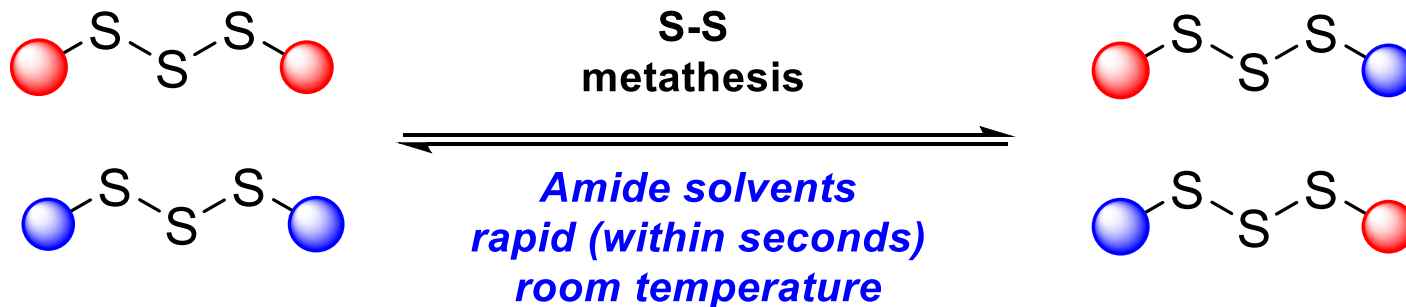


Amide Solvents Induce S-S Metathesis of Organic Trisulfides



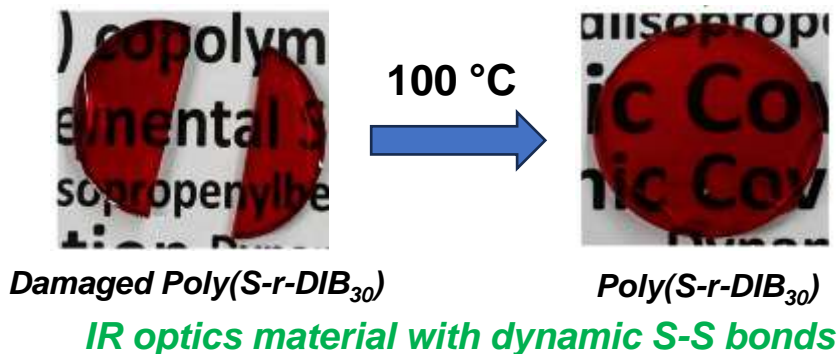
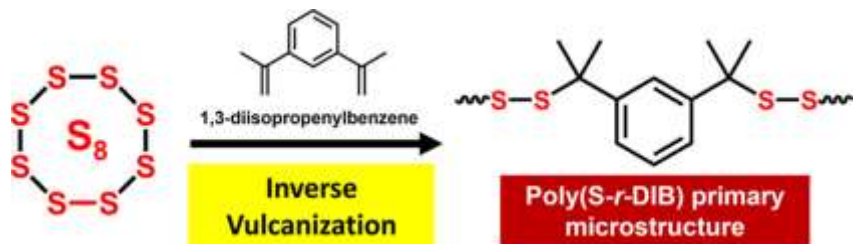
Alfrets D. Tikoalu
PhD Candidate

38th APS, 19 February 2024

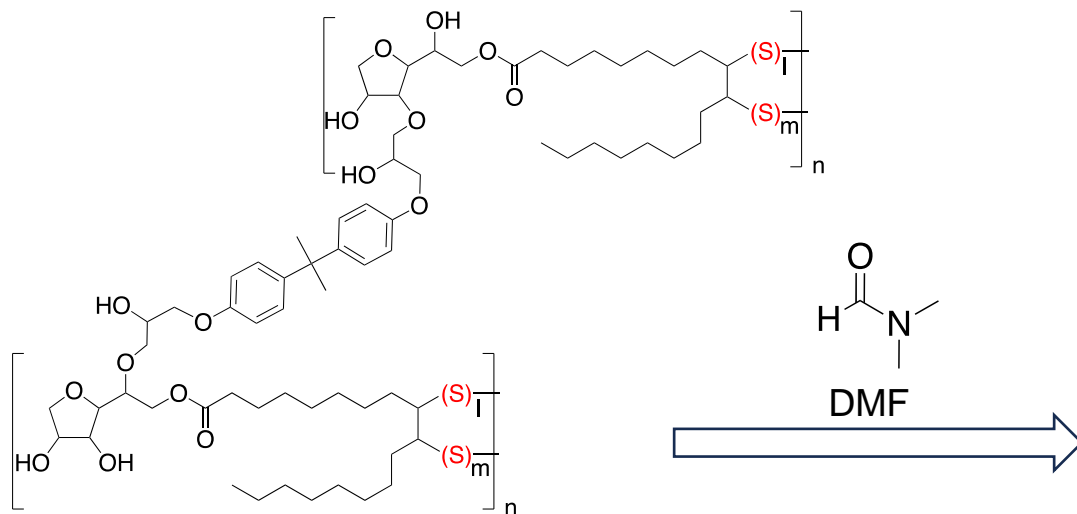
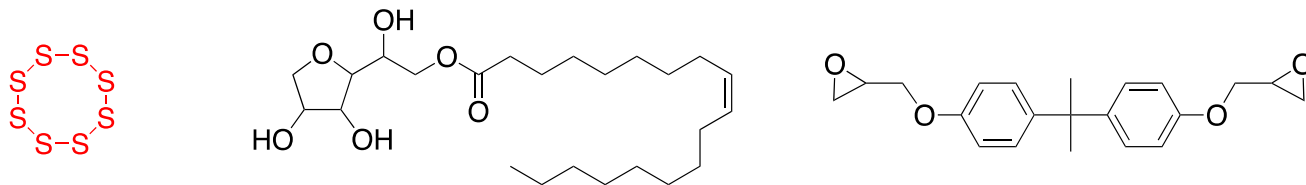
Background: Dynamic sulfur polymers for advanced materials



- **Product of oil refining**
- **Abundant & inexpensive (~ 0.2 USD/kg)**
- **Megatons stockpile**
- **Can be transformed into sulfur polymers:**
 - **Material for IR optics**
 - **Sorbents for toxic metals**
 - **Composites**
 - **Repairable rubbers**



Background: Sulfur polymer M_n changes in DMF



Chemical repair and recycling



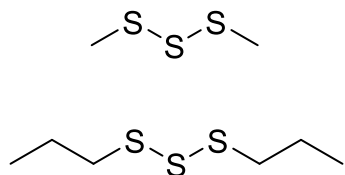
- Soluble (also in DMAc, NMP)
- Reduced M_n (by GPC)

Do these solvents actually break S-S bonds?

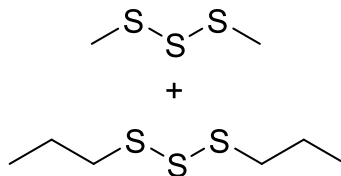
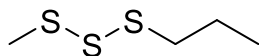
S-S bonds in trisulfides break reversibly in DMF



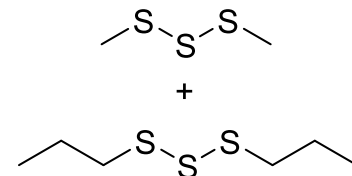
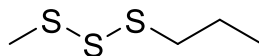
Sam Tonkin



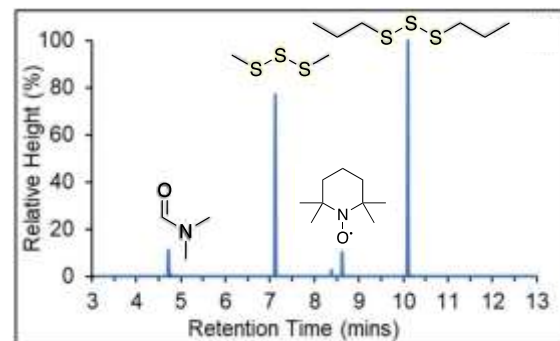
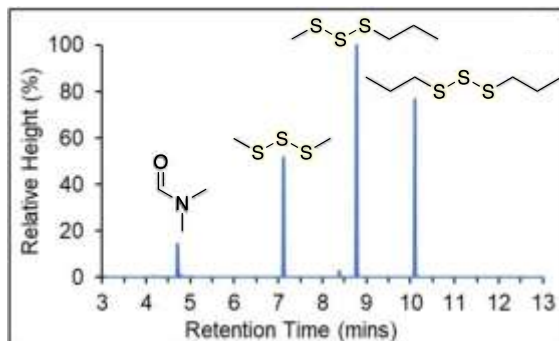
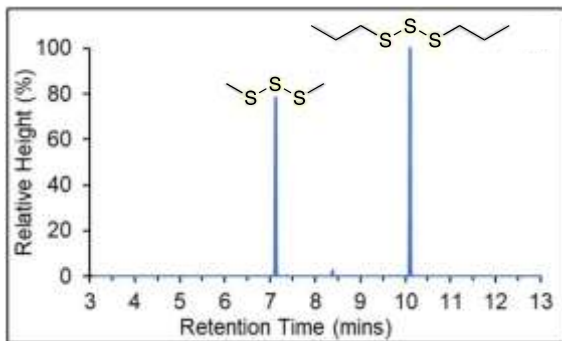
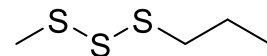
Neat, 20 °C ~~↕~~ up to 24 h



DMF 20 °C ~~↕~~ < 5 min



DMF 20 °C ~~↕~~ TEMPO (10 mol%)

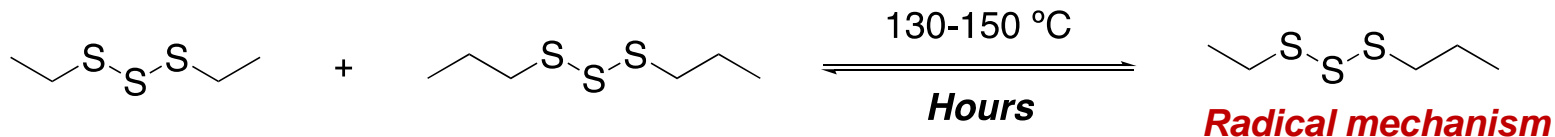


S-S bond metathesis of organic trisulfides

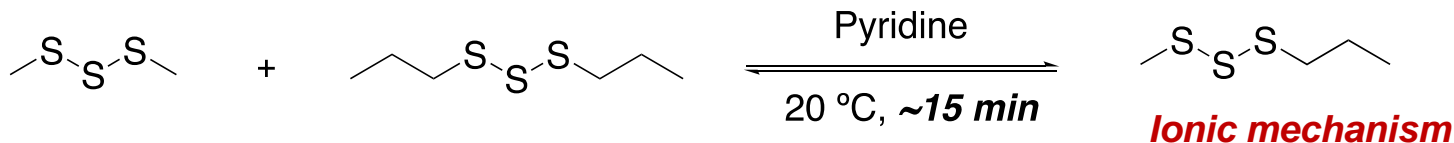


Sam Tonkin

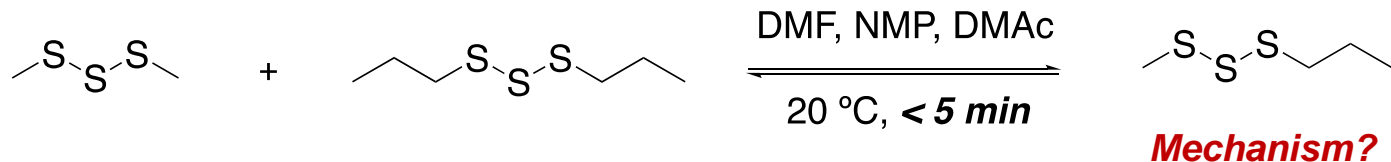
(Trivette and Coran, **1966**)



(Tonkin, Chalker et al., **2020**)

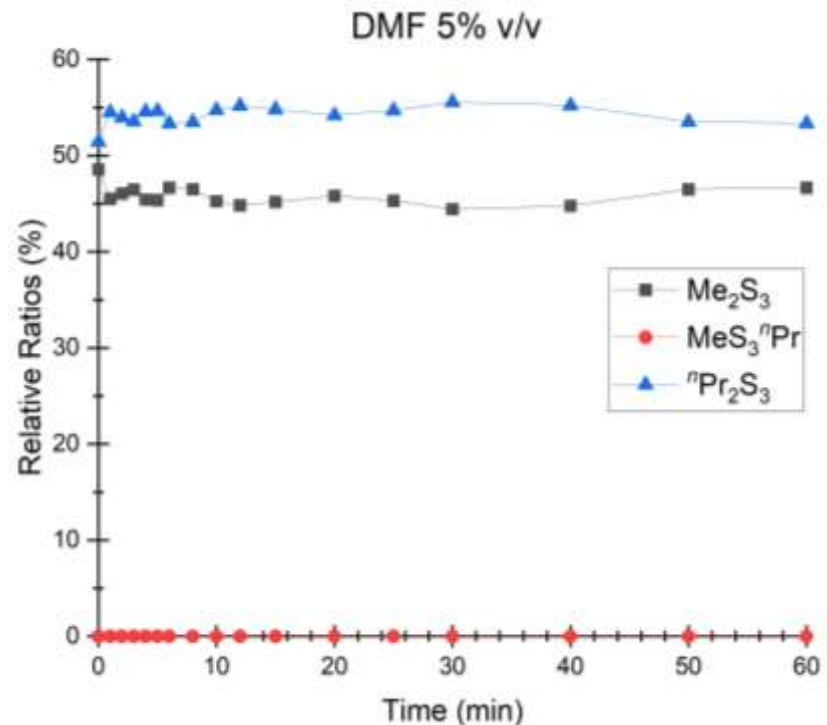
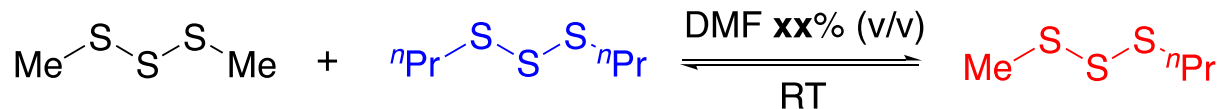


(Tonkin, Chalker, Hasell et al., **2022**)

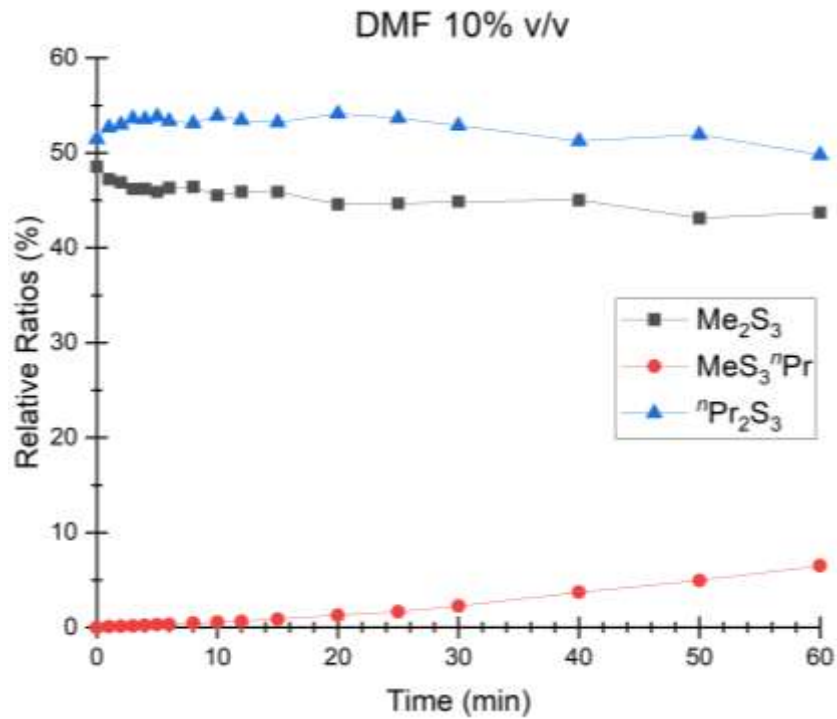
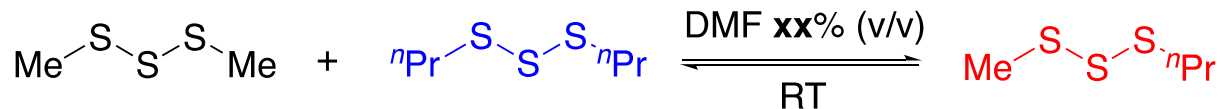


Trivette and Coran, *J. Org. Chem.* **1966**, 31, 100-104; Tonkin, Chalker et al. *Chem. Sci.*, **2020**, 11, 5537-5546; Chalker, J. M., Hasell, T. et al. *Chem. Mater.* **2022**, 34, 3, 1167-1178;

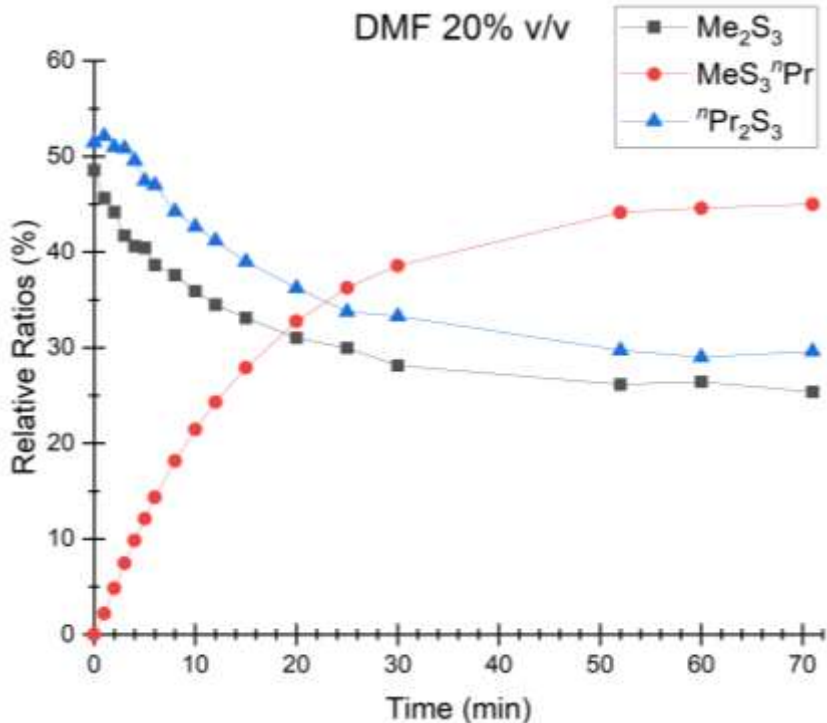
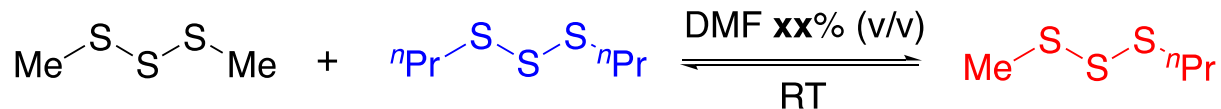
Solvent Investigation – amount of solvent



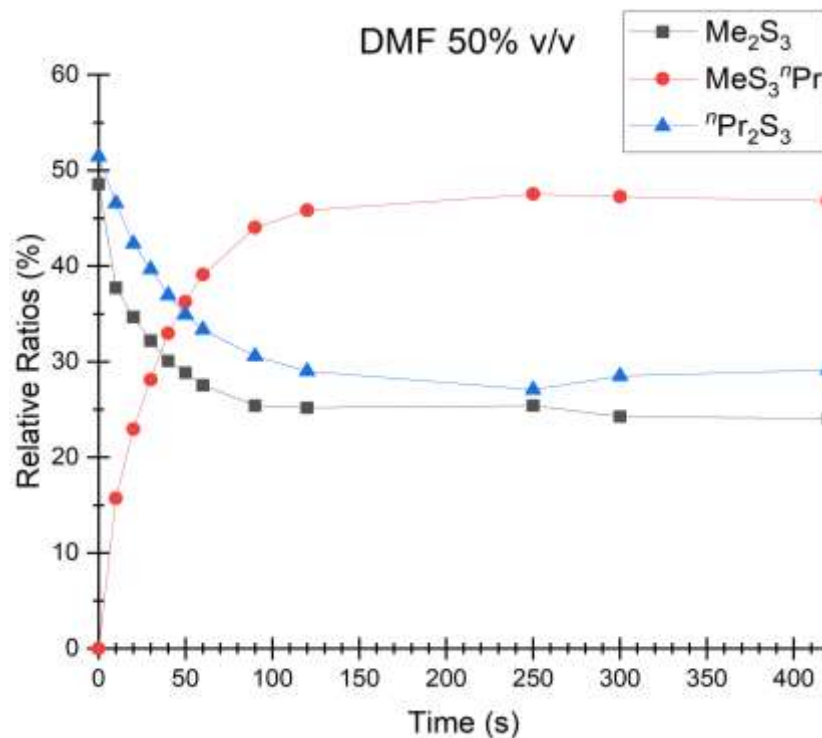
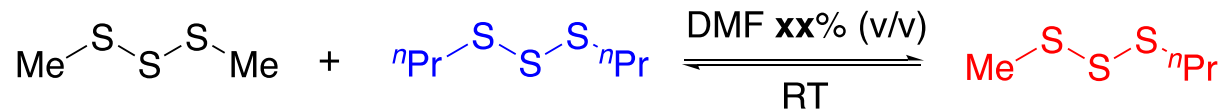
Solvent Investigation – amount of solvent



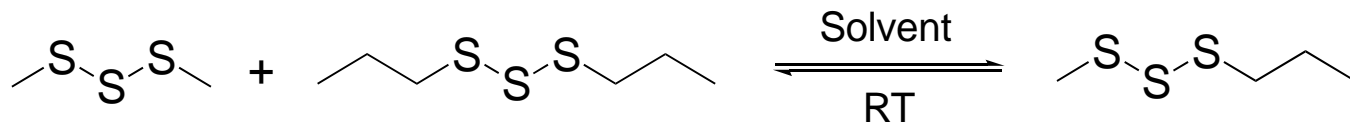
Solvent Investigation – amount of solvent



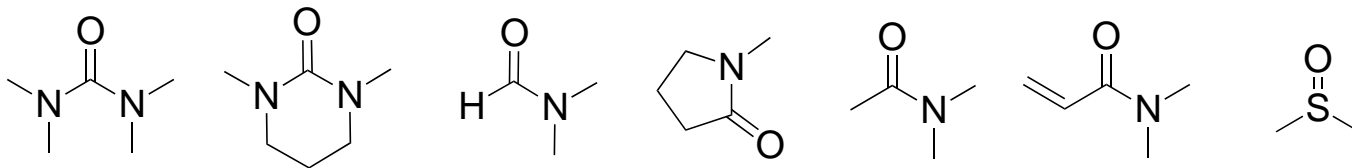
Solvent Investigation – amount of solvent



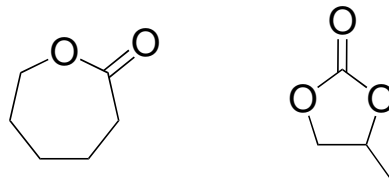
What solvents promote S-S metathesis in trisulfides?



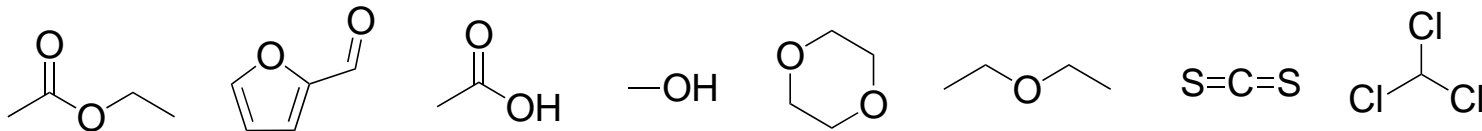
Metathesis within seconds:



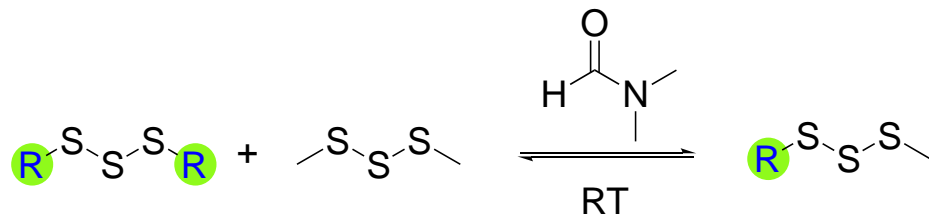
Metathesis within hours:



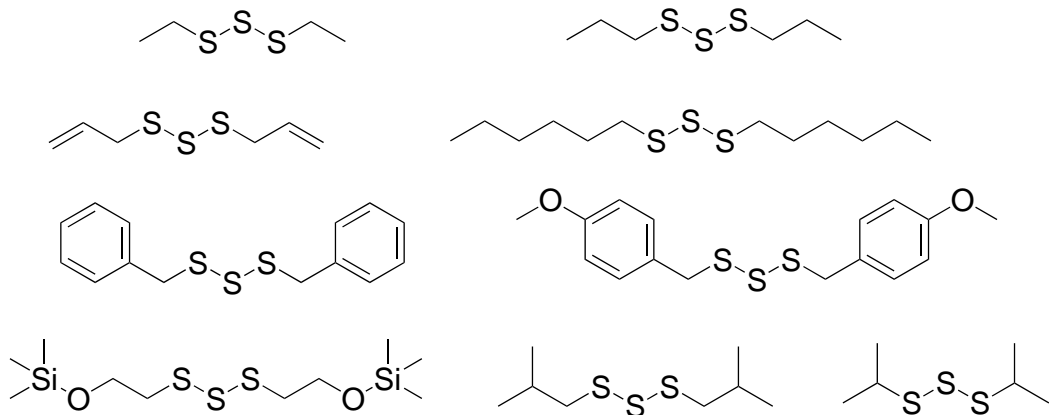
No reaction:



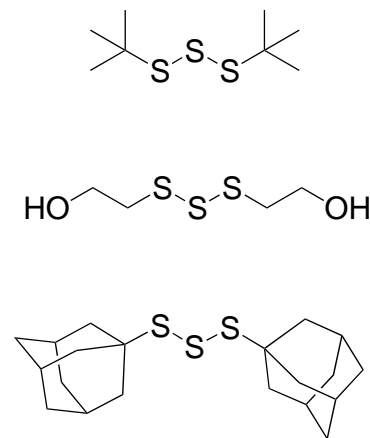
S-S metathesis – substrate scope



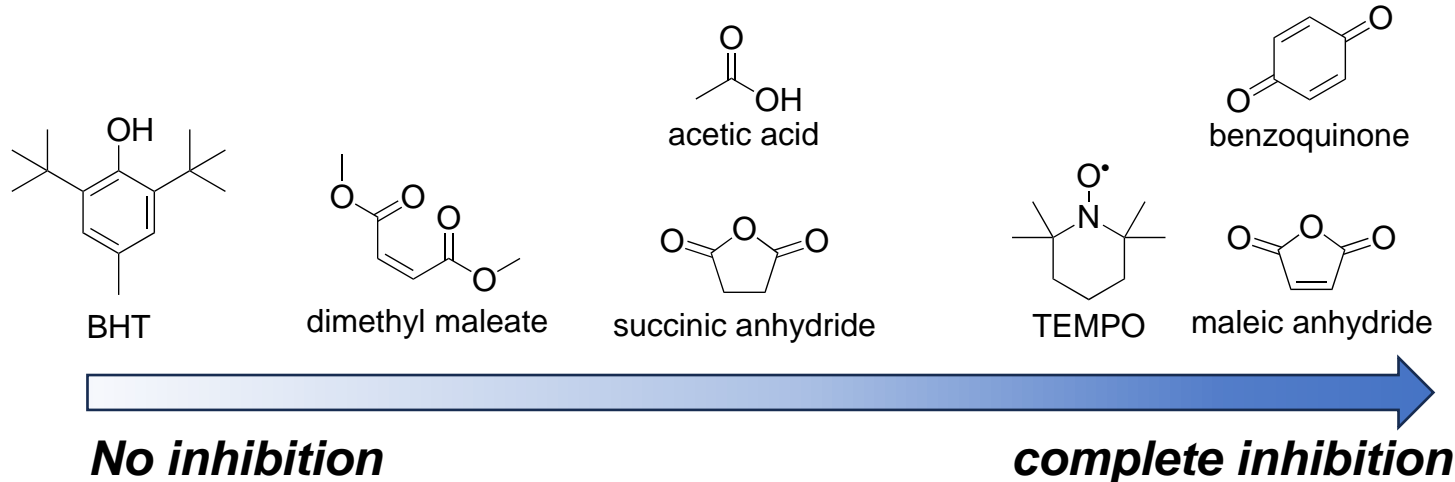
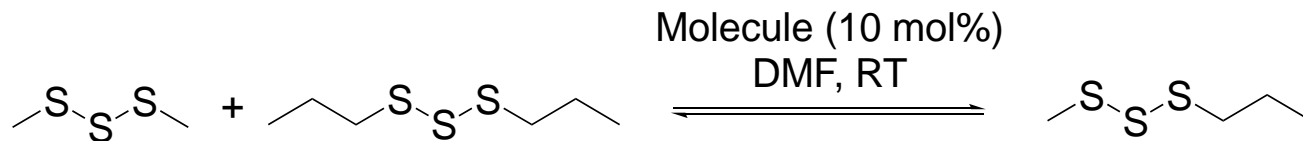
Rapid crossover in seconds



No crossover



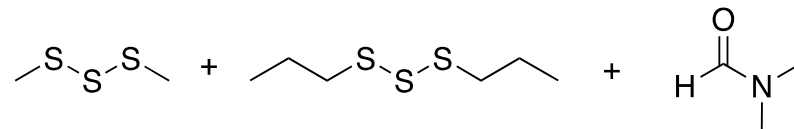
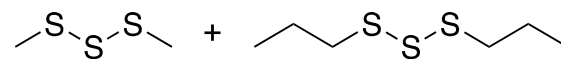
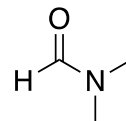
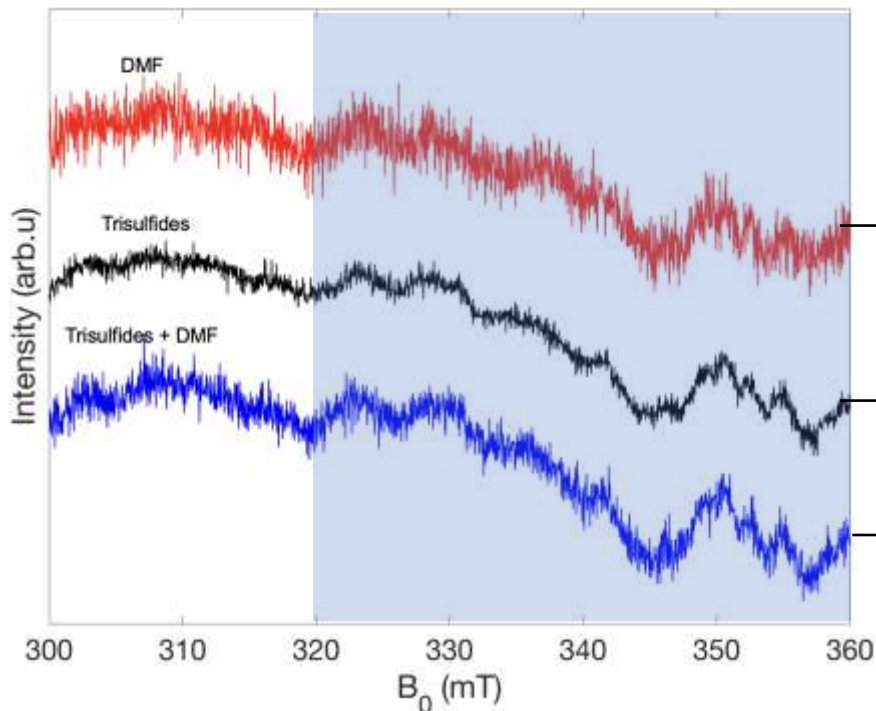
S-S metathesis is inhibited by electrophiles, acid, and oxidants



EPR (Electron Paramagnetic Resonance) spectroscopy – no evidence for radical species



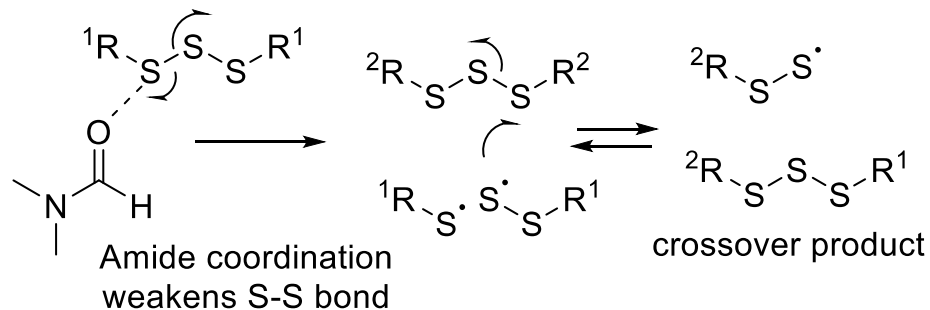
A/Prof. Jeffrey Harmer
(The University of Queensland)



Result:
No S-centered radical signal was observed.

Proposed mechanisms for the S-S metathesis

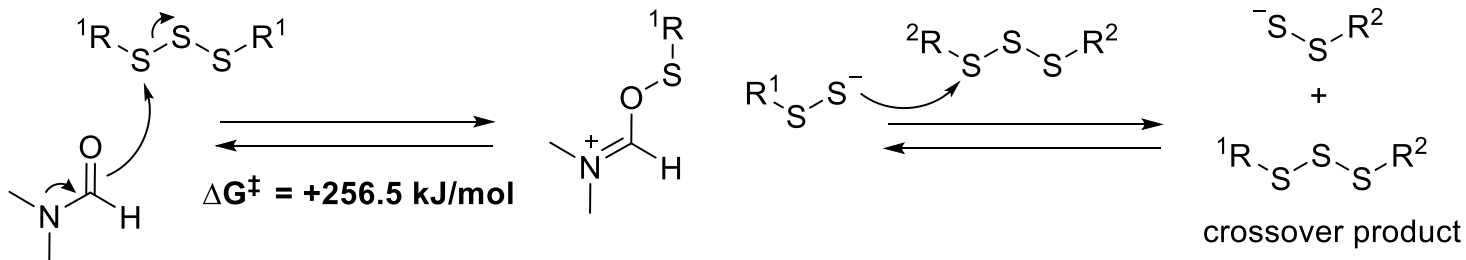
1. Radical mechanism



No evidence
by EPR



2. Ionic mechanism

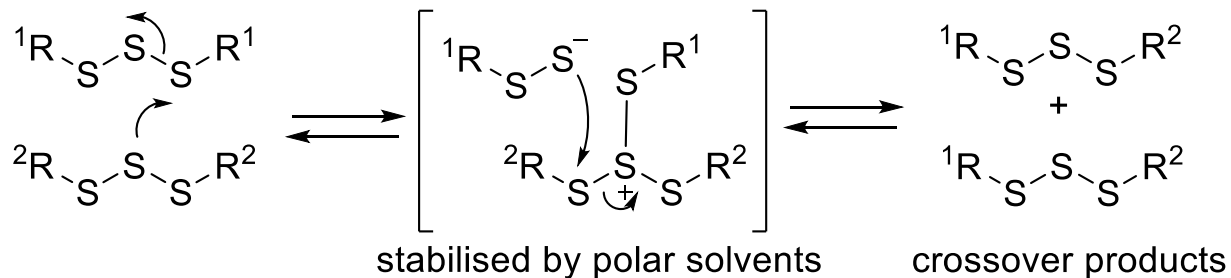


Energy barrier
too high

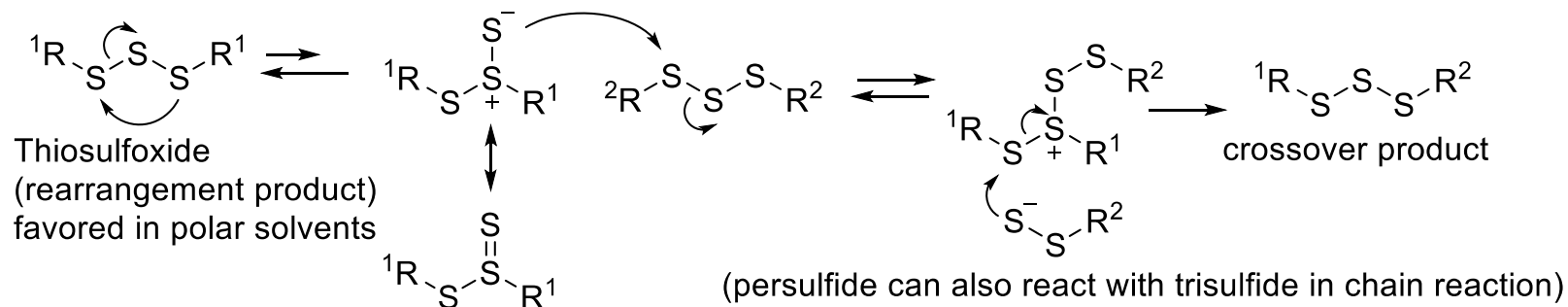


Proposed mechanisms for S-S metathesis

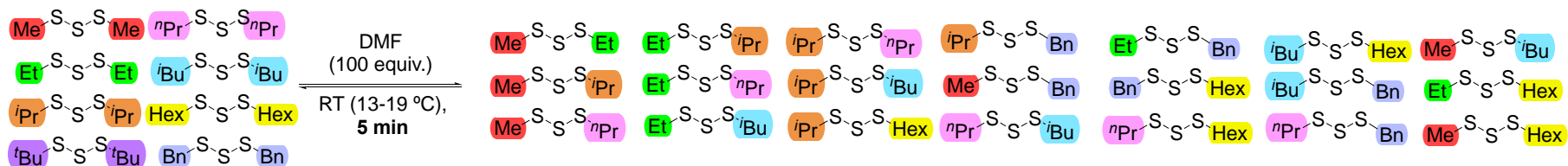
3. Ionic mechanism



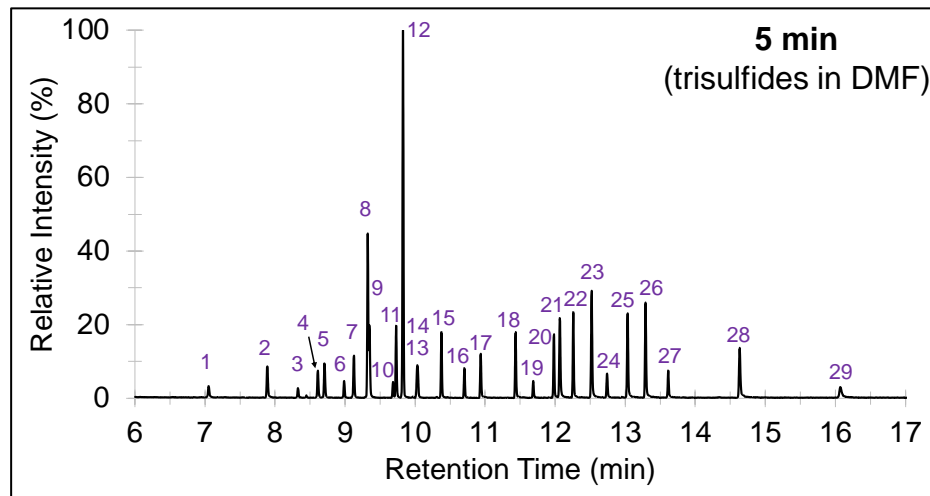
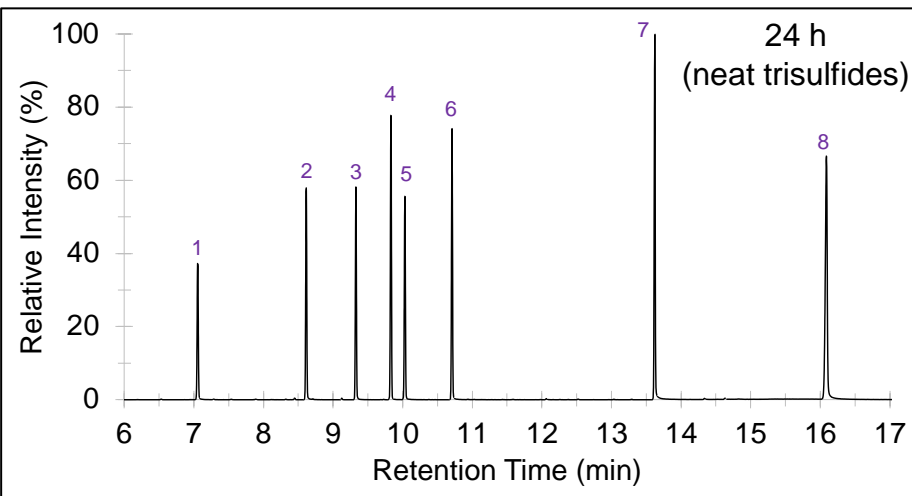
4. Ionic mechanism



Application – Dynamic Combinatorial Library



Rapid formation of dynamic library
8 to 29 trisulfides in < 5 minutes



Tikoalu, A.D., Patel H. D., Smith J., Shapter R., Pei Z., Coote M., Jia Z., Chalker J. M., **2024**. (unpublished results)

Provisional patent **AU2024900381**. Priority date 16 Feb 2024.

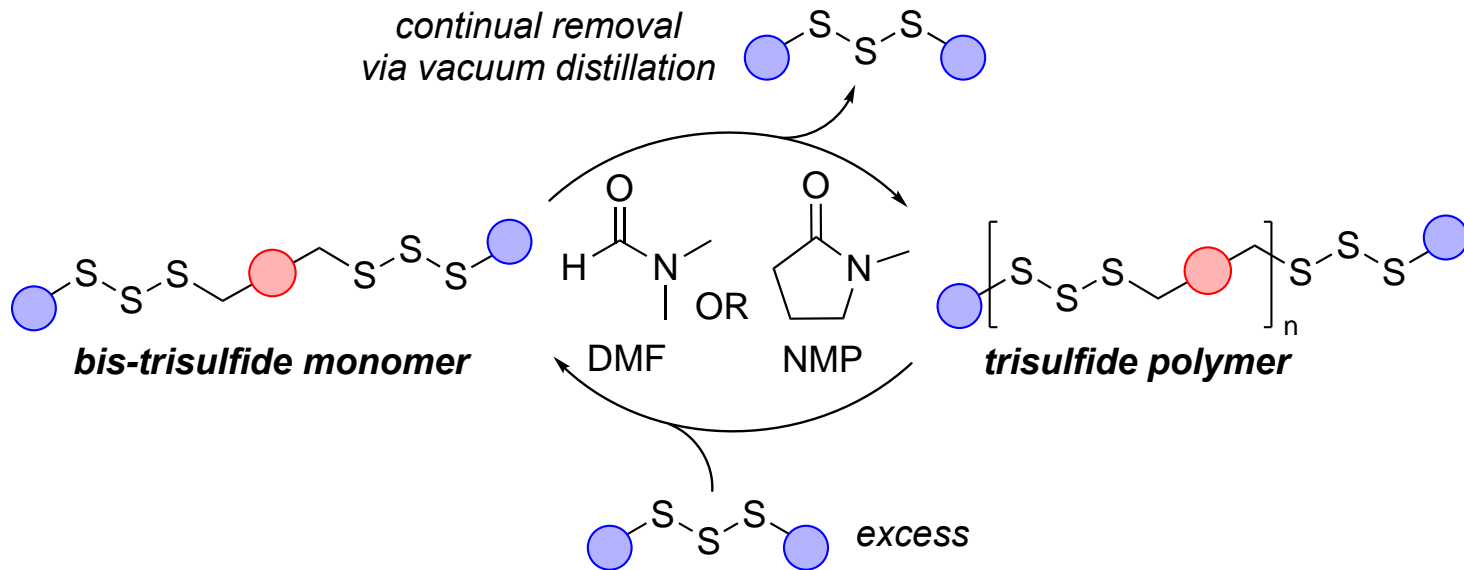
Application to recyclable polymers



Dr. Harshal D. Patel
Tasman 1, Tuesday
4:25-4.40 PM



James N. Smith
Poster Session



Provisional patent **AU2024900381**. Priority date 16 Feb 2024.

Acknowledgments

Prof. Justin M. Chalker

A/Prof. Michael V. Perkins

A/Prof. Zhongfan Jia

A/Prof. Martin R. Johnston

Dr. Harshal Patel

Dr. Witold Bloch

Prof. Michele Coote

A/Prof. Jeffrey Harmer (UQ)

Chalker Lab (past and present members)

Synthesis Super Group at Flinders University



Australian Government

Australian Research Council



UNIVERSITY OF
LIVERPOOL



THE UNIVERSITY
OF QUEENSLAND
AUSTRALIA



**Flinders
University**