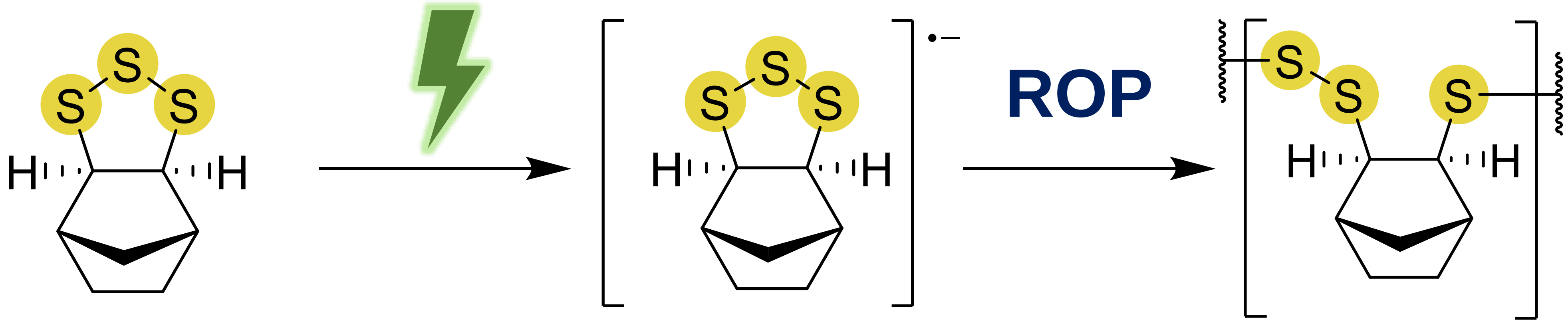
Electrochemical Production of Poly(trisulfides)



South Australia

38APS 19 February 2024

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PhD candidate

Supervisor: Professor Justin Chalker

Flinders University

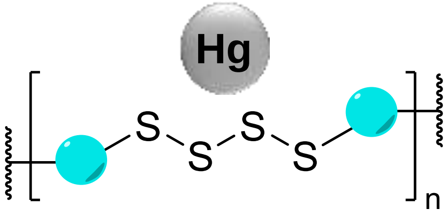
Why Sulfur?

#1 Cheap and highly abundant

< $0.2 USD/kg

#2 Useful properties

Affinity for heavy metals and precious metals



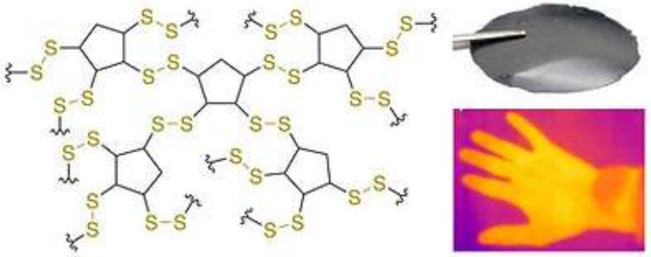
Chalker, **2017**
Chalker, **2021**

Redox activity

Sulfur Copolymer Composite Cathode

Pyun, **2017**

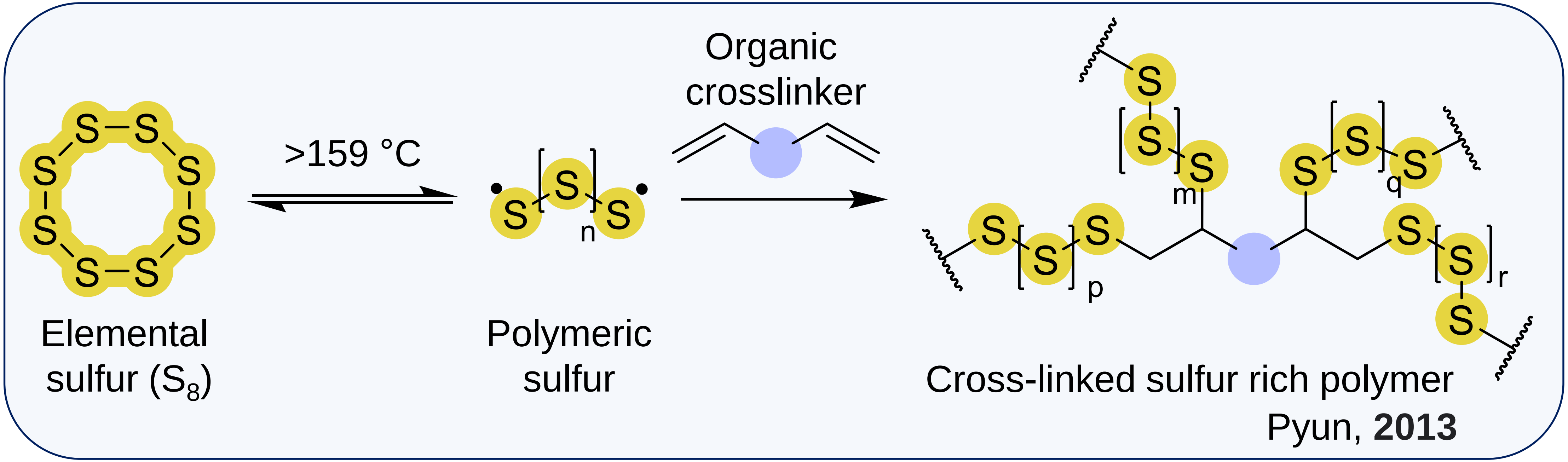
High refractive index and infrared transparency



Pyun, **2014**
Chalker, **2023**

Pyun et al, *Nat. Chem.* **2013**, *5*, 518-524; Chalker et al, *Org. Mater.* **2021**, *2*, 362-373;
Chalker et al, *Chem. Eur. J.* **2017**, *23*, 16219-16230; Pyun et al, *J. Polym. Sci., Part A: Polym. Chem*. **2017**, *10*, 1635.
Pyun et al, *Adv. Mater.* **2014**,*19*,3014-3018; Chalker et al, *Adv. Optical Mater.* **2023**, *11*, 2300058.

Inverse Vulcanisation

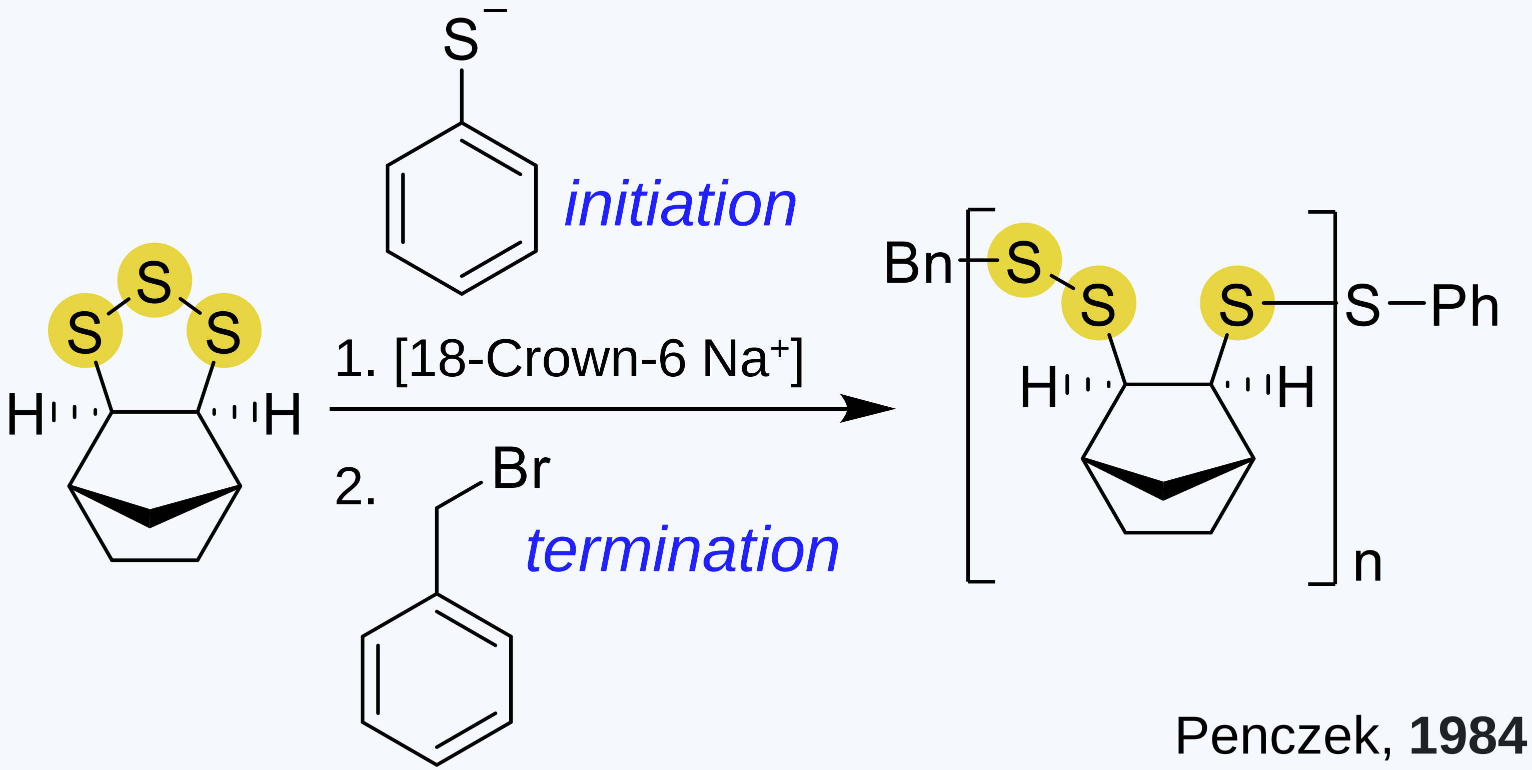


- ✓ Solvent free
- ✓ Operationally simple
- ✓ Dynamic S-S bonds
- ✓ 30-80 wt.% sulfur

- ✷ High temperature
- ✷ Random copolymerization
- ✷ Distribution of sulfur ranks
- ✷ Uncontrolled C-S stereochemistry

Pyun et al, *Nat. Chem.* **2013**, *5*, 518-524;
Pyun et al, *J. Am. Chem. Soc.* **2022**, *144*, 5-22.

Anionic Ring-Opening Polymerisation

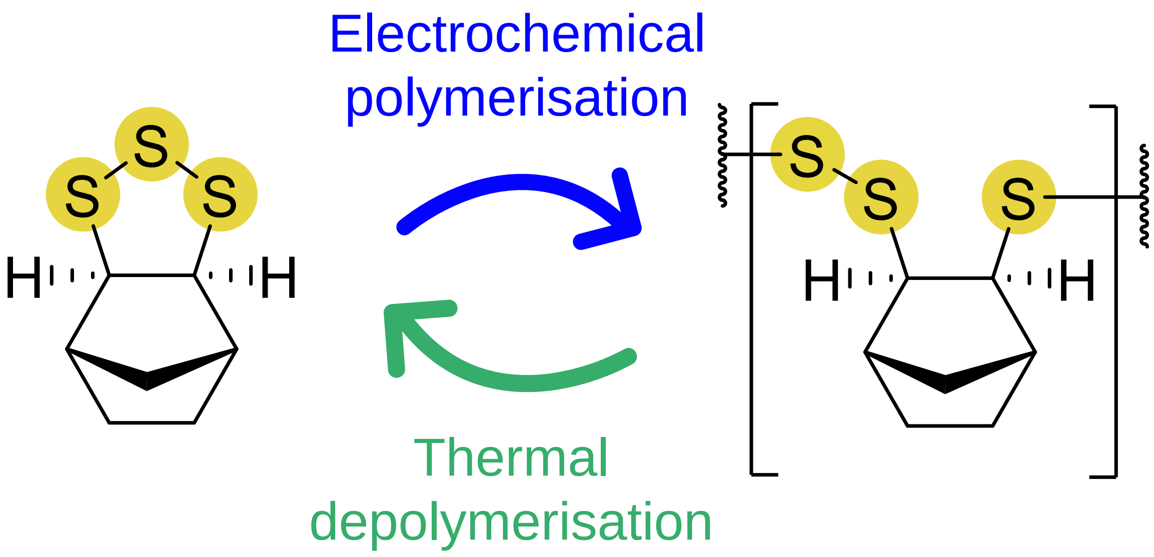


✓ Linear polysulfide
✓ 50 wt.% sulfur
✓ Solvent processable

✷ Highly air and moisture sensitive
✷ Chemical initiation/termination

Penczek et al, *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *5*, 1085-1095.
Penczek et al, *Phosphorus, Sulfur, Silicon Relat. Elem.***1991**. *59*, 47-62.

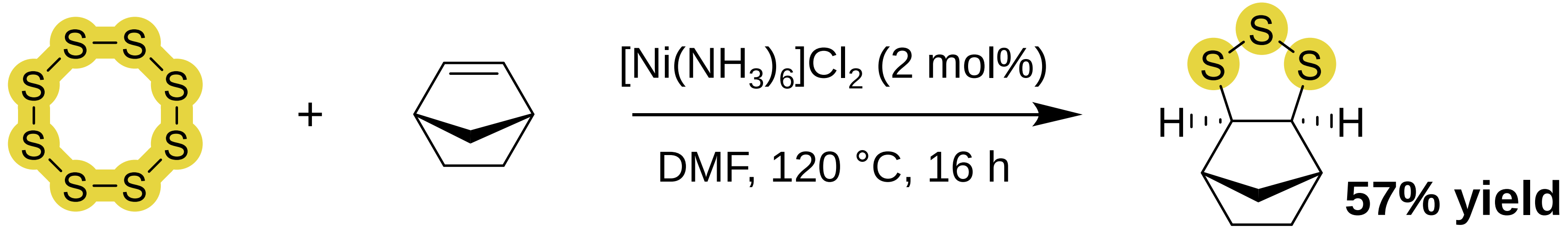
This Work: Electrochemical Ring-Opening Polymerisation



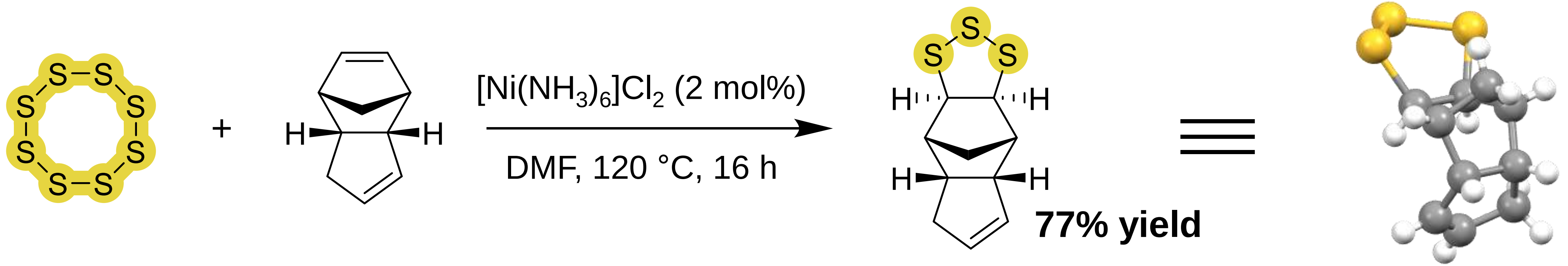
- ✓ Novel electrochemical initiation
- ✓ Well-defined sulfur rank
- ✓ Regioselective propagation
- ✓ Controlled C-S stereochemistry
- ✓ Operationally simple

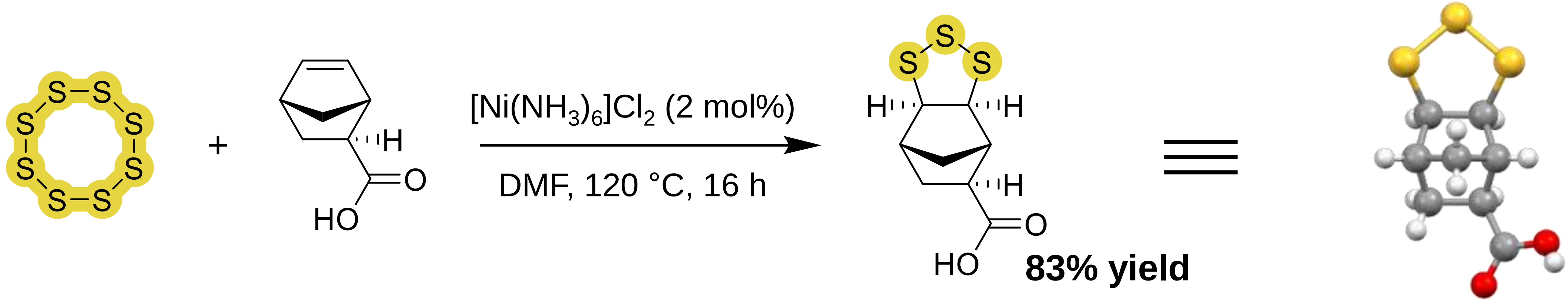
<u>Pople</u>, Nicholls, Pham, Bloch, Lisboa, Perkins, Gibson, Coote, Jia and Chalker, *J. Am. Chem. Soc.* **2023**, *145*, 11798.

Monomer Synthesis



- ✓ 100 g scale
- ✓ Operationally simple
- ✓ Utilises elemental sulfur
- ✓ Functional monomers

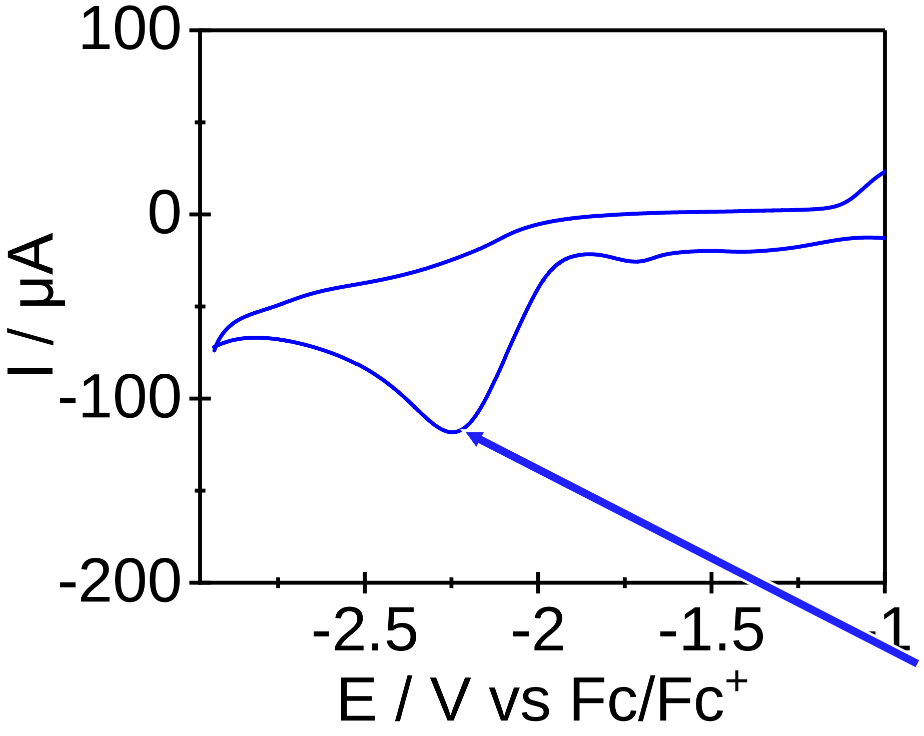




Duñach et al, *Tetrahedron Lett.* **2005**, *46*, 7077-7079; **Pople,** Chalker, et al *J. Am. Chem. Soc.* **2023**, *145*, 11798.

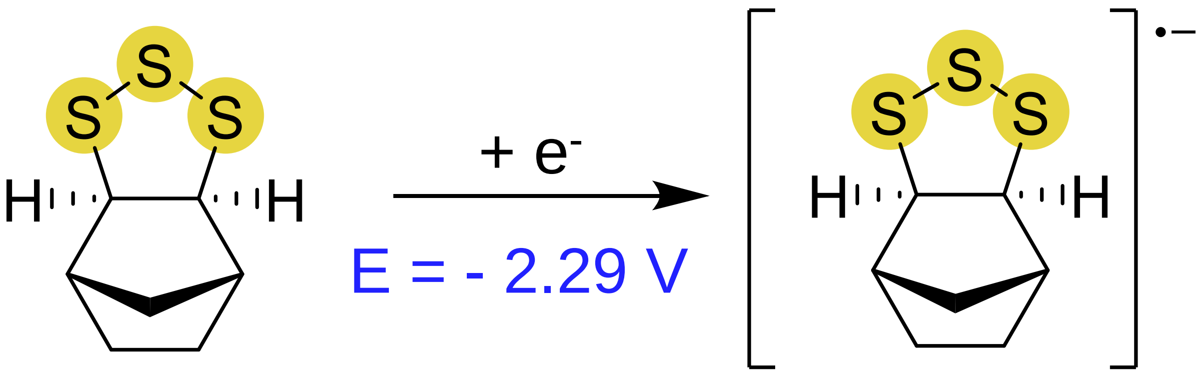
Monomer Redox Activity

Cyclic Voltammetry



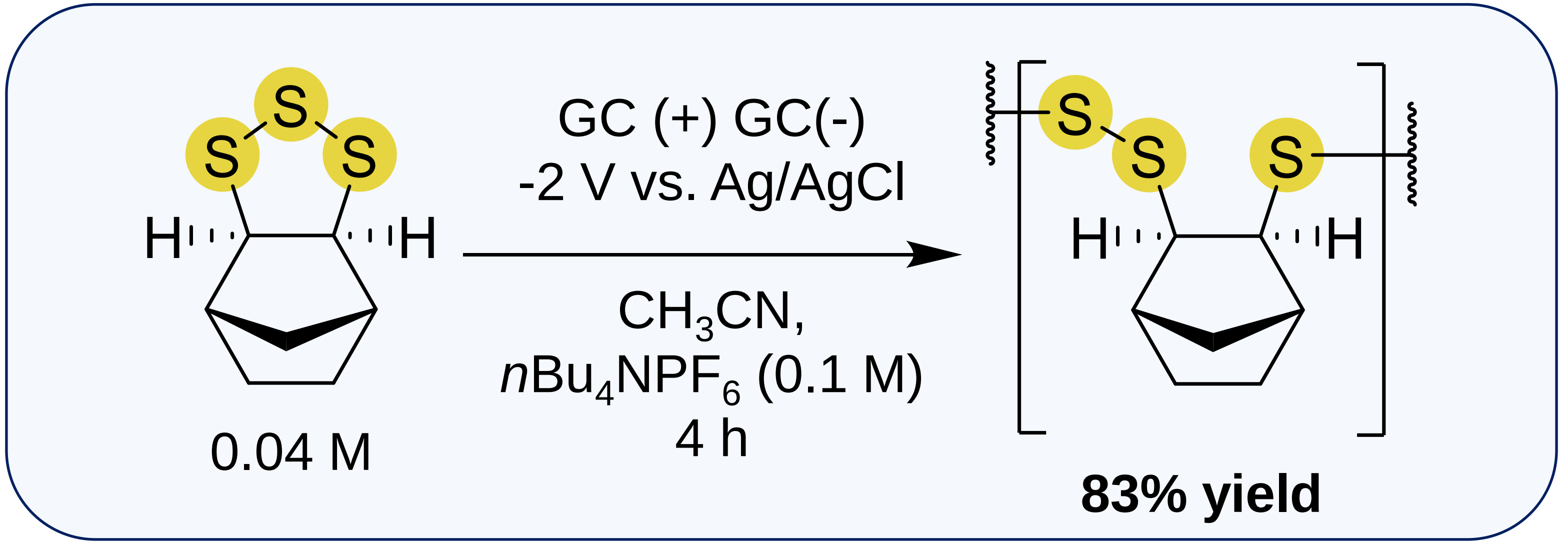
Measured reduction potential: - 2.22 V

Calculated reduction



<u>Pople</u>, Nicholls, Pham, Bloch, Lisboa, Perkins, Gibson, Coote, Jia and Chalker, *J. Am. Chem. Soc.* **2023**, *145*, 11798.

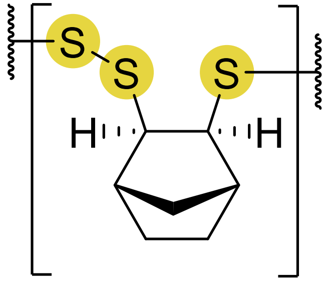
Electrochemical Polymerisation



Initial 15 minutes 30 minutes

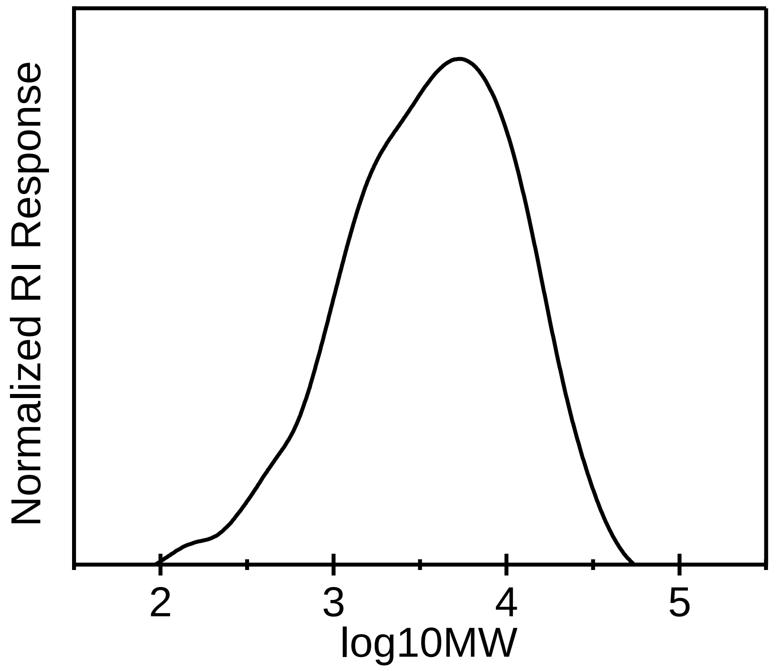
Pople, Nicholls, Pham, Bloch, Lisboa, Perkins, Gibson, Coote, Jia and Chalker, *J. Am. Chem. Soc.* **2023**, *145*, 11798.

Electrochemical Polymerisation

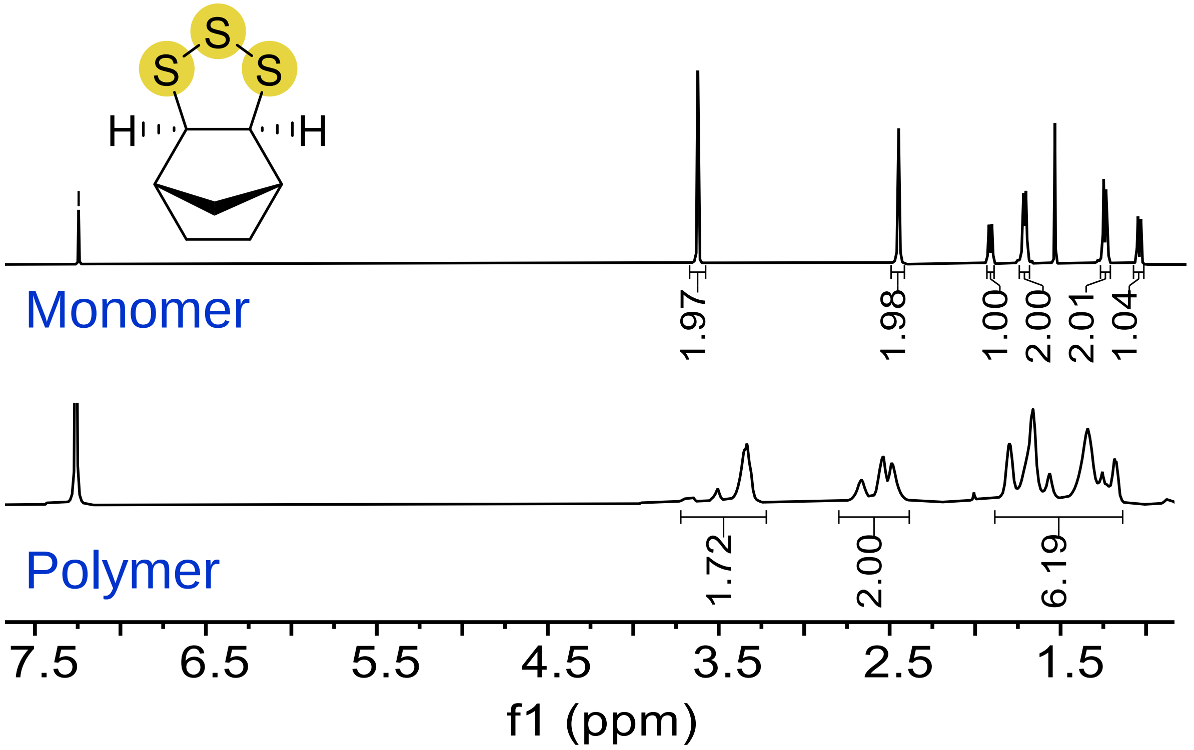


M_w = 6580 g/mol
$Đ$ = 3.08

GPC (THF)



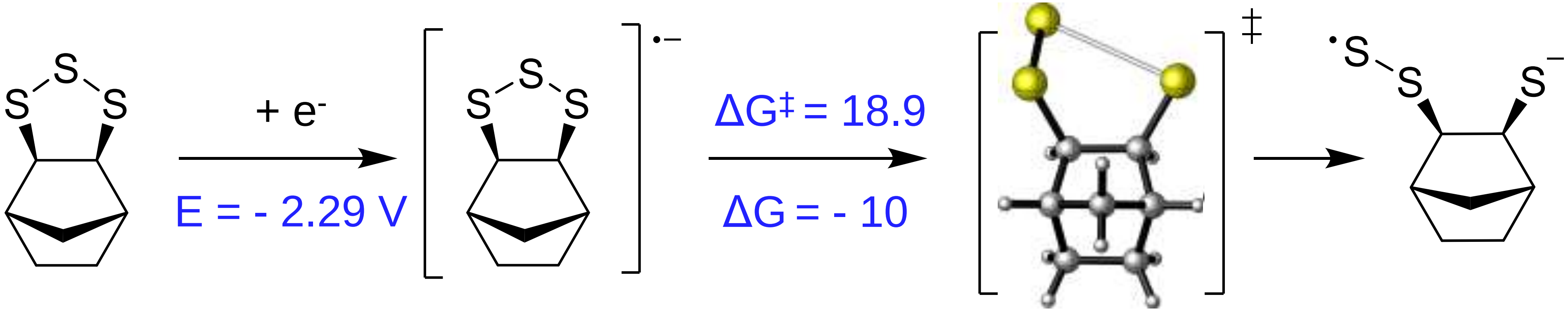
^{1}H NMR (600 MHz, $CDCl_3$)

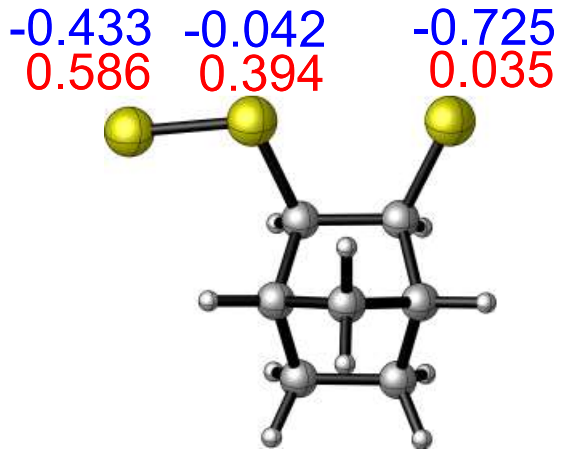


Pople, Nicholls, Pham, Bloch, Lisboa, Perkins, Gibson, Coote, Jia and Chalker, *J. Am. Chem. Soc.* **2023**, *145*, 11798.

Polymer Mechanism

initiation



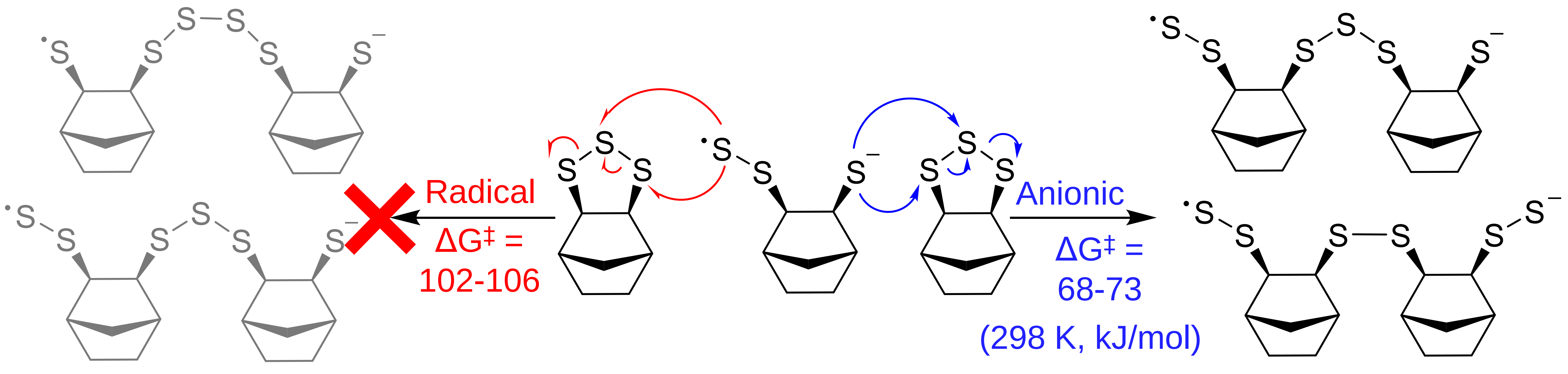


charge (blue) and spin (red) densities on the ring-opened product

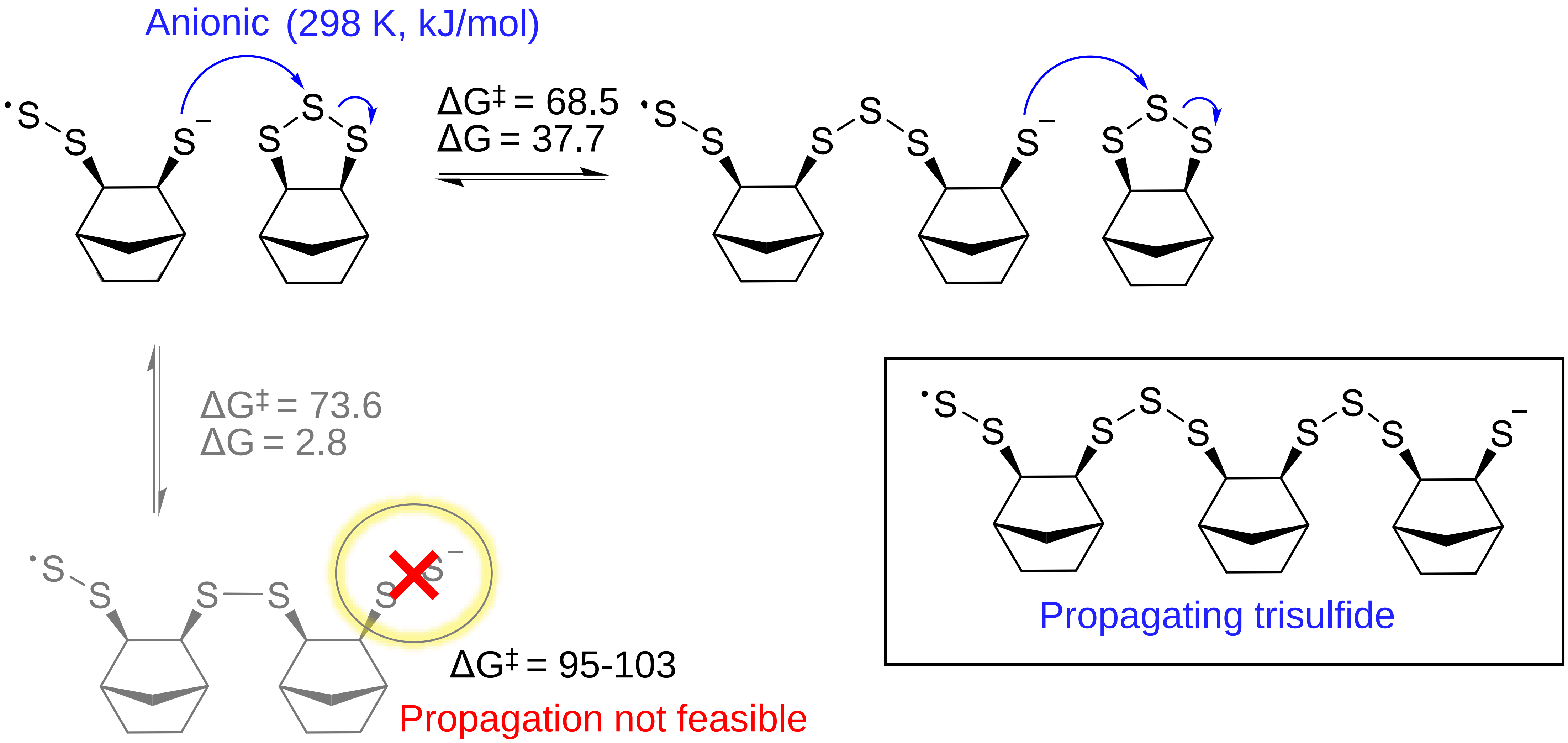
(298 K, kJ/mol)

Pople, Nicholls, Pham, Bloch, Lisboa, Perkins, Gibson, Coote, Jia and Chalker, *J. Am. Chem. Soc.* **2023**, *145*, 11798.

Polymer Mechanism

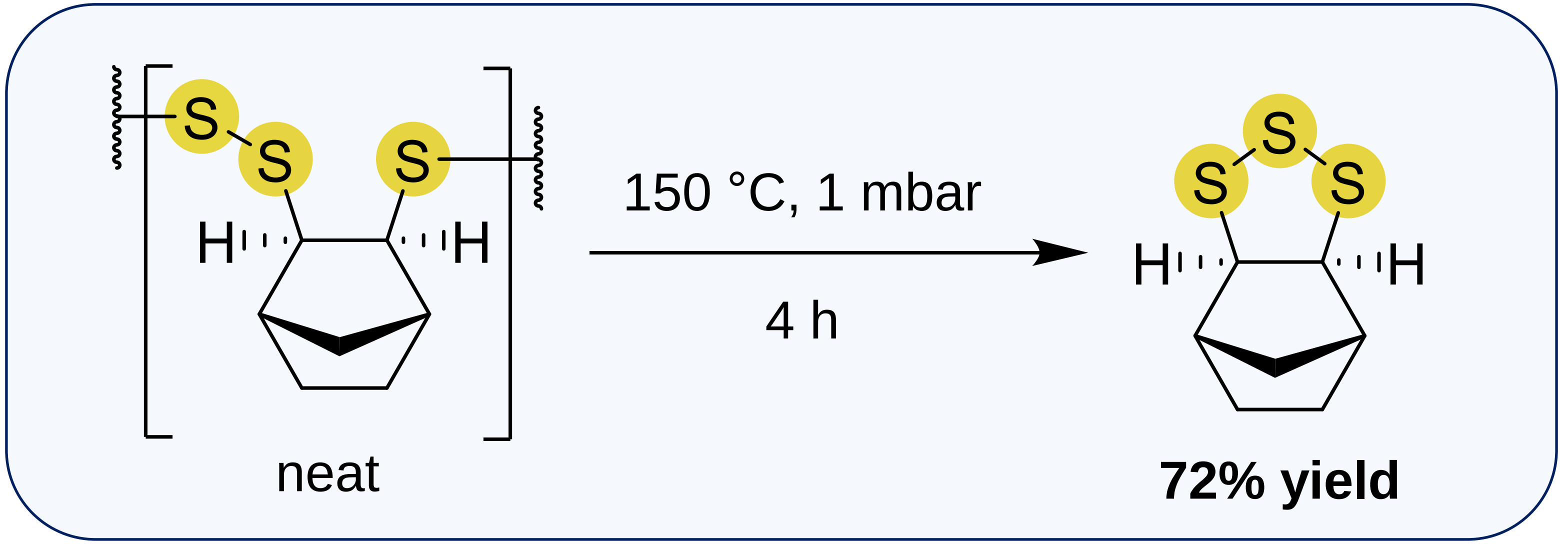


Polymer Mechanism



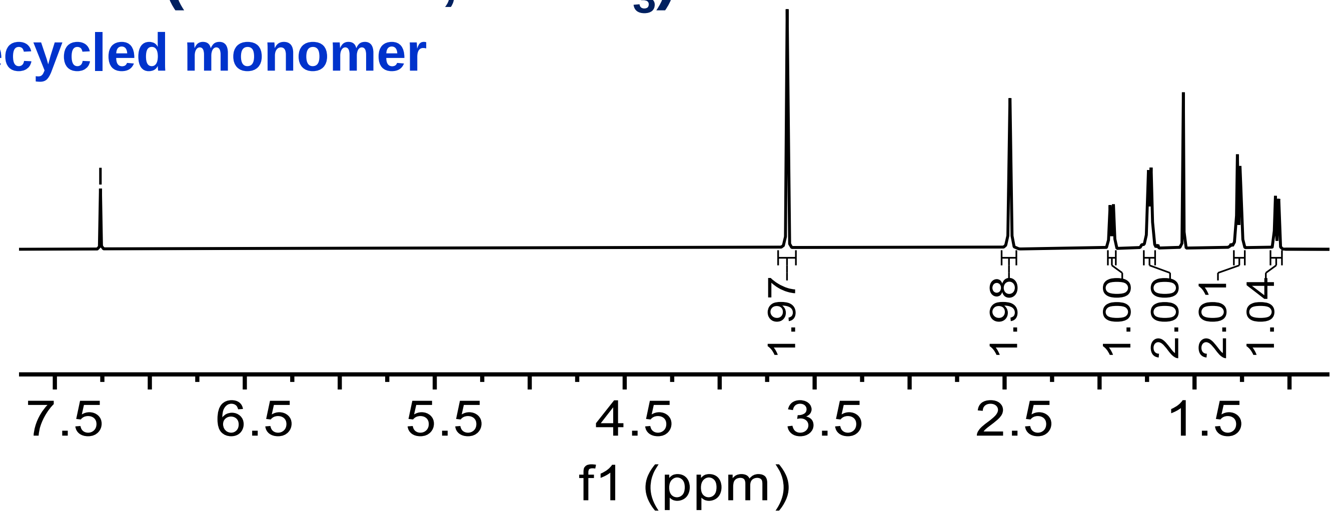
Pople, Nicholls, Pham, Bloch, Lisboa, Perkins, Gibson, Coote, Jia and Chalker, *J. Am. Chem. Soc.* **2023**, *145*, 11798.

Polymer Recycling



^{1}H NMR (600 MHz, $CDCl_3$)

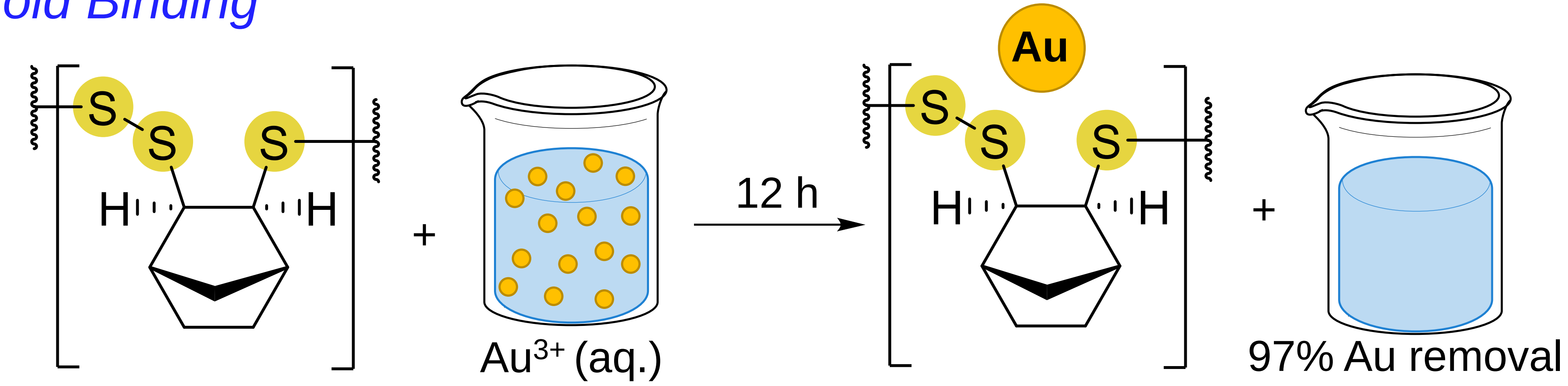
Recycled monomer



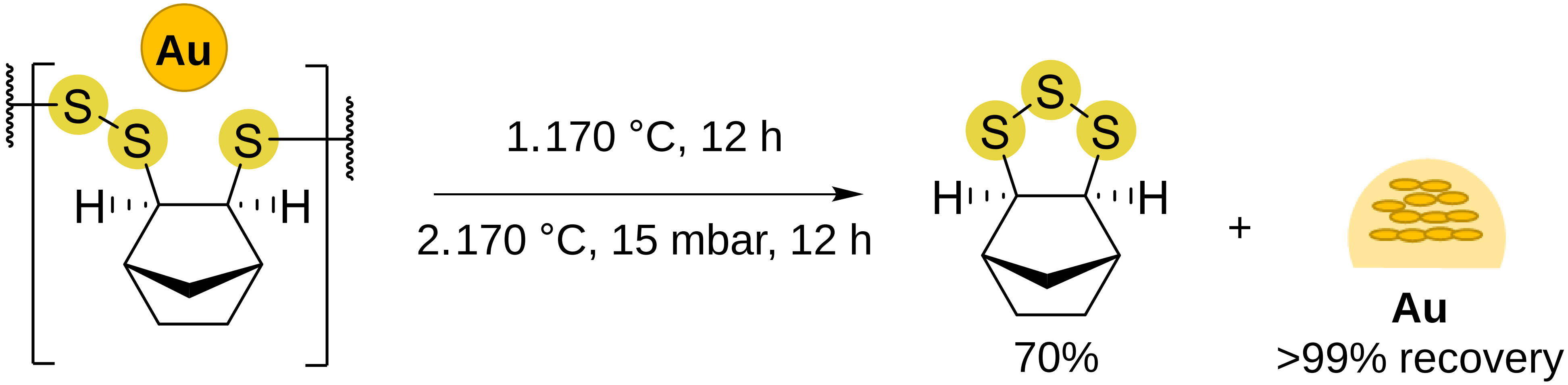
Pople, Nicholls, Pham, Bloch, Lisboa, Perkins, Gibson, Coote, Jia and Chalker, *J. Am. Chem. Soc.* **2023**, *145*, 11798.

Gold Binding and Polymer Recycling

Step 1: Gold Binding



Step 2: Recovery

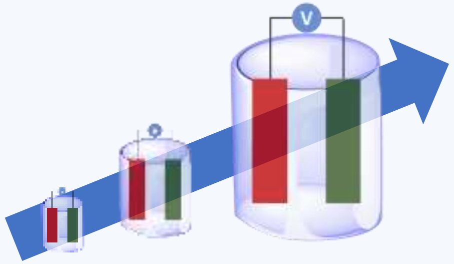


<u>Pople</u>, Nicholls, Pham, Bloch, Lisboa, Perkins, Gibson, Coote, Jia and Chalker, *J. Am. Chem. Soc.* **2023**, *145*, 11798.

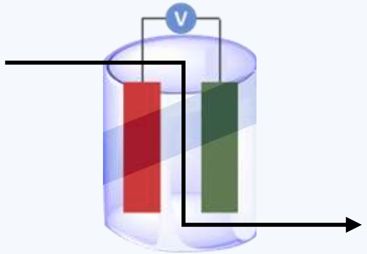
Scaling up Electrochemical Polymerisation

Large Scale Electrochemical Polymerisation

Batch



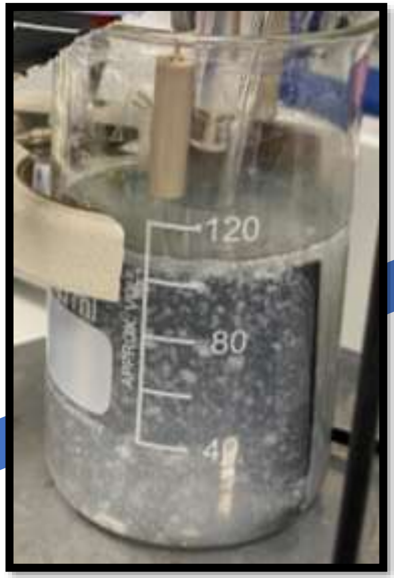
Continuous Flow



200 mg
0.04 M

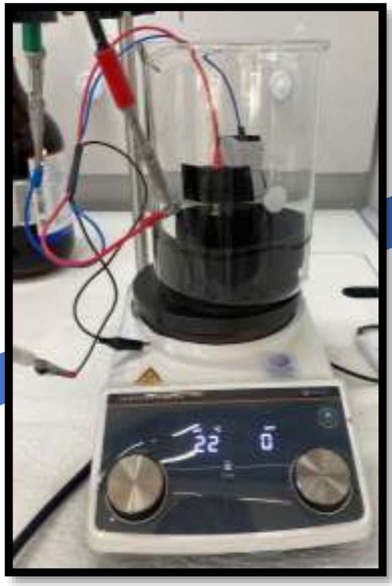
99% conversion,
4 hours

1 g
0.04 M



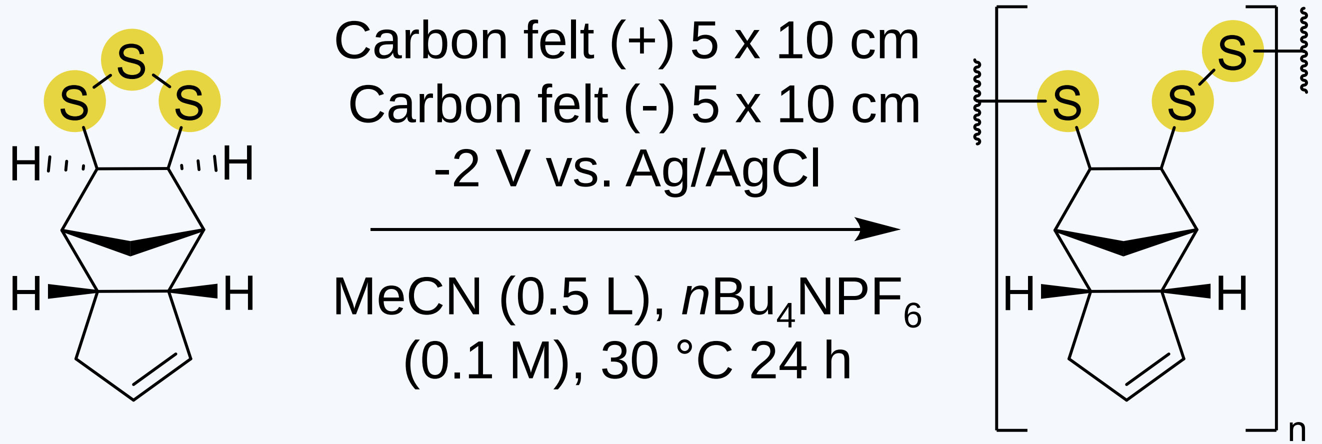
87% conversion,
3 hours

20 g
0.18 M



85% conversion,
24 hours

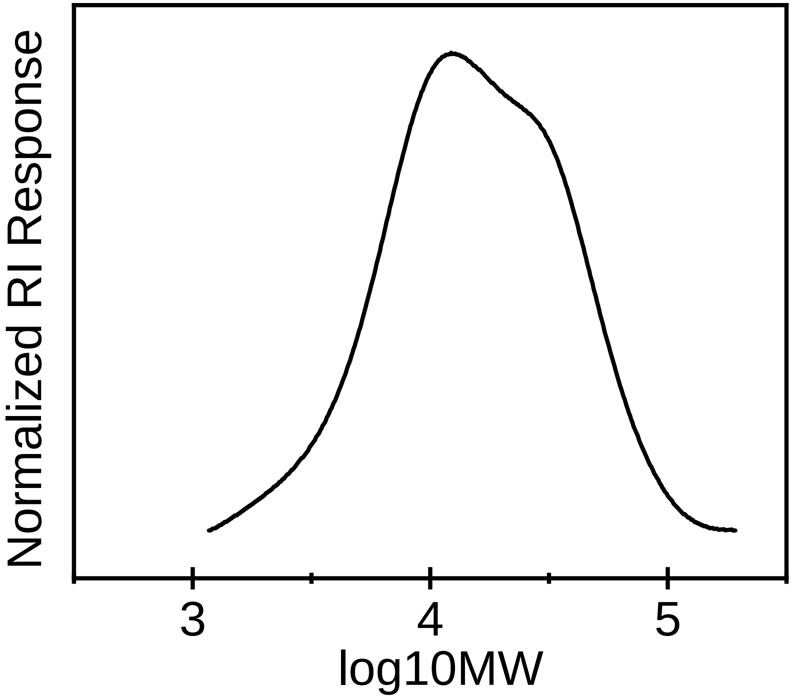
20 g Batch Reaction



0.18 M
20 g

85% conversion
76% yield

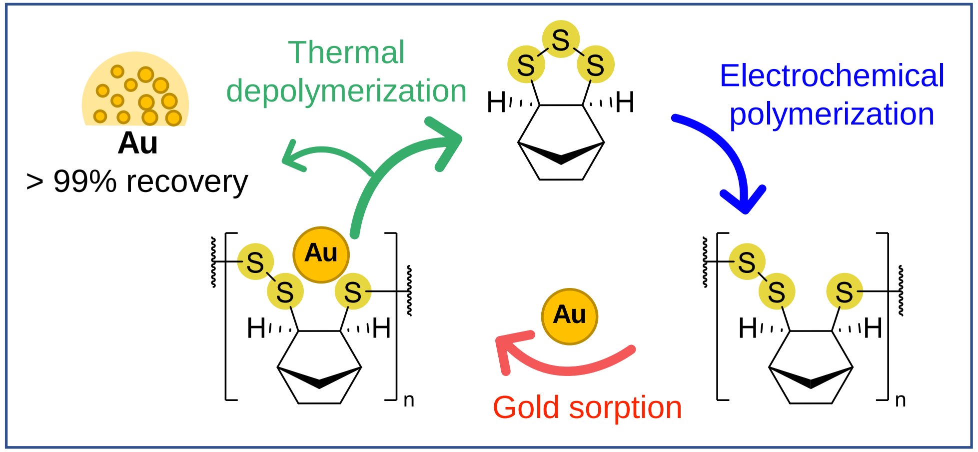
GPC (THF)



M_w = 22000 g/mol
$Đ$ = 1.9

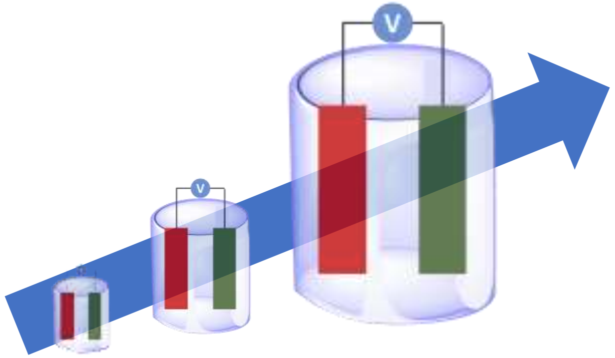
Conclusion and Future Work

#1
Electrochemical synthesis of poly(trisulfides)



- ✓ Well-defined sulfur rank
- ✓ Regioselective propagation
- ✓ Controlled C-S stereochemistry
- ✓ Operationally simple

#2
Scale-up in batch



- ✓ 20 g scale in batch
- ✓ High molecular weight

Future work

Optimise continuous flow conditions.
Poly(trisulfide) applications: antimicrobial studies, high refractive index films, IR optics.

Acknowledgments

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Dr. Max Mann
Dr. Nic Lundquist
Dr. Joseph Wang
Dr. Asya Kroeger
Sam Tonkin
Alfrets Tikoalu
Abbey Mann
Steven Tsoukatos
Caroline Andersson
Jemma Virtue
James Deng
James Smith
Daniel Lewis

Flinders University