Centre for **Sustainable & Circular** Technologies

MONASH University

UNIVERSITY OF BATH

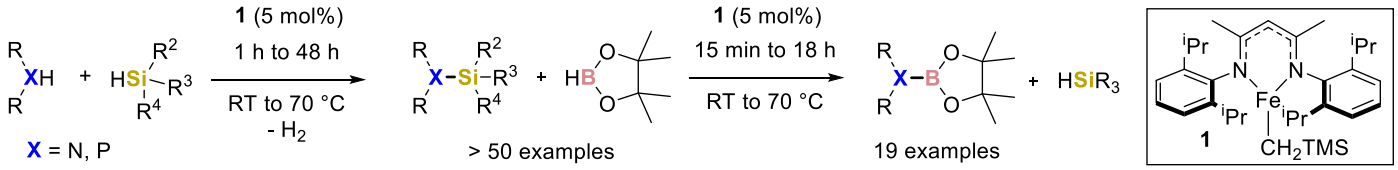
Bath Monash Global PhD Programme in Sustainable & Circular Technologies

Project Title:	Polymerising, depolymerising and repurposing using iron catalysis
Supervisors at Bath: Supervisors at Monash:	Ruth Webster (lead) Sara Kyne
Home Institution:	University of Bath
Indicative period at Host Institution:	2 years at Bath; 18 months at Monash with exact dates to be confirmed

Project Summary

The synthesis and activation of Si-E bonds is increasing due to the importance of silicon chemistry, which has uses that span from materials chemistry (e.g. semiconductors, polymers, composite ceramics) to organosilicon compounds (e.g. protecting groups, coupling partners for cross-couplings). The depolymerisation and reuse of monomers from plastics is important, but is currently limited to hydrocarbon- or biorenewable-based polymers. Also of critical importance are polymers used in ceramics, coatings and lubricants, which are heteroatom rich and, at the end of their lifetime, could have a vast range of uses in modern chemical building block synthesis.

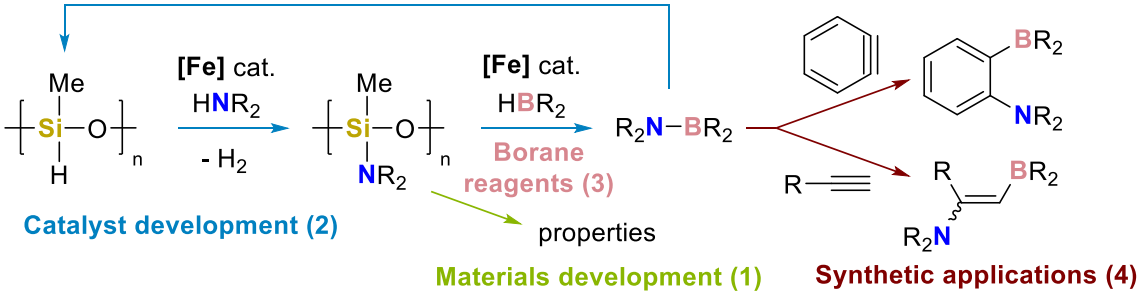
In this context, the dehydrocoupling synthesis and subsequent activation of Si-E bonds by the same well-defined three-coordinate iron(II) β-diketiminate pre-catalyst (**1**) has been discovered by RW.[1] The only by-product from dehydrocoupling is H_2 and this methodology has been extended to depolymerisation of poly(silazanes) (Scheme 1, in collaboration with Merck Durazane® research group). The chemistry is believed to proceed via several iron-hydride intermediates, which SK has used as catalysts for new synthetic methods.[2]



Scheme 1.

This PhD builds upon RW's expertise in iron catalysed main group-main group bond synthesis and experience of polymer chemistry and SK's expertise in iron-hydride chemistry, mechanisms and electrochemistry (Scheme 2). Specifically, this PhD seeks to:

1. Use iron-catalysed dehydrocoupling to transform PMHS into novel poly(siloxysilazanes) and test their physical (RW) and electronic (SK) properties.
2. Determine whether more efficient dehydrocoupling and depolymerisation can take place with more easily prepared, simple iron-hydrides (SK)
3. Determine whether more efficient depolymerisation can take place with more readily accessible, environmentally benign boranes or borohydrides (SK)
4. Investigate uses for depolymerisation monomers of the form $R_2N\text{-}BR_2$ to prepare valuable heteroatom rich building blocks (RW), for example benzyne or alkyne functionalisation.[3]

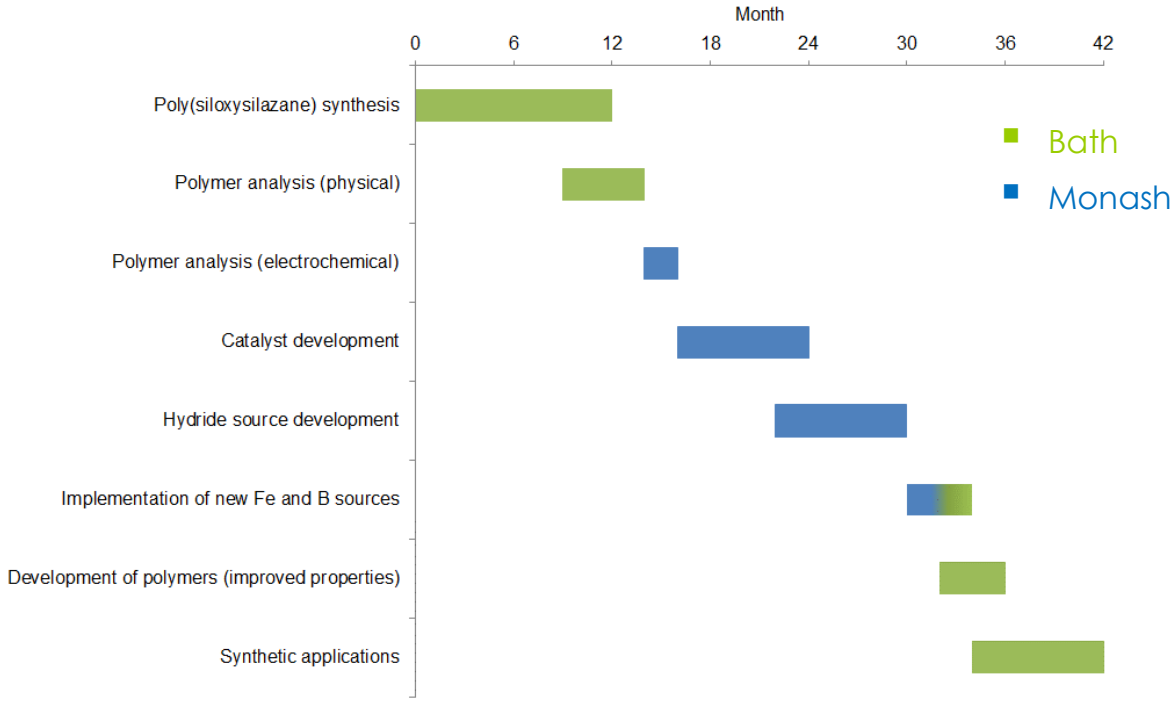


Scheme 2. Polymerisation, depolymerisation catalysis mediated by iron, with onwards repurposing chemical development. Key aims numbered.

Sustainability is built into this project from first principles: iron catalyst, hydrogen gas release, atom economy.

Circular technologies are addressed through a cradle-to-grave-to-cradle approach: new materials with applications, which can then be recycled and the building blocks or monomers reused or repurposed.

The collaborative and training-based approach to this PhD is intrinsic to the project, with the student spending the beginning and end of their PhD at Bath developing experience in polymer synthesis and analysis, and the middle portion at Monash developing iron-hydride chemistry and electrochemistry techniques:



References

1. D. Gasperini, S. E. Neale, A. K. King, S. A. Macgregor and R. L. Webster, unpublished. For previous research involving iron catalysed amine-borane formation see: N. T. Coles, M. F. Mahon and R. L. Webster, *Organometallics*, **2017**, *36*, 2262-2268; M. Espinal-Viguri, S. E. Neale, N. T. Coles, S. A. Macgregor and R. L. Webster, *J. Am. Chem. Soc.*, **2019**, *141*, 572-582.
2. S. H. Kyne, M. Clémancey, G. Blondin, E. Derat, L. Fensterbank, A. Jutand, G. Lefèvre and C. Ollivier, *Organometallics*, **2018**, *37*, 761-771.
3. M. Mesgar, J. Nguyen-Le and O. Daugulis, *J. Am. Chem. Soc.*, **2018**, *140*, 13703-13710; D.-W. Gao, Y. Gao, H. Shao, T.-Z. Qiao, X. Wang, B. B. Sanchez, J. S. Chen, P. Liu and K. M. Engle, *Nature Catalysis*, **2019**, DOI: 10.1038/s41929-019-0384-6.

Features of the programme

- PhD researchers will be registered at both institutions and will be awarded a joint PhD degree.
- PhD researchers will be jointly supervised by academics from both Monash and Bath Universities.
- All PhD researchers in the joint programme will also undertake a bespoke advanced training plan covering a range of topics focusing on sustainability.
- Applicants can apply to either Monash University or the University of Bath as their nominated home institution.
- PhD researchers will undertake a period of no less than 12 months at the partner institution.
- Up to four scholarships/studentships will be offered. Additional and suitably qualified applicants who can access a scholarship/studentship from other sources will be also considered. Evidence of funding must be provided.
- The scholarships/studentships include:
  - a *full tuition fee sponsorship* provided by Monash or Bath for the course duration (up to a maximum 42 months). Note, however, that studentships for Bath-based projects will provide cover for UK/EU tuition fees ONLY.
  - *a living allowance (stipend)* provided by Monash or Bath Universities.

Note: Overseas Student Health Cover (OSHC) must be paid by the student, unless covered by the university.

How to apply

You MUST express interest for three projects in order of preference. Please submit your application at the Home institution of your preferred project ('Home' institution details can be found in the project summary). However, please note that you are applying for a joint PhD programme and applications will be processed as such.

The deadline to submit applications is 23rd February 2020

Monash University

Expressions of interest (EoI) can be lodged through https://www.monash.edu/science/bath-monash-program. The EoI should provide the following information:

CV including details of citizenship, your Official Academic Transcripts, key to grades/grading scale of your transcripts, evidence of English language proficiency (IELTS or TOEFL, for full requirements see: https://www.monash.edu/graduate-research/faqs-and-resources/content/chapter-two/2-2), and two referees and contact details (optional). You must provide a link to these documents in Section 8 using Google Drive (Instructions in Section 8).

University of Bath

Please submit your application through the following link: https://www.csct.ac.uk/bath-monash-global-phd-programme/

Please make sure to mention in the "finance" section of your application that you are applying for funding through the joint Bath/Monash PhD programme for your specified projects.

In the "research interests" section of your application, please name the three projects you are interested in and rank them in order of preference. Please also include the names of the Bath lead supervisors.