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Novel Tamper-Indicating Materials

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2021 ACS Rocky Mountain Regional Meeting

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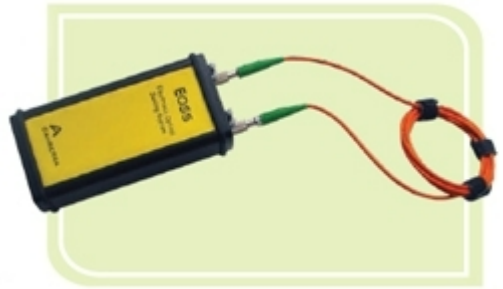
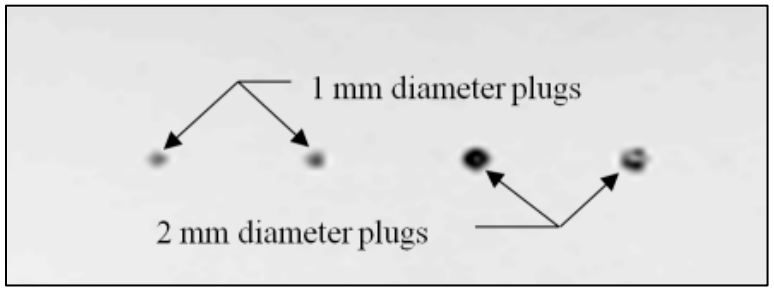
Background

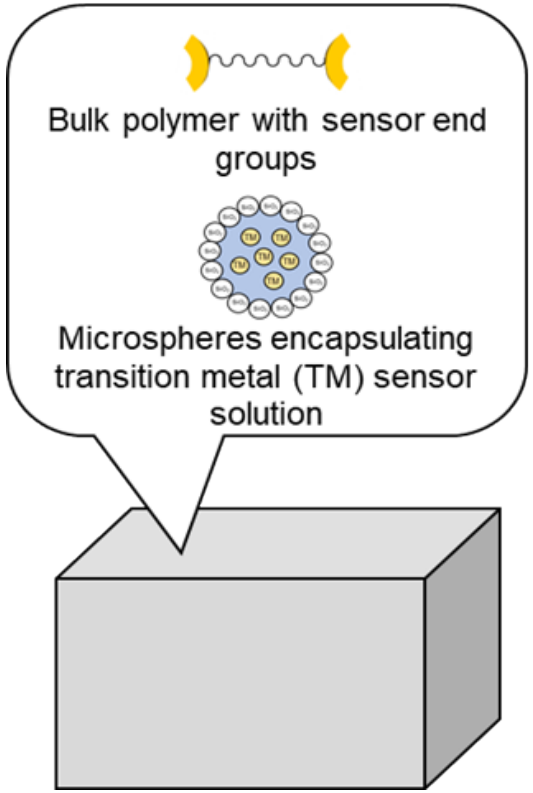
Current tamper-indicating enclosures (TIEs) typically require time consuming and subjective inspections, active monitoring technology, or external verification mechanisms. There are no current approaches that upon tamper, result in obvious responses with only visual inspection needed.

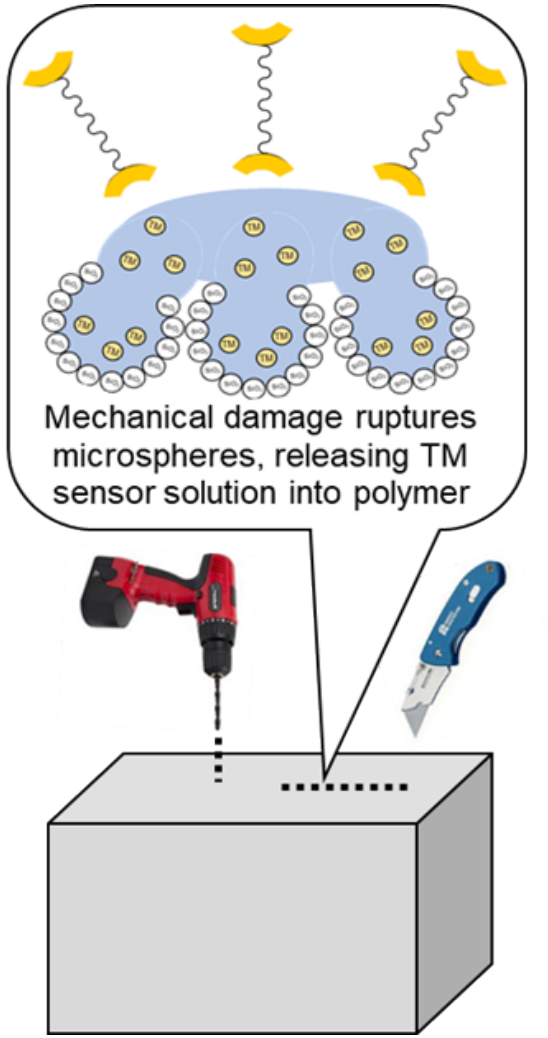


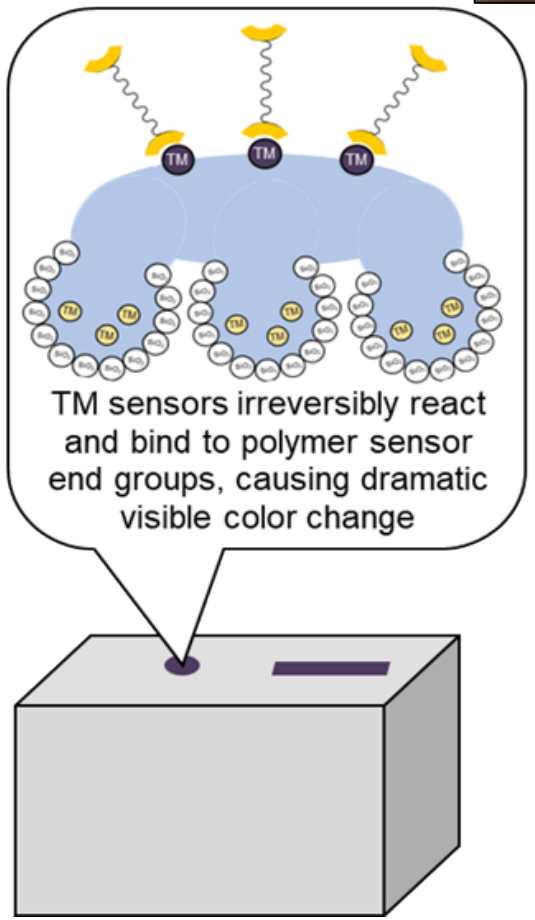


(Left) NGSS surveillance system uses both anodized aluminum, which is verified subjectively on both the outer and inner surfaces via visual inspection and touch, as well as active self-monitoring using conductive materials.
(Middle) The EOSS fiber loop seal uses active self-monitoring using conductive foils. Active methods require power and are not applicable in some scenarios.
(Right) Metal containers can be verified using eddy current – an external electronic instrument capable of finding disturbances in the metal, including drilled and plugged holes.

Concept

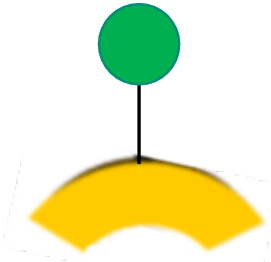

Bulk polymer with sensor end groups
Microspheres encapsulating transition metal (TM) sensor solution


Mechanical damage ruptures microspheres, releasing TM sensor solution into polymer

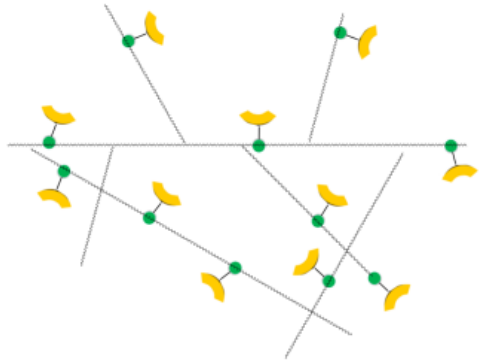

TM
TM
TM
TM sensors irreversibly react and bind to polymer sensor end groups, causing dramatic visible color change

Sensors

General schematic

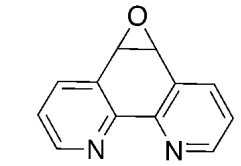


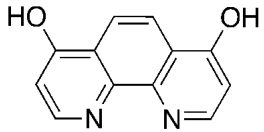
Sensor molecule



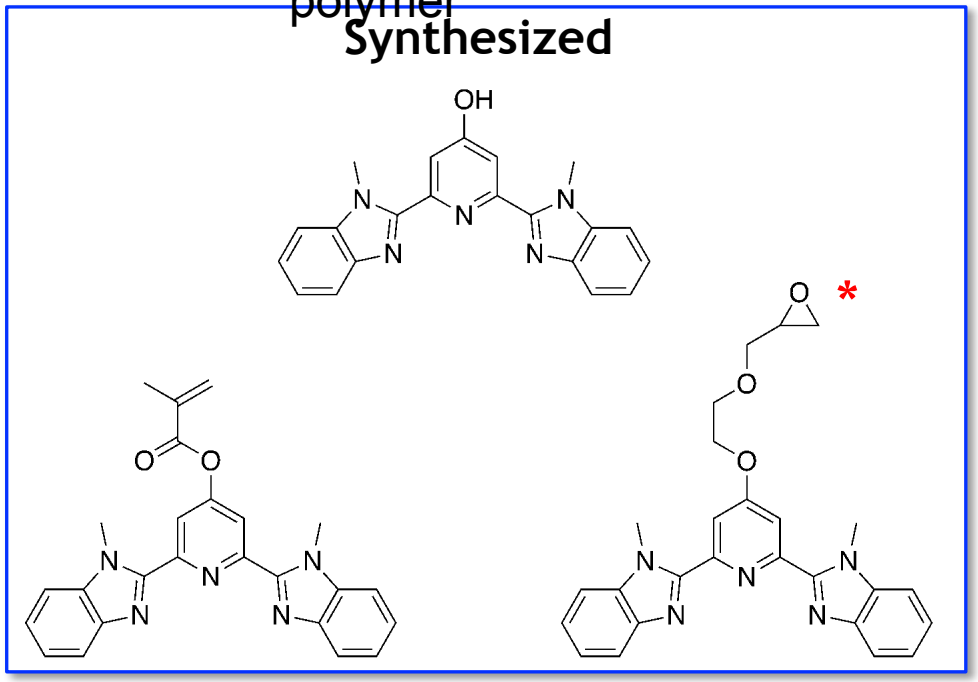
Cross-linked sensing polymer

Commercially Available



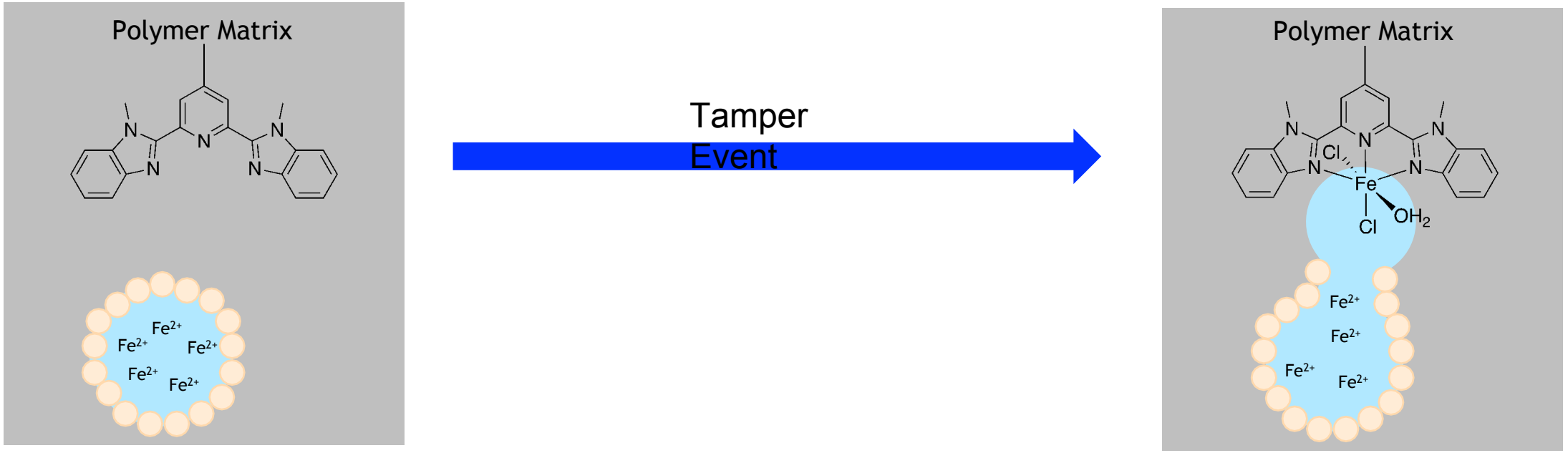


Synthesized



*Attempted

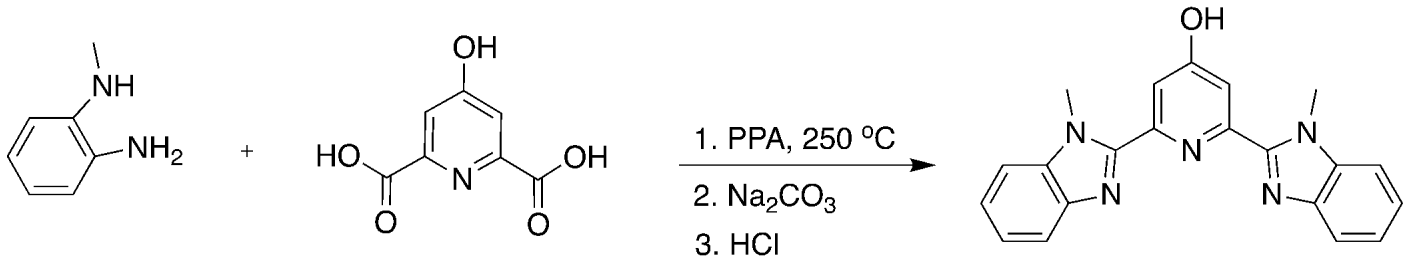
Transition Metal Complexes with Sensor

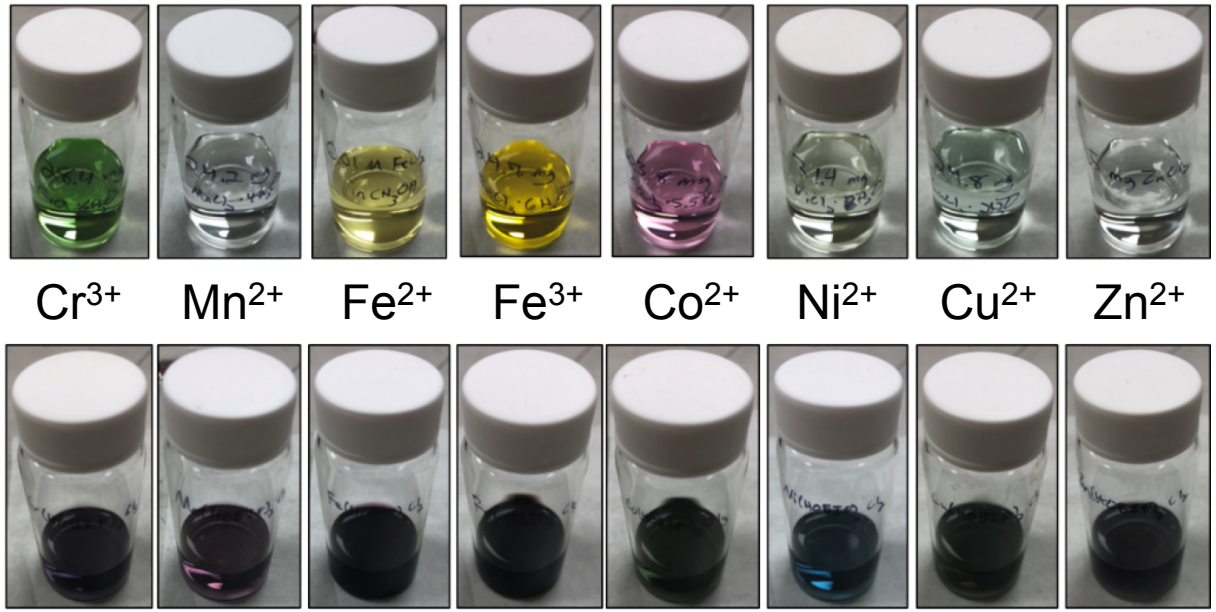


Tamper event releases $FeCl_2 \cdot 4H_2O$ and the sensor chelates to Fe(II) to cause a color change

- Not limited to $FeCl_2 \cdot 4H_2O$
- $FeCl_3 \cdot 6H_2O$ is more robust to oxidation

Investigation of Transition Metal Salts and Sensors





Sensor

- HO-BIP – synthesized
- Produces purple solution

Sensor + TM

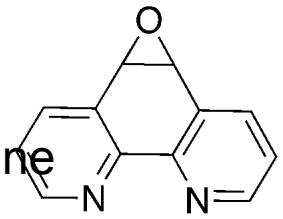
- 1 – 3 mg/mL Metal Chloride Solutions
- Much more dramatic color changes
  - Colored sensor
  - Stronger sensor-transition metal interaction

Chem. Eur. J. **2011**, *17*, 13274.

Investigation of Transition Metal Salts and Sensors

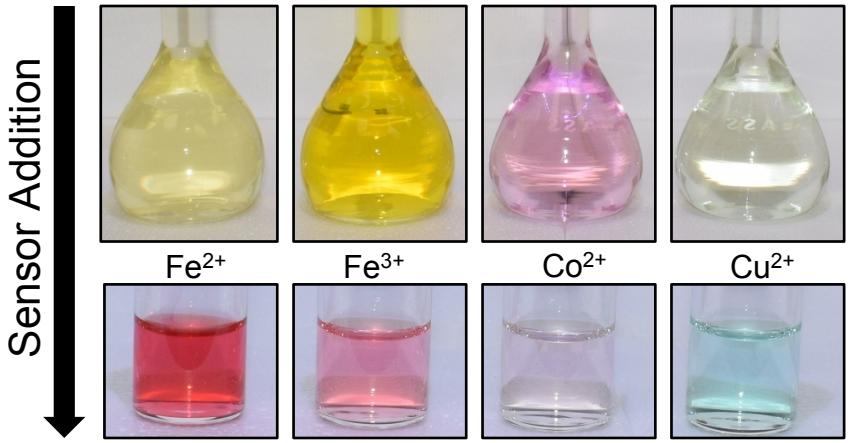
Sensor

- Commercially available phenanthroline

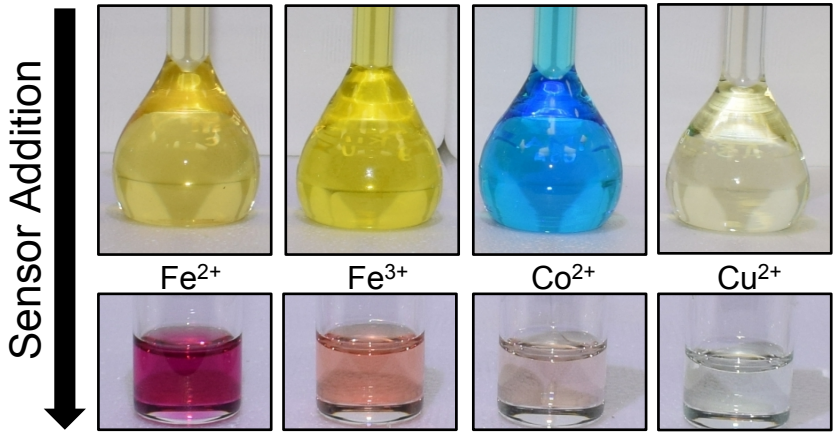


Colorless Sensor Solution

Solutions in Methanol

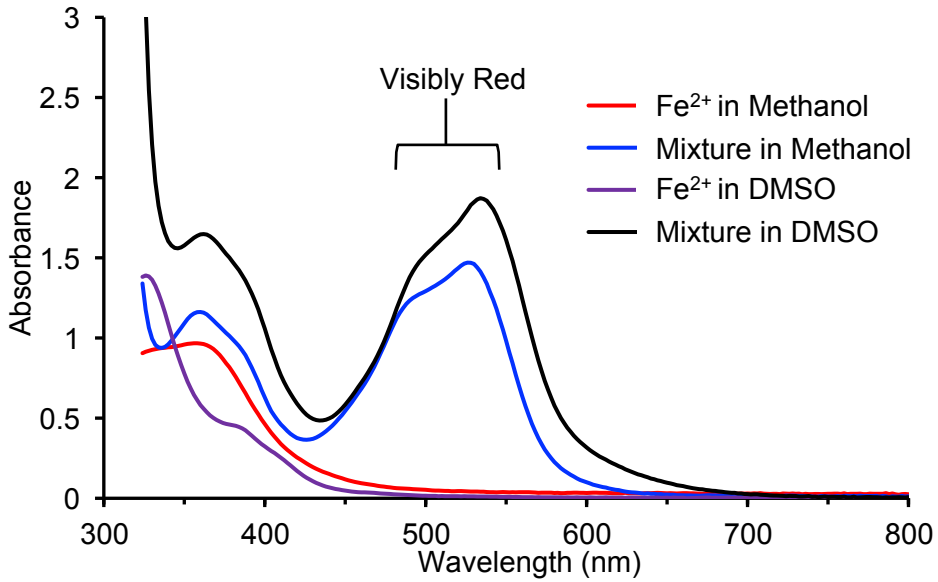


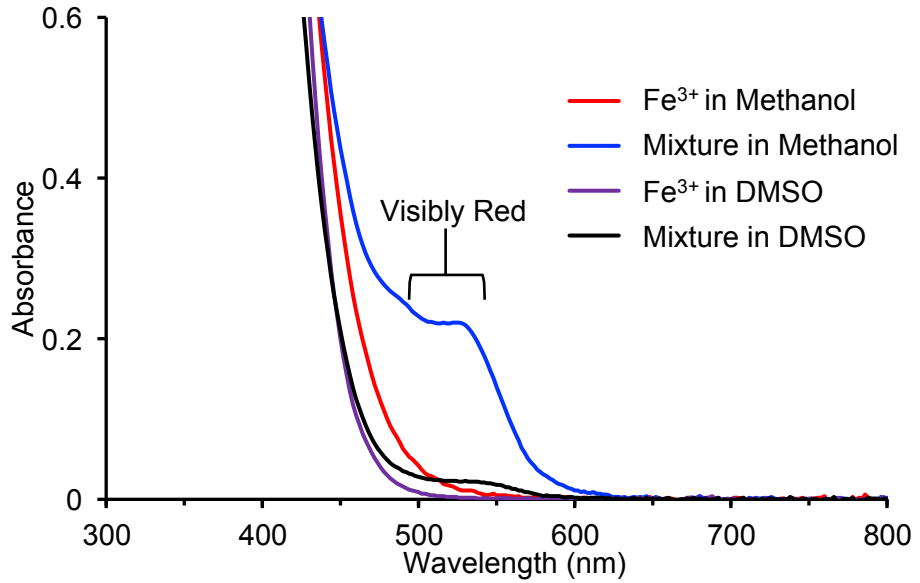
Solutions in DMSO

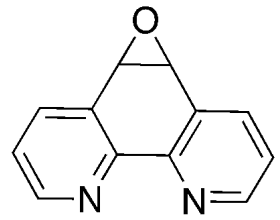


- 1– 3 mg/mL Metal Chloride Solutions; 1:1 ratio of TM to sensor
- Fe^{2+} yields the most dramatic color change, but it is prone to oxidation

Investigation of Transition Metal Salts and Sensors

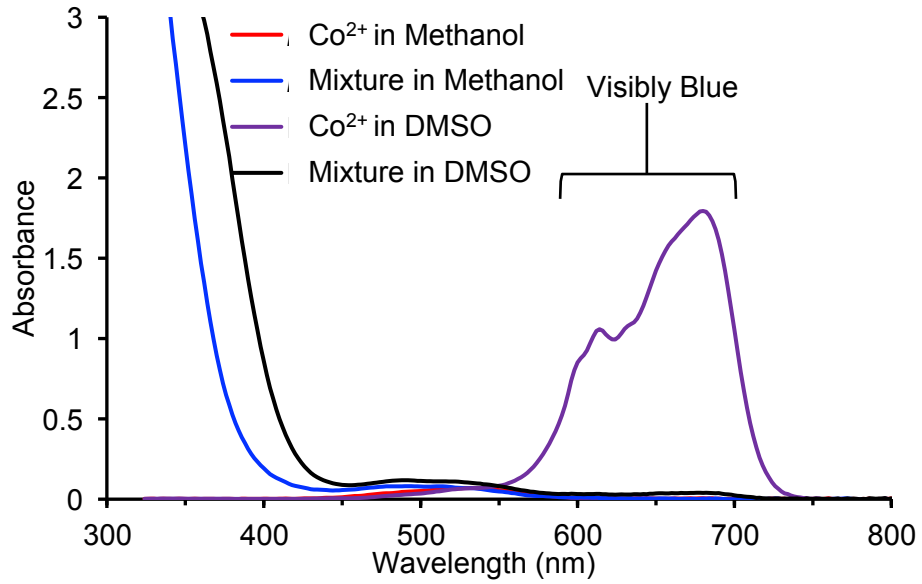


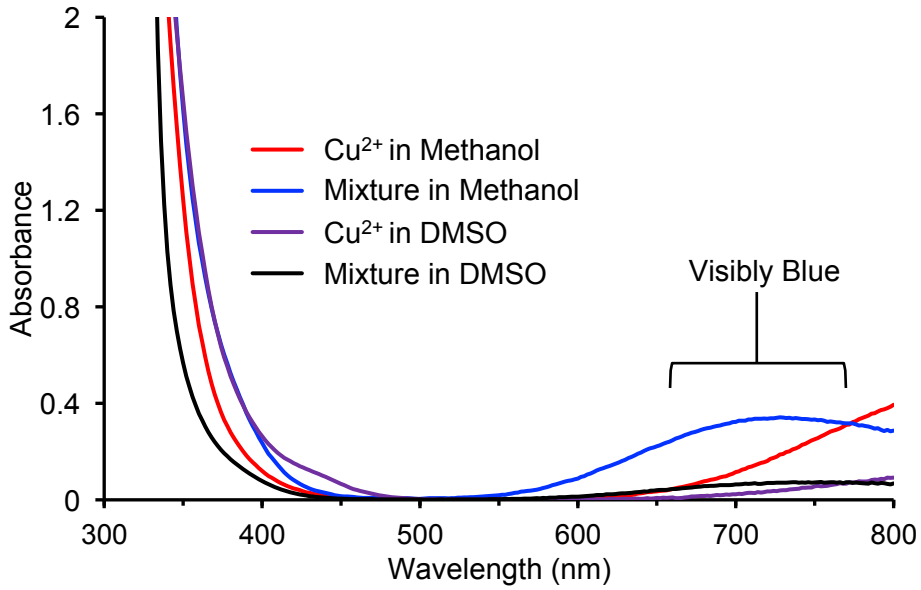




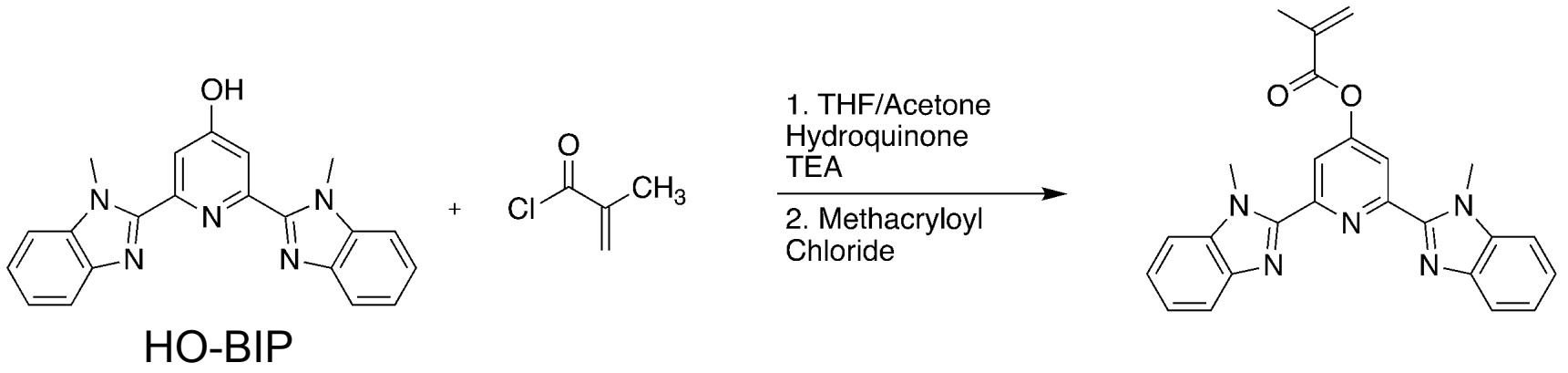
Unfortunately, this molecule did not dissolve into either

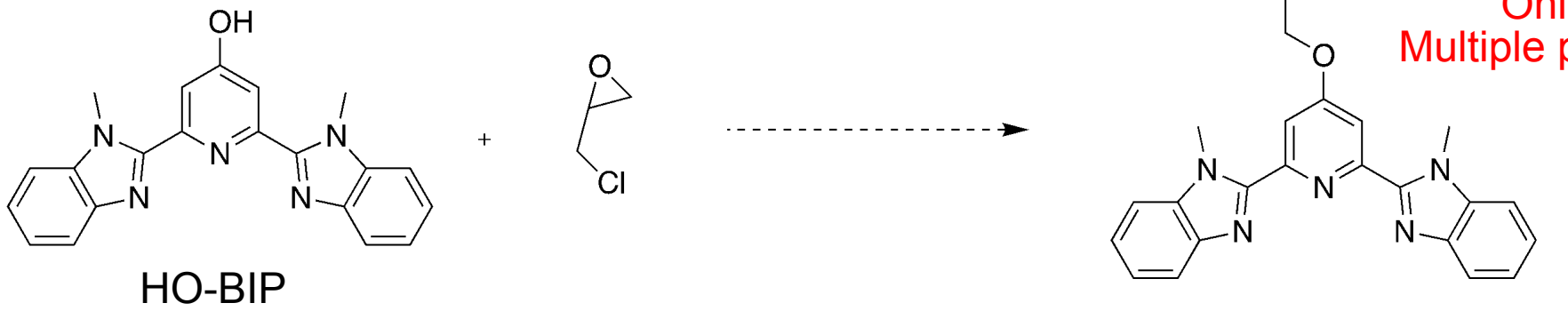
1) the epoxy (room temp or warm)
2) in the T-403 curing agent (room temperature & warm)





Sensor Synthesis





Only ~5% yield
Multiple pathways attempted

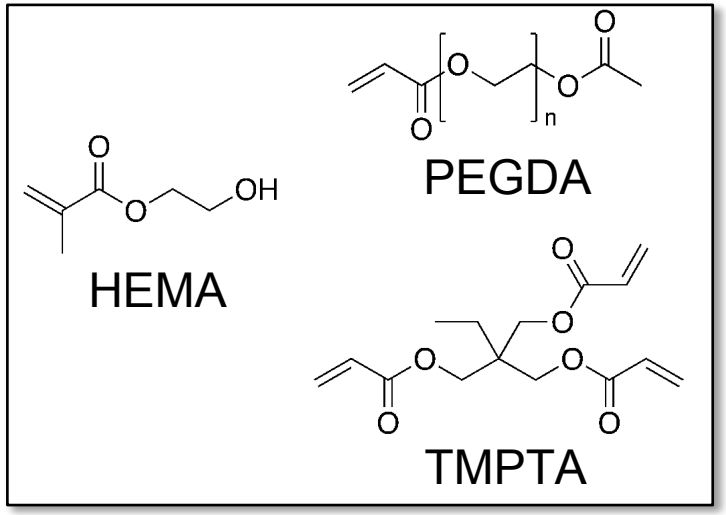
- Solvent, concentration, and temperature were varied with no increase in yield
- Alcohol may not be nucleophilic enough
- Oxygen part of the conjugation into the ring

Krieger, G.; Tieke, B. Macromol. Chem. Phys. **2017**, *218*, 1700052.

Polymer Systems

3 polymer systems and their random copolymers were cured

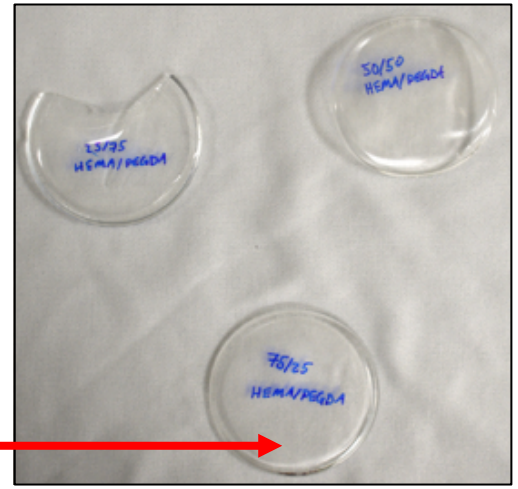
- PEGDA – cheap & crosslinks
- HEMA – polar/water compatible
- TMPTA - crosslinks



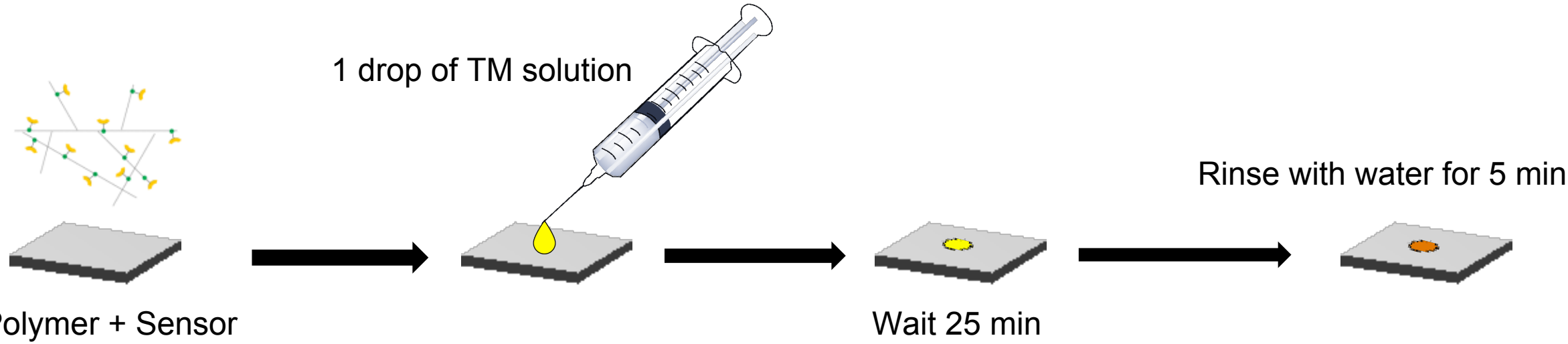
Mixtures of 25/75, 50/50, 75/25

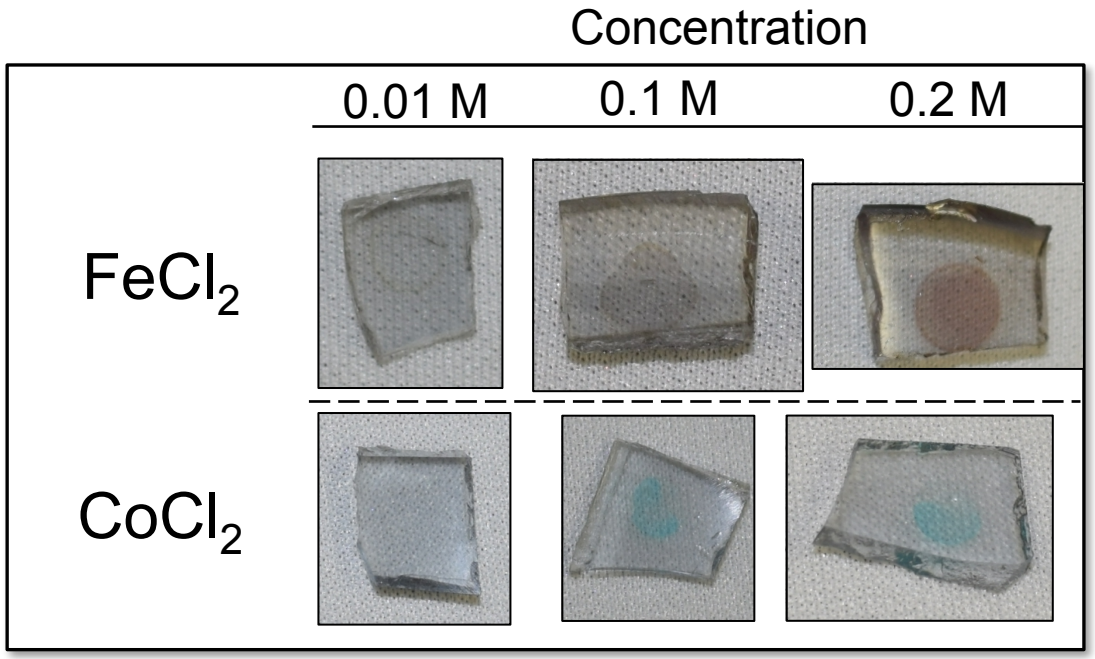
- PEGDA/HEMA – Flexible/Difficult to crack
- PEGDA/TMPTA
- TMPTA/HEMA

Chosen Mixture: 75/25 HEMA/PEGDA



Simulating a Tamper Event





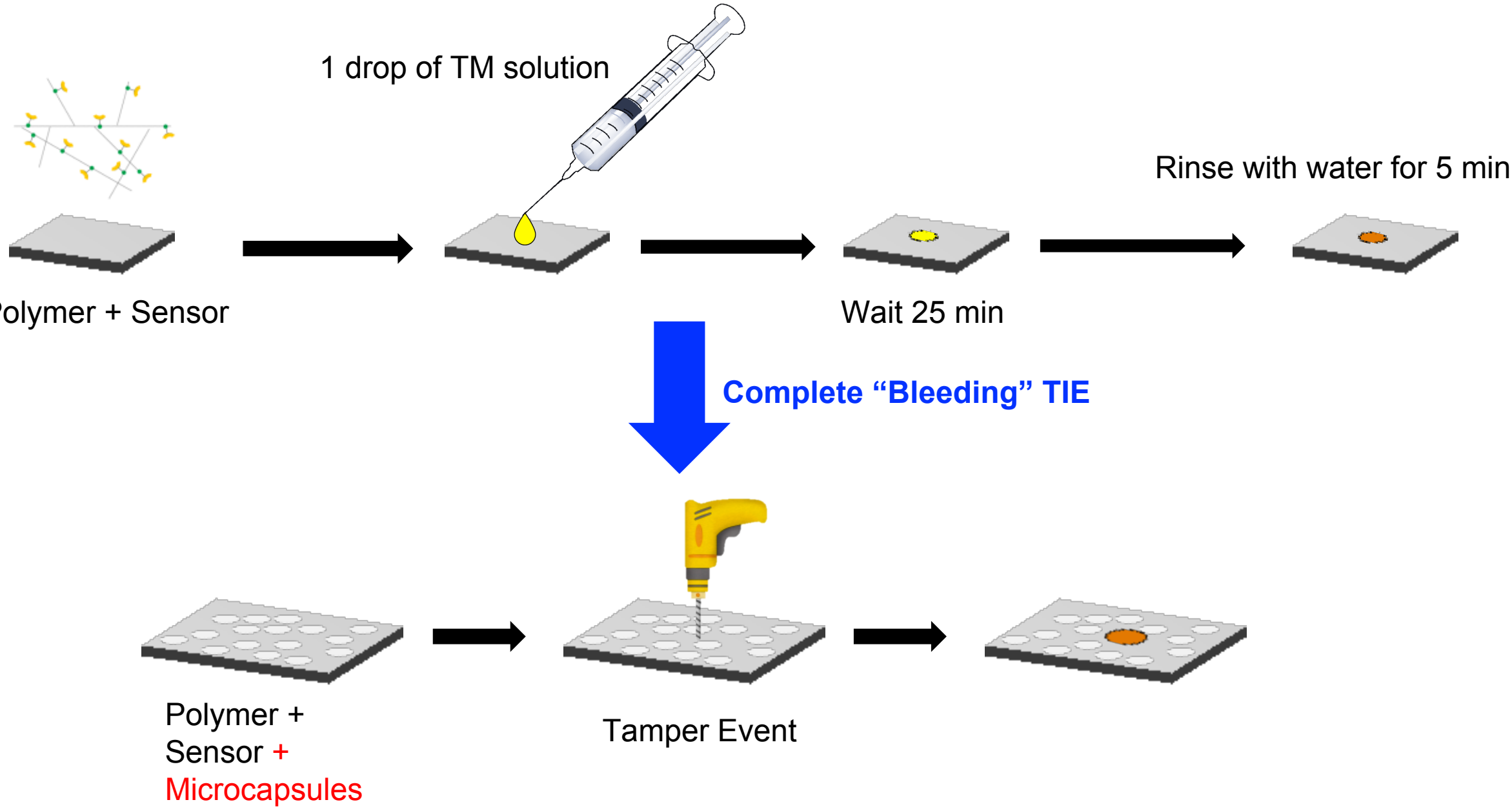
Conclusions

- Strong TM-Sensor bond
- Sensor is bound to polymer
- $FeCl_2$ yields more dramatic change
- 0.2 M is best

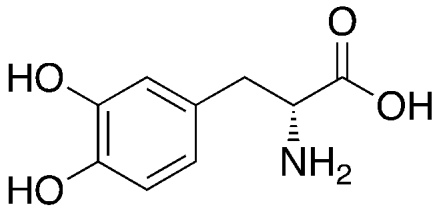
Reversibility

- HCl reverses the TM binding, but destroys polymer

Simulating a Tamper Event

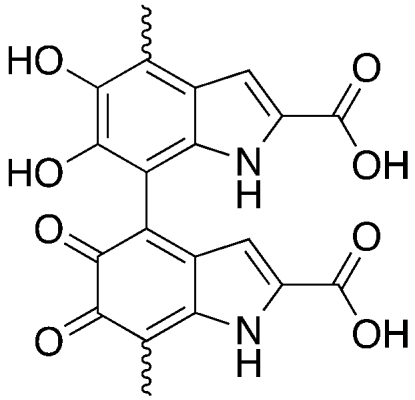


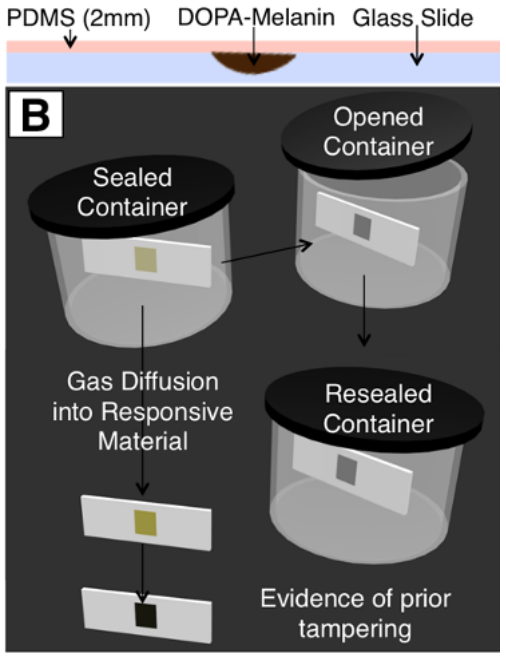
O_2-Sensitive Tamper Indicating Material



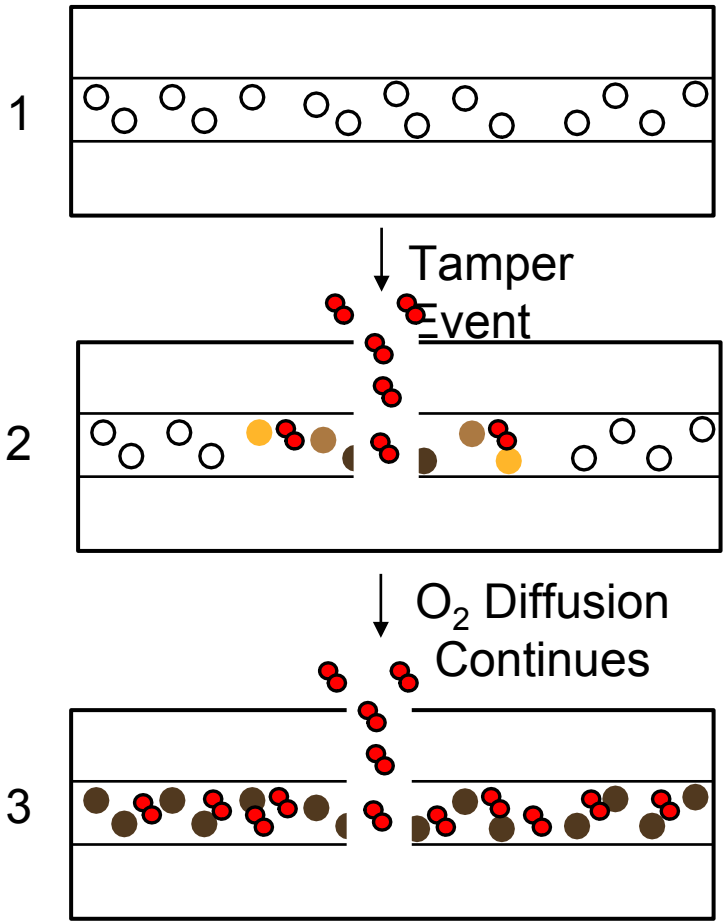
in KOH(aq)

O_2





Clear, Colorless Epoxy Top
Sealed, Clear, Colorless PDMS
Clear, Colorless Epoxy Base



PDMS Layer

- Permeable to oxygen
- Contains bubbles of aqueous L-DOPA/KOH
- Inherently contains unique identifiers

Epoxy Layers

- Minimally permeable to oxygen
- Seals PDMS layer & O_2 sensitive L-DOPA
- Tampering allows oxygen to flow into and diffuse through PDMS
- Inherently contains unique identifiers

ACS Appl. Mater. *Interfaces,* **2016**, 8, 4314−4317

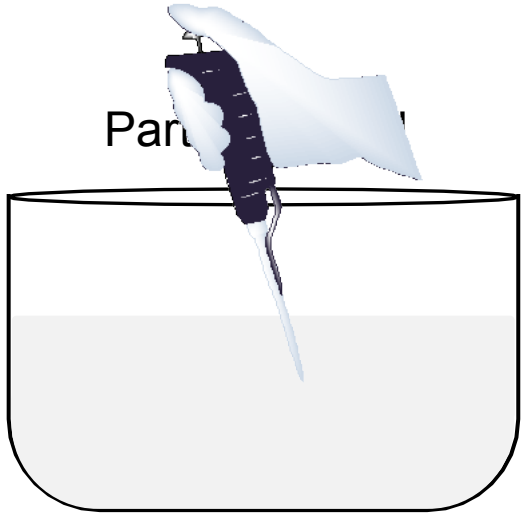
Preparation of 3-Layer System

Mixed PDMS (Sylgard 184)

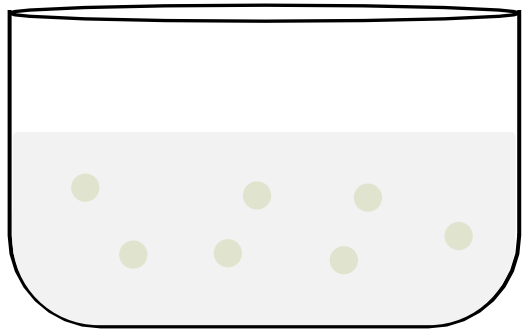
(PDMS components degassed in glovebox antechamber overnight)

60 °C

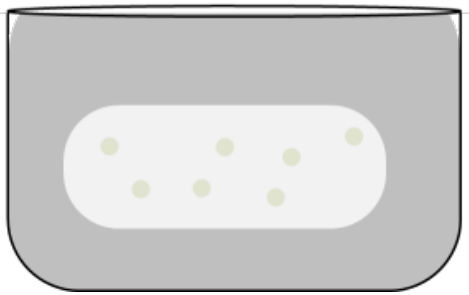
25 min



Addition of ~50 µL of L-DOPA to PDMS

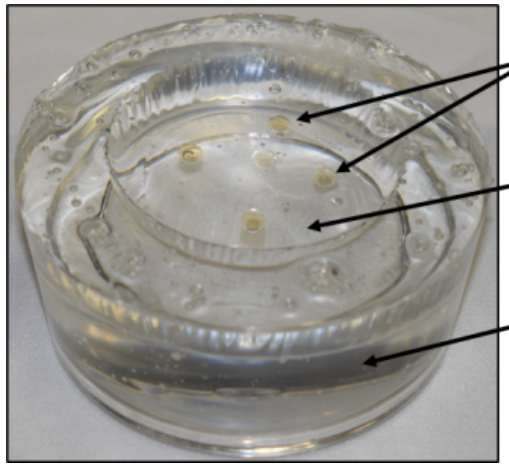


Allowed to fully cure in glovebo



Epoxy: Epon 828/Jeffamine T403

- Partially cured for 4 hours
- ½ material poured then PDMS was set on top
- Other half poured over

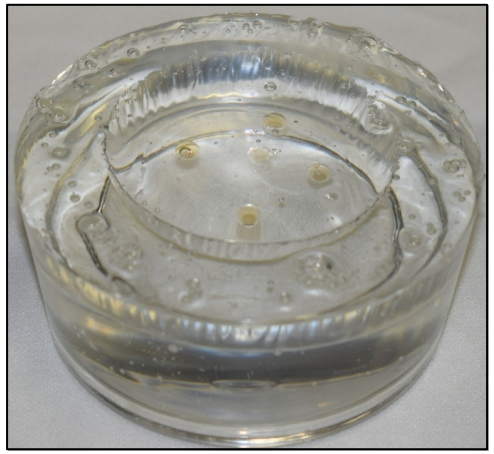


(Epoxy components degassed in glovebox antechamber over a weekend)

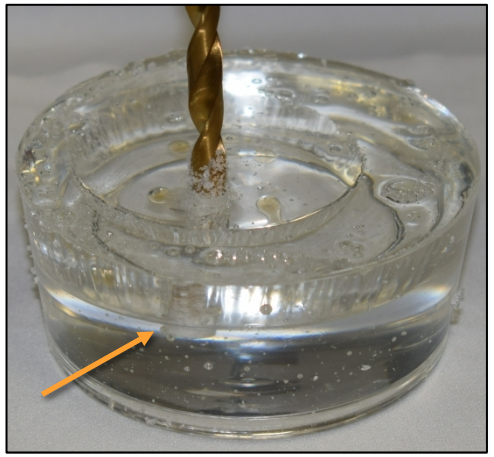
L-DOPA Tamper Event

Bubbles from mixing are inherent unique identifiers

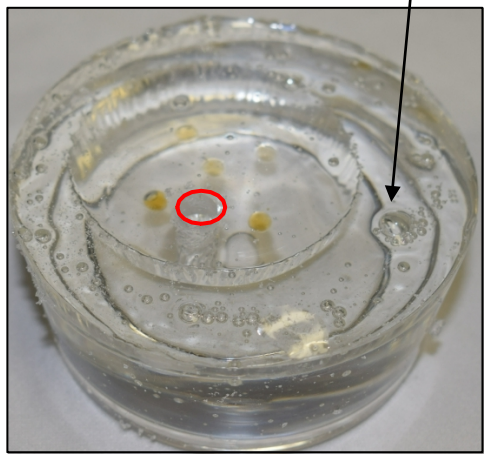
= tamper hole



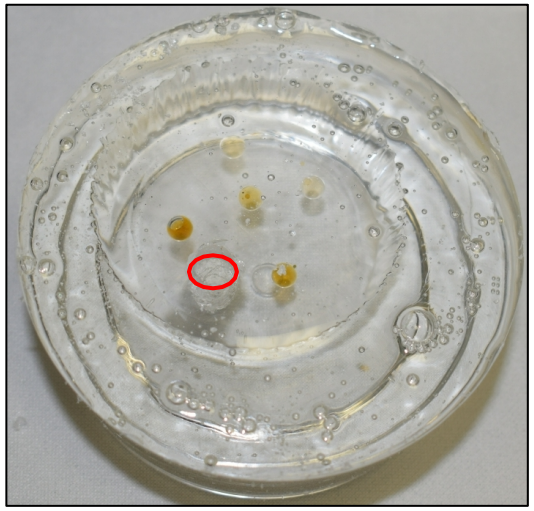
Before Tamper



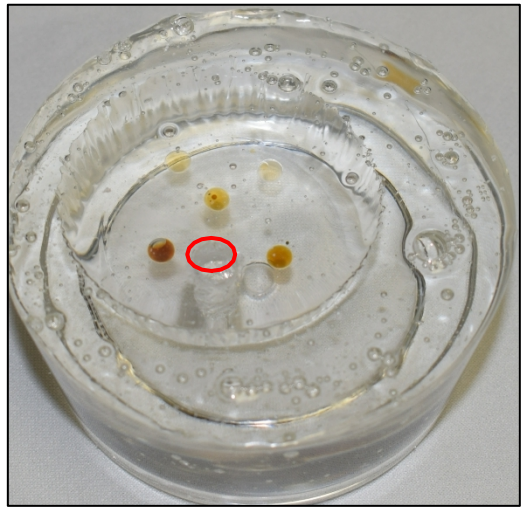
Tamper event introducing oxygen



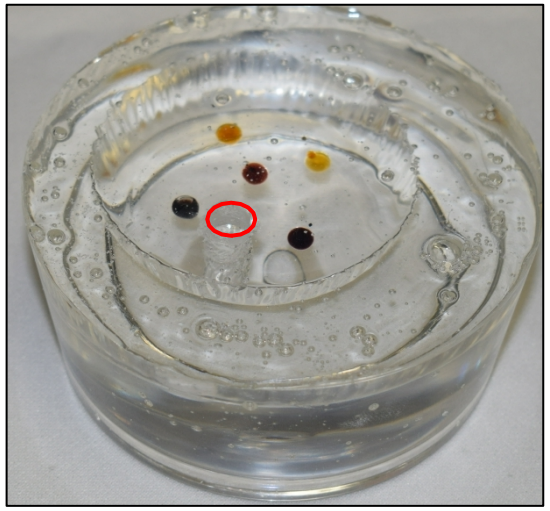
2 hours



4 hours



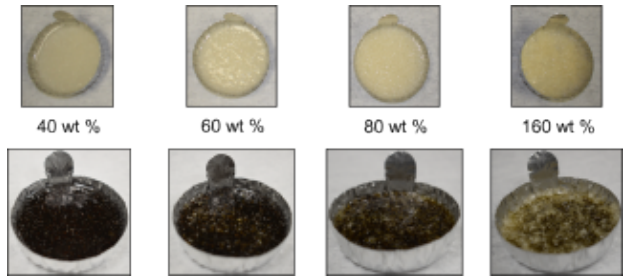
6 hours



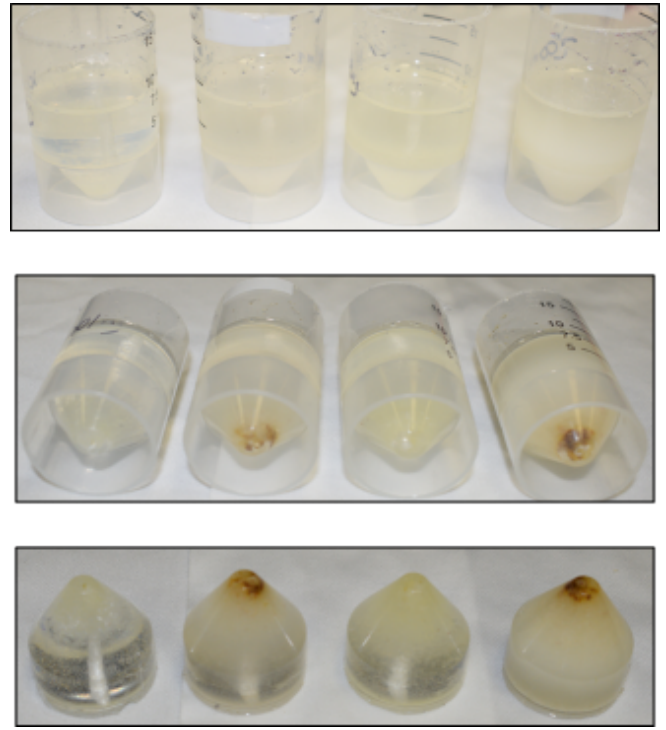
22 hours

Process Improvements

Polymer Substrate - Silicone



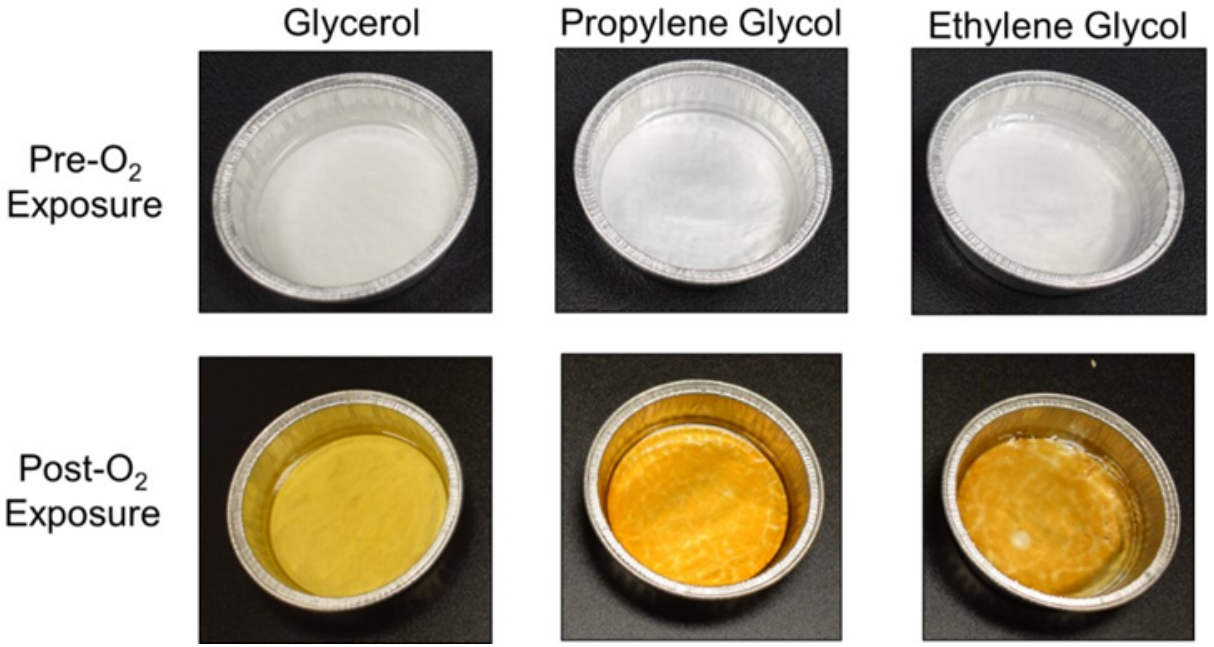
Polymer Substrate - Epoxy

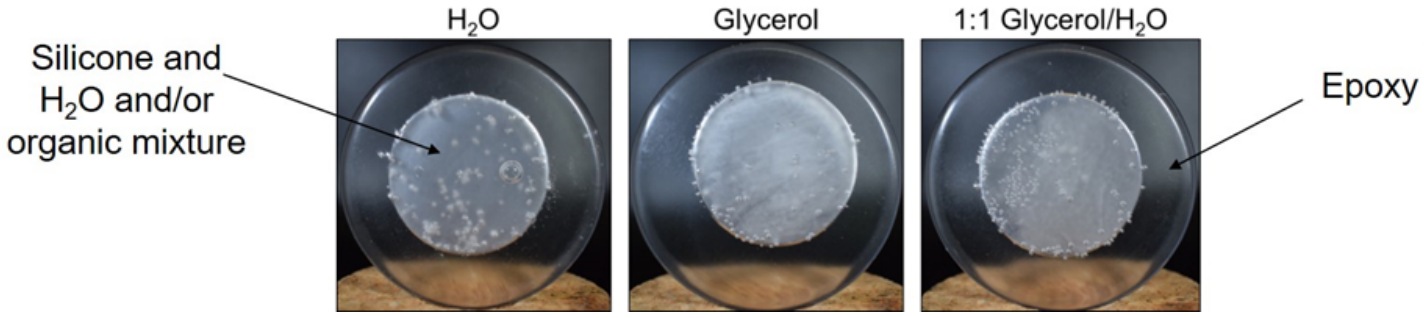


High-boiling Polyprotic Organics

Using high-boiling polyprotic solvents rather than water was expected to allow both L-DOPA and KOH solubility while expanding the temperature range at which these materials can be utilized.

- To test this, water was replaced with;
  - Glycerol (T_b = 290 °C, T_f = 18 °C)
  - Propylene glycol (T_b = 187 °C, T_f = -60 °C)
  - Ethylene glycol (T_b = 197 °C, T_f = -13 °C

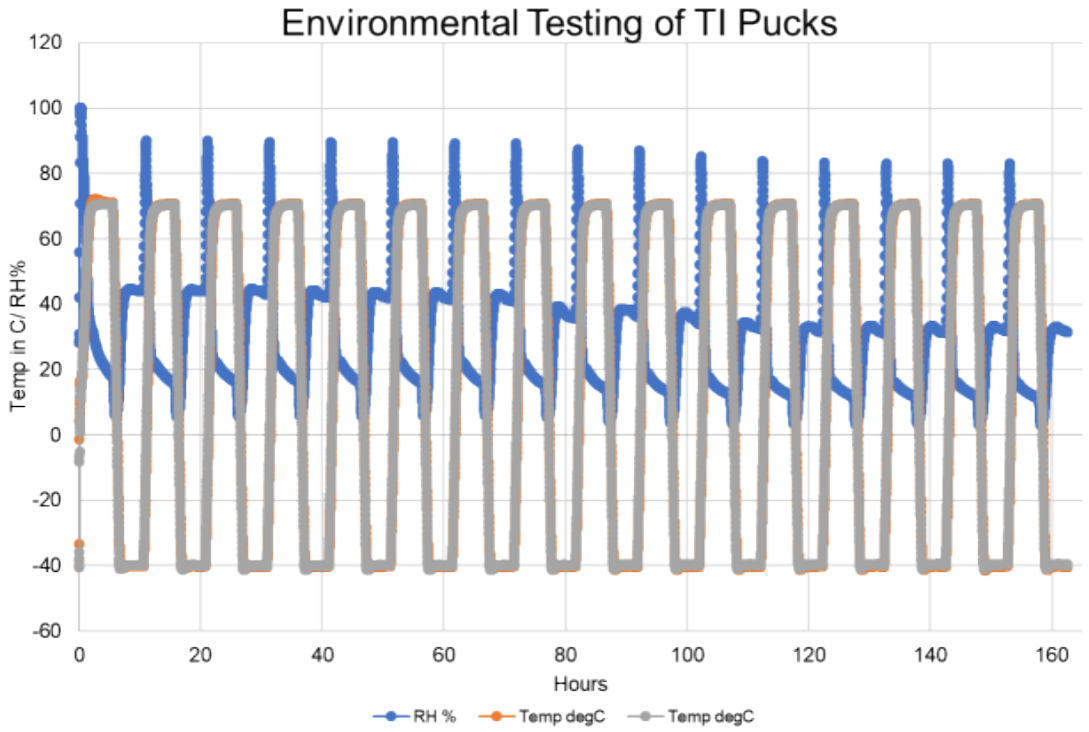




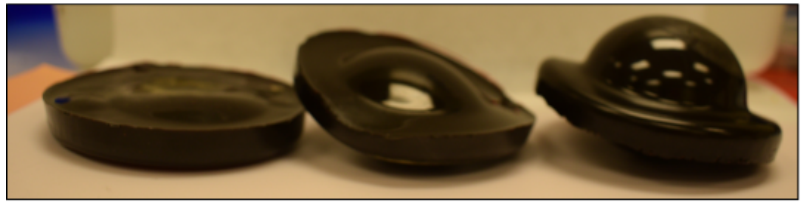
Once pure organic solvents were proven with the same O_2 mechanism established with H_2O, the final solvent experiments had relevant combinations of H_2O and polyprotic organics to yield a balance of solubility and thermal properties

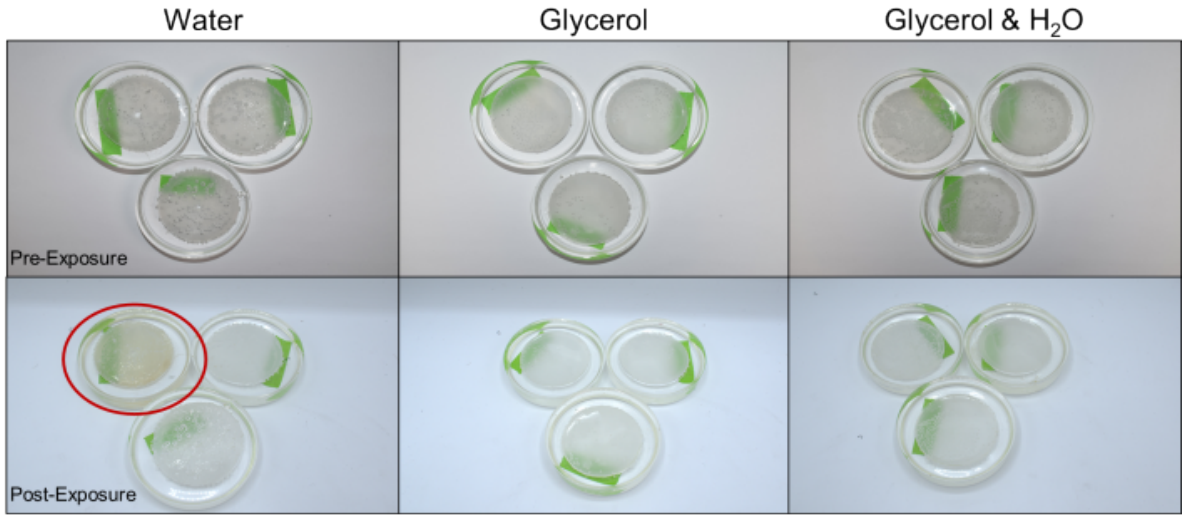
Bubbles formed during processing lead to inherent areas that would be difficult to replicate

Thermal Cycling and Gamma Irradiation of Coupons



^{60}Co Gamma Irradiated – Dose Rate = 641.4 rads/s - 190 hours





L-DOPA solution absorbed by beads & placed in Sylgard/Epoxy

Acknowledgements

Collaborators

Heidi Smartt – PI of project

Matt Humphries– Postdoc (now SNL staff)

Annabelle Benin

Patrick Feng

Amanda Jones

Nicholas Myllenbeck

Jason Livesay

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National Nuclear Security Administration
Office of Defense Nuclear Nonproliferation