The University Of Queensland
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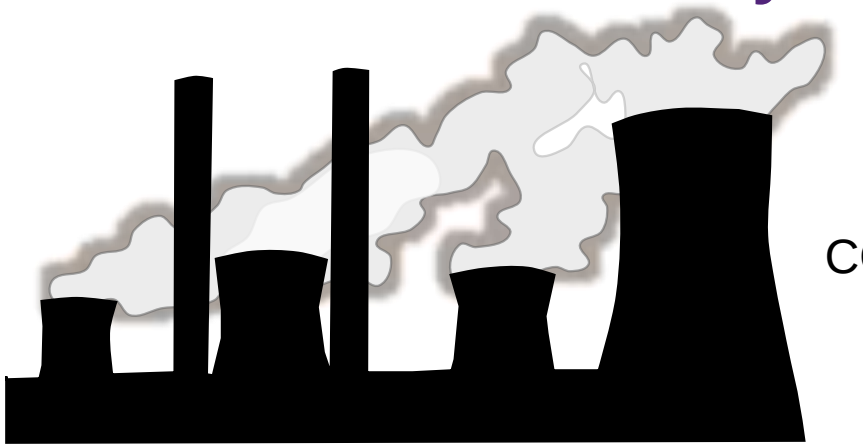
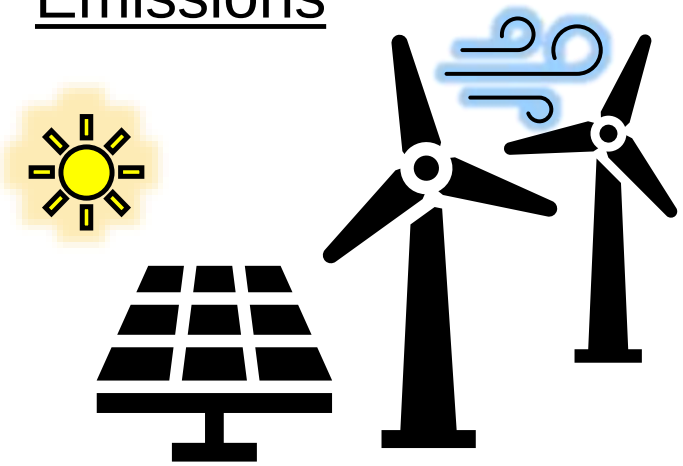
Enhancing the Durability of Polymeric Materials via Sequential Infiltration Synthesis

Francis McCallum

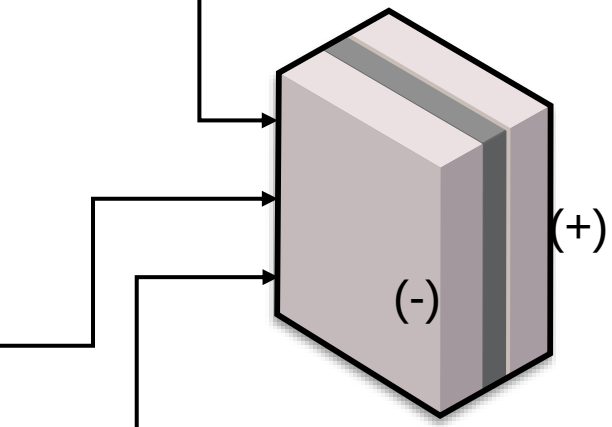
Durable Electrolysers for a Sustainable Future



Emissions



Renewables

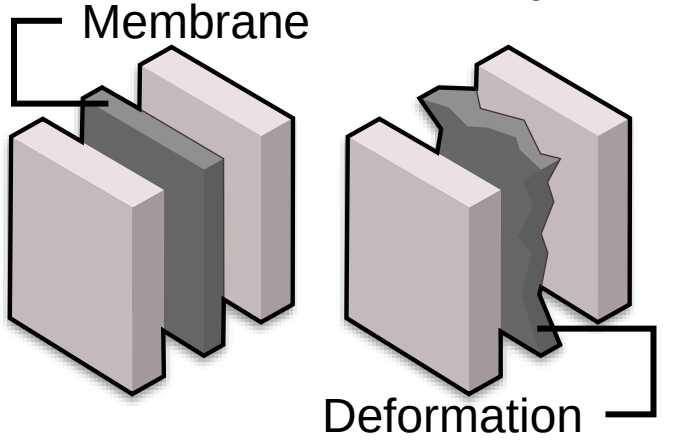


Electrolysers

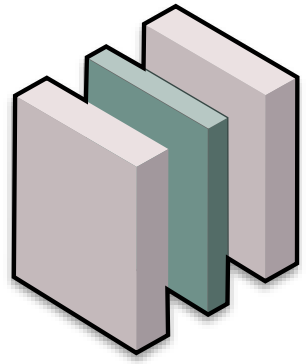
Useful Products

- Hydrogen
- Formic acid
- Carbon monoxide
- Ethanol
- Ethylene

Durability



Sequential Infiltration Synthesis



Improved Durability

- Thermal
- Mechanical
- Chemical

International Journal of Hydrogen Energy, vol. 46, no. 35, 2021, pp. 18489–510

Background

What Is SIS?

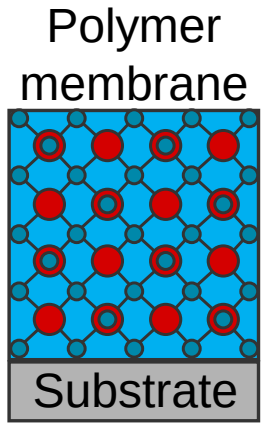
Improved Durability

- Thermal
- Mechanical
- Chemical

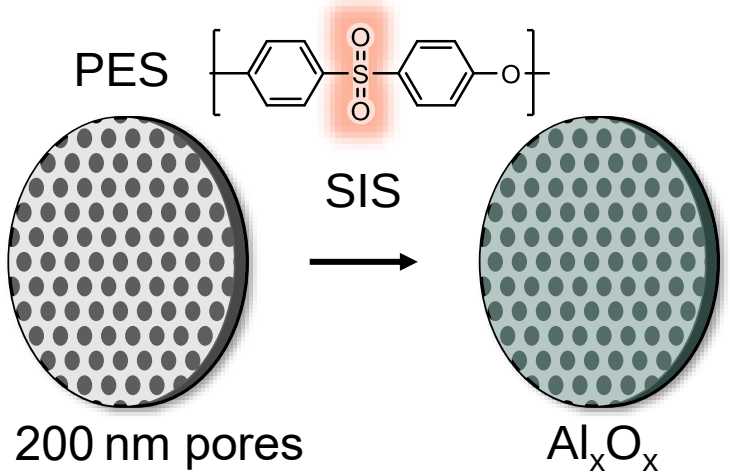
*Introducing metal oxides

*Minimal sacrifice of form & function

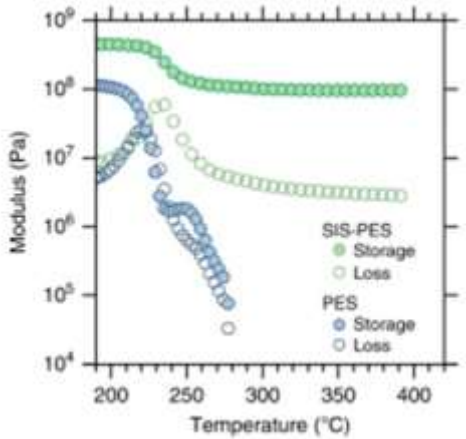
M_xO_x



Microporous Membranes



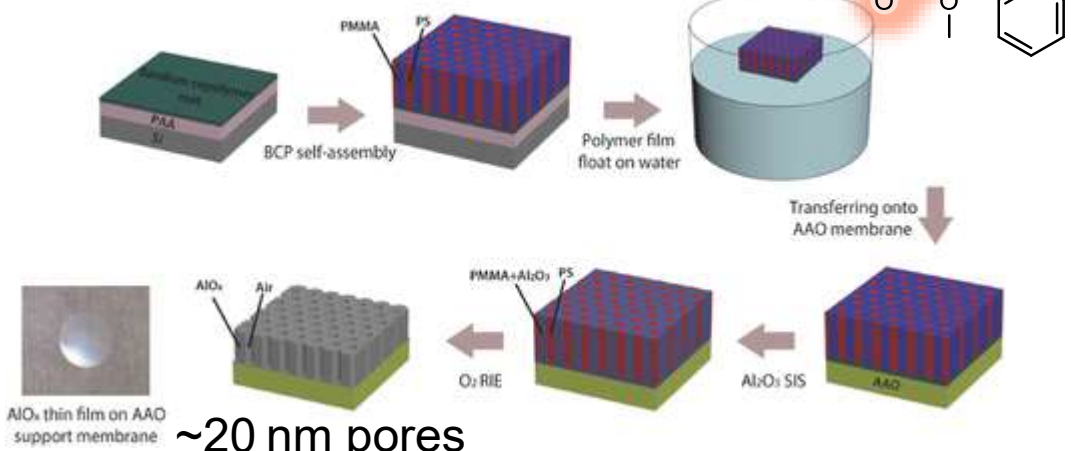
***Enhancing materials**



Nanoporous Membranes

***Template**

PMMA & PS

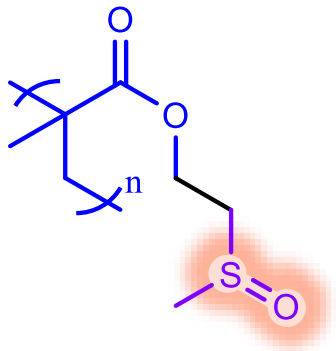


~20 nm pores

New Candidate for SIS

Poly(2-(methylsulfinyl)ethyl methacrylate)

***PMSEMA**



How to SIS?

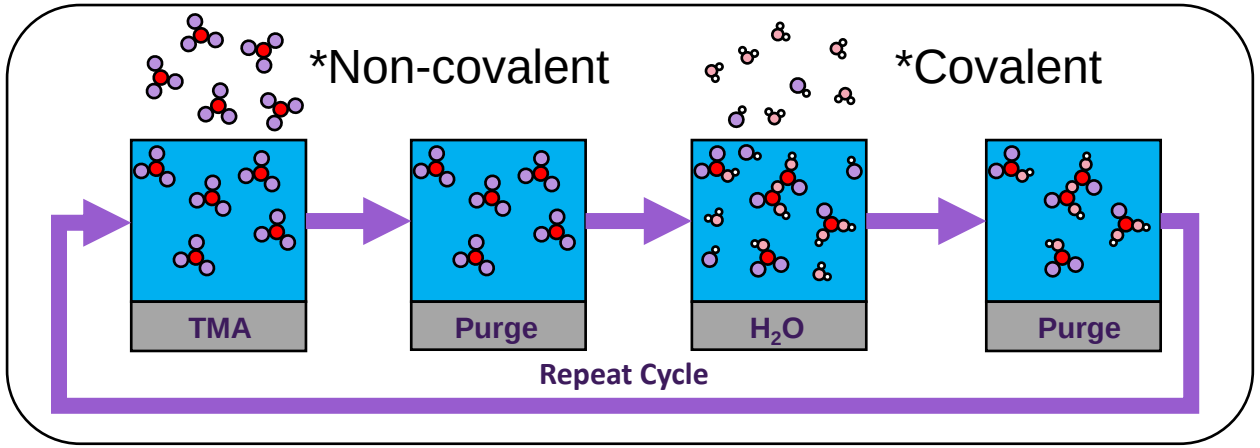
Nature Communications, vol. 11, no. 1, 2020

Advanced Functional Materials, vol. 27, no. 34, 2017

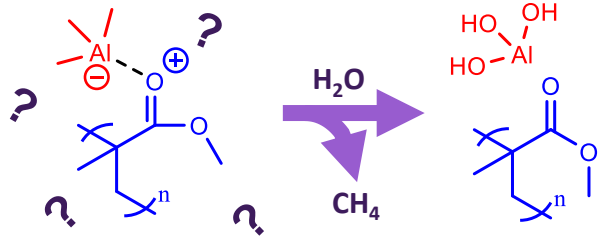
How Does it Work?

SIS

Low Pressure Chamber



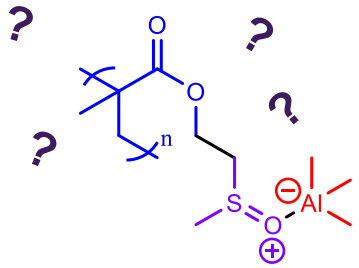
Lewis base group C=O



Lewis acid-base adduct

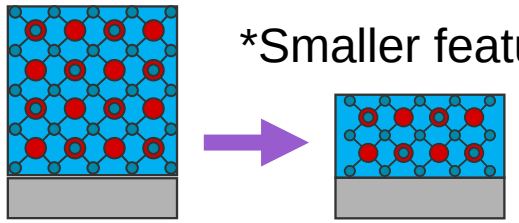
Lewis acid-base reaction

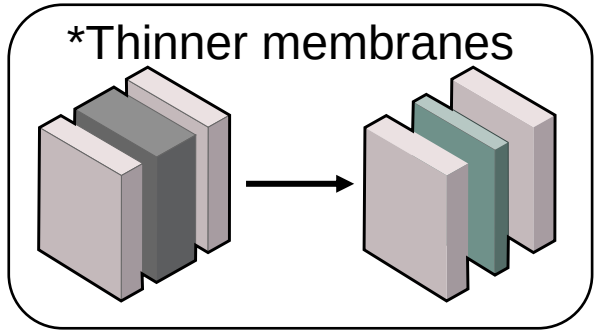
Stronger group S=O



***PMSEMA**

Application





Characterise?

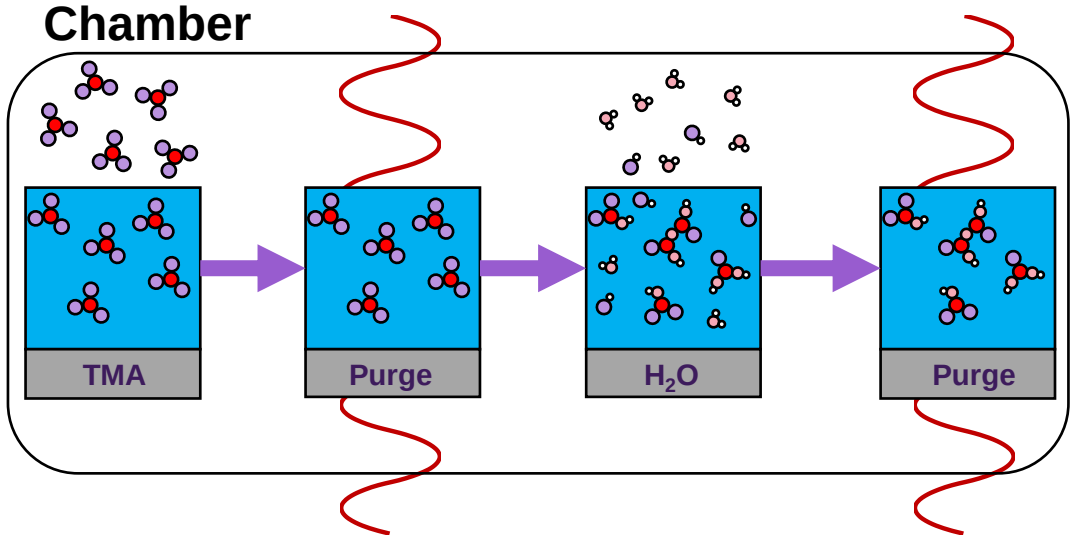
Chemistry of Materials, vol. 31, no. 15, 2019, pp. 5509–5518.
Journal of Power Sources, vol. 375, 2018, pp. 170–84.

Characterisation Techniques in SIS

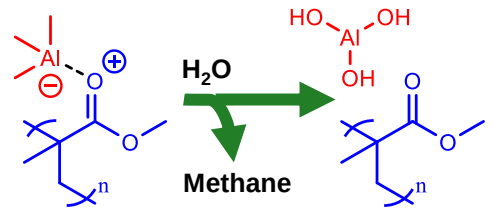
- Observable peak shifts
  - Carbonyl (C=O)
- Pros vs cons
  - ✓ Dosage
  - ✓ Temperature
  - × Stoichiometric
  - × Signal
  - × Structure

New techniques?

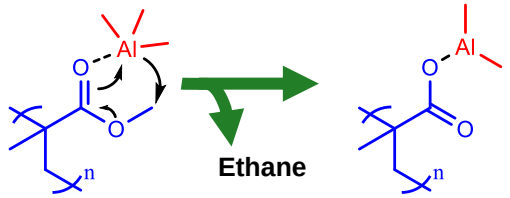
In-situ Transmission FTIR

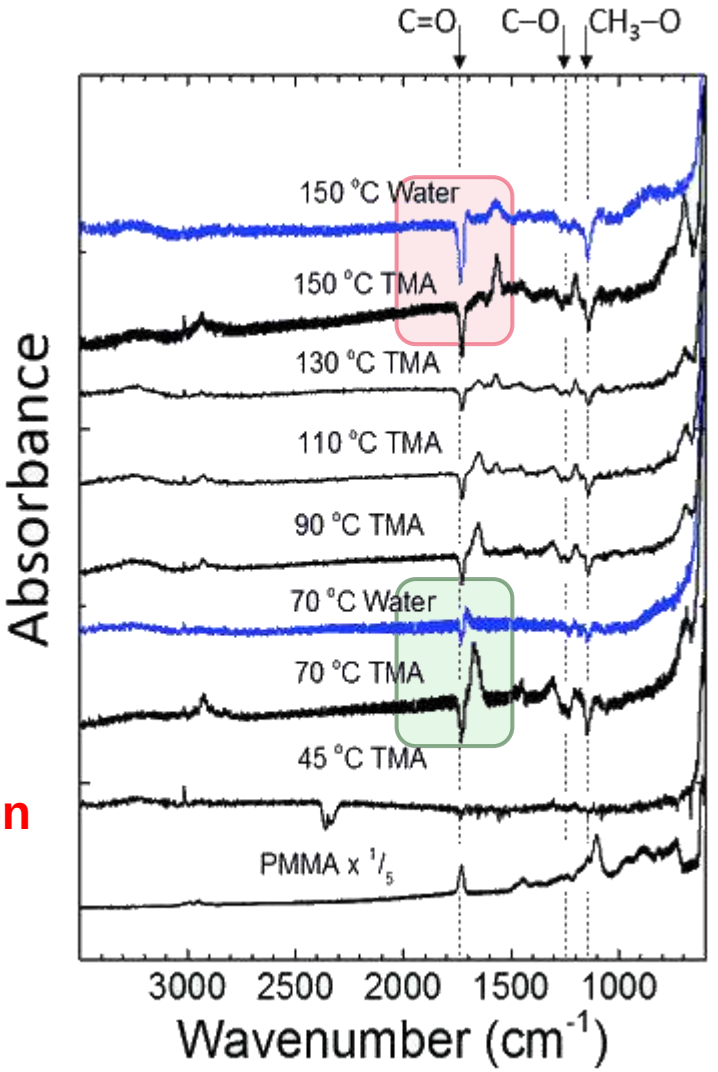


Lewis acid-base adduct

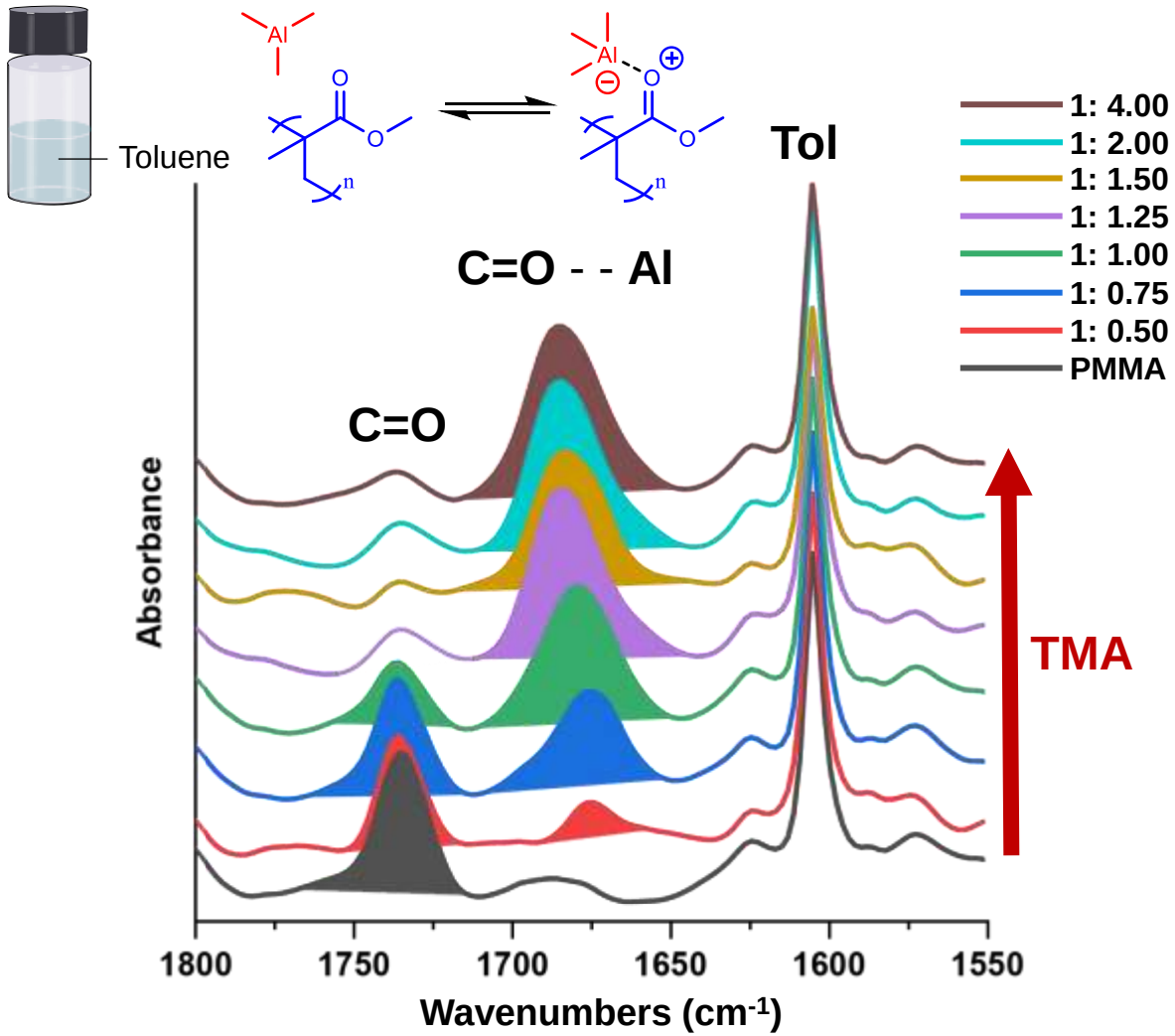


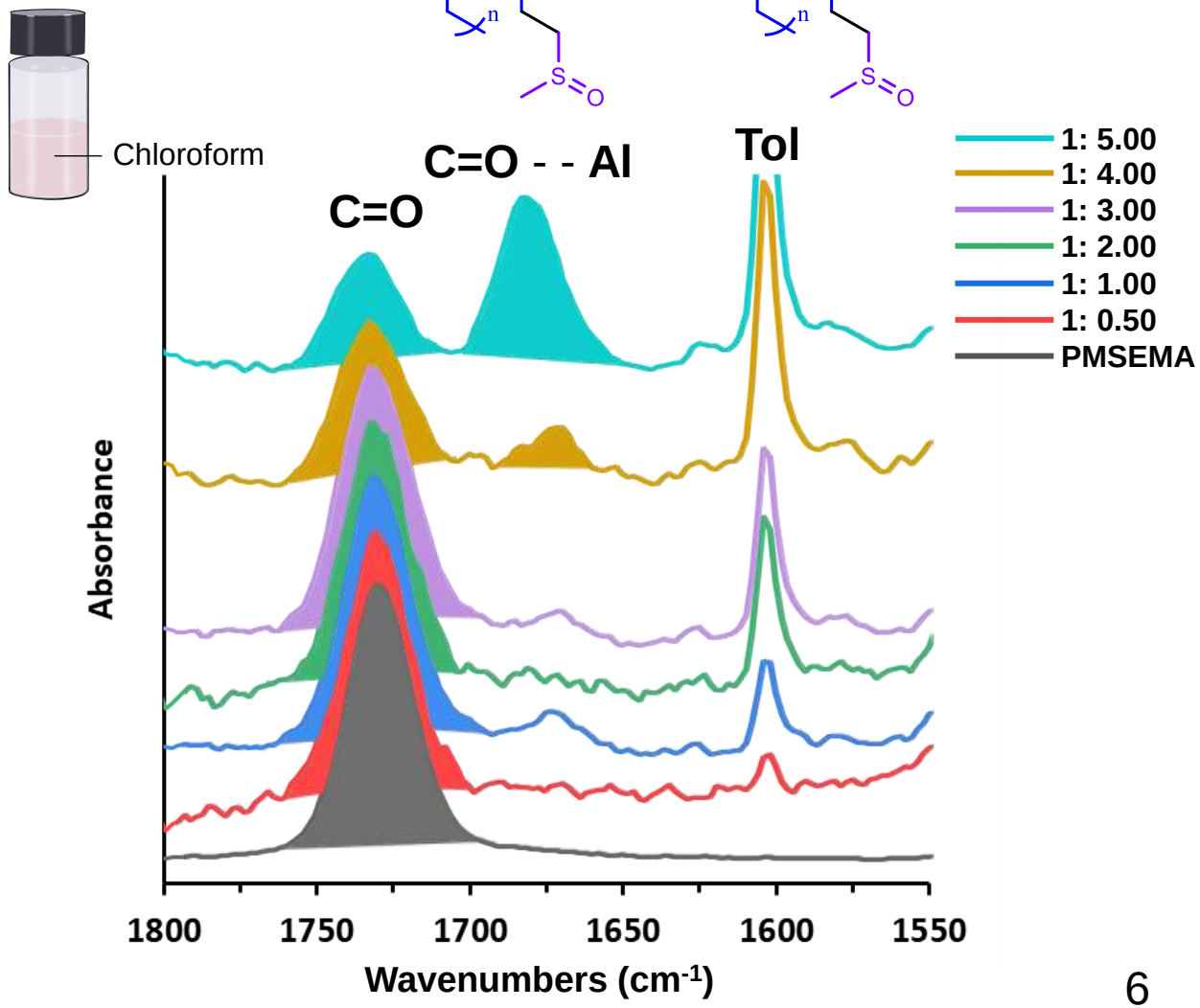
Lewis acid-base reaction



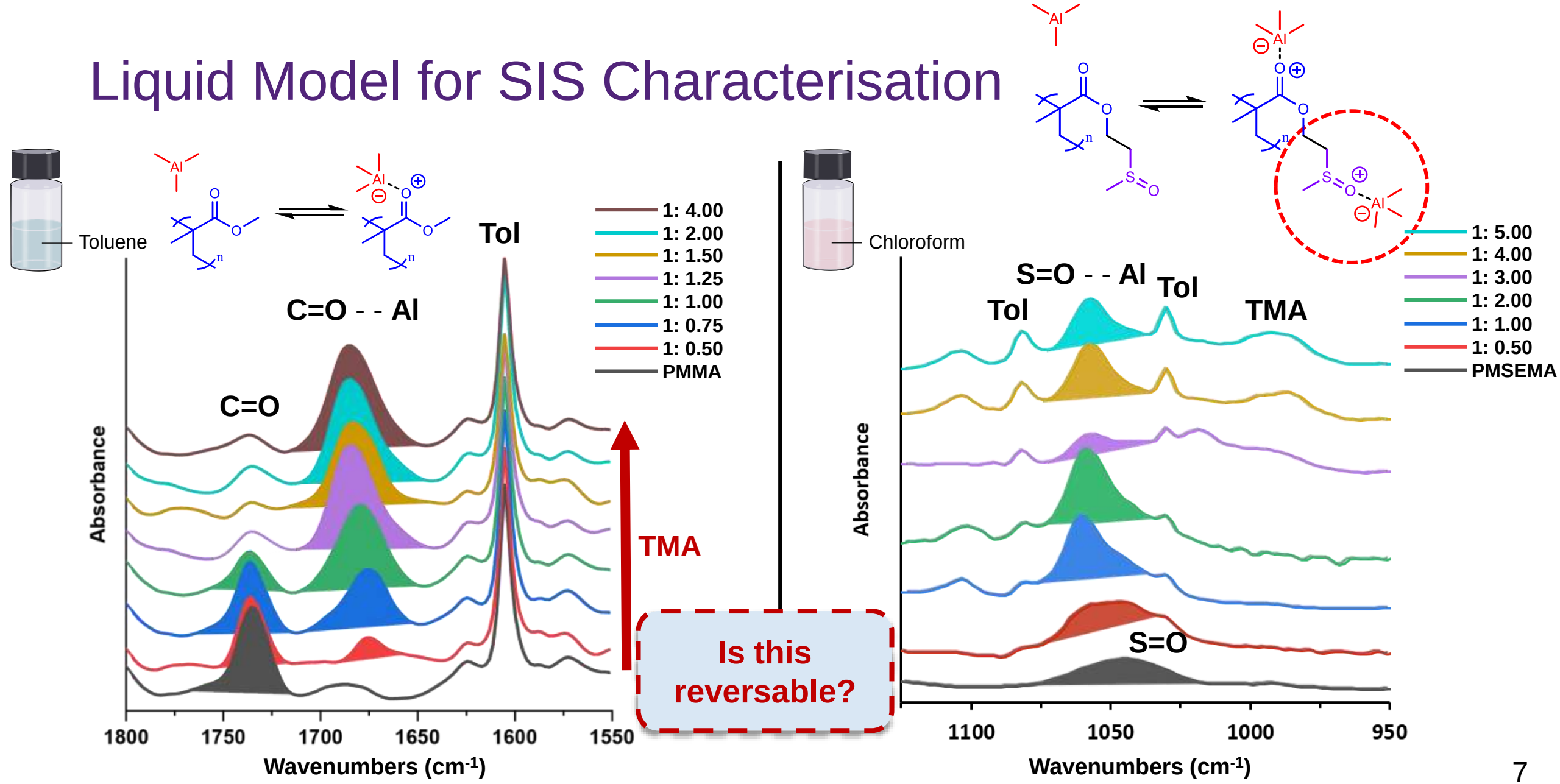


Liquid Model for SIS Characterisation

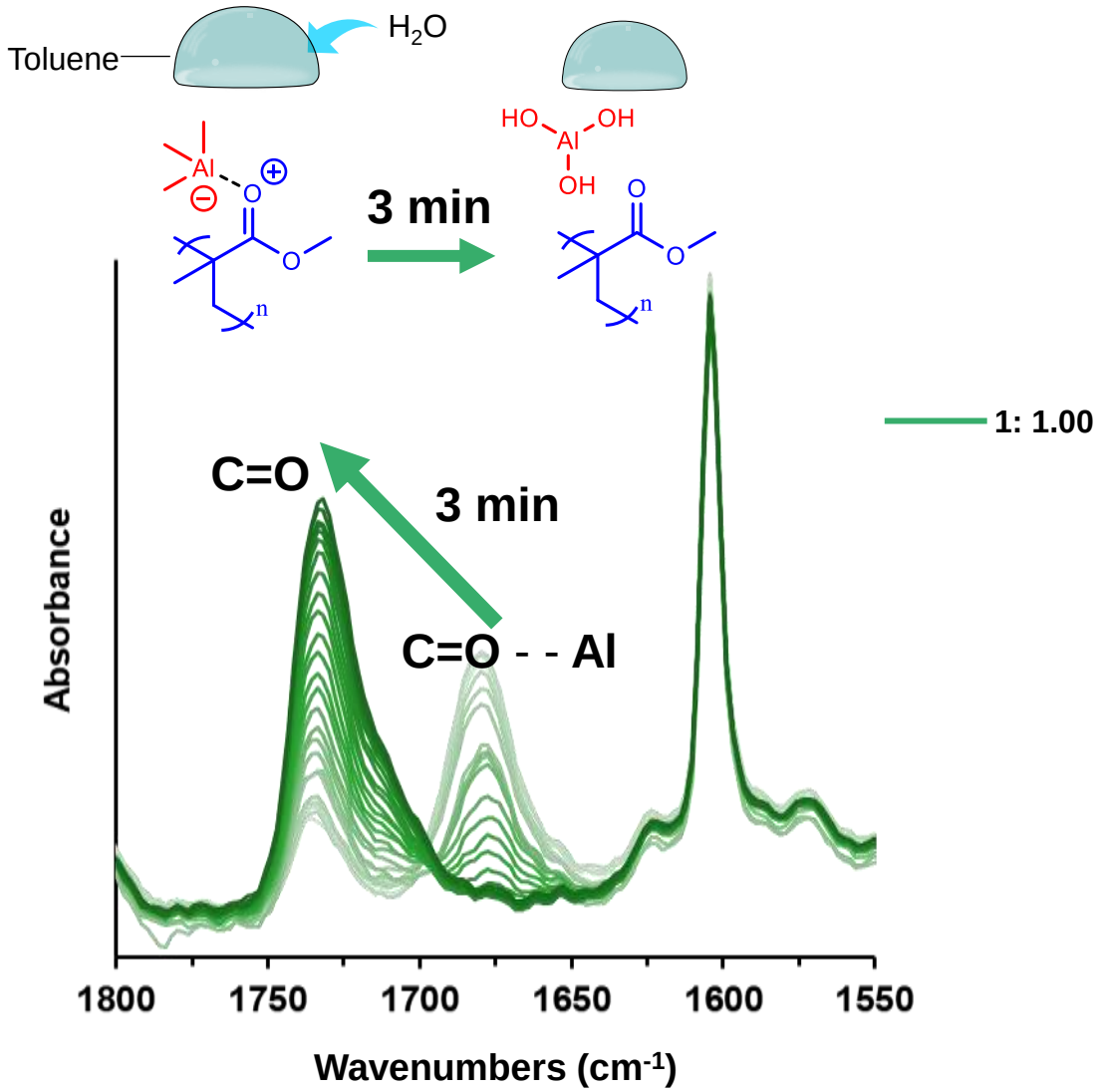


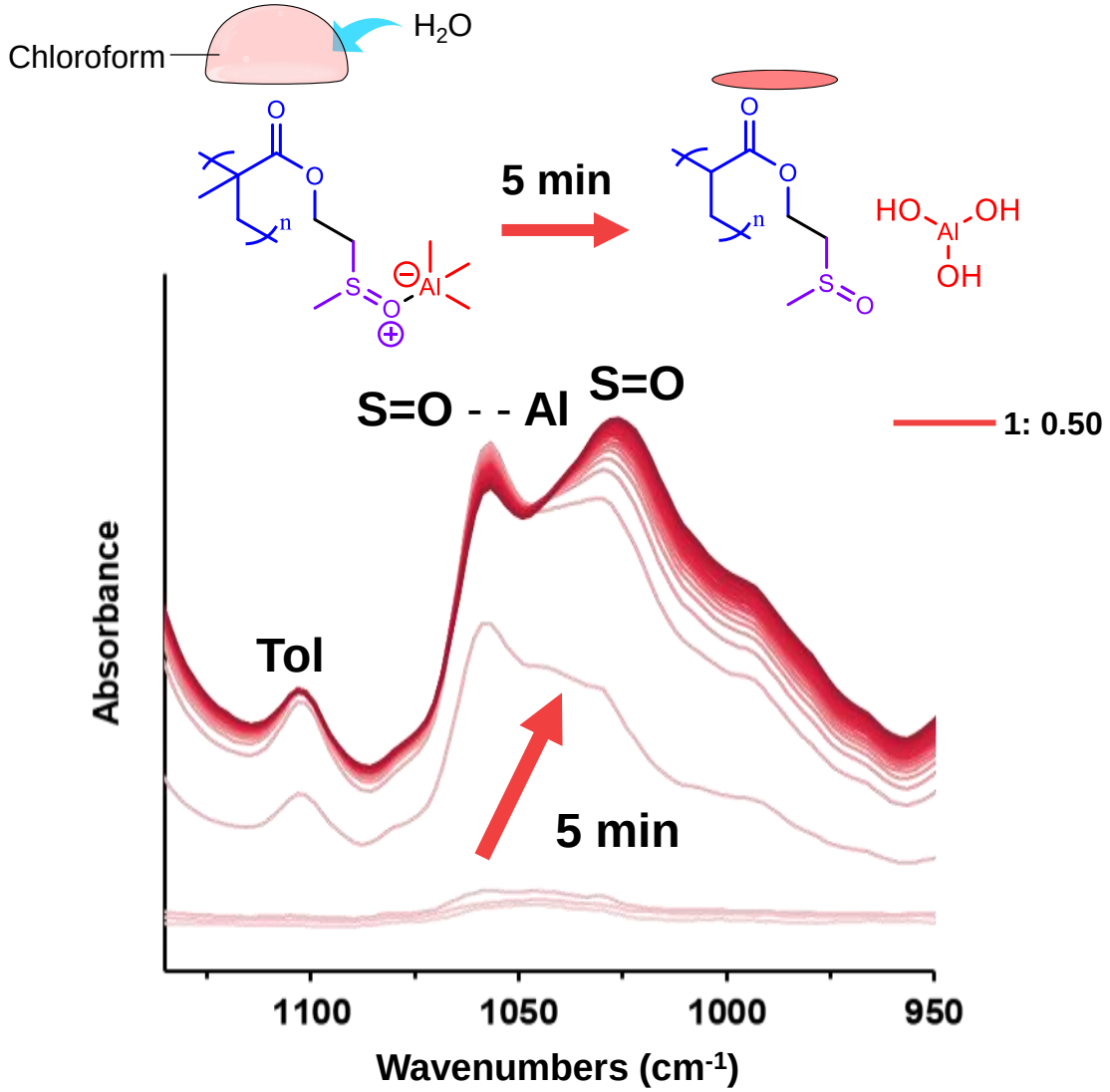


Liquid Model for SIS Characterisation



Reversibility of the Adduct





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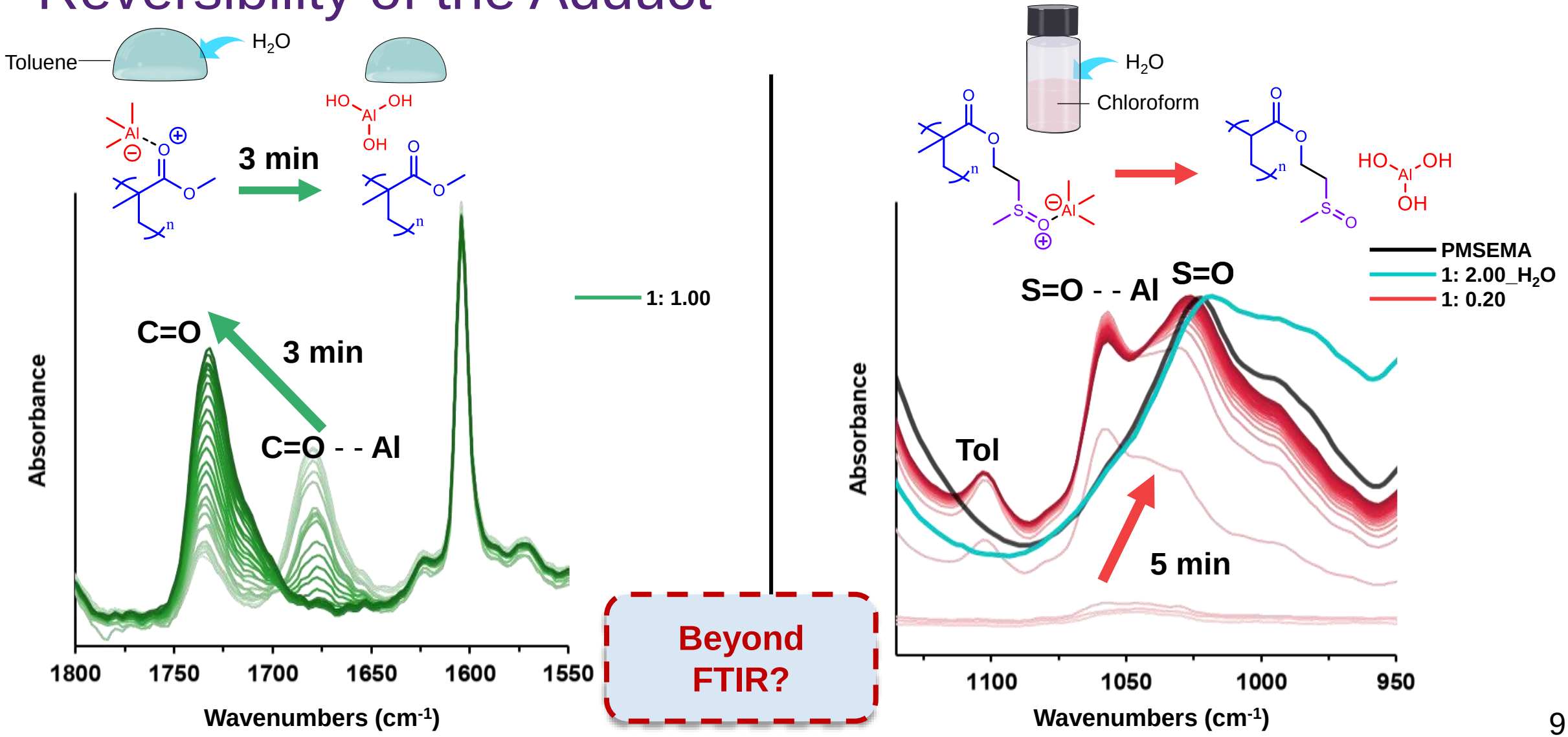
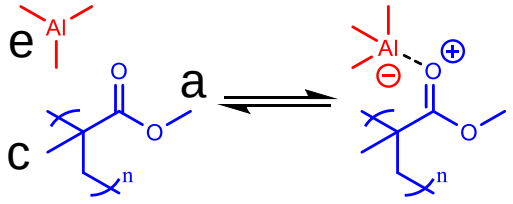
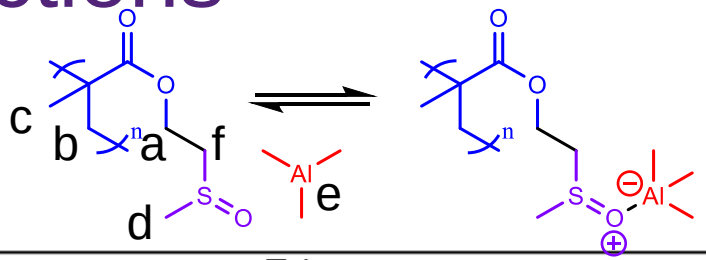
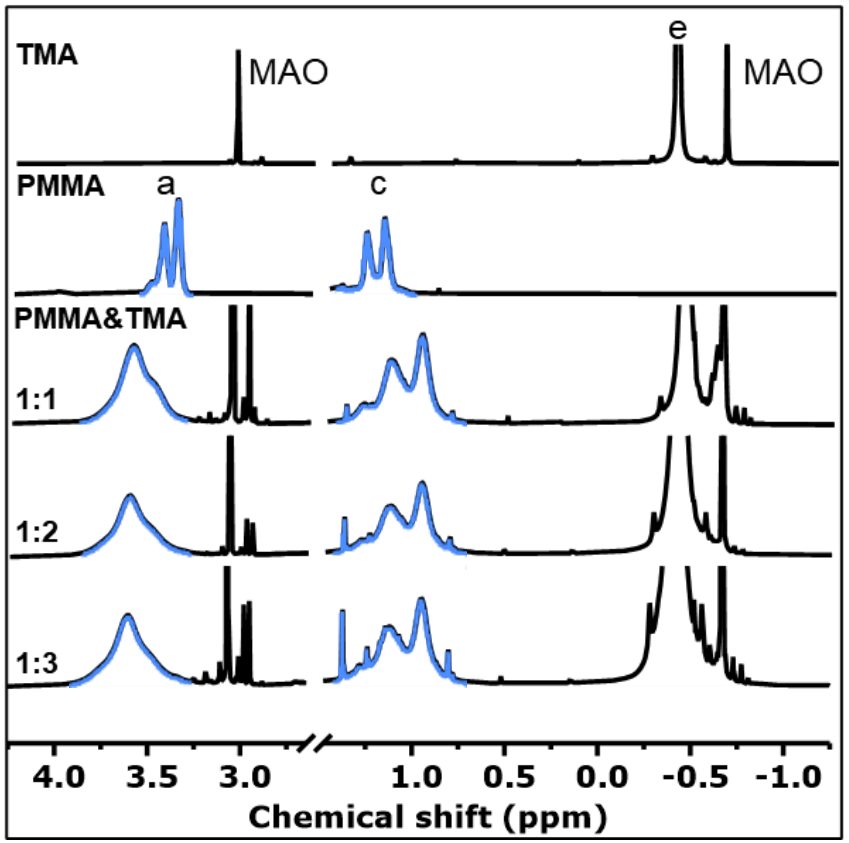


A Clearer View of Molecular Interactions

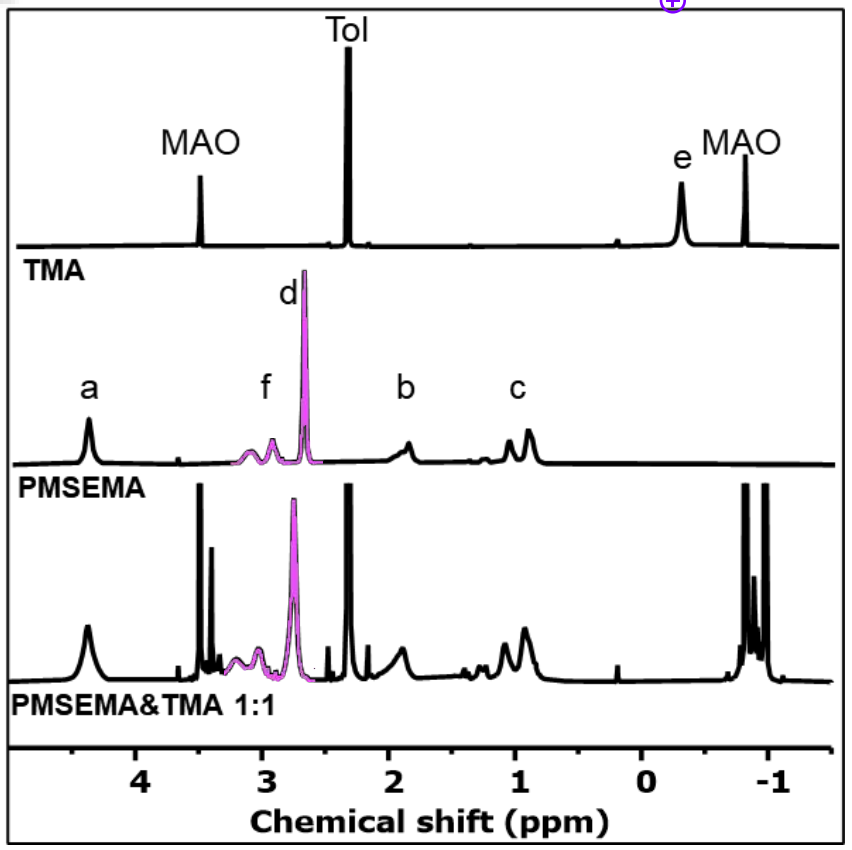


Is TMA bound to the polymer?



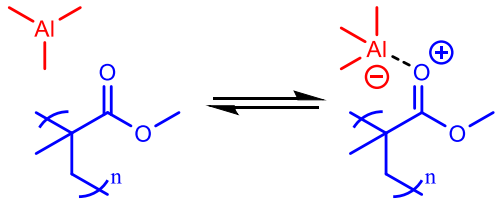


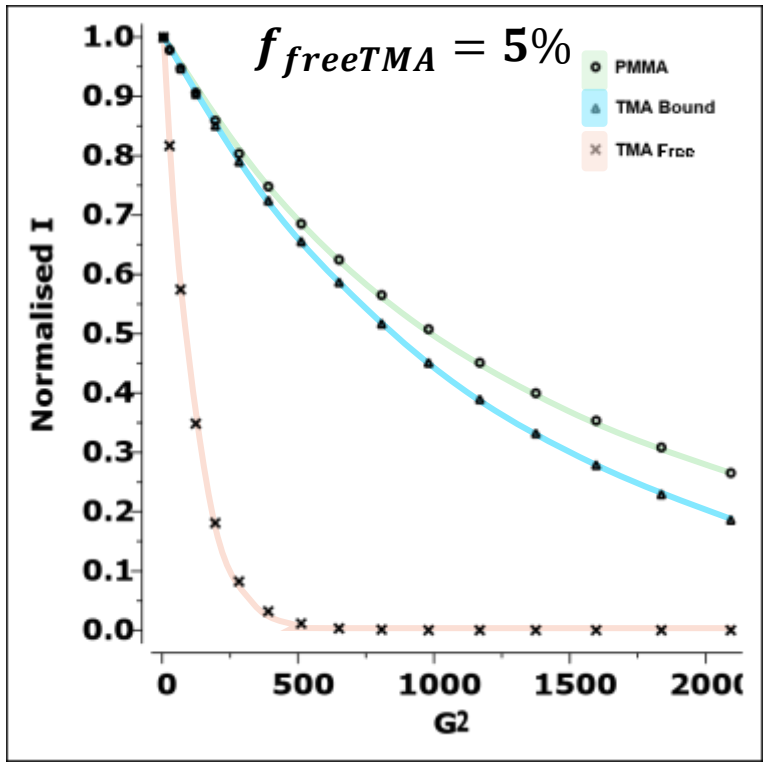
In toluene



In chloroform

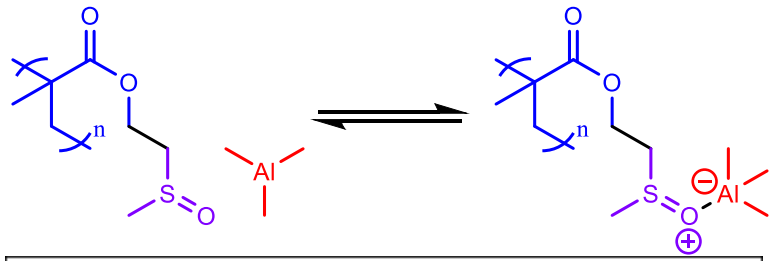
Diffusion Analysis of TMA Binding

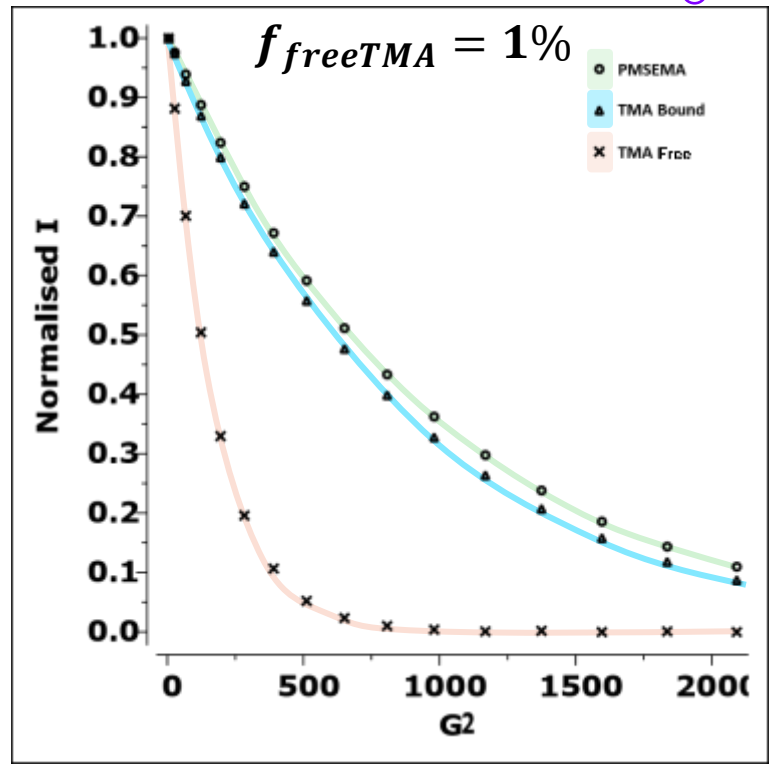




In toluene PMMA & TMA (1:1)

PMSEMA Good SIS Candidate?



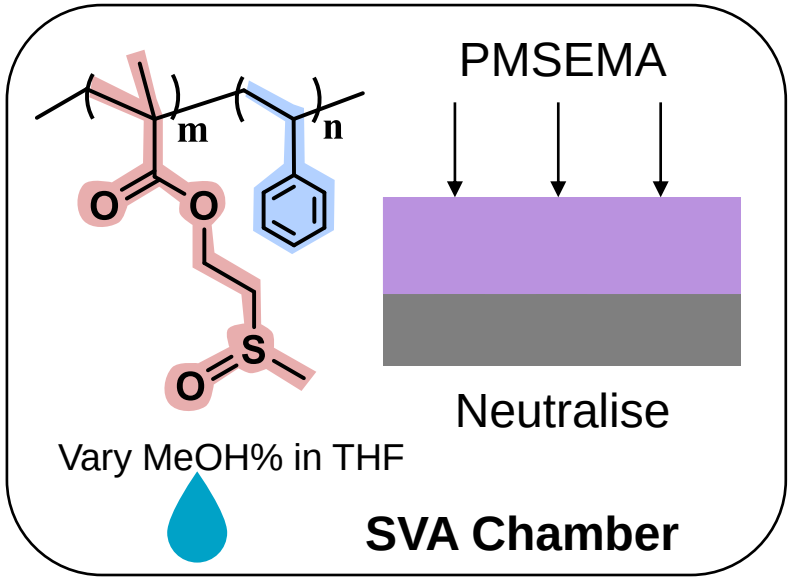


In chloroform PMSEMA & TMA (1:1)

$$D_{observed} = f_{free} D_{free} + (1 - f_{free}) D_{polymer}$$

Facilitating Phase Separation in PMSEMA-*b*-PS

Improve thermal via SIS

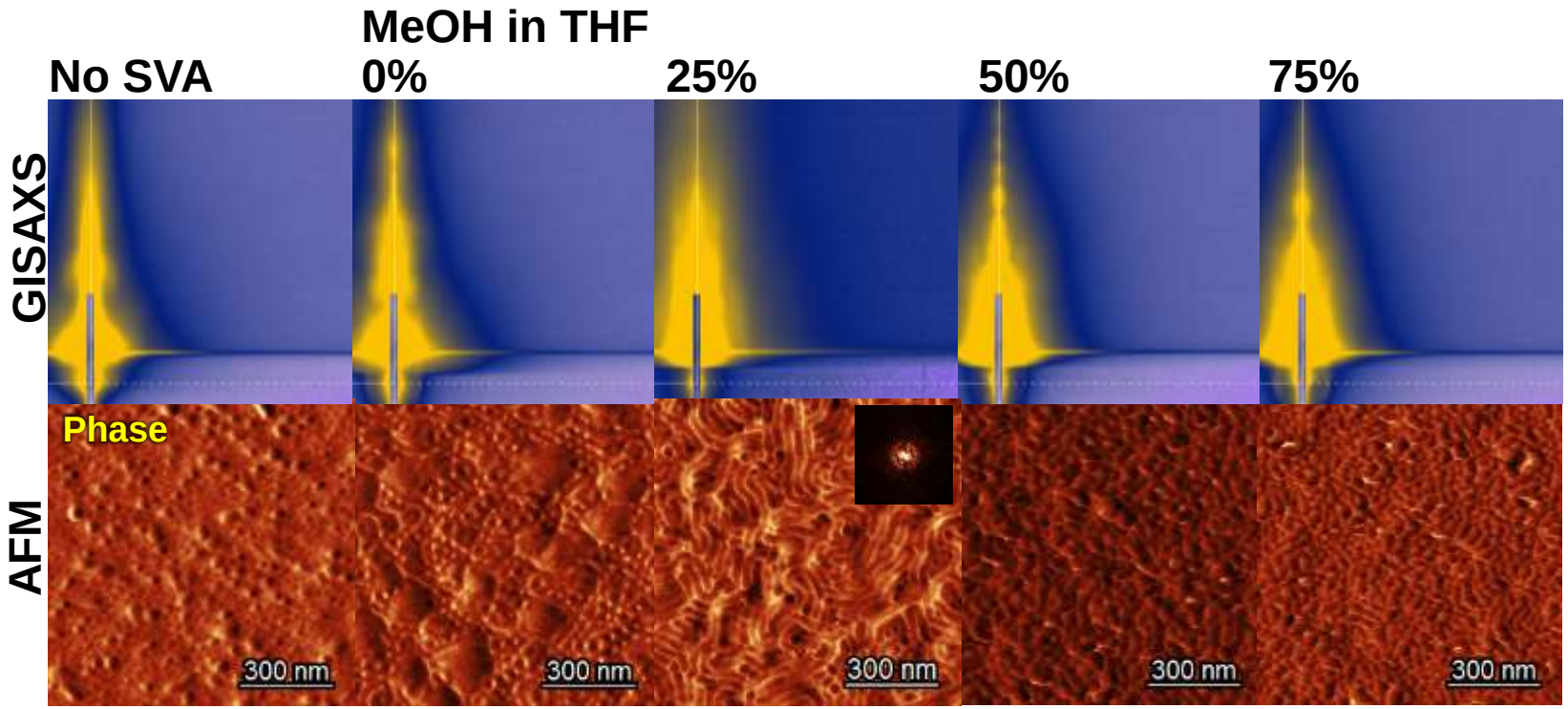


PMSEMA

- Hydrophilic
  - MeOH

PS

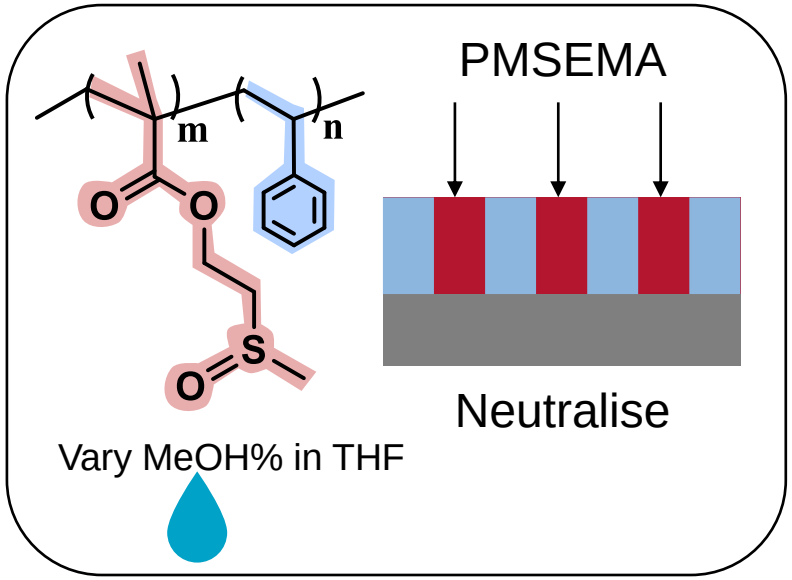
- Hydrophobic
  - THF



$PMSEMA_{44}$-*b*-PS_{13}

Facilitating Phase Separation in PMSEMA-*b*-PS

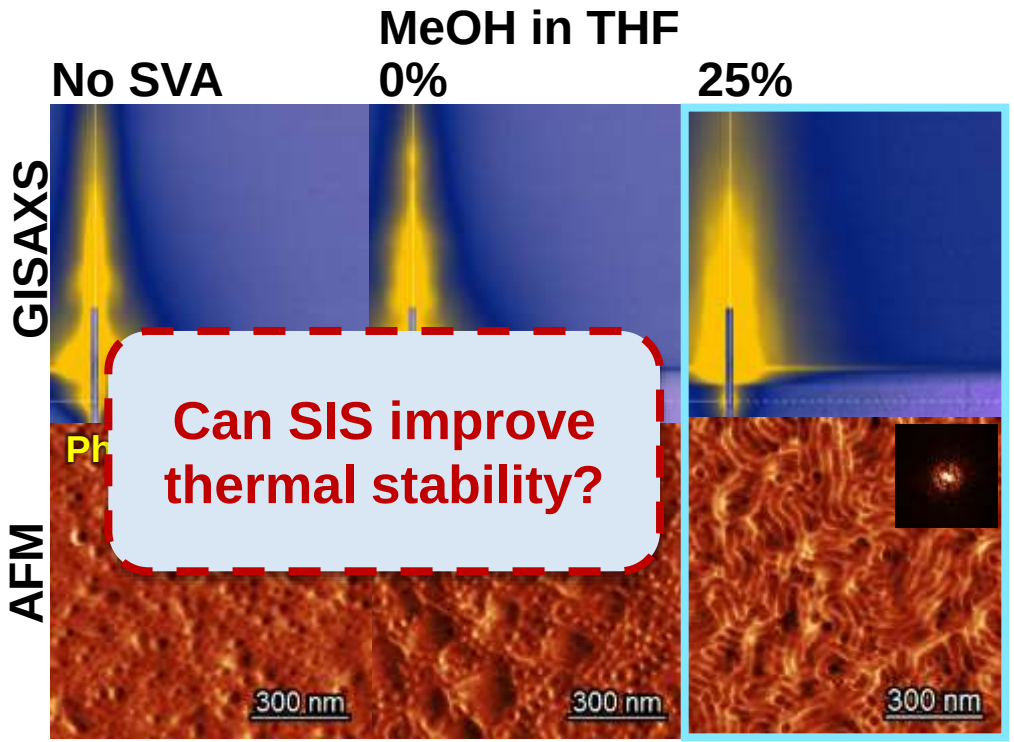
Chamber



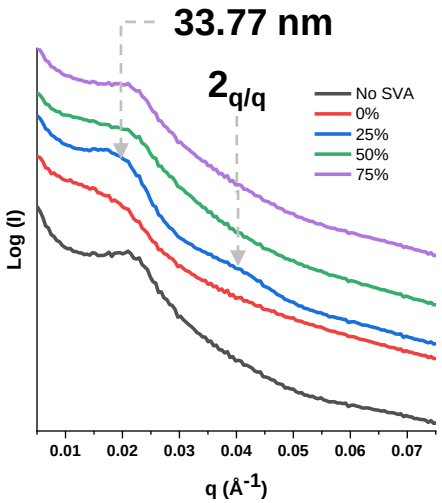
PMSEMA
- Hydrophilic
  - MeOH
- TMA "philic"

PS
- Hydrophobic
  - THF
- TMA "phobic"

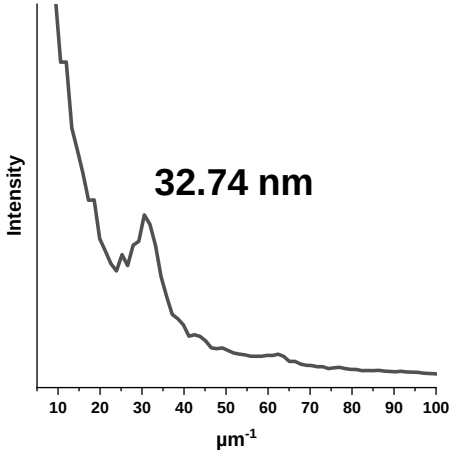
$PMSEMA_{44}$-*b*-PS_{13}



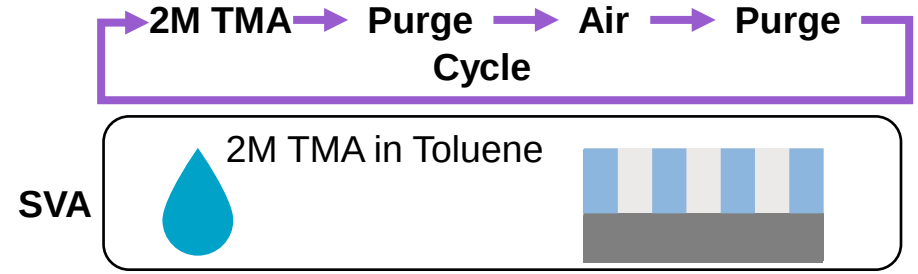
GISAXS Profile



AFM Profile of Phase FFT



Stability of TMA-Annealed Films



$PMSEMA_{44}$-*b*-PS_{13}

105 °C

No treatment

105 °C x1

105 °C x2

105 °C x4

Height

Phase

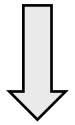
300 nm

Traditional SIS?

Stability of SIS Treated Films

$PMSEMA_{26}$-*b*-PS_{19}

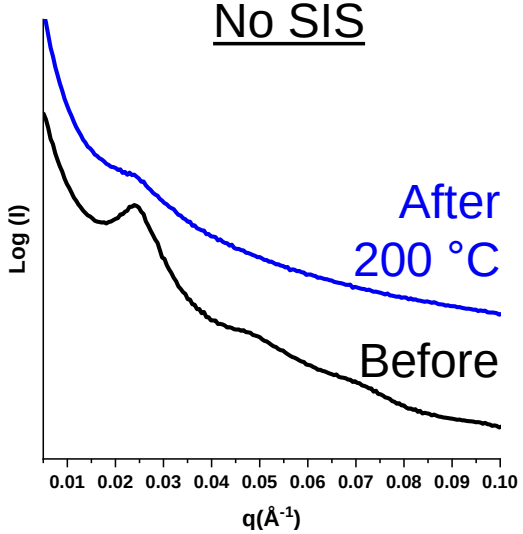
No SIS



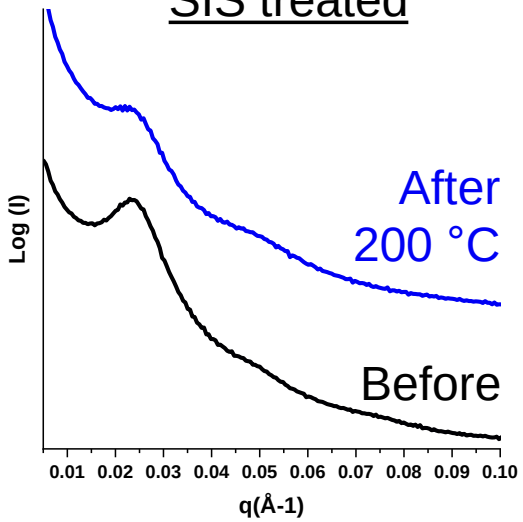
SIS x1

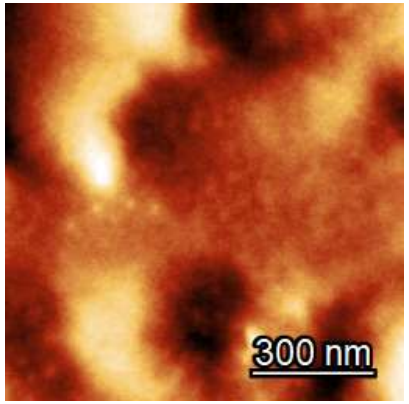
TMA → Purge → H_2O → Purge
Cycle

No SIS

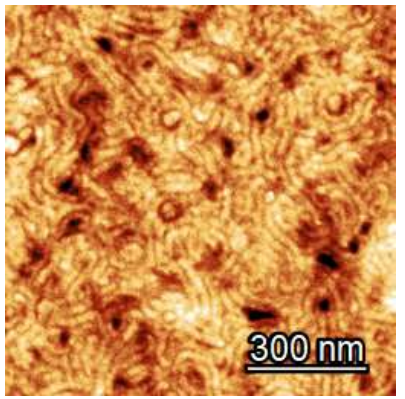


SIS treated





After 200 °C



After 200 °C

PMSEMA is a strong candidate for SIS

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Acknowledgments

Advisory Team

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Assoc Prof Idriss Blakey

Dr Hui Peng

Dr Md Daloar Hossain

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ANFF

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Indigenous
HDR Development Grant

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CREATE CHANGE

THANK YOU!