

# Towards the Optimization of Nanoporous Copolymer Membranes for Use as Heavy Metal Adsorbers

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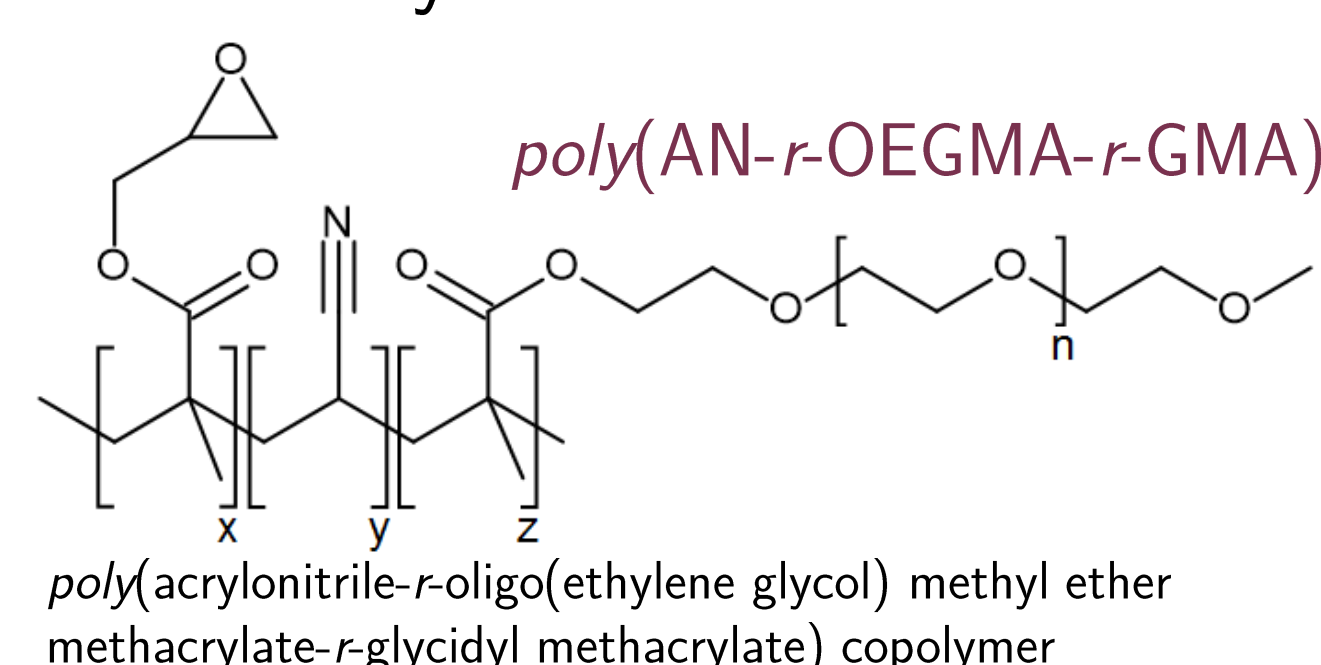
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## Introduction & Motivations

- ▶ Removal of **small, aqueous contaminants** is a substantial challenge in water and wastewater treatment
- ▶ Species such as dissolved **heavy metal ions**, pharmaceuticals and personal care products (PCPPs) are particularly concerning due to their **potential toxicity** to humans and aquatic ecosystems
- ▶ There is a global need for technologies which can **easily and economically** remove such contaminants
  - ▷ **Membranes** are playing an increasingly-important role
- ▶ Developing membrane technologies for water treatment include:
  - ▷ Membrane bioreactors
  - ▷ Mixed matrix membranes
  - ▷ Antifouling technologies
  - ▷ **Adsorptive membranes**
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  - ▷ **Filtration**
- ▶ In adsorptive membranes, the selective capture of difficult-to-remove aqueous contaminants can be enabled by introducing **toxin-specific binding sites** (*i.e.* for targeting heavy metals)
  - ▷ Facilitates a two-fold separation ability
  - ▷ Reduced unfavorable diffusional mass transfer limitations
  - ▷ **Improved separation efficiency** compared to other adsorbers

## Nanoporous Block Copolymer Membranes

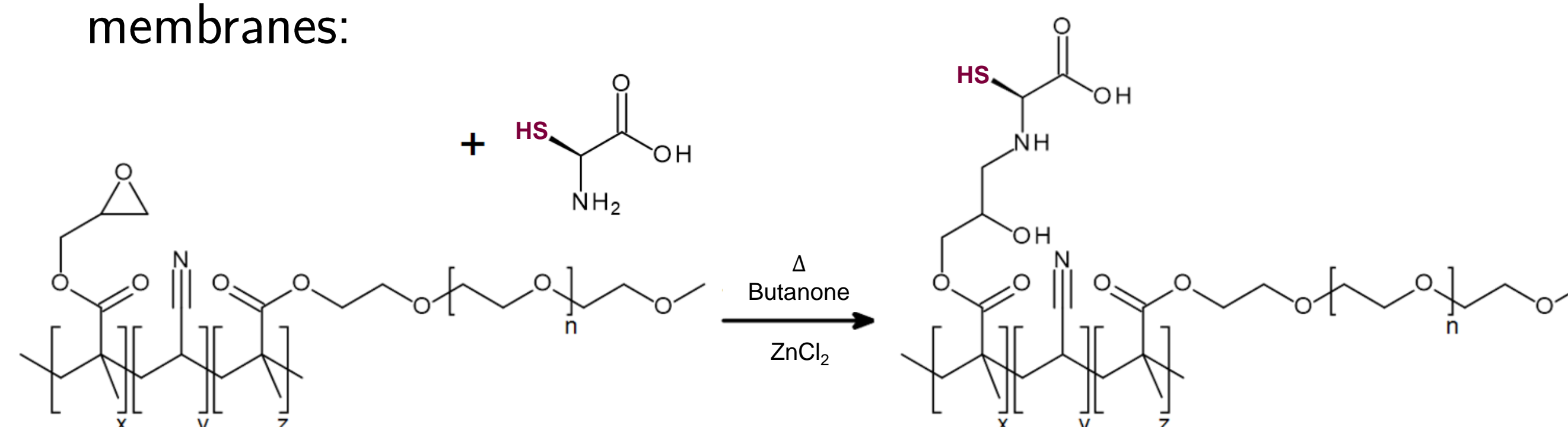
- ▶ The **self-assembly and nonsolvent-induced phase separation technique (SNIPS)** can be used to create block copolymer membranes with **tunable and well-defined nanostructures**
- ▶ Membrane formation via the SNIPS procedure relies on the **incompatibility of polymer "blocks"** in order to form a structured, nanoporous system
- ▶ Microphase separation and membrane formation relies on the copolymer composition, kinetic/thermodynamic considerations



- ▶ Free radical polymerization with AIBN initiator  $n \approx 8, x \approx 0.2, y \approx 0.4, z \approx 0.4$
- ▶ Membrane cast on ultrafiltration membrane substrate using dimethyl sulfoxide solvent
- ▶ Immersion in isopropanol (non-solvent) induces the membrane to "self-assemble"

## Membrane Synthesis

- ▶ The tunable nature of *poly(AN-*r*-OEGMA-*r*-GMA)* membranes makes them amenable to **chemical modification**
- ▶ For example, **amino acids** have shown to form complexes with heavy metals
  - ▷ **L-cysteine** (R = SH): Pb(II), Cd(II), Cu(II)
- ▶ Amino acid moieties can be grafted onto the copolymer membranes:

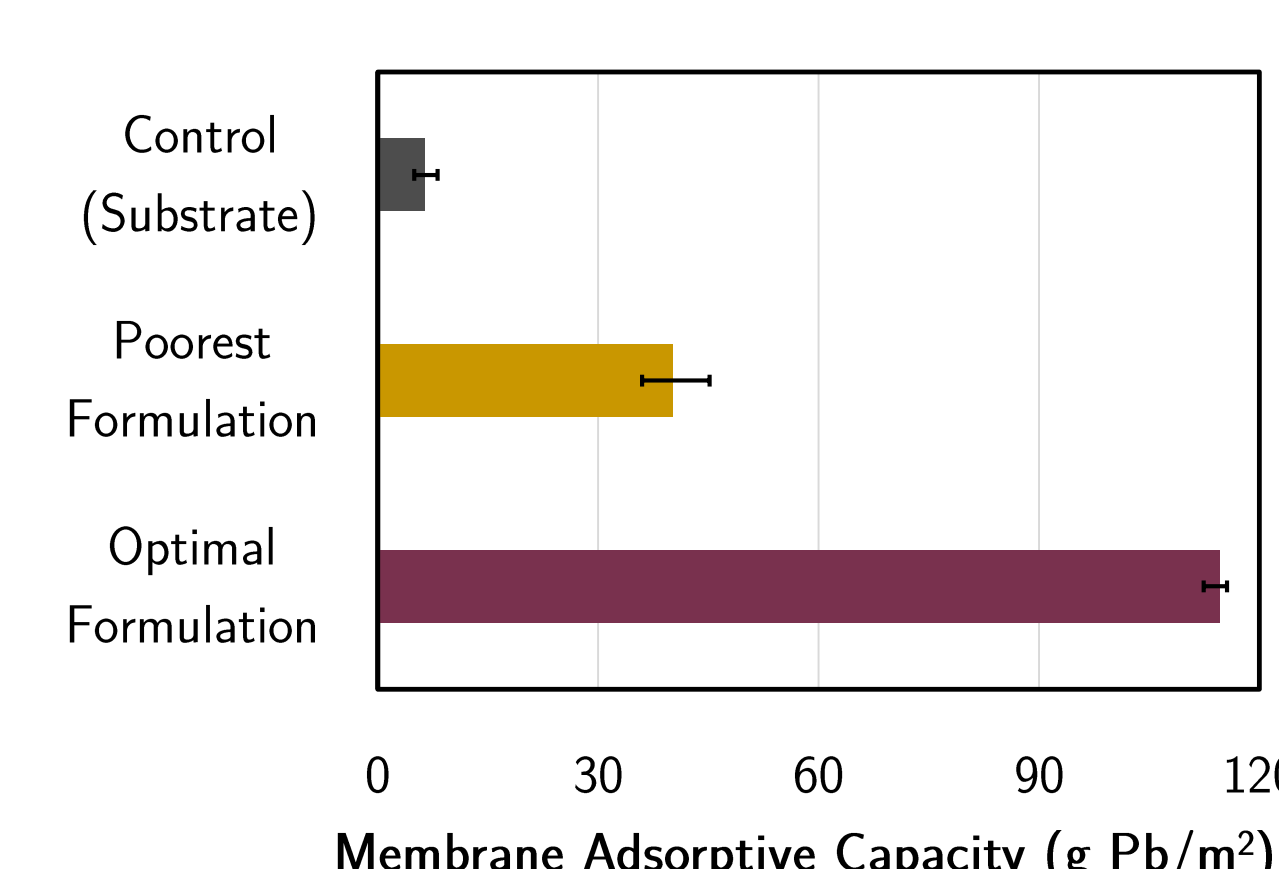
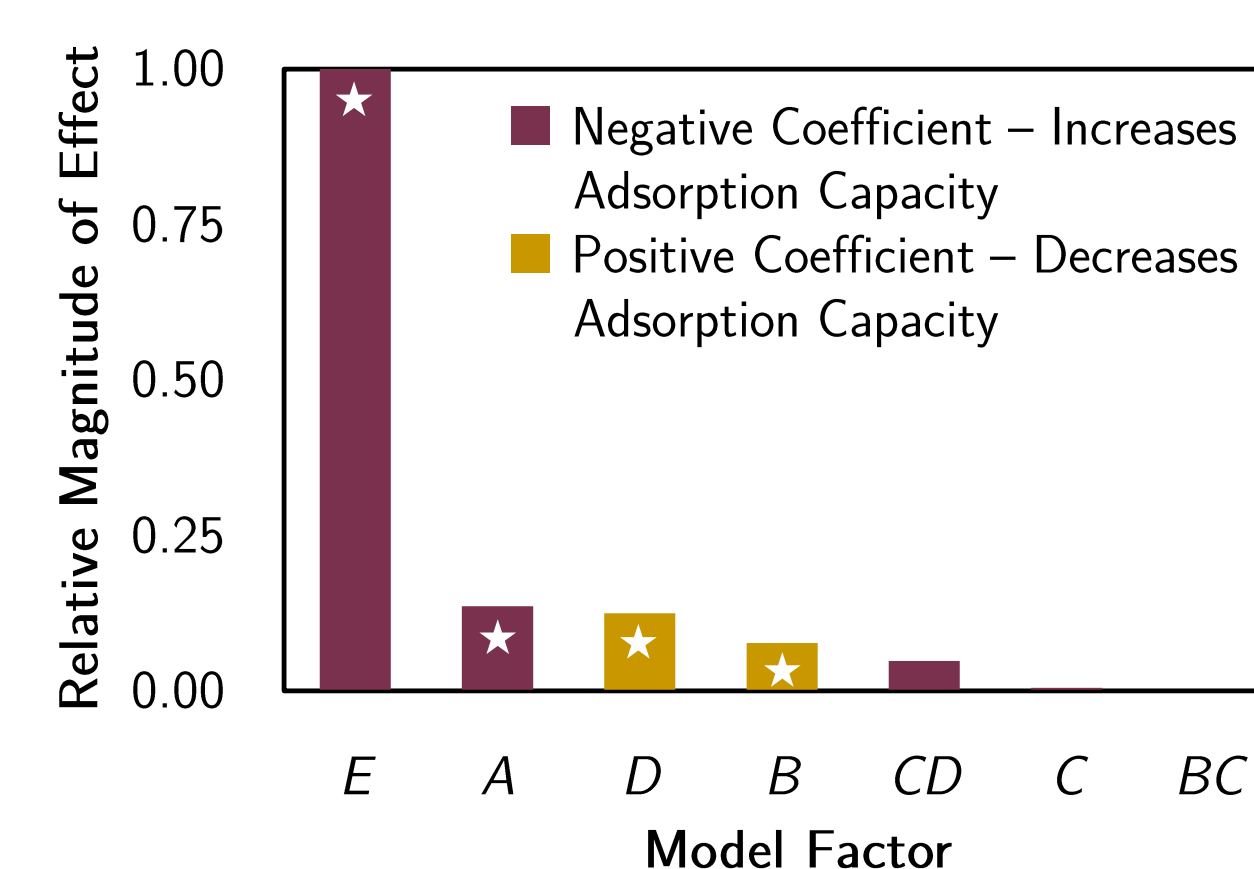


- ▶ A  $2^{5-2}$  fractional-factorial **design-of-experiments** architecture was used to improve the conjugation of cysteine onto the membranes
- ▶ Degree of functionalization estimated via **static lead adsorption capacity** experiments

Factor	Name	-/+
A	Reaction Temperature	40°C / 60°C
B	[Cysteine]	0.01 M / 0.1 M
C	[ZnCl <sub>2</sub> Catalyst]	5 mol% / 10 mol%
D = AB	Reaction Time	6 h / 18 h
E = AC	Reducing Agent* (DL-dithiothreitol)	No / Yes

\*0.02 M DL-dithiothreitol in 0.02 M HEPES buffer (pH = 8) was used as a reducing agent.

- ▶ Unmodified membrane discs (diameter = 14 mm) were reacted according to the DOE architecture
- ▶ Cys-modified membranes were immersed in agitated 25 ppm Pb solutions (pH = 5) for 18 h
- ▶ Pb adsorption was quantified via inductively-coupled plasma optical emission spectroscopy (ICP-OES) at  $\lambda = 220.353$  nm
- ▶ Each experiment was performed in *at least* duplicate



- ▶ **Result: greater lead adsorption capacities** (*i.e.* more bound cysteine) can be obtained:
  - ▷ Using the reducing agent, at higher temperature levels, using lower cysteine concentrations and lower reaction times
  - ▷ The catalyst concentration is insignificant
- ▶ The DOE-"optimized" **adsorption capacity** was found to be  $115 \pm 2$  mg Pb/m<sup>2</sup> membrane

## Membrane Characterization

### Composition Analysis

- ▶ **Atomic composition** of the membrane for both native and cysteine-modified *poly(AN-*r*-OEGMA-*r*-GMA)* copolymers
  - ▷ Analysis via **x-ray photoelectron spectroscopy (XPS)**

Element	Carbon	Oxygen	Nitrogen	Sulfur
Peaks	C1s	O1s	N1s	S2p
Unmodified Membrane <sup>†</sup>	69.22%	23.27%	6.62%	0.12%
Cys-Modified Membrane <sup>†</sup>	68.62%	21.88%	8.53%	0.43%

<sup>†</sup>Elemental composition expressed in atomic percent

- ▶ **Result: 70% of GMA functional groups** are grafted with cysteine

### Pore Size Characterization

- ▶ **Pore size characterization** via solute rejection experiments:
    - ▷ Feed solution: 1 g/L polyethylene glycols/oxides (1–35 kDa)
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- ▶ Actual rejection coefficients  $R_a$  shown
  - ▶ Calculated molecular weight cutoff (MWCO) values:
    - ▷ **Unmodified membrane:**  $MWCO \approx 5.1$  kDa  $\approx 5.3$  nm
    - ▷ **Cys-modified membrane:**  $MWCO \approx 20.3$  kDa  $\approx 8.3$  nm

- ▶ Membrane permeabilities,  $L_p$ :
  - ▷ **Unmodified membrane:**  $L_p = 0.36 \pm 0.05$  LMH/bar
  - ▷ **Cys-modified membrane:**  $L_p = 0.86 \pm 0.05$  LMH/bar
- ▶ **Result: Evidence to suggest a change in pore structure** during the reaction

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