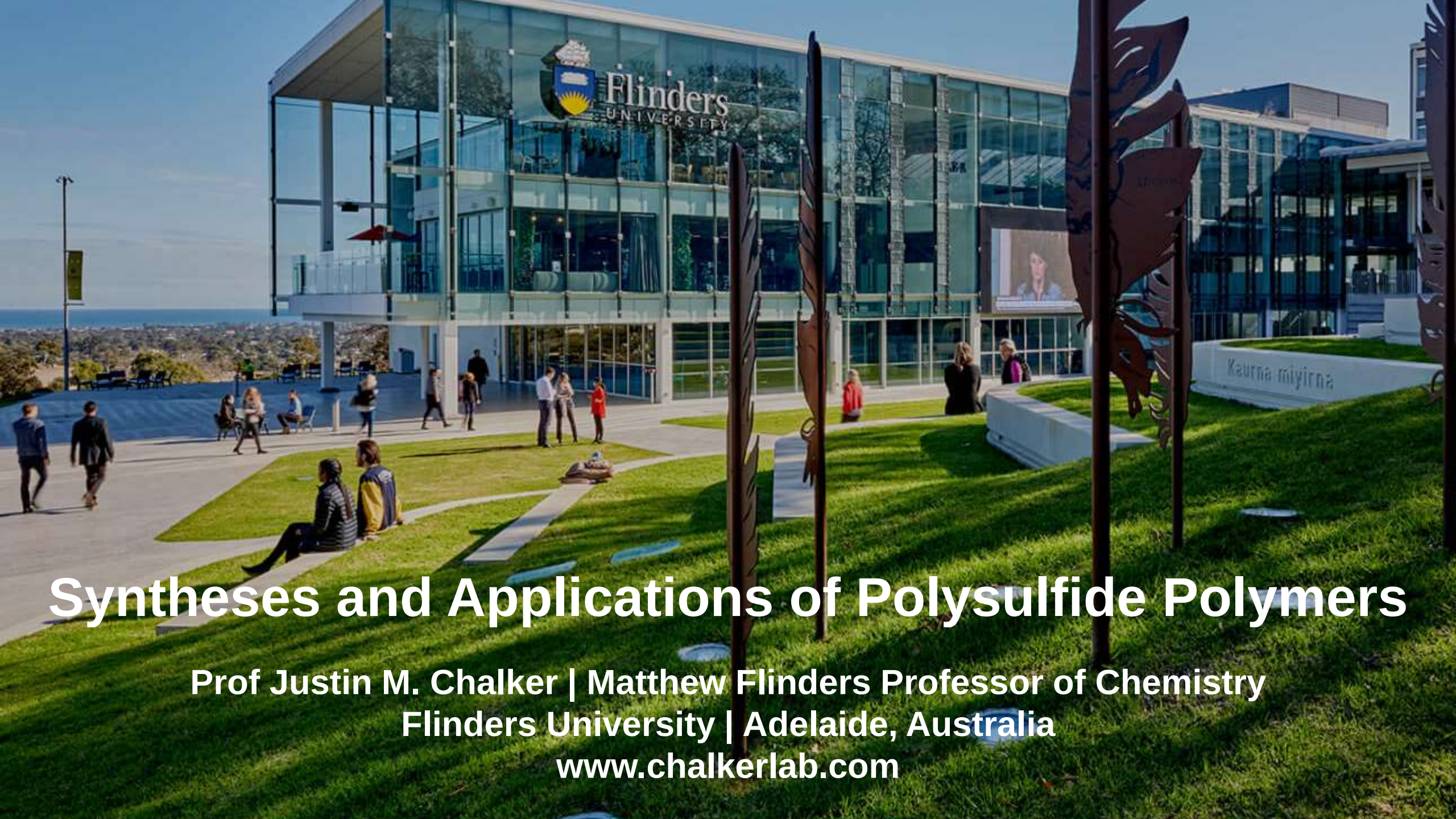
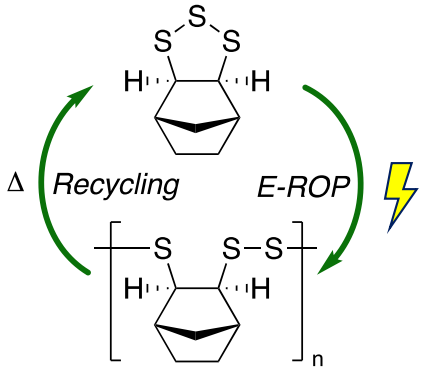


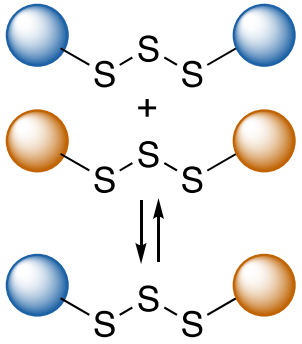
Syntheses and Applications of Polysulfide Polymers

Prof Justin M. Chalker | Matthew Flinders Professor of Chemistry
Flinders University | Adelaide, Australia
www.chalkerlab.com

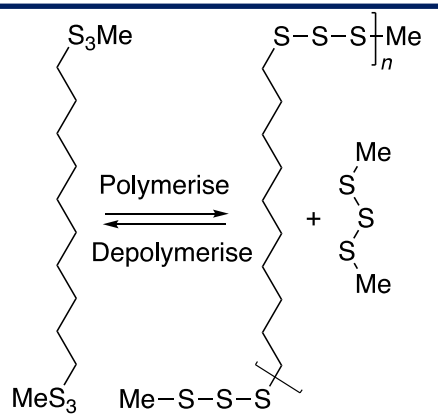
38th Australasian Polymer Symposium – Chalker Lab



Electrochemical ROP
Jasmine Pople
Coromandel, Monday, 15:05



Reagent-Free Trisulfide Metathesis
Alfrets Tikoalu
Coromandel, Monday, 15:20



Trisulfide Metathesis Polymerisation
James Smith
Poster, Monday, 18:00

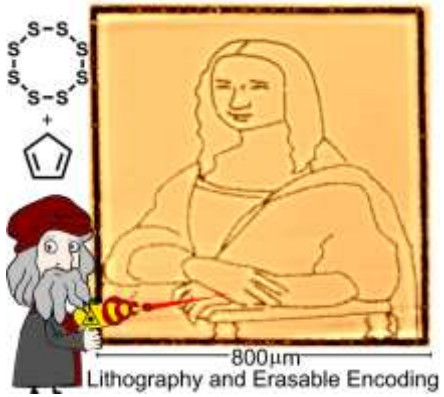
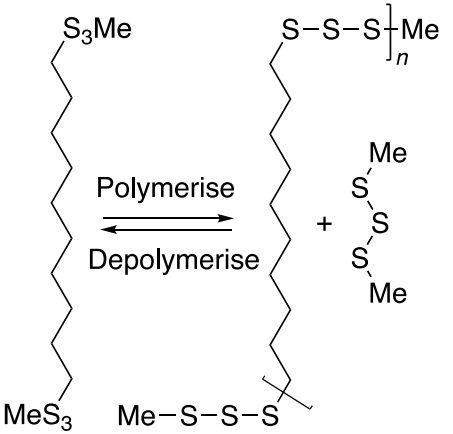


Photo-Responsive Polysulfides
Dr Lynn Lisboa
Coromandel, Monday, 16:55

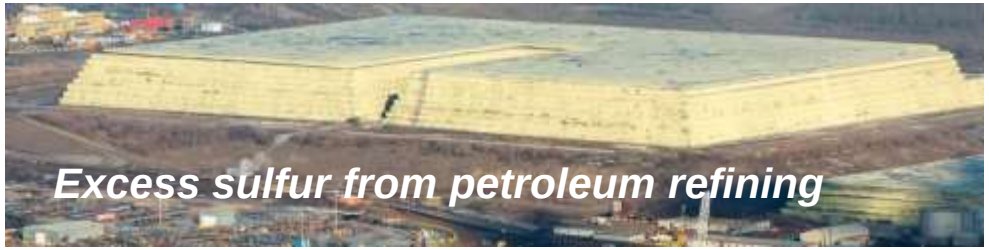
Polysulfides for Safer Gold Mining
Prof Justin Chalker
Coromandel, Monday, 17:10



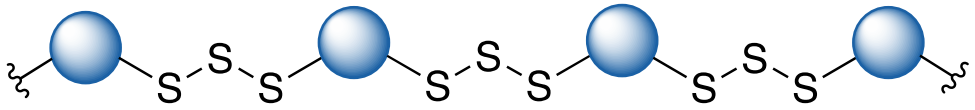
Trisulfide Metathesis Polymerisation
Dr Harshal Patel
Tasman 1, Tuesday, 16:25

Overview and Takeaway Messages

1: Sulfur is an abundant, useful feedstock for polymer synthesis



Polysulfides (made from sulfur) have useful properties



Useful chemical, thermomechanical, optical, and metal binding properties

Overview and Takeaway Messages

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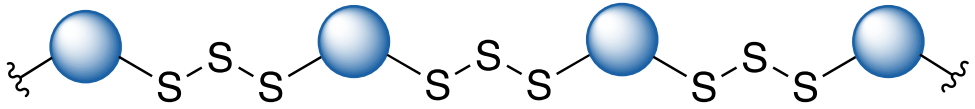
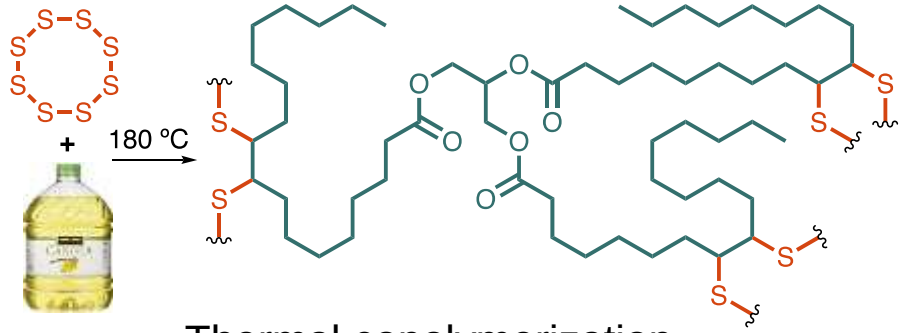
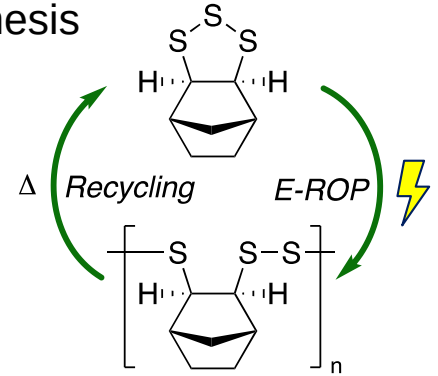


Useful chemical, thermomechanical, optical, and metal binding properties

2: There are complementary methods for polysulfide synthesis



Thermal copolymerization



Electrochemical-ROP

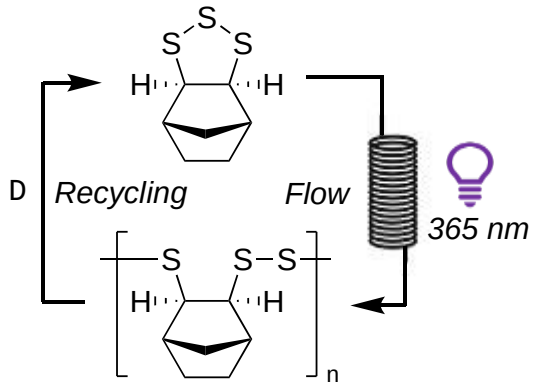


Photo-ROP

Overview and Takeaway Messages

1: Sulfur is an abundant, useful feedstock for polymer synthesis

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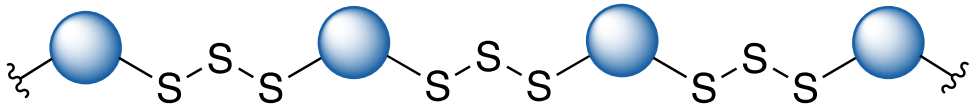
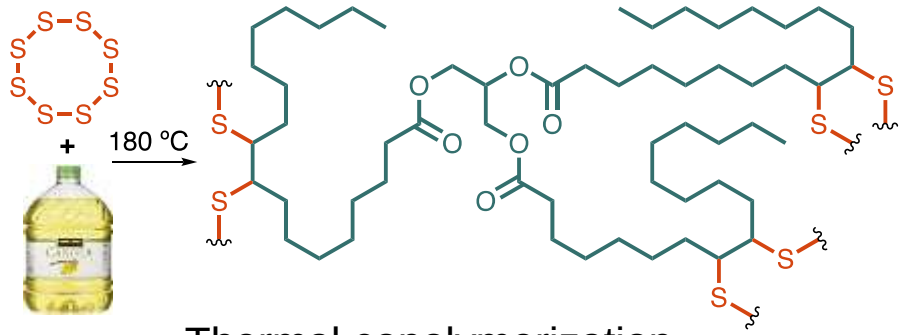
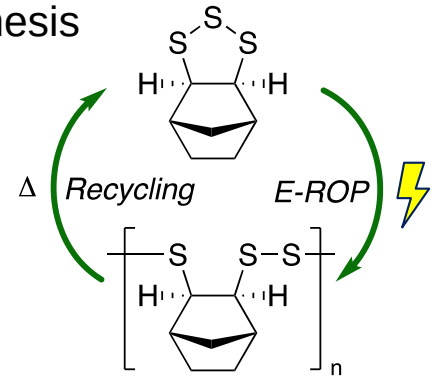


Useful chemical, thermomechanical, optical, and metal binding properties

2: There are complementary methods for polysulfide synthesis



Thermal copolymerization



Electrochemical-ROP

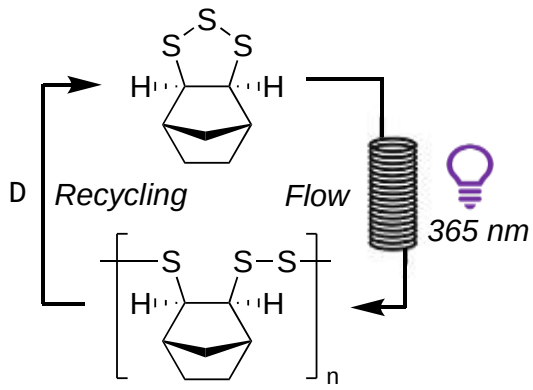


Photo-ROP

3: Polysulfide polymers are promising materials for safer gold mining and e-waste recycling

For foundations of inverse vulcanization and sulfur-derived polymers: Pyun et al, *Nat. Chem.* 2013, 5, 518 and *J. Am. Chem. Soc.* 2022, 144, 5

Sulfur: abundant, low-cost precursor to functional polymers

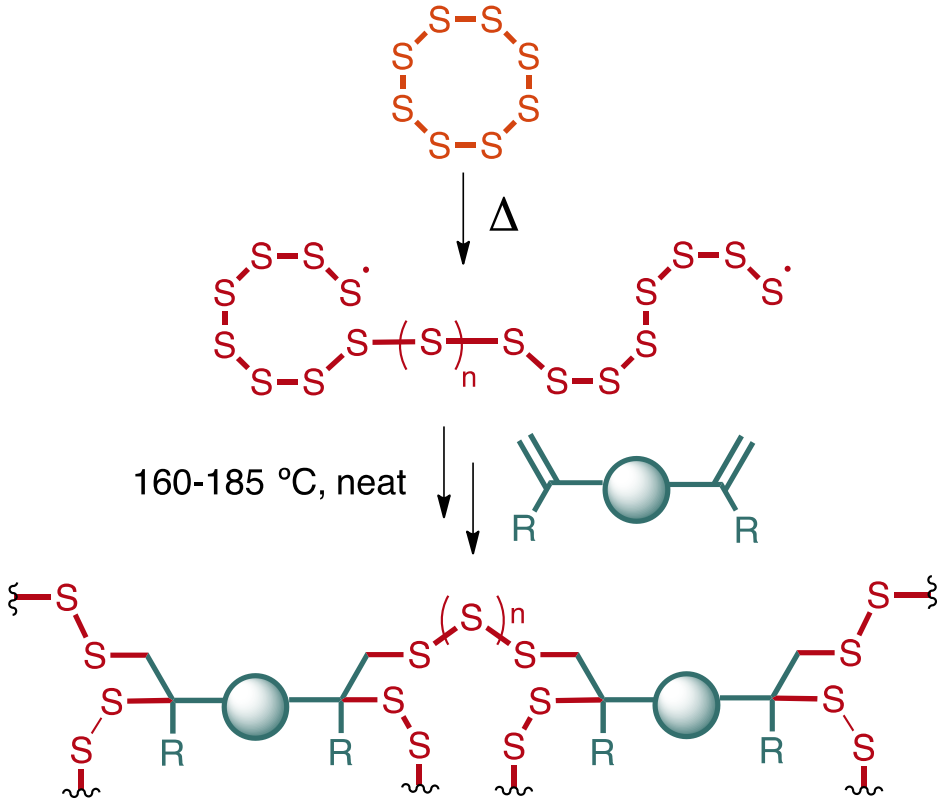
Elemental sulfur

~80 million tonnes produced each year (petroleum refining)

~$0.2 USD per kilogram

Megaton stockpiles

Source: US Geological Survey, 2022 Mineral Commodities Summary



Polysulfide polymers

Dynamic S-S networks

High refractive index

Metal binding

Redox active

For conception and prospects of ***inverse vulcanization*** and related copolymerizations see Pyun et al, *Nat. Chem.* 2013, 5, 518 and *J. Am. Chem. Soc.* 2022, 144, 5

Flinders University

Polymerization Method 1: Inverse vulcanization using sulfur and canola oil

Mercury sorbent
US Patent 11,167,263
Chem. Eur. J. 2017, 23, 16219
Adv. Sustainable Syst. 2020, 4, 1900111
Chem. Commun. 2021, 57, 6296-6299

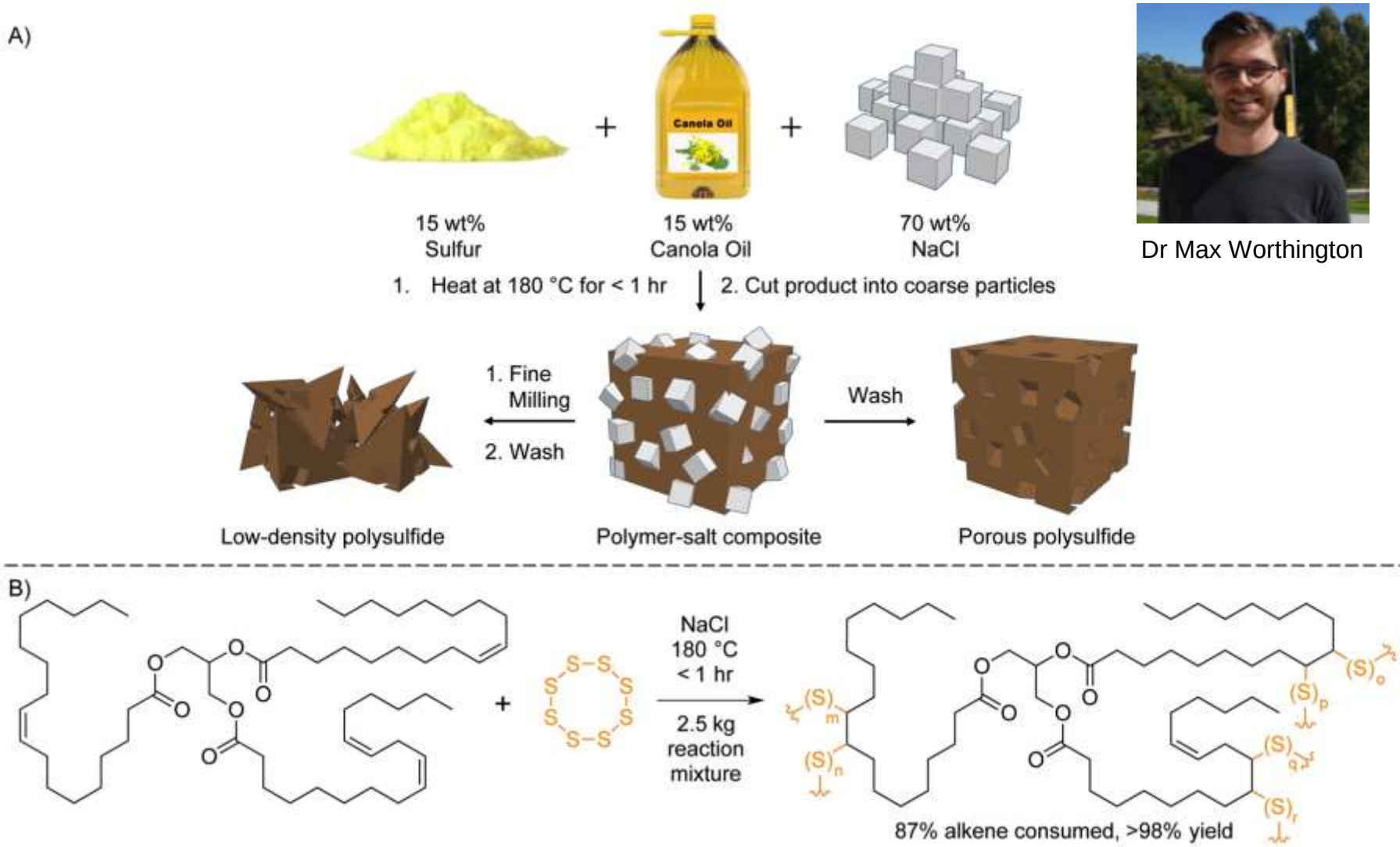
Oil spill remediation
Adv. Sustainable Syst. 2018, 2, 1800024

Fertilizer vehicle
Org. Biomol. Chem. 2019, 17, 1929

Repairable composites
Chem. Eur. J. 2020, 26, 10035-10044
Polym. Chem. 2022, 13, 5659
Sustain. Mater. Techno. 2022, 32, e00400
Macromol. Mater. Eng. 2023, 2300298

Thermal insulation
ChemSusChem 2021, 14, 2352

Gold sorbent
WO/2020/198778



Dr Max Worthington

Flinders University

Polymerization Method 1: Scale-up (10 kg)

Control unit

Canola oil preheating unit

Drill press

Torque control & Foaming impeller

10 kg reactor in oven

Dr Louisa Esdaile

Dr Max Mann

ADELAIDE CONTROL ENGINEERING

Flinders University

Polymerization Method 1: Scale up (1000 kg/day) via reactive extrusion

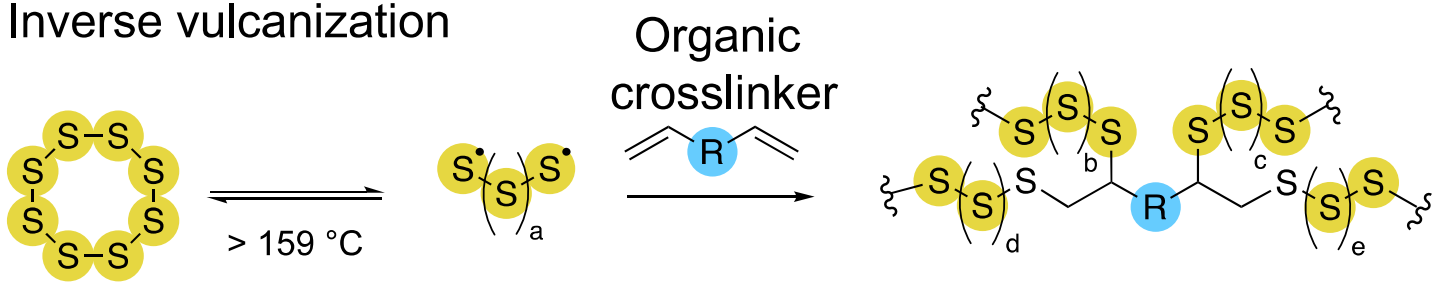
Flinders University

ACE ADELAIDE CONTROL ENGINEERING

CleanEarth™ Technologies

Polymerization Method 2: Electrochemical Ring-Opening Polymerization

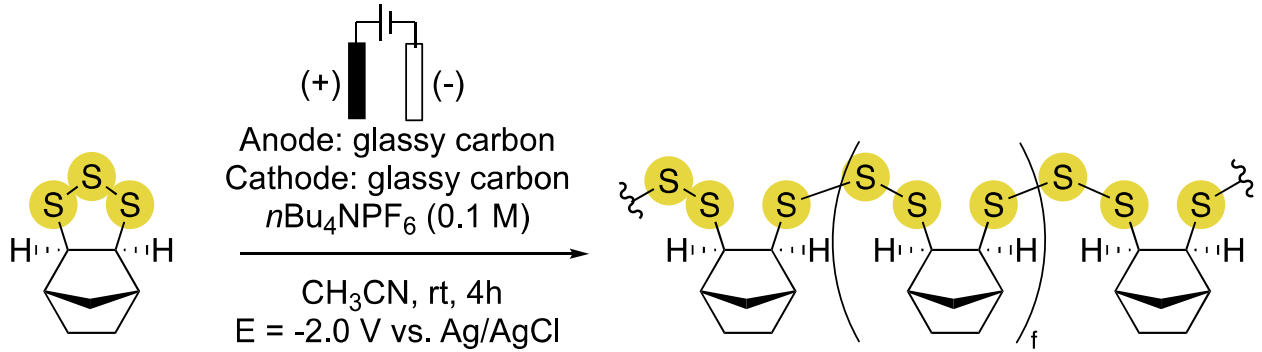
A) Inverse vulcanization



Elemental sulfur (S_8) — Polymeric sulfur — Cross-linked sulfur rich polymer

- ✷ High temperature
- ✷ Hazardous
- ✷ Random copolymerization
- ✷ Distribution of sulfur ranks

B) This work: electrochemical ring opening polymerization



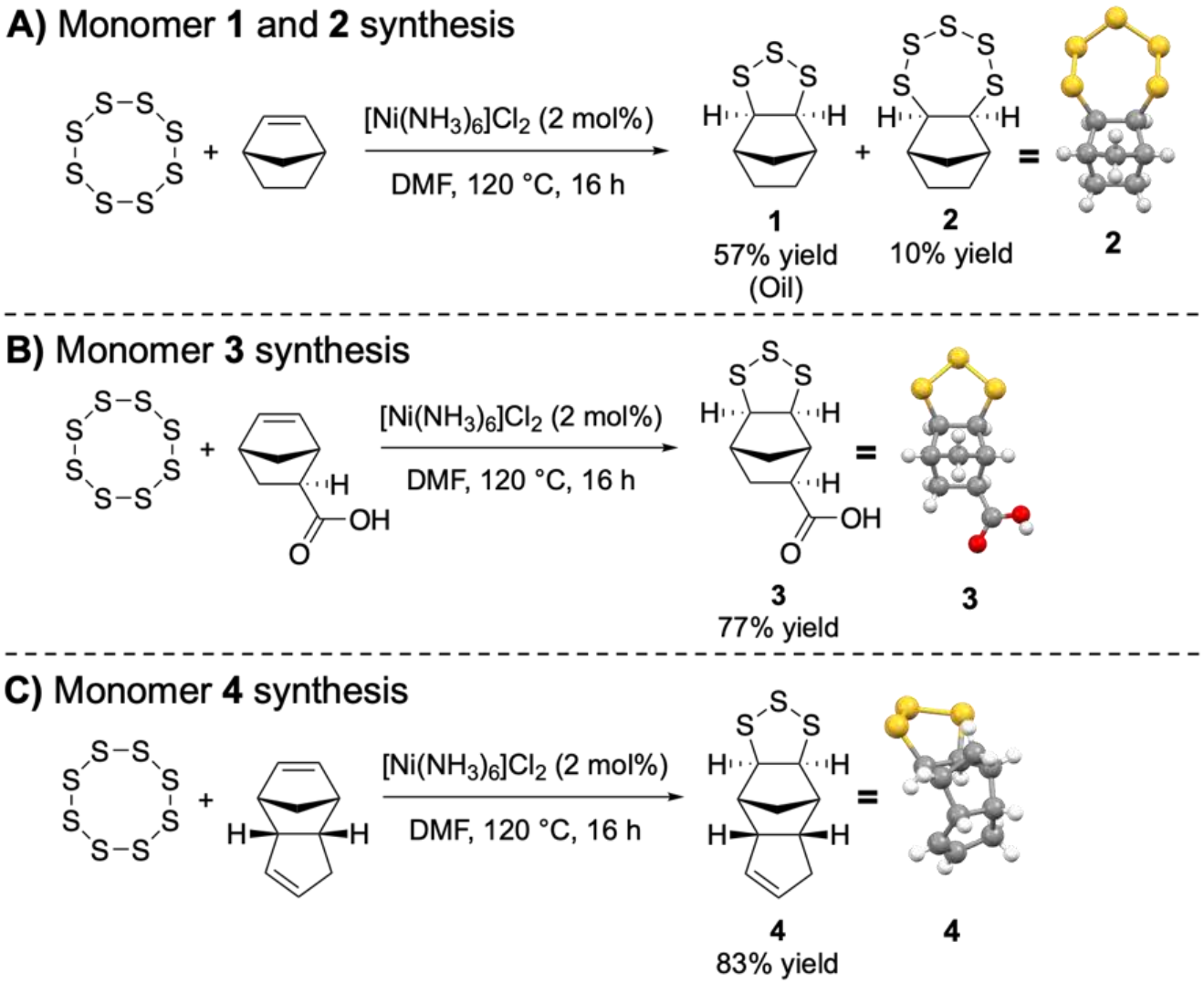
Cyclic trisulfide — Poly(trisulfide)

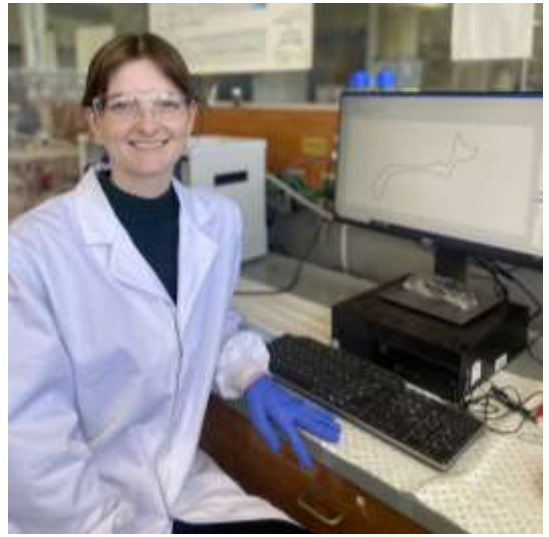
- ✓ Low temperature
- ✓ Novel electrochemical initiation
- ✓ Operationally simple
- ✓ Well-defined sulfur rank

For previous studies of *anionic* ROP see Penczek et al:
Nature 1978, 273, 738 and *J. Polym. Sci., Polym. Chem. Ed.* 1984, 5, 1085

Flinders University

Polymerization Method 2: Monomer Synthesis



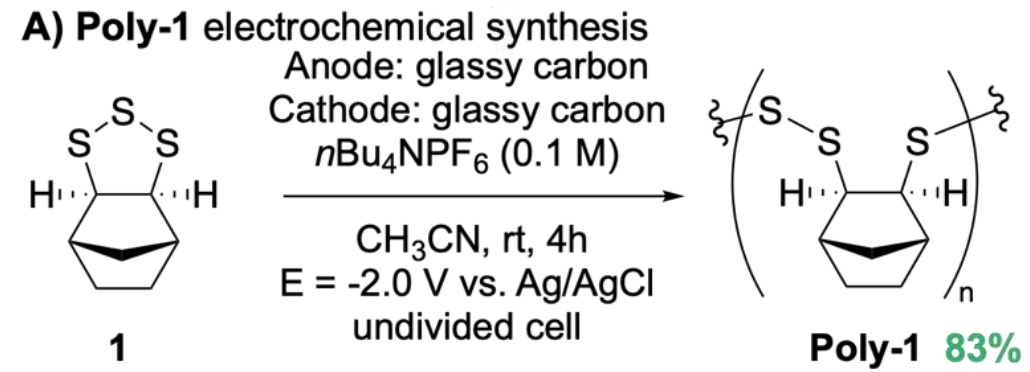


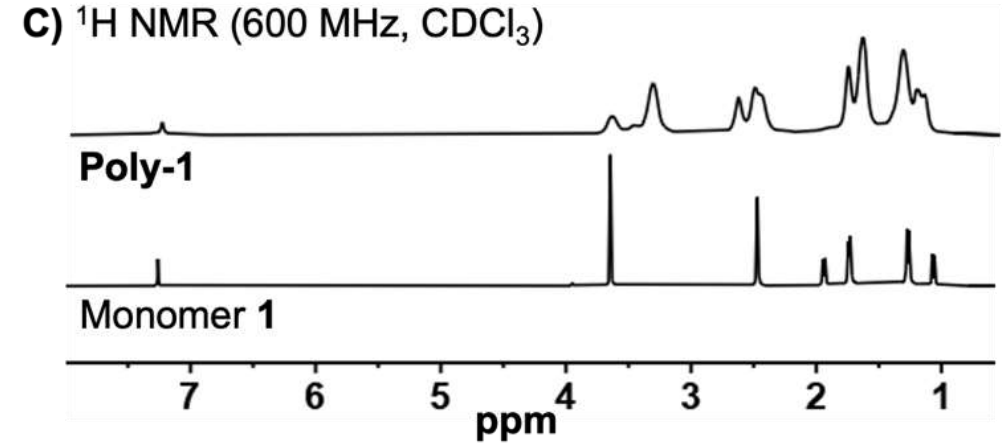
Jasmine Pople

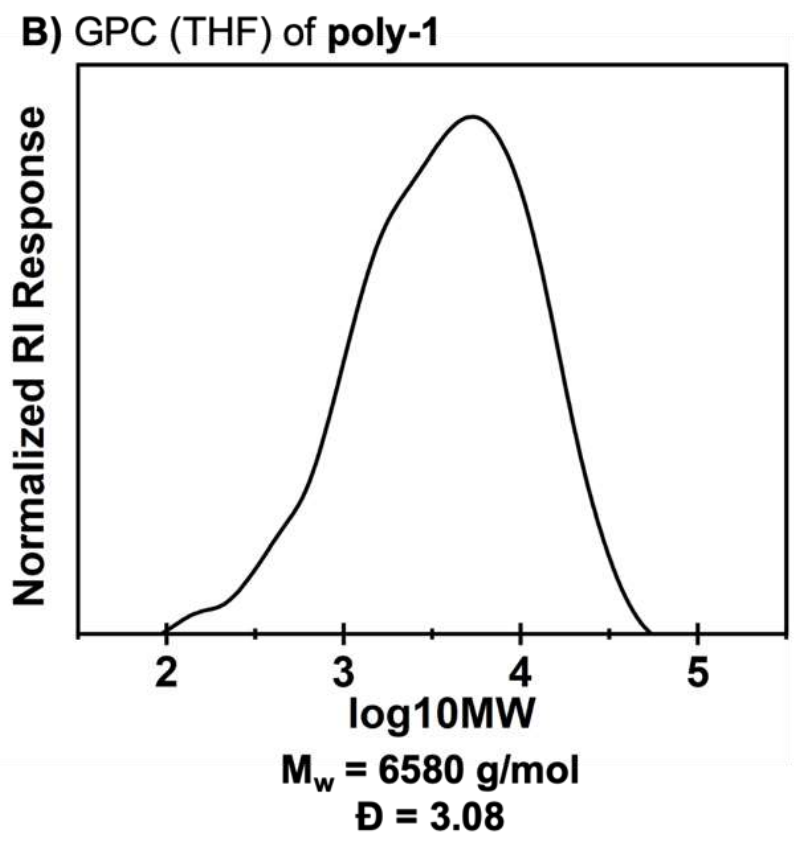
Pople, Nicholls, Pham, Bloch, Lisboa, Perkins, Gibson, Coote*, Jia* and Chalker*
J. Am. Chem. Soc. 2023, 145, 11798-11810

Flinders University

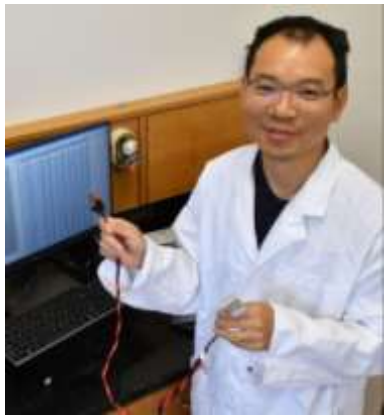
Polymerization Method 2: Electrochemical Ring-Opening Polymerization







Jasmine Pople
Thomas Nicholls



Zhongfan Jia

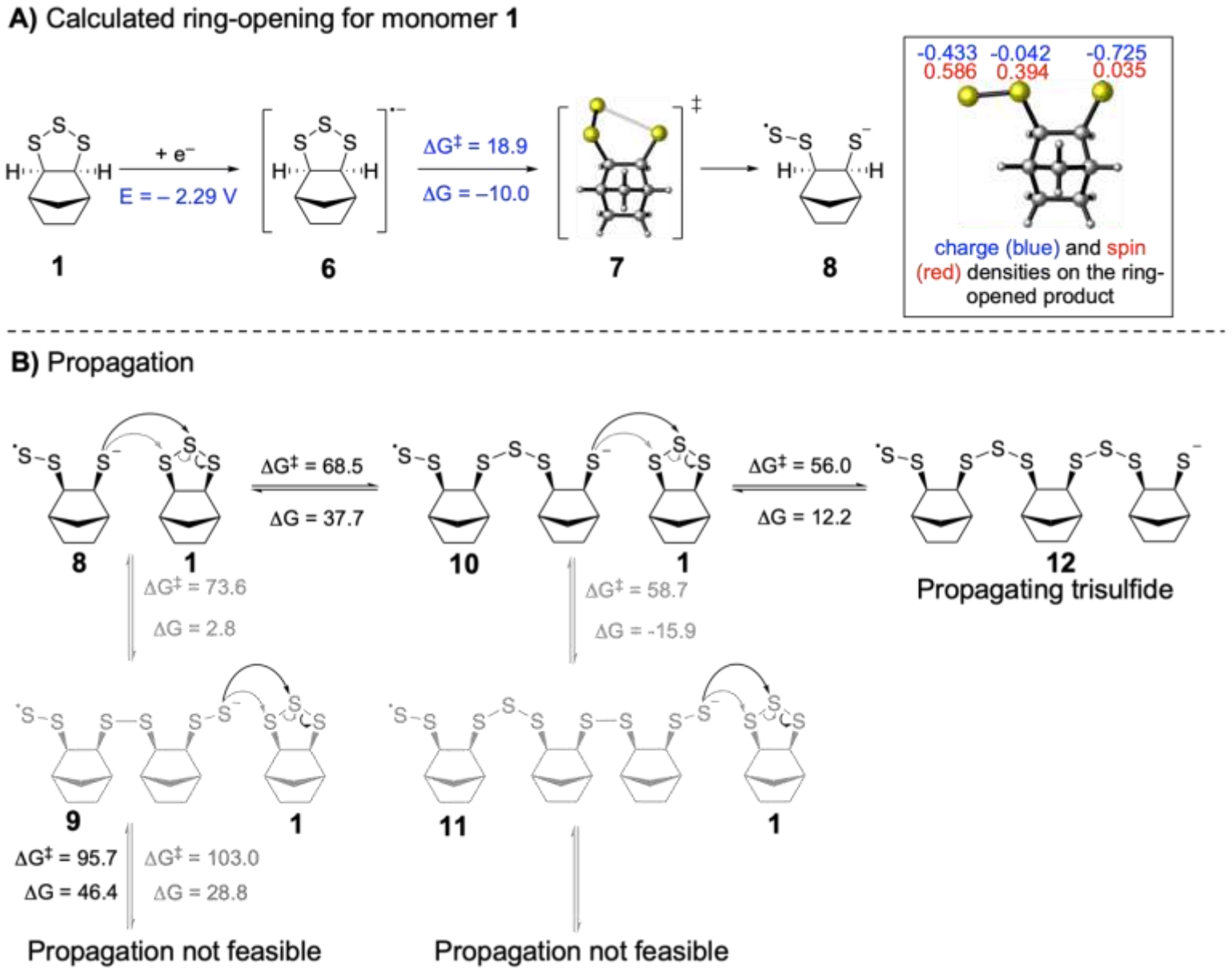
Pople, Nicholls, Pham, Bloch, Lisboa, Perkins, Gibson, Coote*, Jia* and Chalker*
J. Am. Chem. Soc. 2023, 145, 11798-11810

Flinders University

Polymerization Method 2: Electrochemical Ring-Opening Polymerization Mechanism

Michelle Coote

Le Nhan Pham



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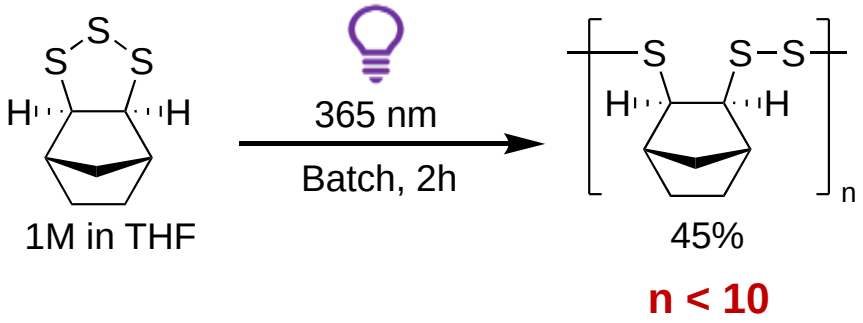
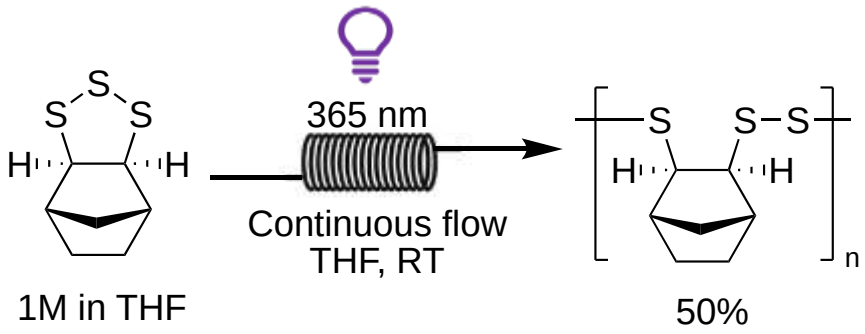
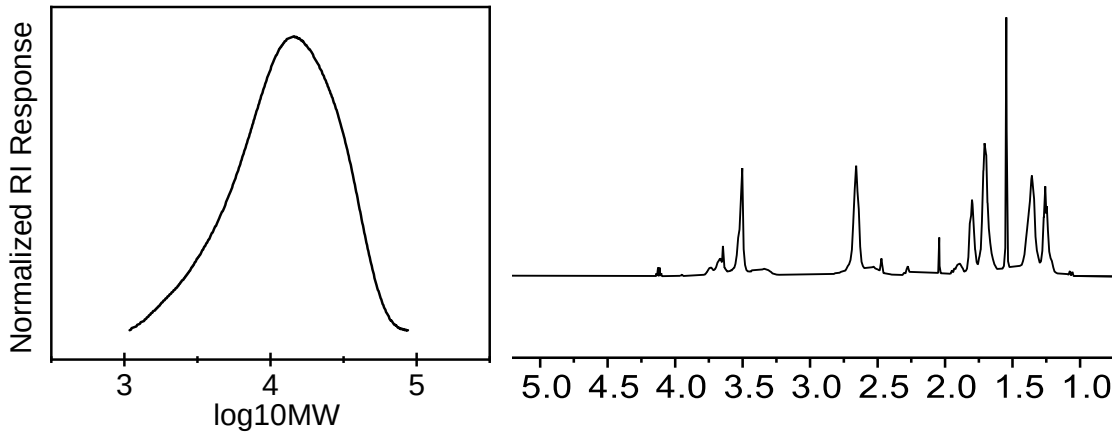
Polymerization Method 3: Photochemical Ring-Opening Polymerization



- **Oligomers major product in batch (< 2k g/mol)**
- **365 nm light breaks down polymer**

Jasmine Pople

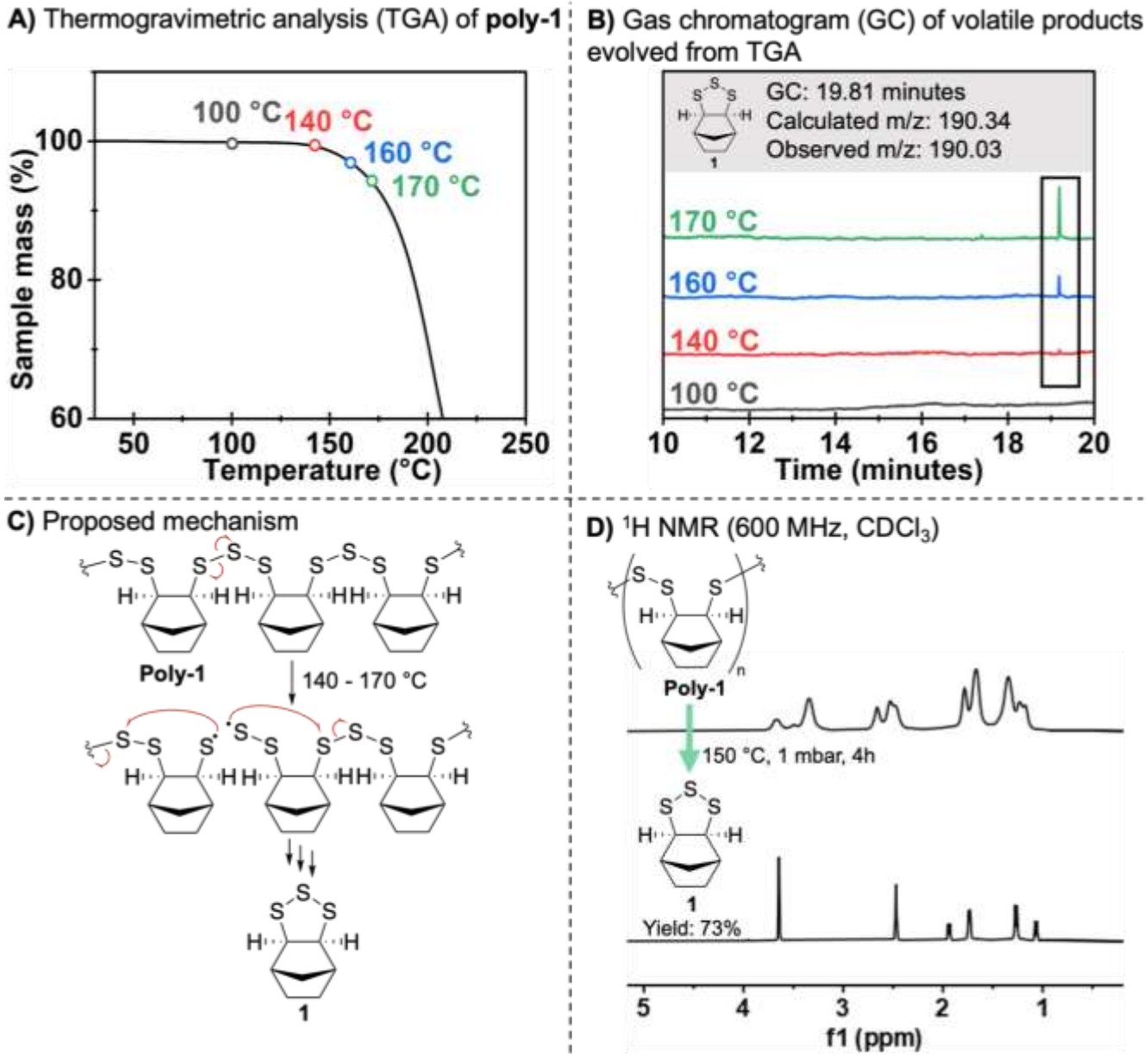


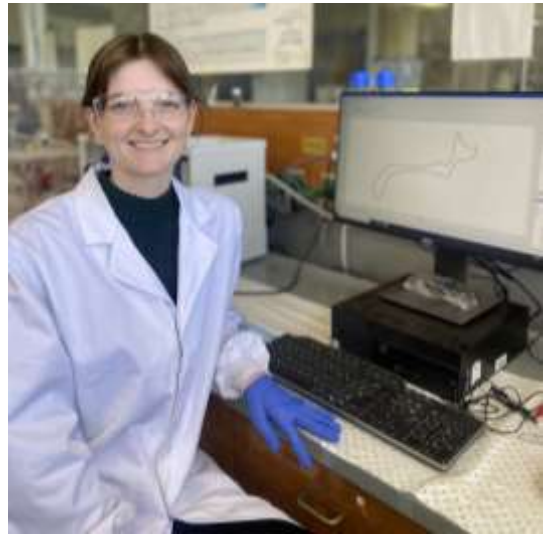


Pople, Nicholls, Coote, Jia and Chalker, *unpublished results*

For previous studies on photochemical synthesis of polysulfides:
Emsley, Griffiths, *Phosphorus, Sulfur Relat. Elem.* 1980, 9, 227 and Wu, Hasell, Quan, *Nat. Chem.* 2022, 14, 1249

Thermal depolymerisation of a poly(trisulfide)

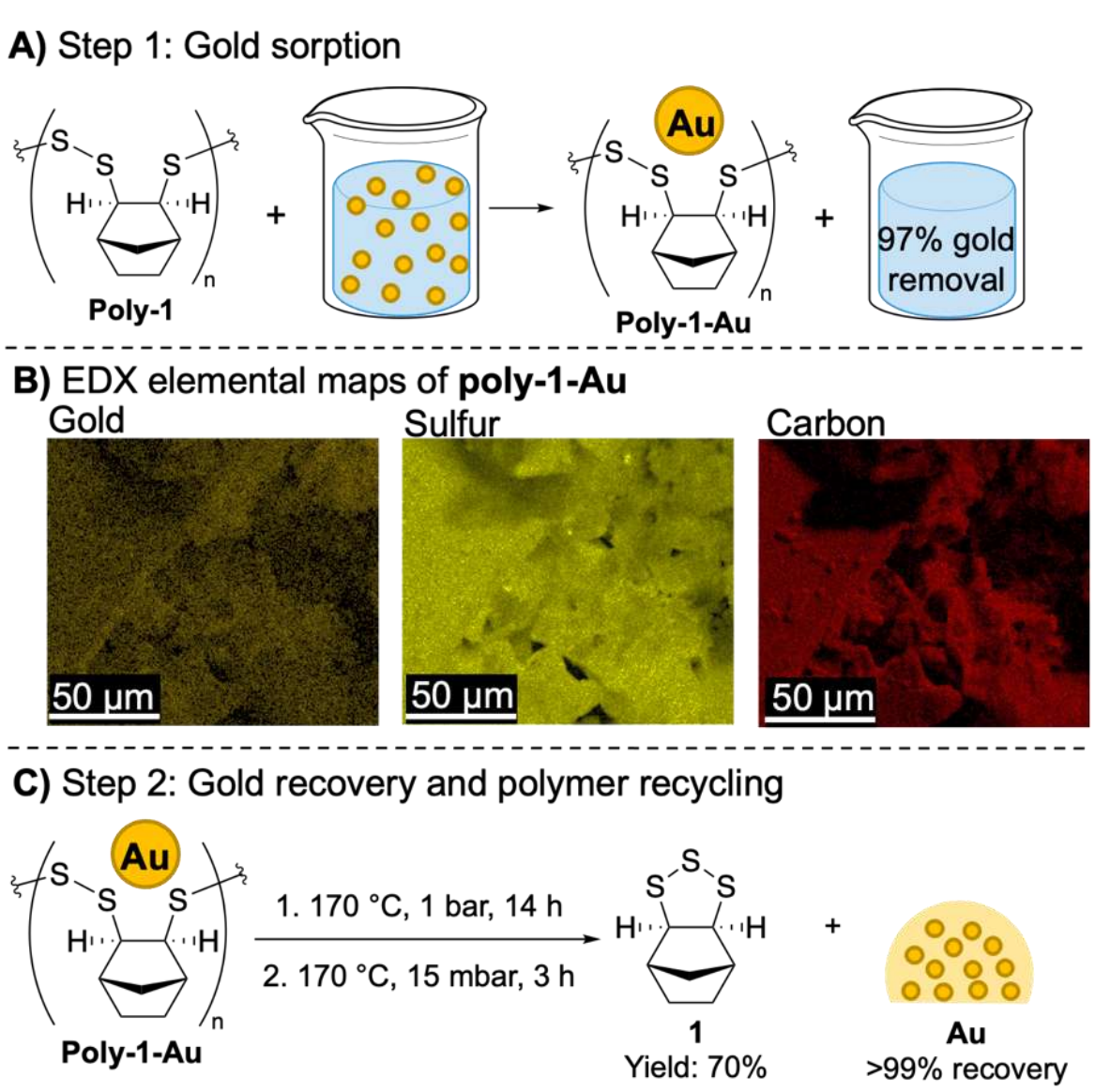


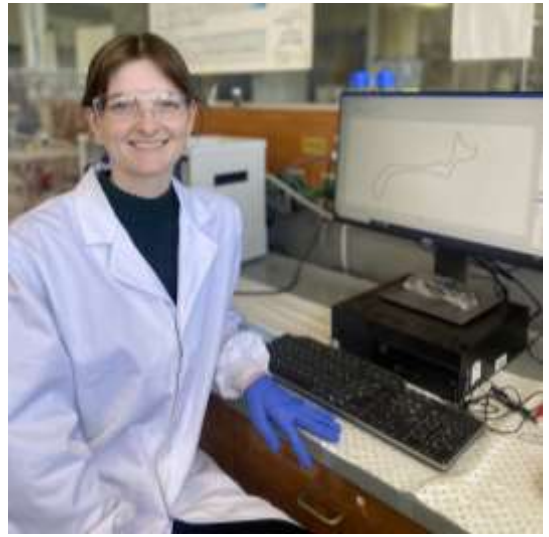


Jasmine Pople

Flinders University

Gold recovery using poly(trisulfide) sorbent





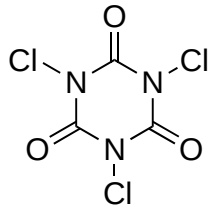
Jasmine Pople

Flinders University

Towards mercury- and cyanide-free gold mining

Maximilian Mann

Gold metal
50 mg



(TCCA, 0.05M)

catalyst, H_2O
4-12 h

Aqueous
Au(III)

Sequester Au on bunded polymer
4-12 h

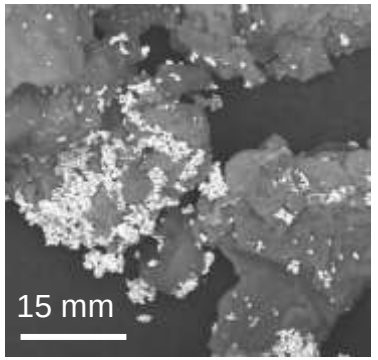
Harshal Patel

Lynn Lisboa

>90%
gold recovery

Pyrolysis

or depolymerisation



Au nanoparticles
on polymer surface

Thomas Nicholls

Mann, Chalker WO/2020/198778


Sign in
NORTHERN TERRITORY
Linger and Die Gold Mine
Australia
QUEENSLAND
WESTERN AUSTRALIA
SOUTH AUSTRALIA
NEW SOUTH WALES
Great Australian Bight
VICTORIA
ACT
Map
Google

Mercury- and cyanide-free gold mining using polysulfide sorbents

Dr Maximilian Mann

Concentrates
(4 kg, 300 mg gold)

Polysulfide sorbent

Filter + 30 g
polysulfide

1. Incinerate or
   depolymerise
2. Refine

>90% gold recovery

1. Magnet (remove magnetite)
2. Leach: 2 L H_2O + 65 g TCCA + catalyst

Mann, Chalker WO/2020/198778

Gold recovery from electronic waste – urban mining





Sort, collect gold-rich e-waste → Mill, concentrate → Leach, recover → Refine


Dr Max Mann


Dr Lynn Lisboa

Multi-tonne pilot demonstration completed

Mann, Chalker WO/2020/198778

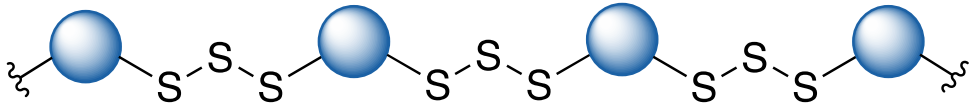

Dr Harshal Patel


Dr Tom Nicholls

Overview and Takeaway Messages

1: Sulfur is an abundant, useful feedstock for polymer synthesis

Polysulfides (made from sulfur) have useful properties



Useful chemical, thermomechanical, optical, and metal binding properties

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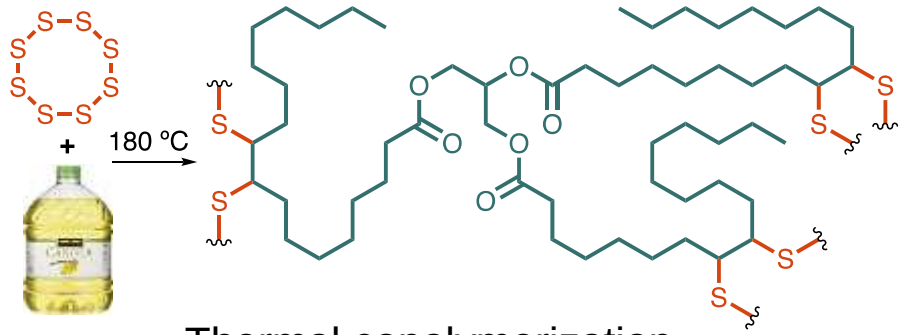
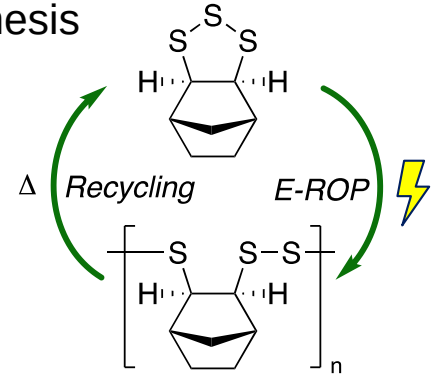


Thermal copolymerization



Electrochemical-ROP

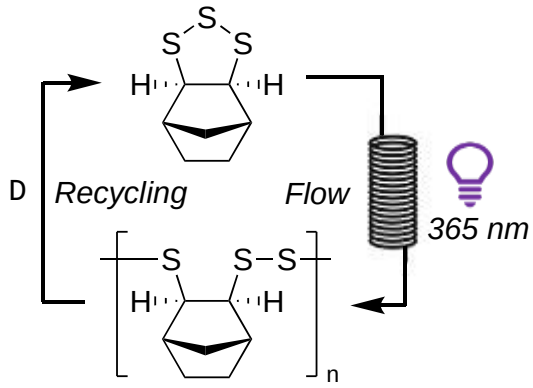
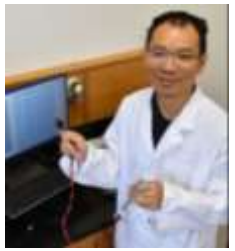


Photo-ROP

3: Polysulfide polymers are promising materials for safer gold mining and e-waste recycling

Acknowledgments










Honours & MS Students

Federico Muller
Jemma Virtue

PhD Students

Alfrets Tikoalu
Sam Tonkin
Jasmine Pople
Abbey Mann
James Smith

Research Fellows

Thomas Nicholls
Lynn Lisboa
Harshal Patel
Max Mann
Nic Lundquist
Yanting Yin

Academic Collaborators

Zhongfan Jia
Michelle Coote
Chris Gibson
Gunther Andersson
Louisa Esdaile
Wit Bloch
Mike Perkins
Martin Johnston
David Lewis
Jonathan Campbell
Jason Gascooke
Tom Hasell
Luke Henderson
Munish Puri

For more, please visit our website:
www.chalkerlab.com

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Clean UrbanMining

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ADELAIDE CONTROL ENGINEERING
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justin.chalker@flinders.edu.au
www.chalkerlab.com

Thank You!