Building, David Brewster Road, University of Edinburgh, UK



Introduction

- Controlled radical polymerisation (CRP) is an extremely important development in polymer chemistry, able to achieve control over molecular weight, dispersity and macromolecular architecture whilst maintaining high functional group tolerance.
- Our group aim to control the polymerisation through the use of a metal mediator to reversibly trap a growing polymer chain. This creates a dynamic equilibrium between the dormant species and active radicals thus suppressing termination reactions.
- This is achieved through either **Atom Transfer Radical Polymerisation (ATRP)**, where the metal mediator reversibly transfers a halogen atom to the propagating radicals, or **Organometallic Mediated Radical Polymerisation (OMRP)**, where the metal mediator itself deactivates the propagating radicals *via* formation of a metal-carbon bond.
- Whilst work in this field has been dominated by copper, iron presents an exciting area of research as it is inexpensive, non-toxic and has the potential to act through both ATRP and OMRP mechanisms.
- There is considerable mechanistic interplay during an OMRP, including both reversible and irreversible termination reactions (Figure 1). Different conditions promote different pathways.

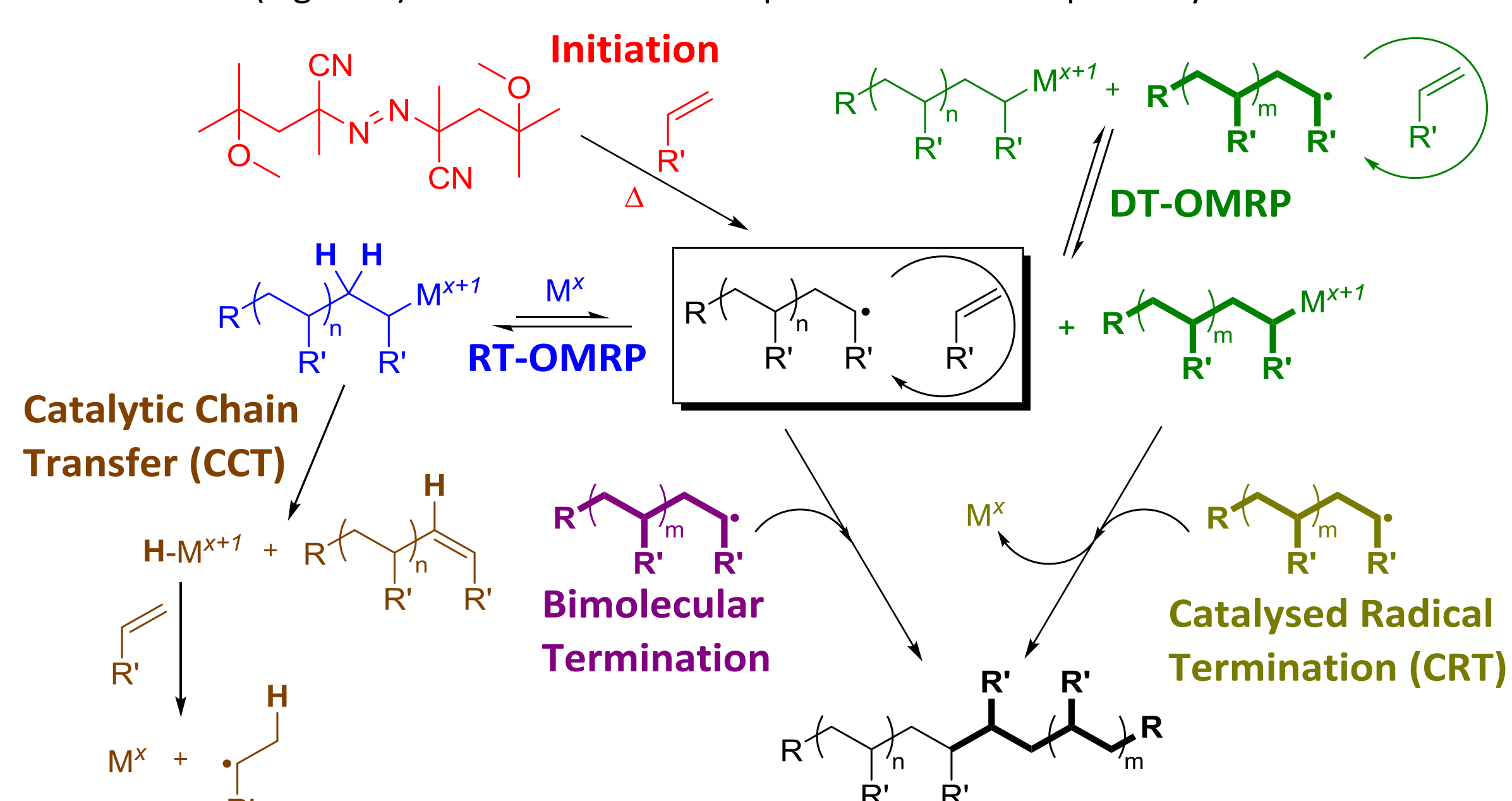


Figure 1: Mechanisms involved in OMRP.

Amine-bis(phenolate) Iron

- Amine-bis(phenolate) (ABP) iron complexes (Figure 2) have been thoroughly explored as CRP mediators and are excellent mediators of the polymerisation of both substituted styrenes and methyl methacrylate.¹⁻⁴
- A wide variety of substituents on the phenyl rings, along with different amine bridges, have been screened with the best mediators achieving dispersities as low as 1.07.
- Mechanistic studies have shown that a multimechanism system is in play – both ATRP and OMRP are acting in cooperation to control the polymerisation.²
- Iron(II)-amine bis(phenolate) complexes (Figure 3) have also been synthesised, so that the ATRP and OMRP mechanisms can be differentiated and individually isolated.³
- This contribution discusses the mechanistic investigations into understanding how the OMRP of vinyl monomers are mediated by the aforementioned iron ABP complexes.⁵
- Particular focus is paid to understanding the equilibrium between propagation and termination reactions in OMRP at different temperatures.

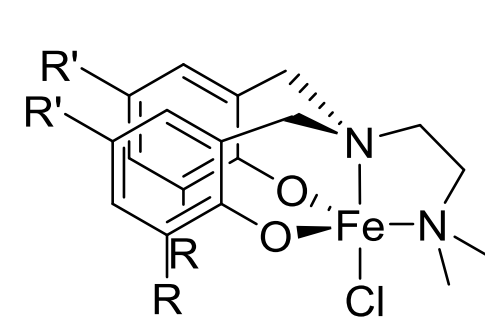


Figure 2: Fe(III)-amine bis(phenolate).

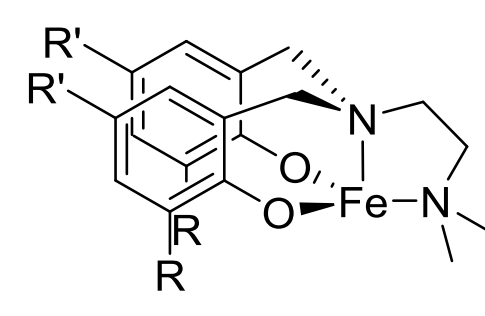


Figure 3: Fe(II)-amine bis(phenolate).

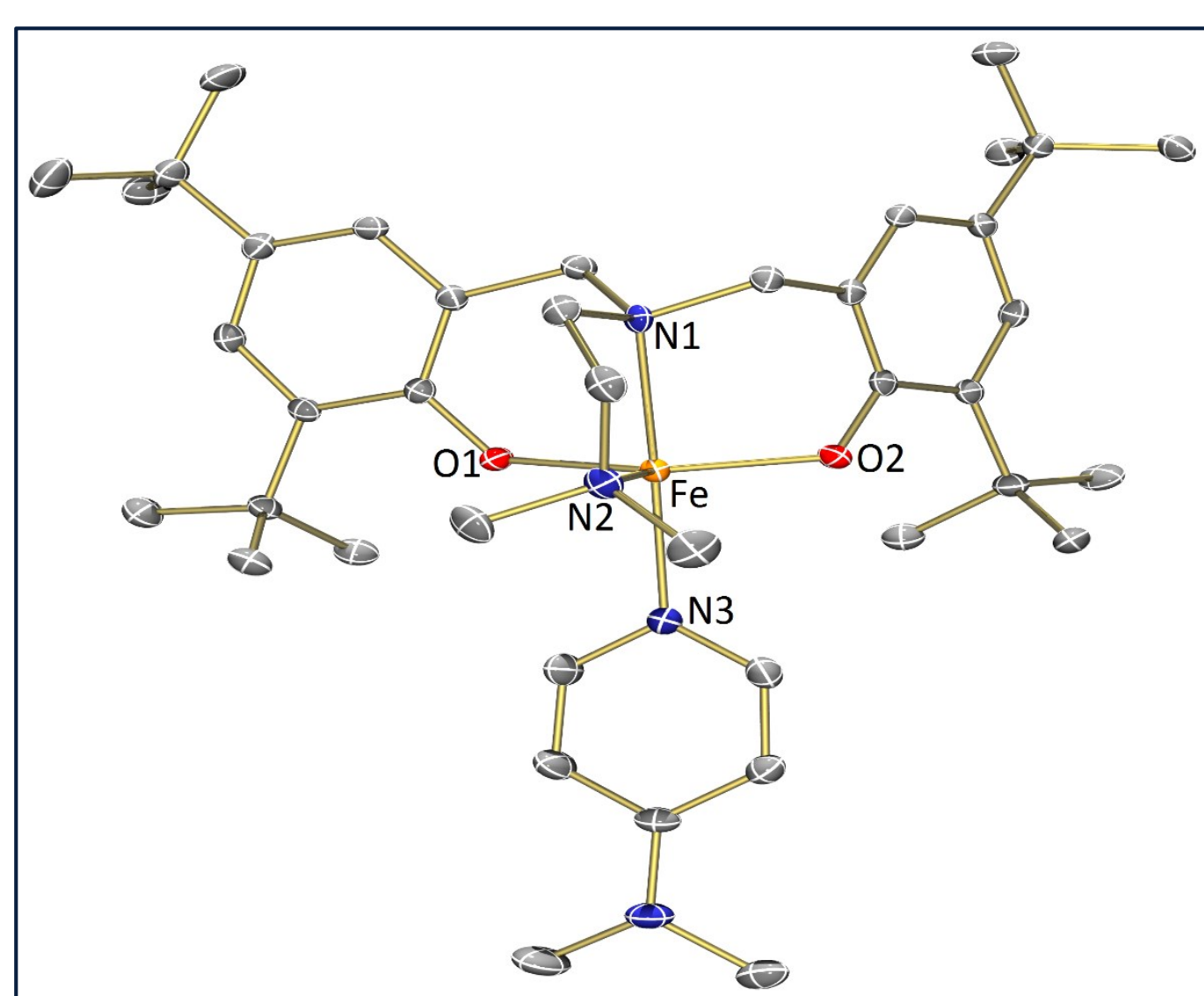


Figure 4: Molecular structure of tert-butyl substituted amine-bis(phenolate) iron(II) used within this work.

Polymerisation Procedure

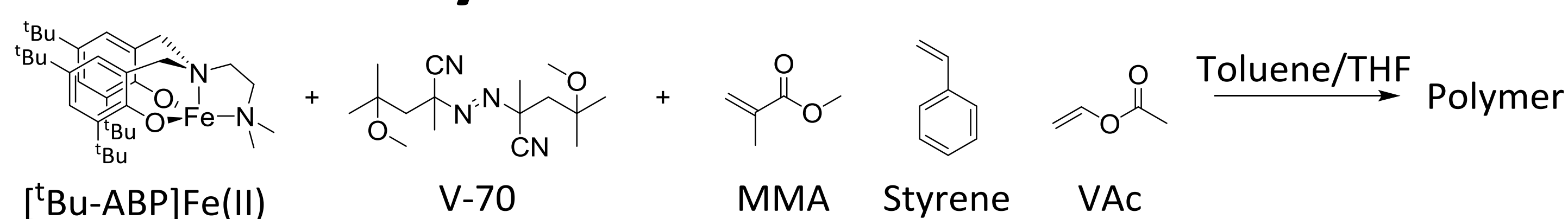


Figure 5: Representative polymerisation procedure.

References

- L. E. N. Allan, J. P. MacDonald, A. M. Reckling, C. M. Kozak and M. P. Shaver, *Macromol. Rapid Commun.*, 2012, **33**, 414–418.
- L. E. N. Allan, J. P. MacDonald, G. S. Nichol and M. P. Shaver, *Macromolecules*, 2014, **47**, 1249–1257.
- H. Schroeder, B. R. M. Lake, S. Demeshko, M. P. Shaver and M. Buback, *Macromolecules*, 2015, **48**, 4329–4338.
- R. Poli and M. P. Shaver, *Inorg. Chem.*, 2014, **53**, 7580–7590.
- D. L. Coward, B. R. M. Lake and M. P. Shaver, *Manuscript in Preparation*.



OMRP of Methyl Methacrylate (MMA)

- Initial kinetic studies, at high temperature and fast initiation, show some living behaviour (Figure 6).
- Rate of conversion slows as time increases.
- Noticeable onset of bimolecular termination, which increases dispersity.
- Optimisation studies show iron complex concentration has little effect on polymerisation, but increasing initiator concentration reduces molecular weights.
- Kinetic studies show improved living behaviour with increased monomer concentration (Figure 7).
- Chain extension experiment saw increase in molecular weight whilst maintaining control, showing good chain end fidelity.
- Polymerisation at lower temperature saw high conversions reached, with significantly longer reaction times.

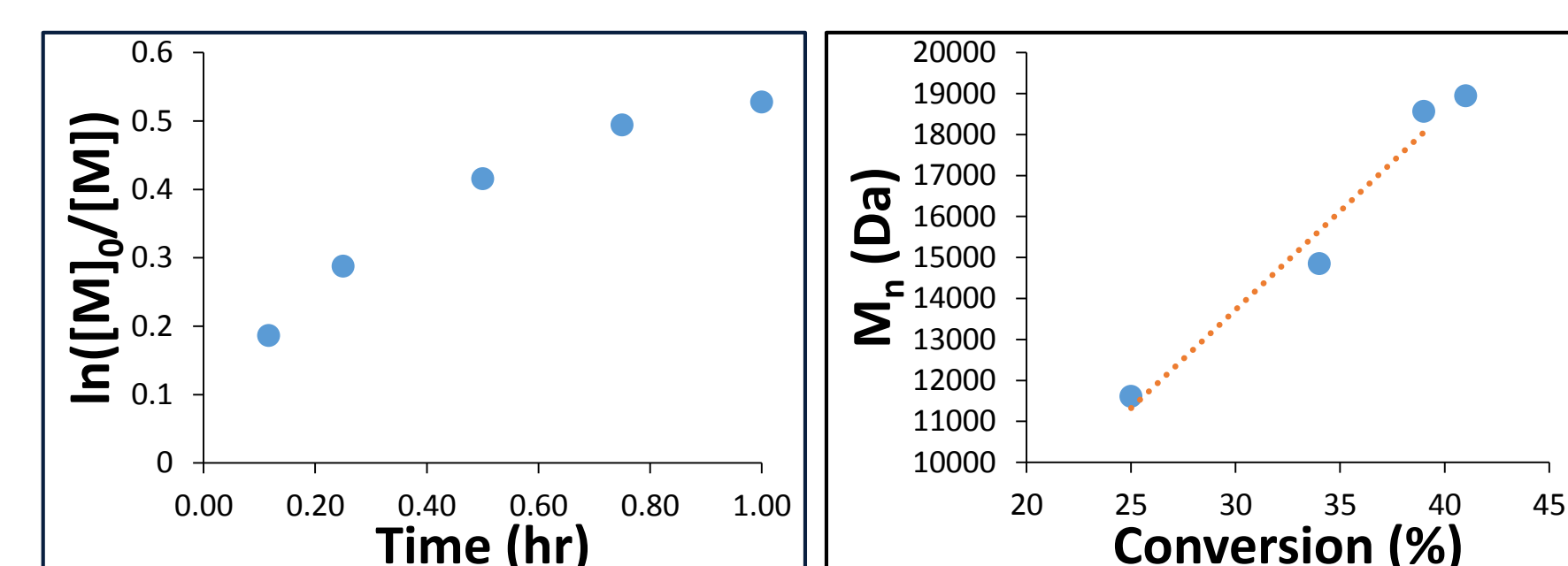


Figure 6: Plots of (left) $\ln([M]_0/[M]_t)$ vs time and (right) molecular weight vs conversion for MMA polymerisation. $[MMA]:[Fe^{II}]:[V-70] = 100:1.00:1.00$, $MMA:toluene = 1:1$ (v/v), $75^\circ C$.

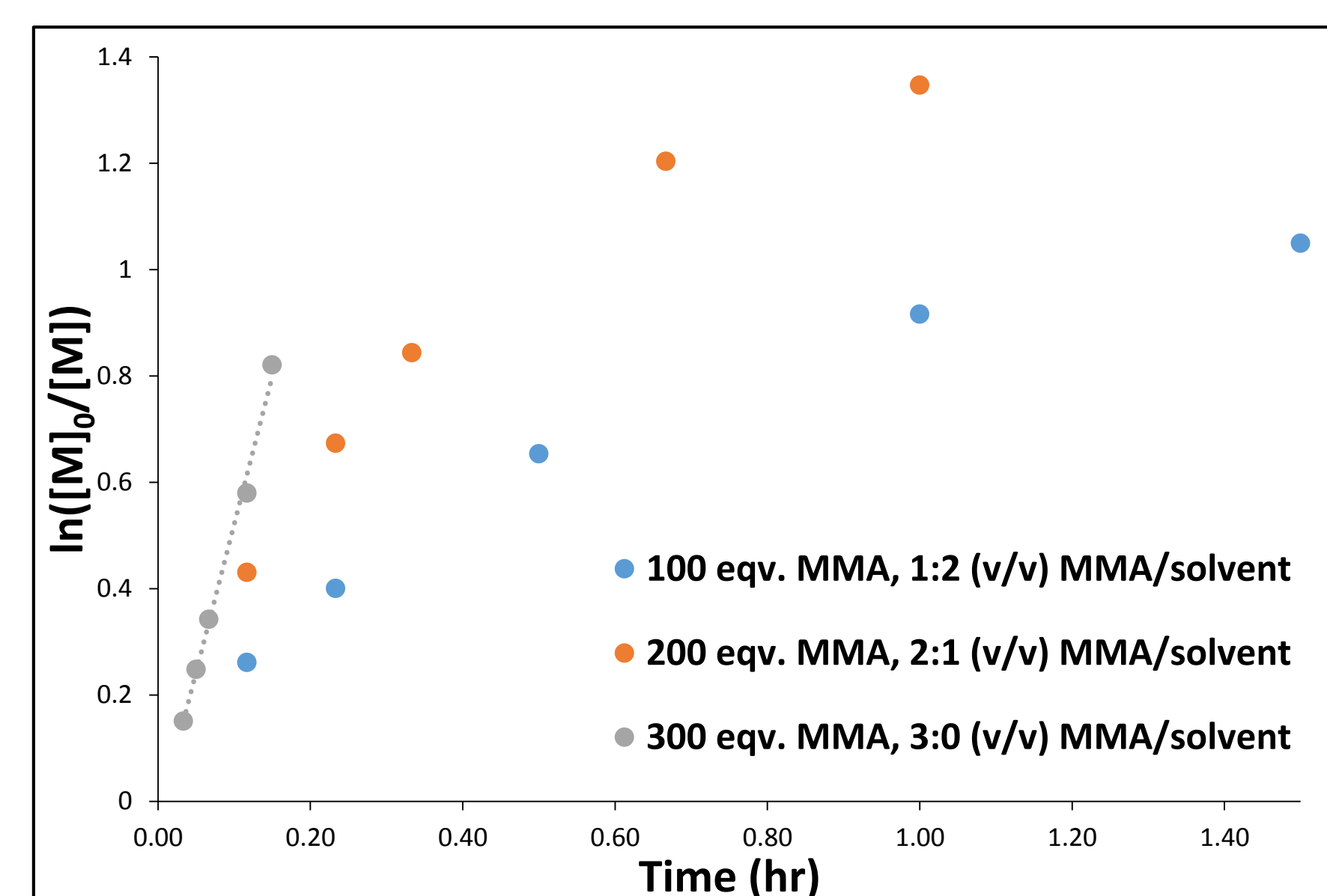


Figure 7: Plot of $\ln([M]_0/[M]_t)$ vs time for MMA polymerisations at $75^\circ C$. $[Fe^{II}]:[V-70] = 1.00:5.00$. Constant total volume.

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

Table 1: Data for polymerisation of MMA at low temperature. $[MMA]:[Fe^{II}]:[V-70] = 100:1.00:1.00$, $MMA:toluene = 1:2$ (v/v), $30^\circ C$.

OMRP of Styrene

- Difficult to control styrene polymerisation using OMRP.
- Lowering the temperature greatly improves control.
- Using an excess of initiator in dilute conditions gave a low dispersity of 1.30.
- Kinetic studies showed an initial rapid polymerisation, before linear increase in conversion with time.
- Molecular weights increased linearly with conversion, suggesting a well-controlled living polymerisation.
- This is the first example of a well-controlled living OMRP of styrene mediated by iron, and perhaps by any metal.

Temp. ($^\circ C$)	Equiv. V-70	Conv. (%)	$M_{n,th}$ (Da)	M_n (Da)	\bar{D}
75	1	50	5200	13200	2.67
50	1	45	4700	7700	2.04
30	1	30	3100	7200	1.54
30 ^a	3.5	39	4100	3500	1.30

Table 2: Effect of temperature, initiator concentration, and solvent on styrene polymerisation. $[Sty]:[Fe^{II}]:[V-70] = 100:1.00:x$, $Sty:THF = 1:1$ (v/v), 18hr. ^a $Sty:THF = 1:3$ (v/v).

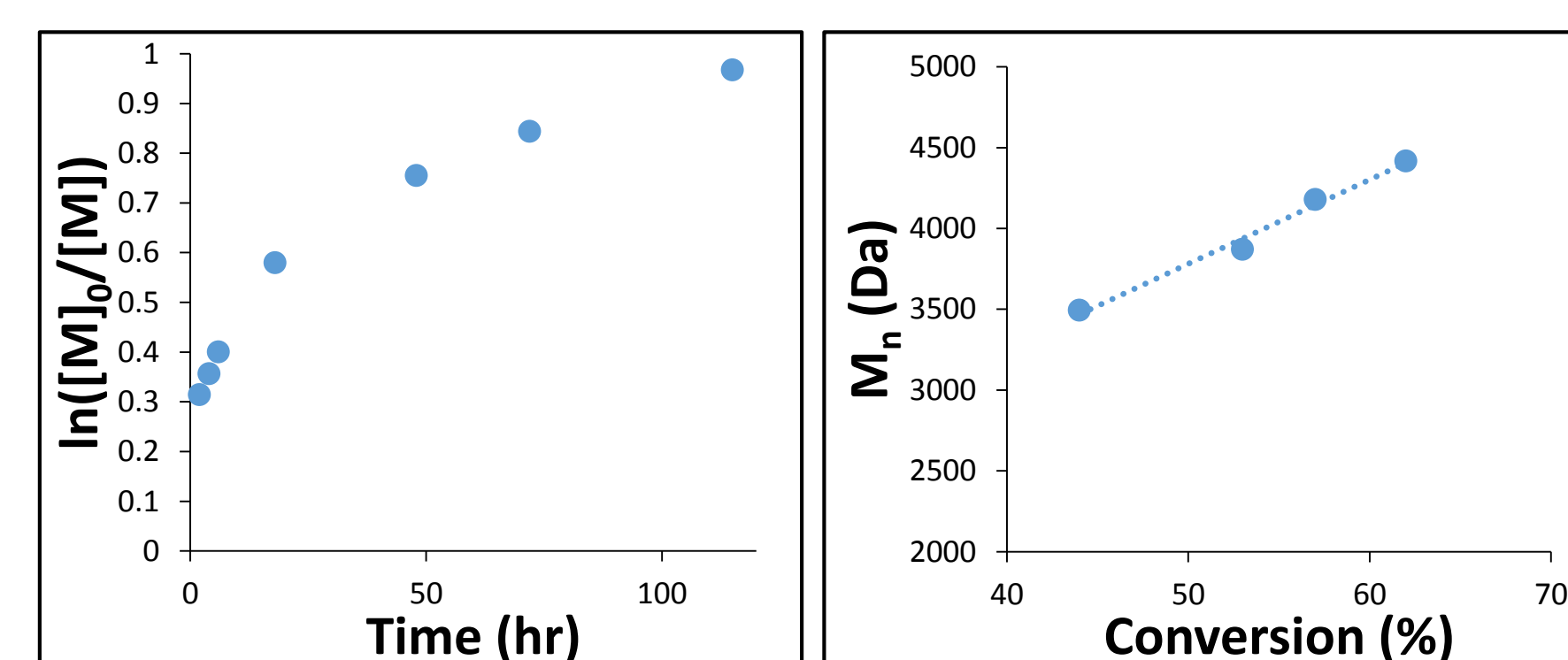


Figure 8: Plots of (left) $\ln([M]_0/[M]_t)$ vs time and (right) molecular weight vs conversion for styrene polymerisation. $[Sty]:[Fe^{II}]:[V-70] = 100:1.00:3.50$, $Sty:THF = 1:3$ (v/v), $30^\circ C$.

OMRP of Vinyl Acetate (VAc)

- Using the iron(II) ABP complex under OMRP-conditions yielded negligible poly(vinyl acetate), even under forcing conditions.
- A distinct colour change was observed, suggesting that initiation has taken place, but very quickly forms an extremely stable inactive species.
- This is likely to be an iron(III)-vinyl acetate species, stabilised by either a five- or six-membered ring achieved through carbonyl donation from the monomer to the metal (Figure 9).

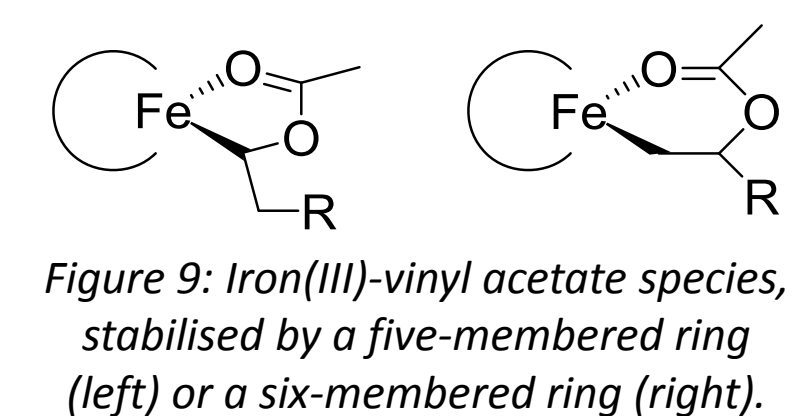


Figure 9: Iron(III)-vinyl acetate species, stabilised by either a five-membered ring (left) or a six-membered ring (right).

Conclusions & Future Work

- In this work the OMRP of styrene, methyl methacrylate and vinyl acetate, mediated by an iron(II) ABP complex, have been thoroughly explored.
- The mechanistic temperature profile is now well-understood, with different reactions promoted at different temperatures.
- Future work will focus on exploring the range of block copolymers which are possible to synthesise due to the metal-capped polymer afforded by OMRP.

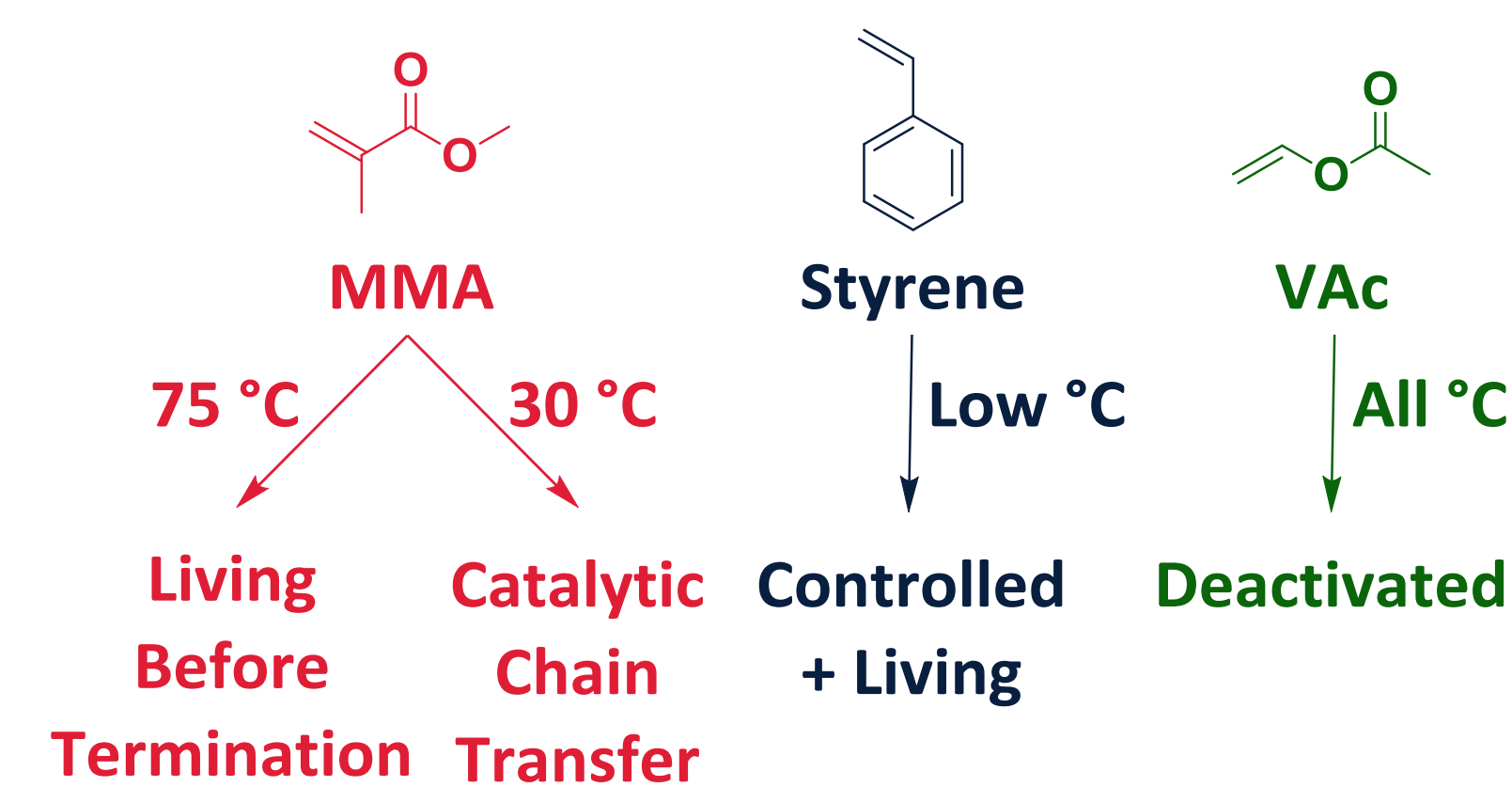


Figure 10: Conclusions from this contribution.