SAND2019-10333PE

Tamper-Indicating Enclosures with Visually Obvious Tamper-Response: Sensor Synthesis Strategies

PRESENTED BY

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Overview

Desired polymer matrix characteristics

- Crosslinked
- Easily processed (3-D Printed, spray coated, mold cured)

Desired sensor characteristics

- Compatible with polymer matrix
- Dramatically changes color with tamper event
- Irreversible

Systems Tested

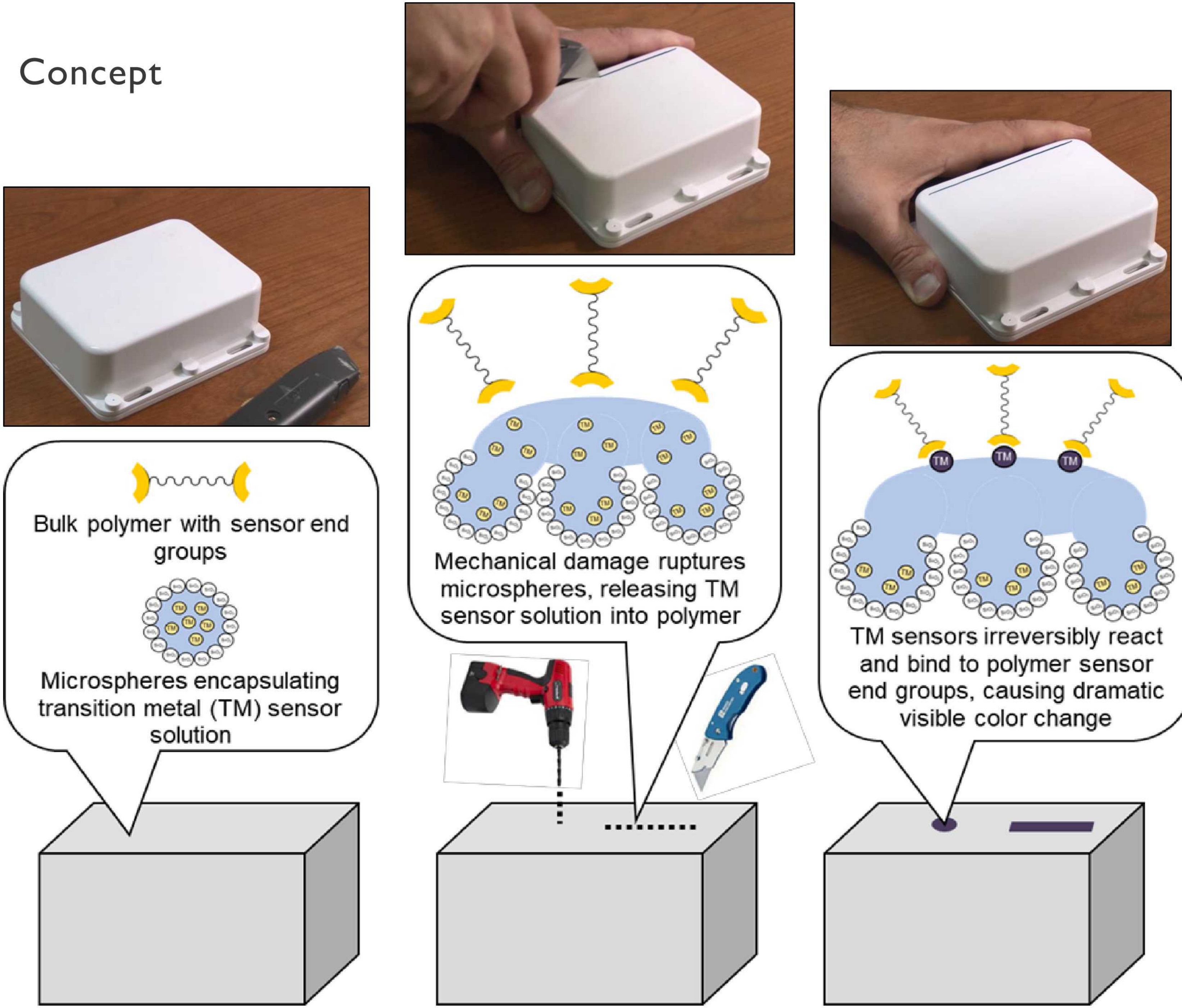
Heat/UV curable crosslinked polymer

- Sensor easily incorporated
- Simple to modify
- Cheap
- Weak to moderate color change

L-DOPA O_2 sensing spheres

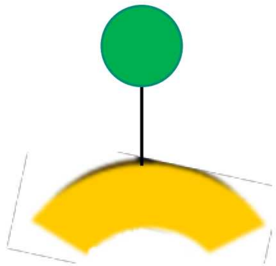
- Cheap COTS materials only
- Sensitive to O_2
- Dramatic color change
- Difficult processing – inert environment required

Concept

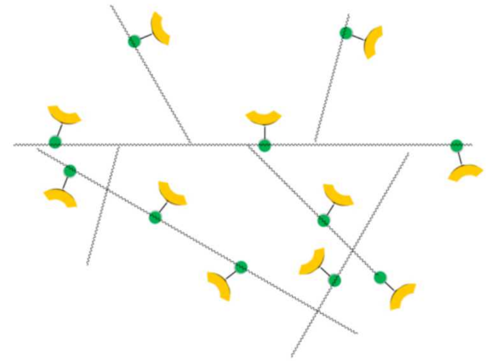

Bulk polymer with sensor end groups
Microspheres encapsulating transition metal (TM) sensor solution
Mechanical damage ruptures microspheres, releasing TM sensor solution into polymer
TM sensors irreversibly react and bind to polymer sensor end groups, causing dramatic visible color change

Sensors

General schematic

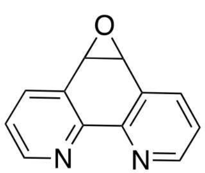


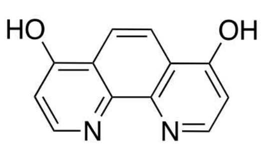
Sensor molecule



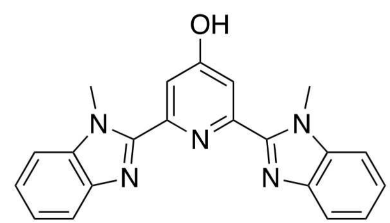
Cross-linked sensing polymer

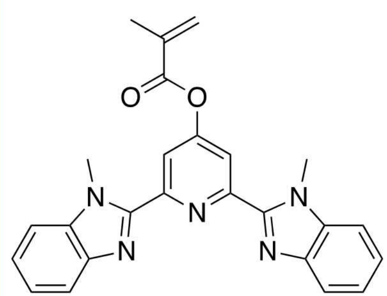
Commercially Available

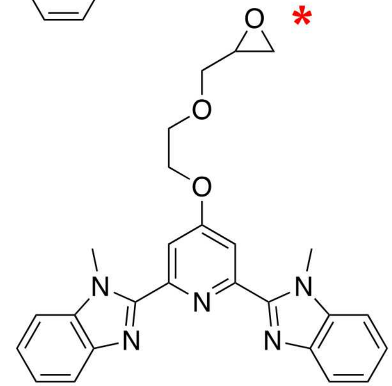




Synthesized







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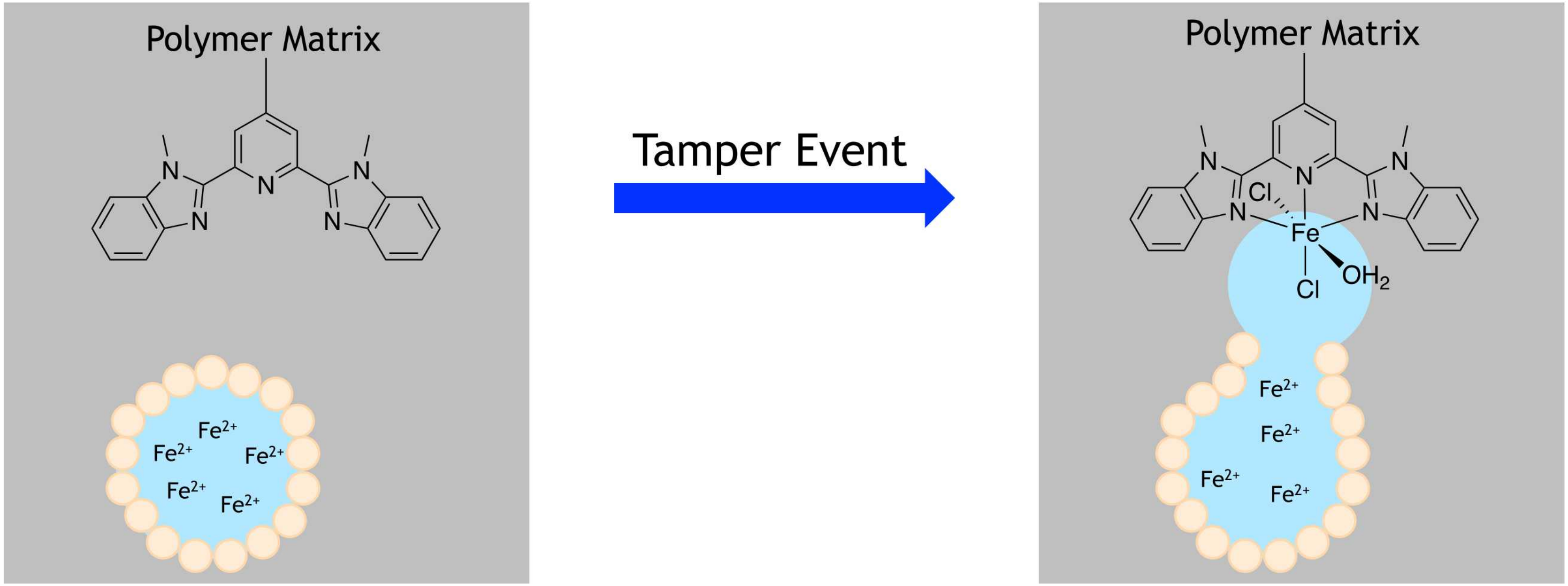
* Planned

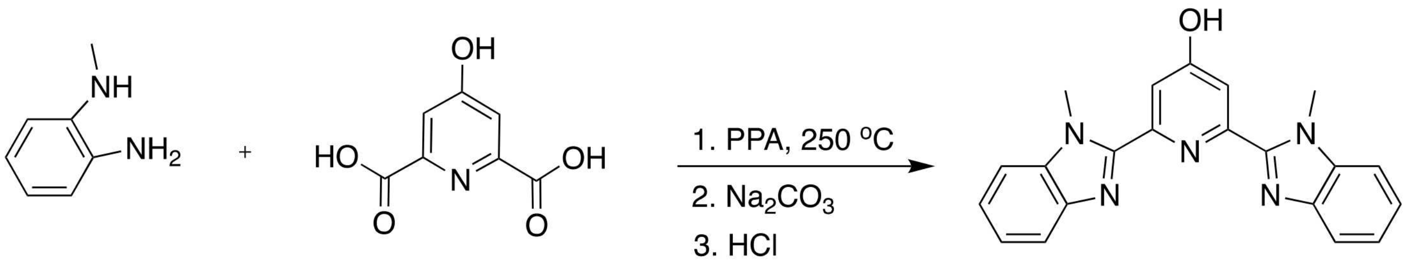
Transition Metal Complexes with Sensor



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

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

Investigation of Transition Metal Salts and Sensors

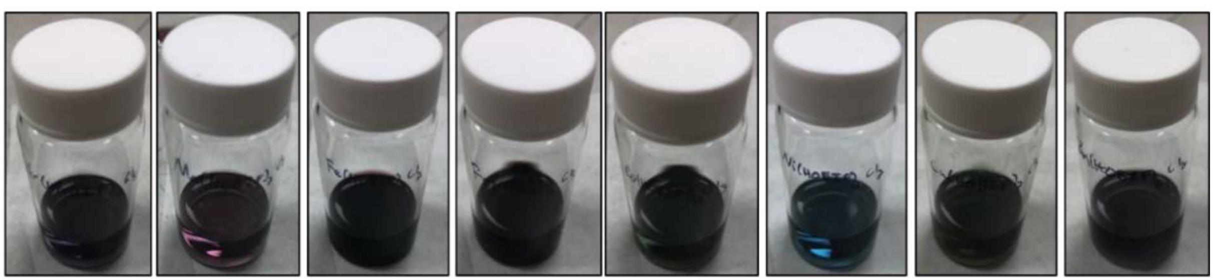


Largy, E. et. al. Chem. Eur. J. **2011**, *17*, 13274.

Sensor

- HO-BIP – synthesized
- Produces purple solution

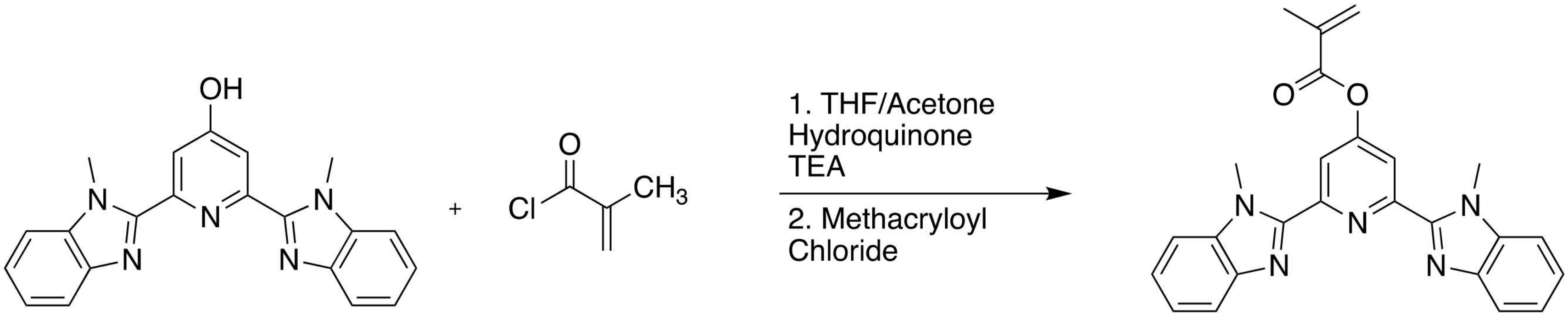
Cr^{3+} Mn^{2+} Fe^{2+} Fe^{3+} Co^{2+} Ni^{2+} Cu^{2+} Zn^{2+}



Sensor + TM

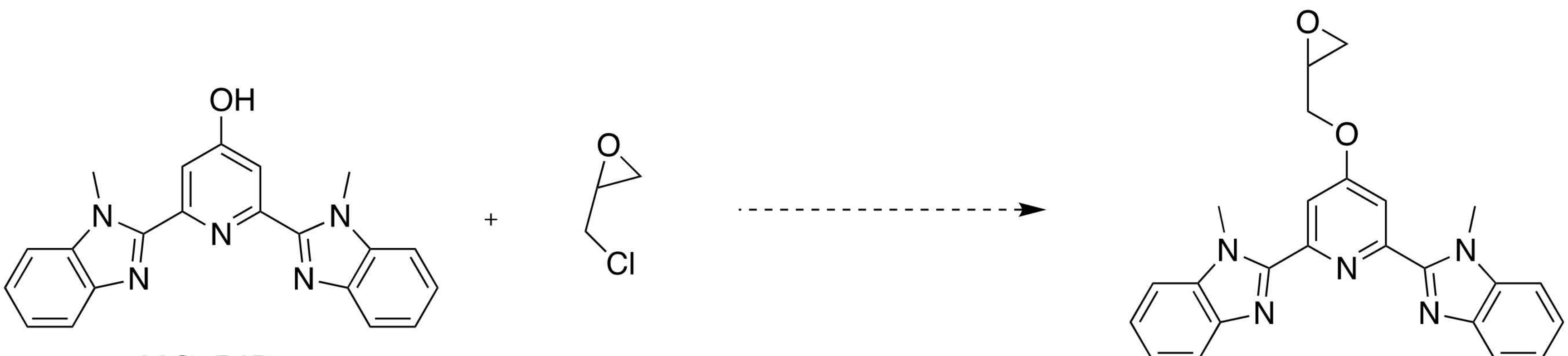
- 1 – 3 mg/mL Metal Chloride Solutions
- Much more dramatic color changes
  - Colored sensor
  - Stronger sensor-transition metal interaction

Sensor Synthesis



HO-BIP

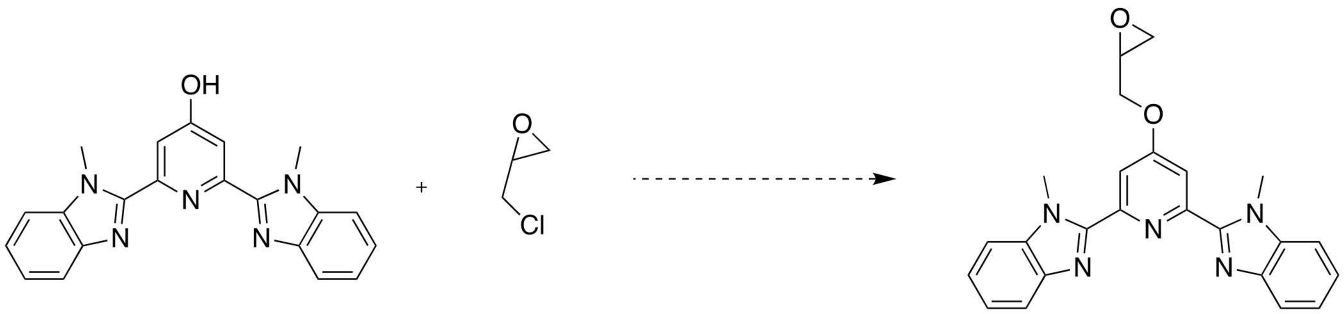
Krieger, G.; Tieke, B. Macromol. Chem. Phys. **2017**, *218*, 1700052.



HO-BIP

Only ~5% yield

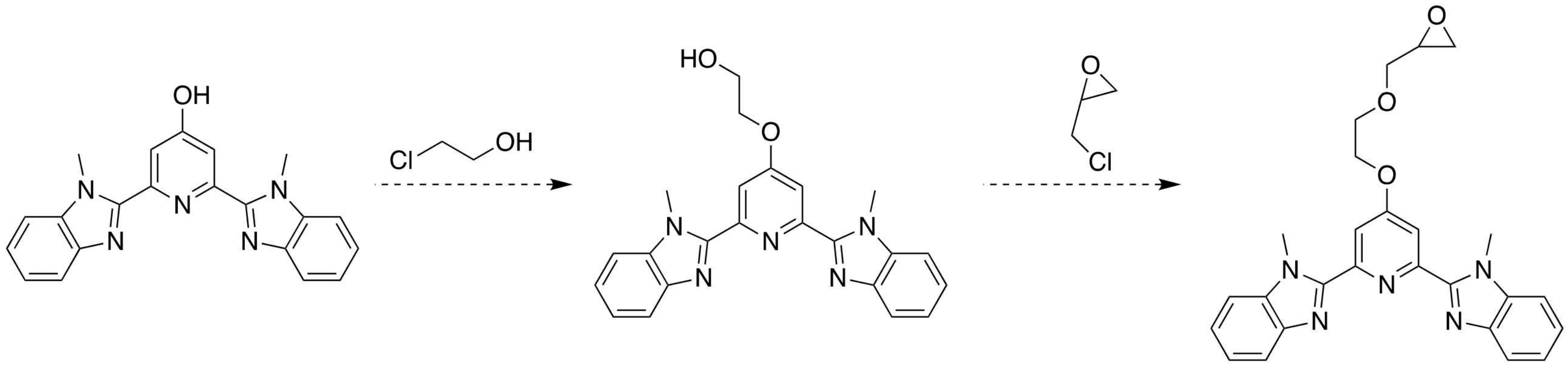
Future Epoxide Syntheses



Only ~5% yield

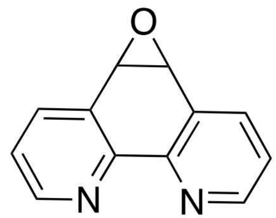
- Solvent, concentration, and temperature were varied with no increase in yield
- Alcohol may not be nucleophilic enough
- Oxygen part of the conjugation into the ring

New route extends the epoxide away from the aromatic ring



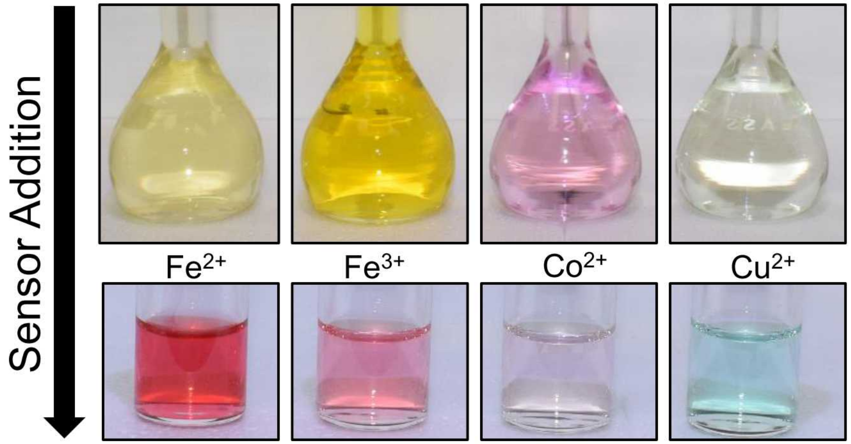
Investigation of Transition Metal Salts and Sensors

Sensor
- Commercially available phenanthroline

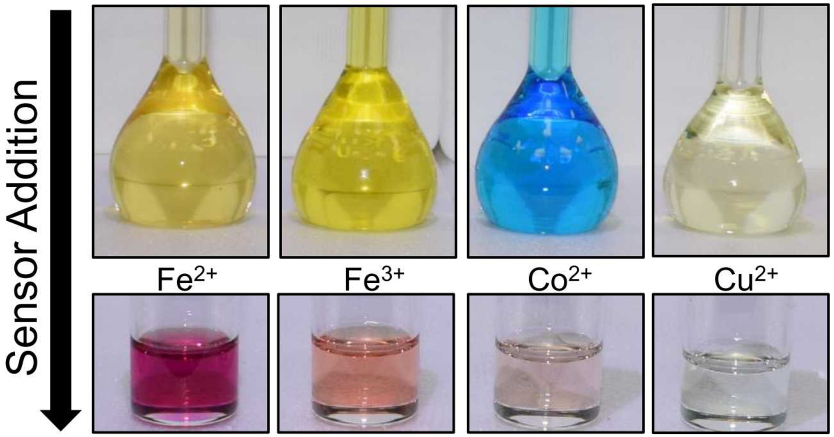


Colorless Sensor Solution

Solutions in Methanol

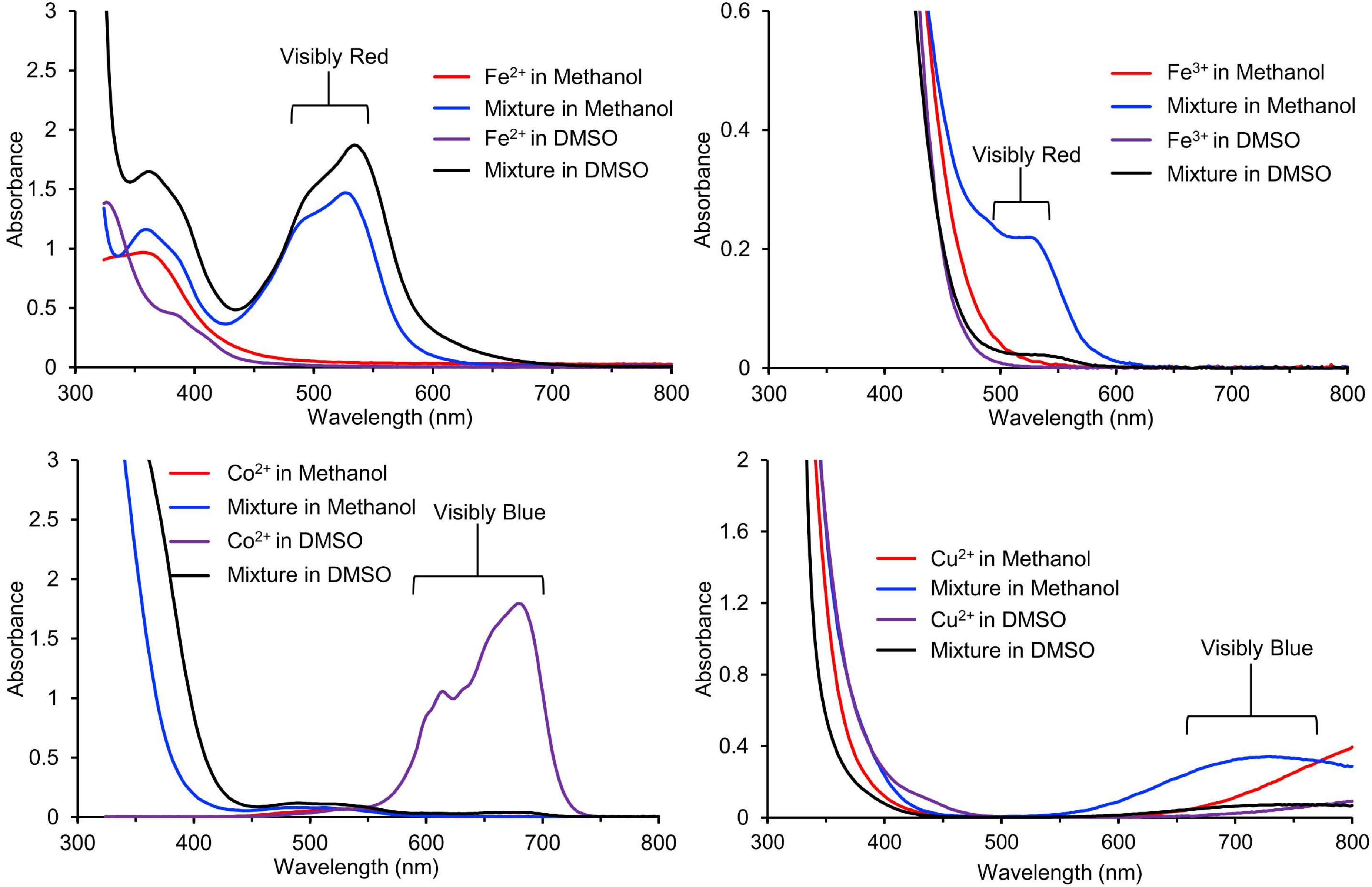


Solutions in DMSO

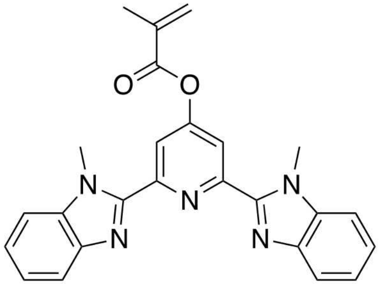


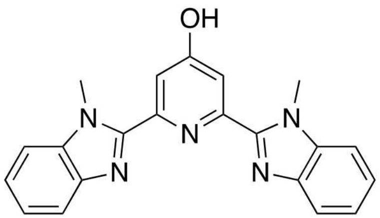
- 1– 3 mg/mL Metal Chloride Solutions; 1:1 ratio of TM to sensor
- Fe^{2+} yields the most dramatic color change, but it is prone to oxidation

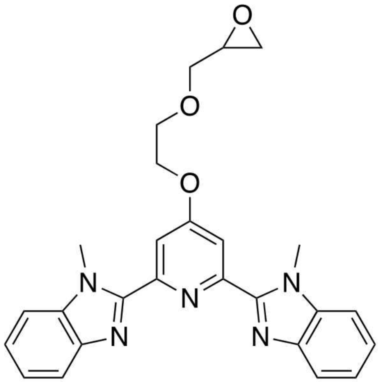
Investigation of Transition Metal Salts and Sensors



Methods for Sensor Linkage to Polymer







Acrylate
for spray coating/molding

Progress

- HEMA:PEGDA; 25:75 system works best - heat & UV curable

Urethane
for spray coating/molding

Progress

- EN4/EN7 with sensor

Control

w/Sensor

Epoxy
for molding

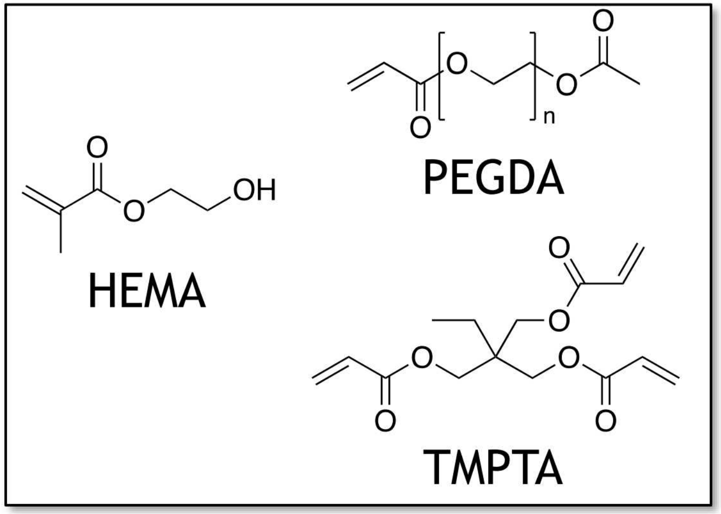
Progress

- Sensor synthesis ongoing
- 828/T403 – viable epoxy system

Polymer Systems

3 polymer systems and their random copolymers were cured

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



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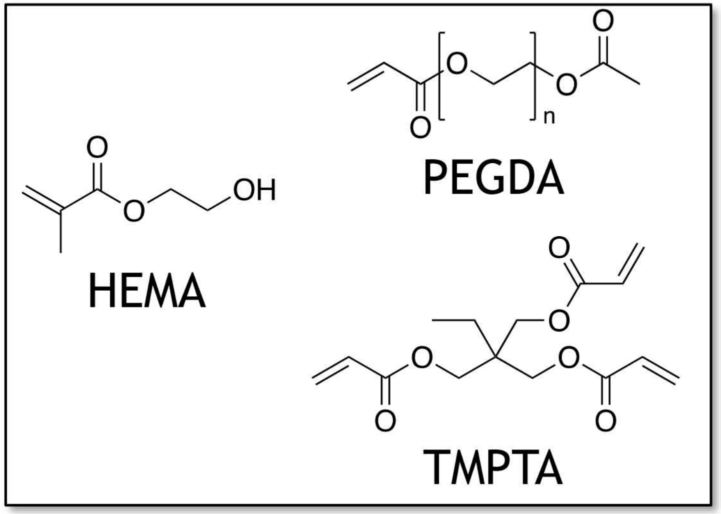
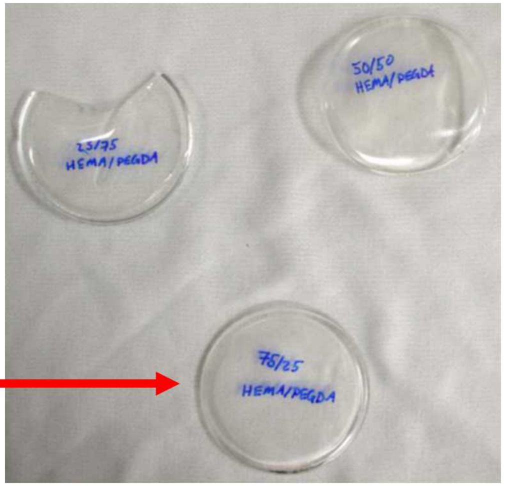


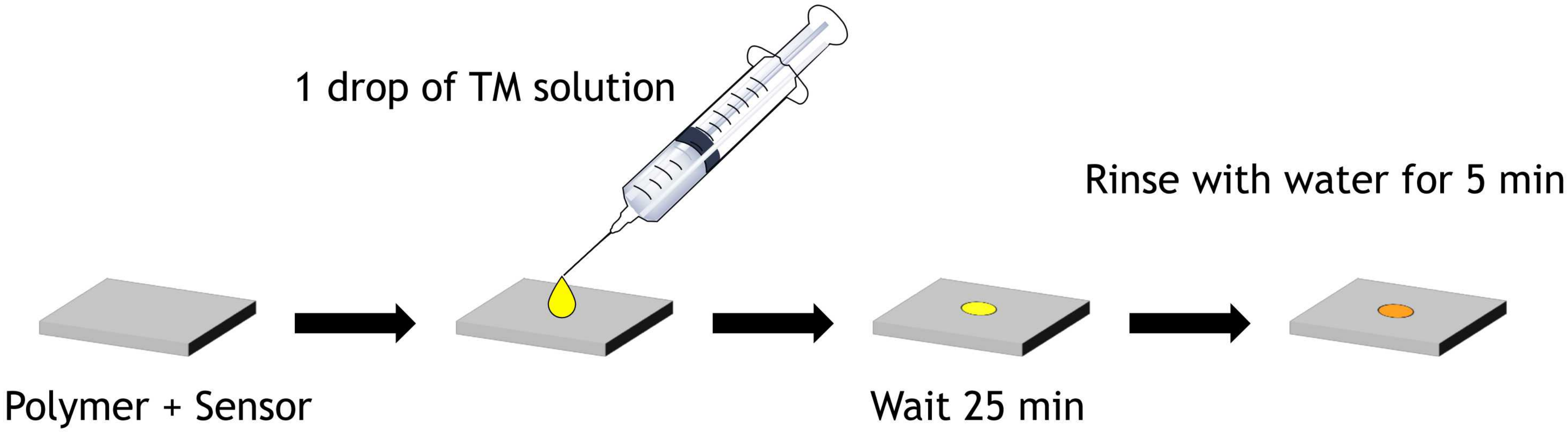
Mixtures of 25/75, 50/50, 75/25

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

Chosen Mixture: 75/25 HEMA/PEGDA



Simulating a Tamper Event



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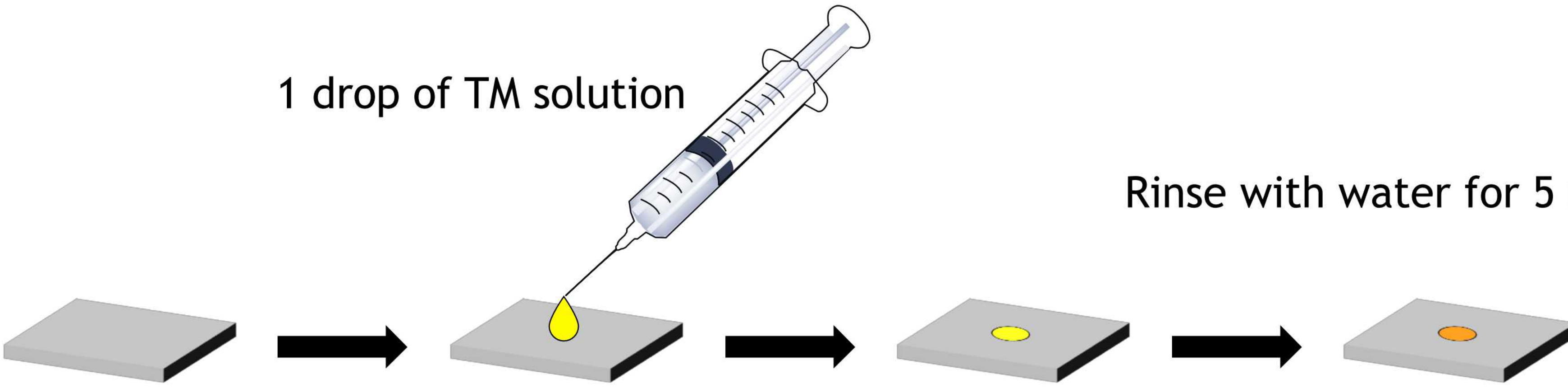
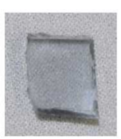
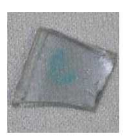


Concentration

	0.01 M	0.1 M	0.2 M
$FeCl_2$			
$CoCl_2$			

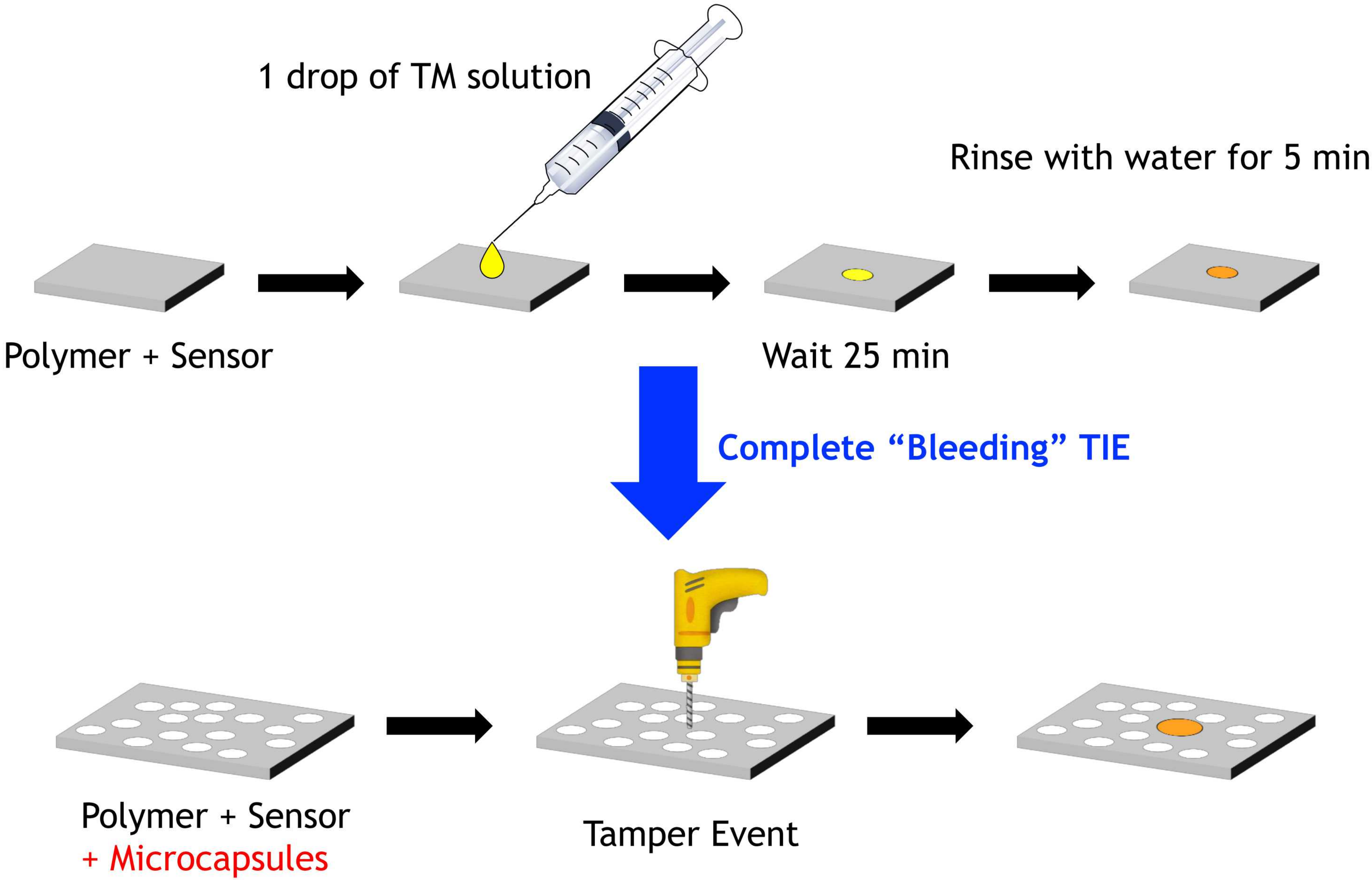
Conclusions

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

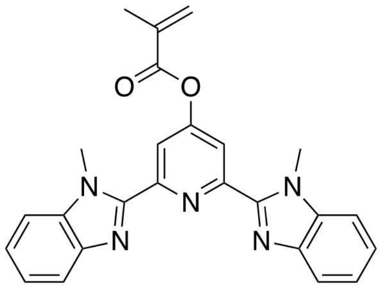
Reversibility

- HCl reverses the TM binding, but destroys polymer

Simulating a Tamper Event



Summary of Sensors



Acrylate
for spray coating/molding

Progress

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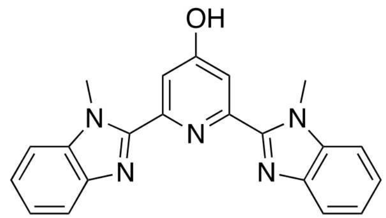
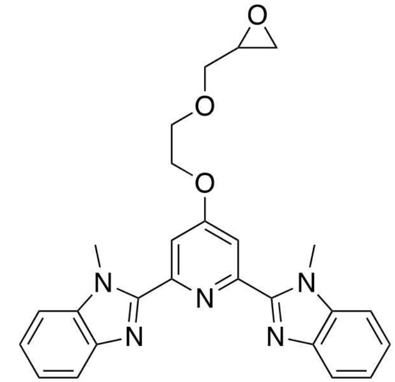


Polyurethane
for spray coating/molding

Progress

- EN4/EN7 with sensor



Epoxy
for molding

Progress

- Sensor synthesis ongoing
- 828/T403 – viable epoxy system

Difficulties & Ongoing Work

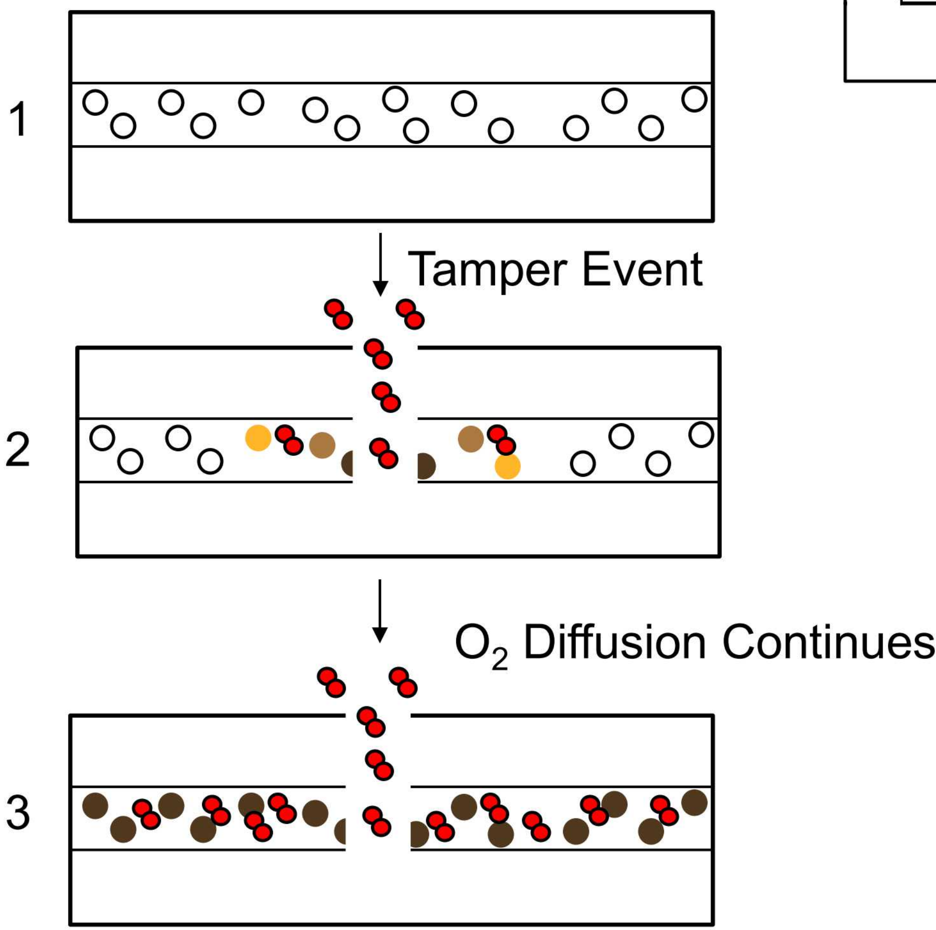
Solubility:

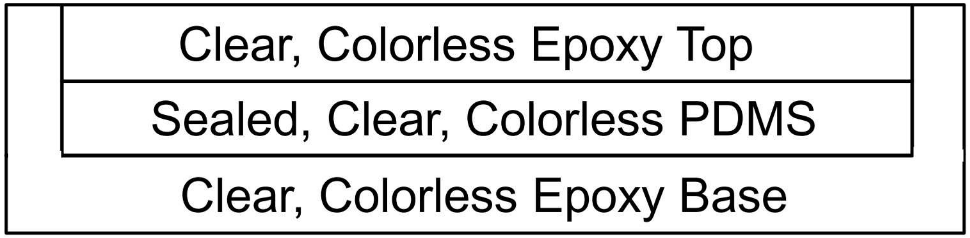
- Sensor in solvent
  - Commercial sensors and HO-BIP have low solubility
- Sensor in polymer systems
  - Max solubility of HO-BIP in PEGDA/HEMA is 0.3 wt. %
  - Poor solubility of HO-BIP in polyurethane systems
    - HO-BIP had to be dissolved overnight in polyol (EN7)

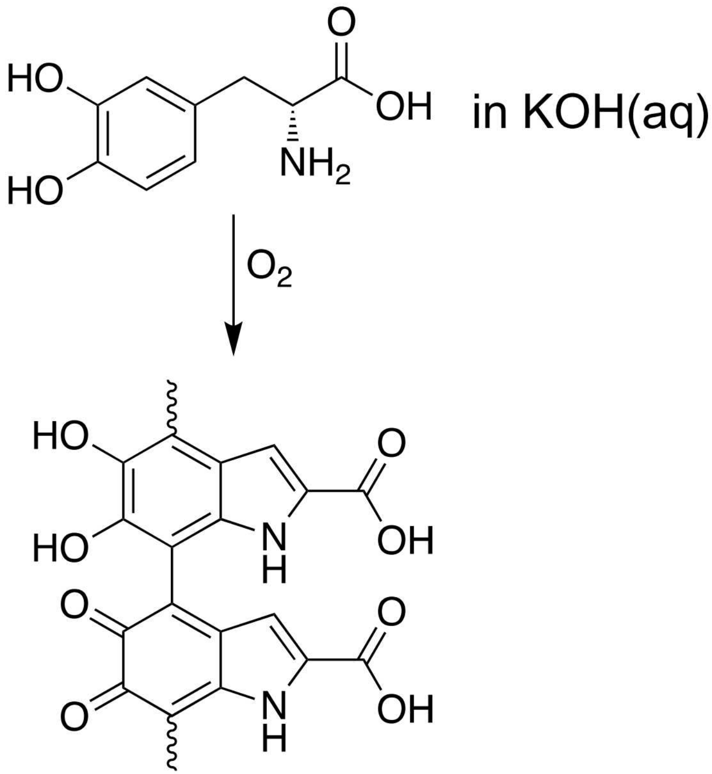
Syntheses:

- Epoxide derivative of HO-BIP low yielding & difficult to purify
- Epoxide derivatives of phenanthroline have yielded no conversion

O_2 Sensitive Tamper Indicating Material

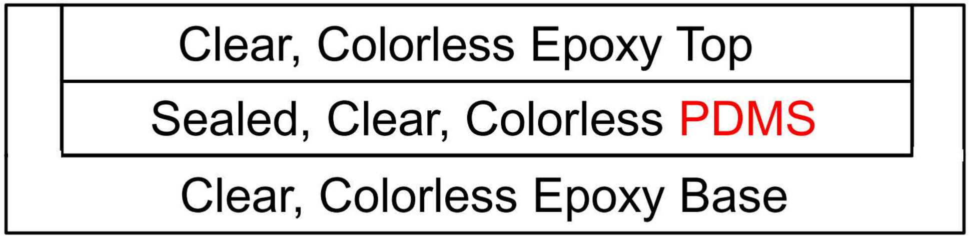






ACS Appl. Mater. *Interfaces,* **2016**, 8, 4314–4317

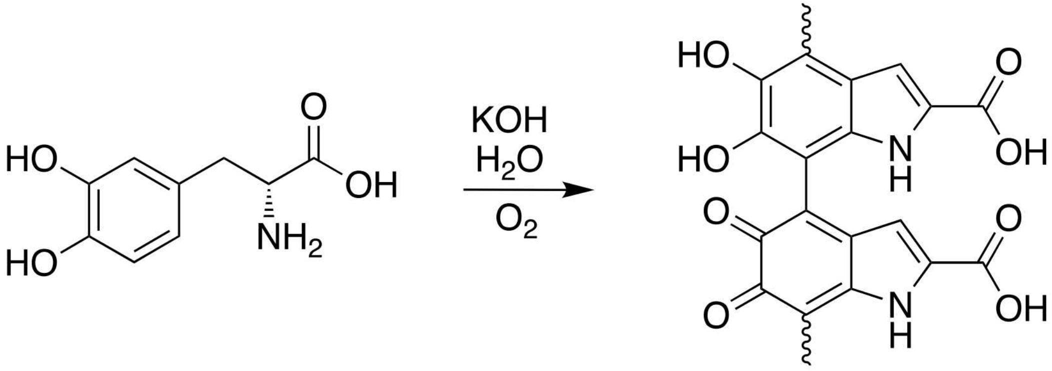
L-DOPA 3-Layer System Concept



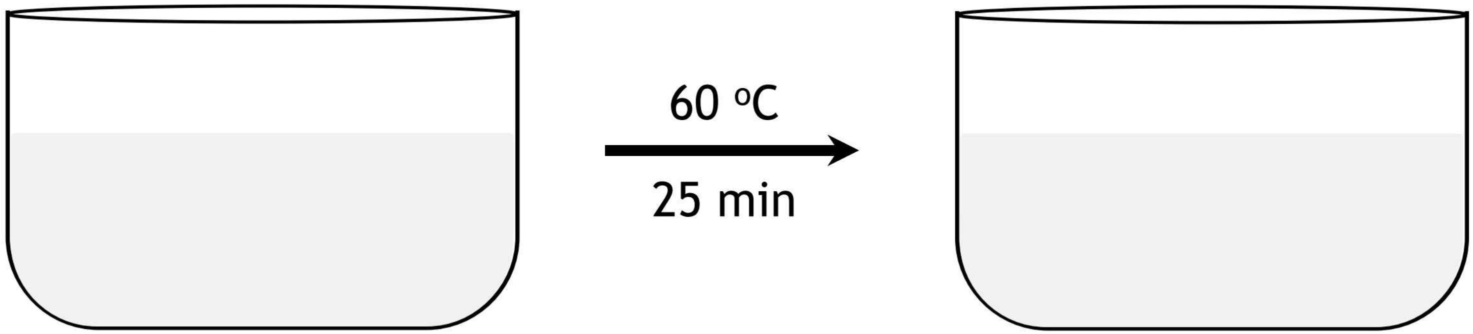
3-Layer Thermoset System
- Top and bottom: **epoxy**
- Center: **PDMS**

PDMS Layer
- Permeable to oxygen
- Contains bubbles of aqueous L-DOPA/KOH

Epoxy Layers
- Minimally permeable to oxygen
- Seals PDMS layer & O_2 sensitive L-DOPA
- Tampering allows oxygen to flow into and diffuse through PDMS



Preparation of 3-Layer System



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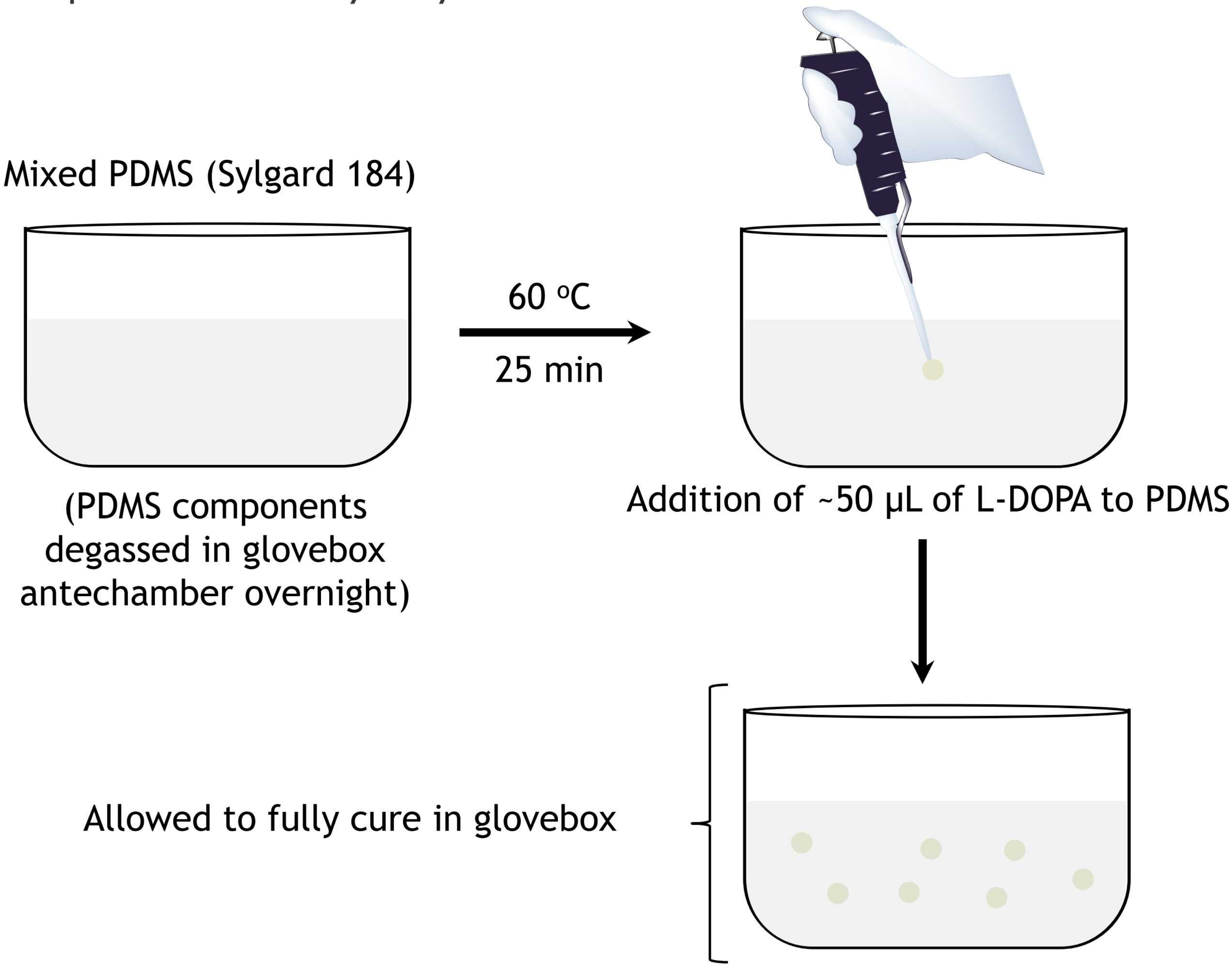

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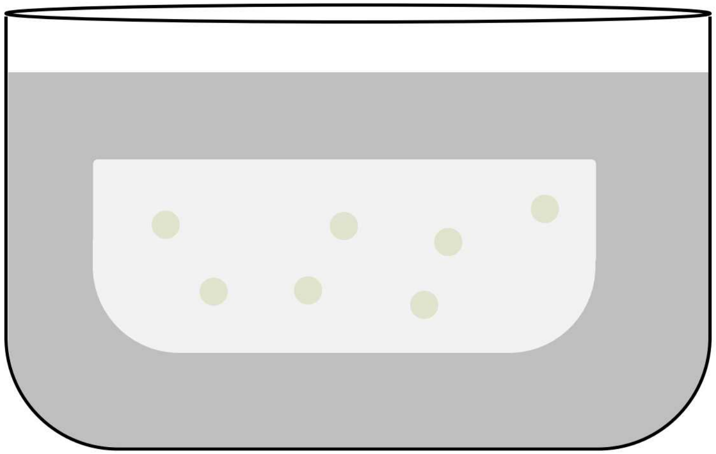

Epoxy: Epon 828/Jeffamine T403

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

(Epoxy components degassed in glovebox antechamber over a weekend)

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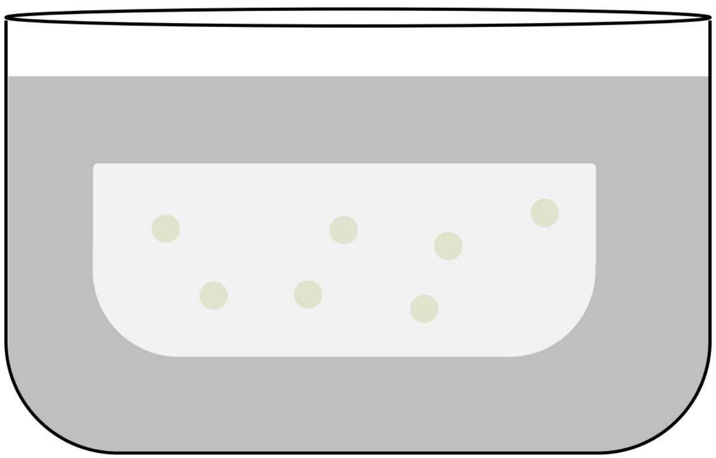

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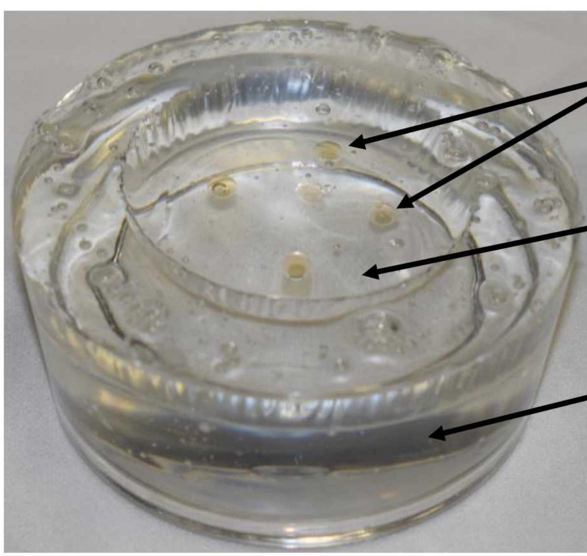
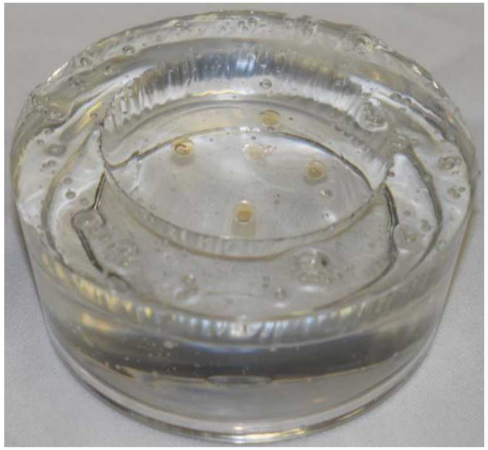


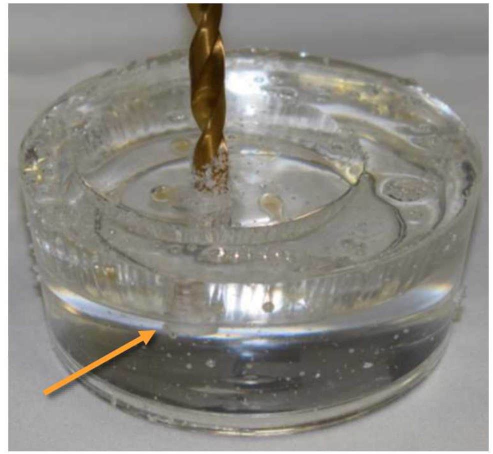
(Epoxy components degassed in glovebox antechamber over a weekend)

L-DOPA Tamper Event

⭕ = tamper hole



Before Tamper



Tamper event introducing oxygen

2 hours

4 hours

6 hours

22 hours

Ongoing Work/Future Directions

- How do we disperse L-DOPA bubbles more easily?
  - Current method requires physically distributing each bubble
  - Can L-DOPA be simply mixed in to PDMS?
- Can we decrease processing time? Is there a way to batch process?
- Can L-DOPA be formed into a thin film?