Evaluation of polymer-penetrant interactions to elucidate contaminant uptake and retention in polymer coatings

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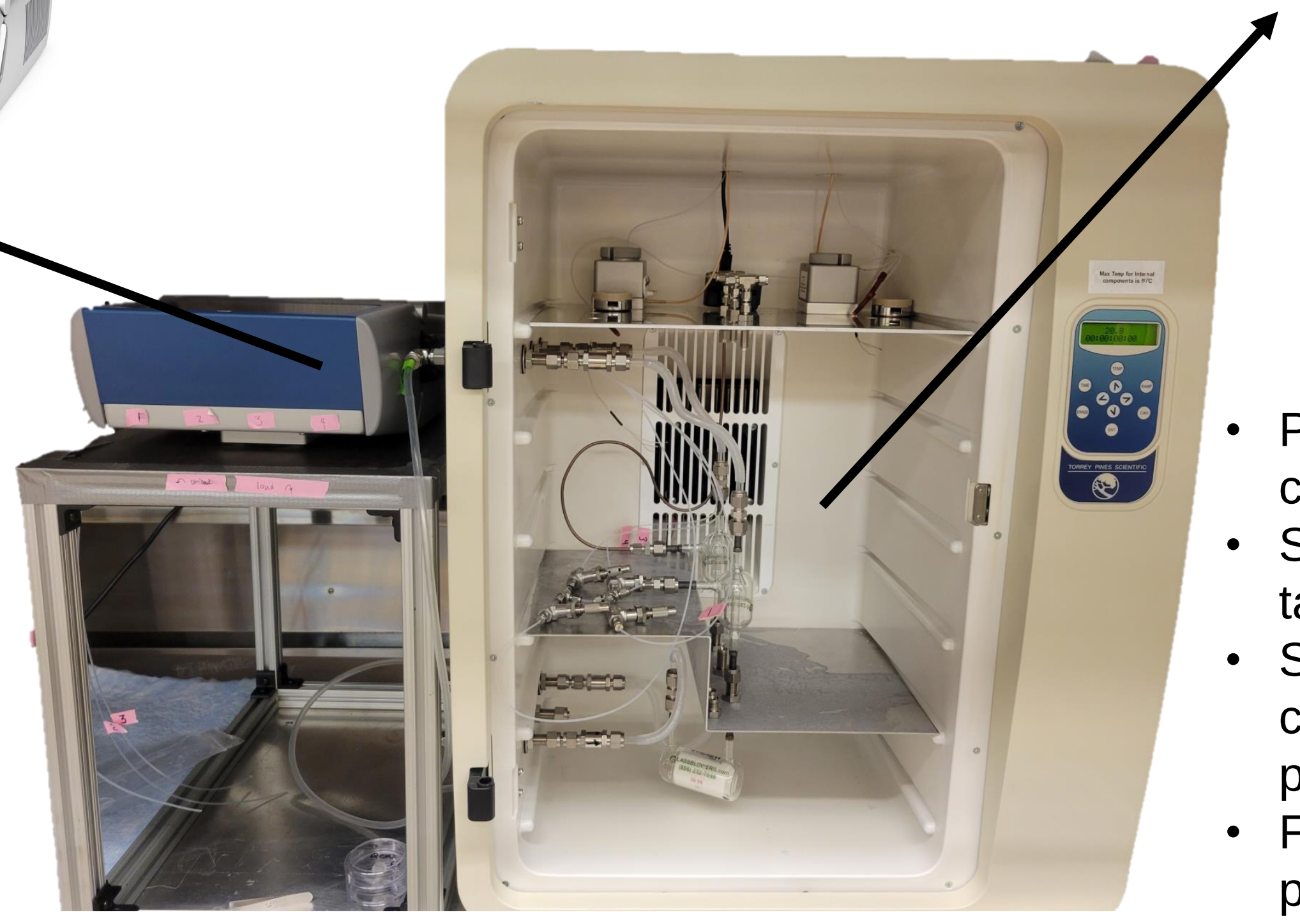
Instrumentation and Innovations



Quartz Crystal Microbalance with Dissipation

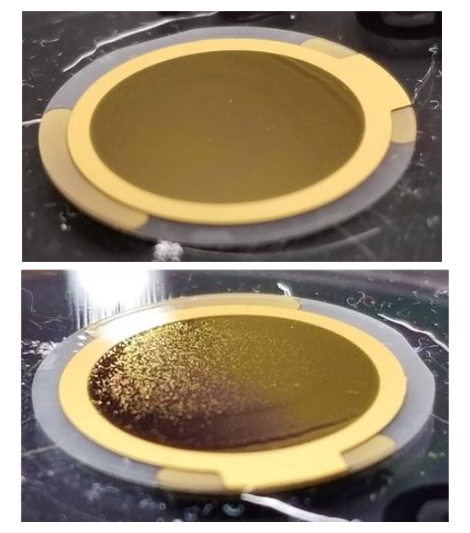
- Evaluation of mechanical properties of polymers and solvents (e.g., protective coatings / polymeric films)
- QCM: measurement of mass uptake of thin films (<1 μm)
- QCM-D: evaluation of mechanical properties of thicker films (<10 μm)
- Common use: evaluation of polymer and liquid penetrant

CHALLENGE: MODIFY FOR USE WITH VAPOR EXPOSURES

Vapor Saturation and Mixing Manifold

- Pure N_2 enters saturator cell (bottom right)
- Saturator cell: N_2 flows over target penetrant 3x
- Saturated N_2 enters mixing chamber (right), mixes with pure N_2
- Flows of saturated N_2 and pure N2 manipulated for desired penetrant concentration
- After mixing, vapor exists thermal enclosure to QCM-D

Polymer Film Formulation



- Gold-coated crystals 14 mm diameter
- Evaluation of controllable parameters (relative humidity, polymer concentration in solvent, solvent selection and evaporation rate, cure conditions, cure time length
- For mass uptake: film thickness target is ~100 nm
- For mechanical properties: film thickness target is >1 μm
- Spin casting parameters: spin rate, spin ramp rate, cure in situ or elsewhere

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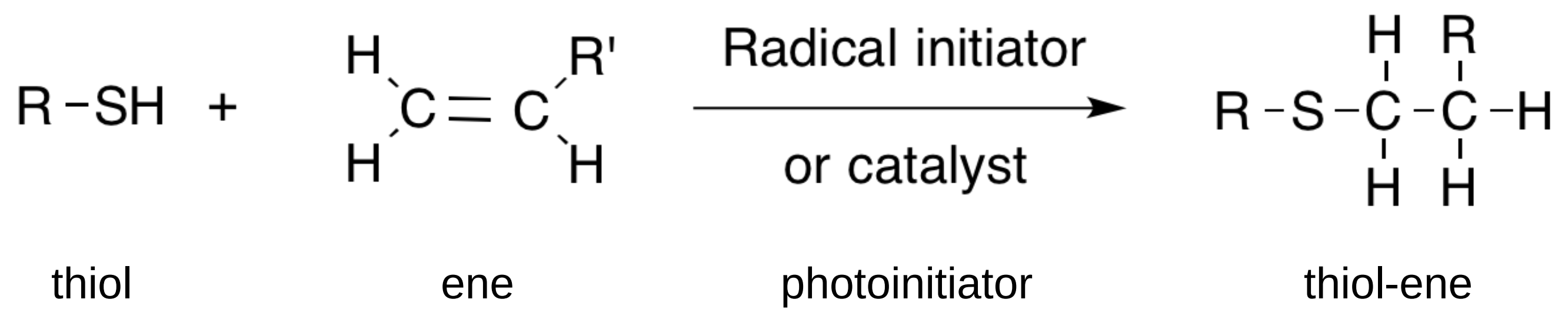
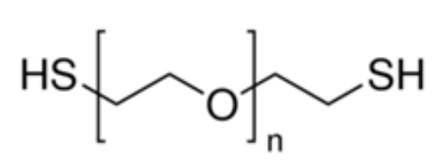
Polymer Platform Selection

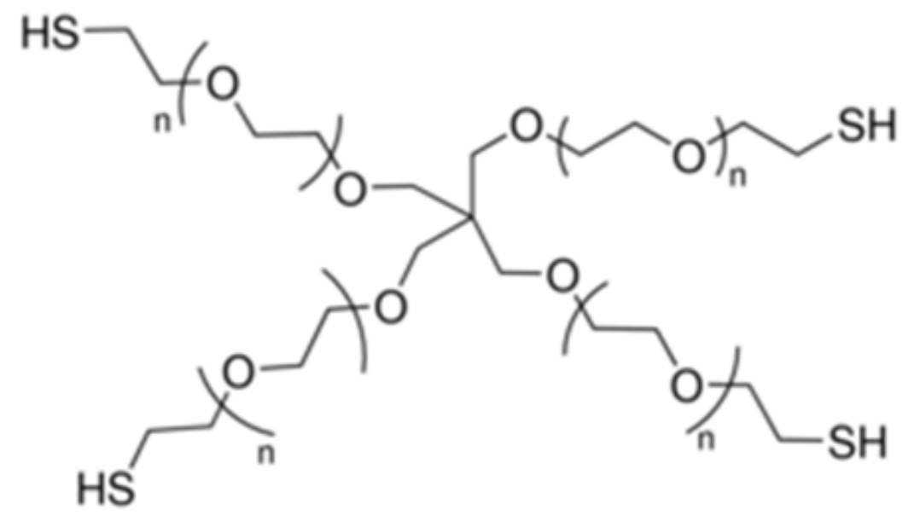
- Thiol-ene chemistry ("click chemistry")
- Highly tunable
- Easy formulation and spin casting
- Base materials widely available
- Thiols and enes added in 1:1 stoichiometric ratio with ~0.01-0.10 wt% photoinitiator.



$$\mathrm{R{-}SH} + \mathrm{H_2C{=}CHR'} \xrightarrow[\text{or catalyst}]{\text{Radical initiator}} \mathrm{R{-}S{-}CH_2{-}CHR{-}H}$$

Thiol and Ene Selection



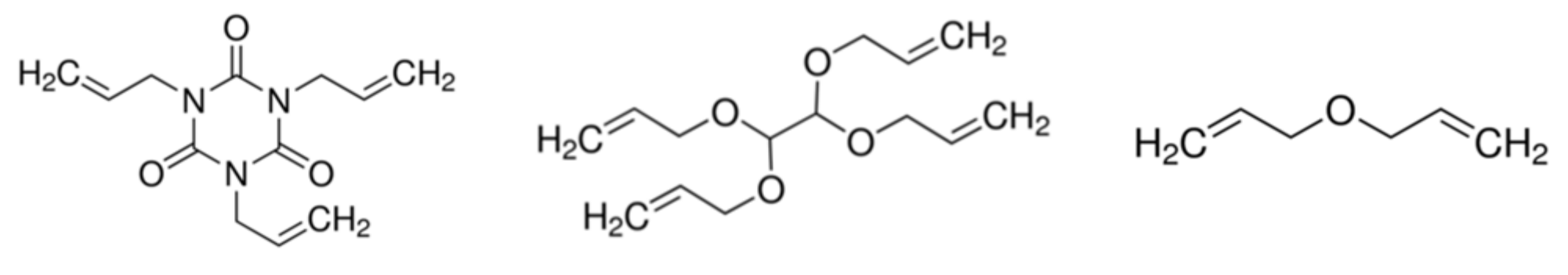


THIOLS

- Poly(ethylene glycol) dithiol (PEG dithiol) with average Mn = 1000, 3400, and 8000 g/mol (shown left).
- For increased heterogeneity, consider 4-arm PEG dithiols (Mn = 5000, 10,000, and 20,000 g/mol), as shown (right).

ENES

- initial choices for cross-linker:
  - 1,3,5-triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (3T)
  - glyoxal bis(diallyl acetal) (4T)
  - Optional: allyl ether (AE)
- Solvents chosen to increase heterogeneity based on number of crosslinking 'ene' locations.



Crosslinkers:3T (left), 4T (middle), and AE (right).

Solvents Selection

Objectives to evaluate:

1. Impact of molecular weight (Hexane and octane series probe molecules)
2. Influence of chlorine functional groups (Chloro- and dichloro-additions)
3. Influence of –OH groups (hexanol/octanol series)
4. Molecular geometry (evaluation of cyclic molecular geometries)
5. Comparison with HD simulant (CEES)

Initial solvent selection includes:

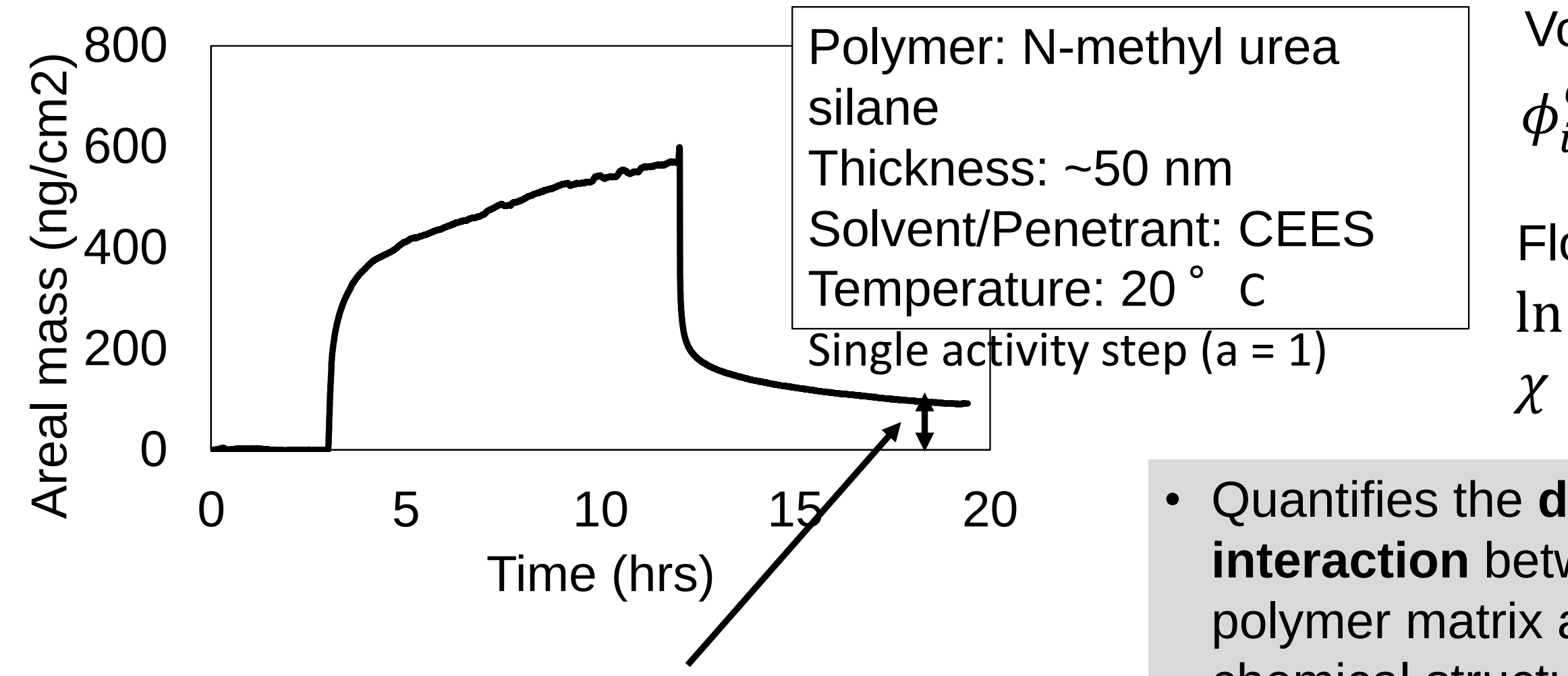
- **Hexane**
- **1-chlorohexane**
- **1,6-dichlorohexane**
- 1-hexanol
- Cyclohexane
- Octane
- 1-chlorooctane
- 1,6-dichlorooctane
- 1-octanol
- Cyclooctane
- **2-chloroethyl ethyl sulfide (CEES)**

Hypotheses

(1) By increasing cross-link density, we hope to improve material resistance to solvent penetration. If solvent penetration through polymer systems is sterically or geometrically driven, then manipulating the molecular porosity by controlling the crosslink density should allow us to control the solvent penetration through the system.

(2) By increasing the polymer heterogeneity, we will be able to control material resistance to solvent penetration. The more straightforward a path is through a polymer, the more easily a solvent is expected to penetrate the composite. By increasing the effective tortuosity of a polymer film, we can provide a hindrance to the solvent mobility through the system.

Chemical Penetration into Polymer Film



Polymer: N-methyl urea silane
Thickness: ~50 nm
Solvent/Penetrant: CEES
Temperature: 20 ° C
Single activity step (a = 1)

- Possible CEES entrainment within polymer sample – sign of irreversible change?

Volume fraction:

$$\phi_i^{avg} = \frac{\Delta m_i}{L_{QCM}}\left(\frac{\bar{V}_i}{MW}\right)=0.107$$

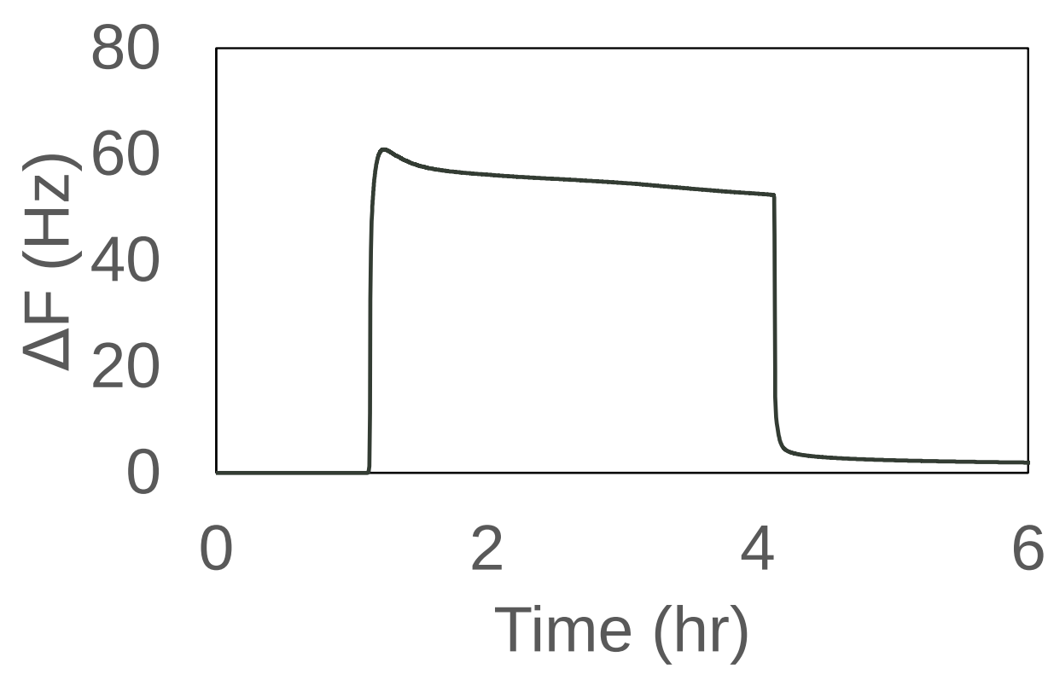
Flory-Huggins:

$$\ln(a_1) = \ln(1-\phi_2) + \phi_2 + \chi\phi_2^2$$

$$\chi = 1.68$$

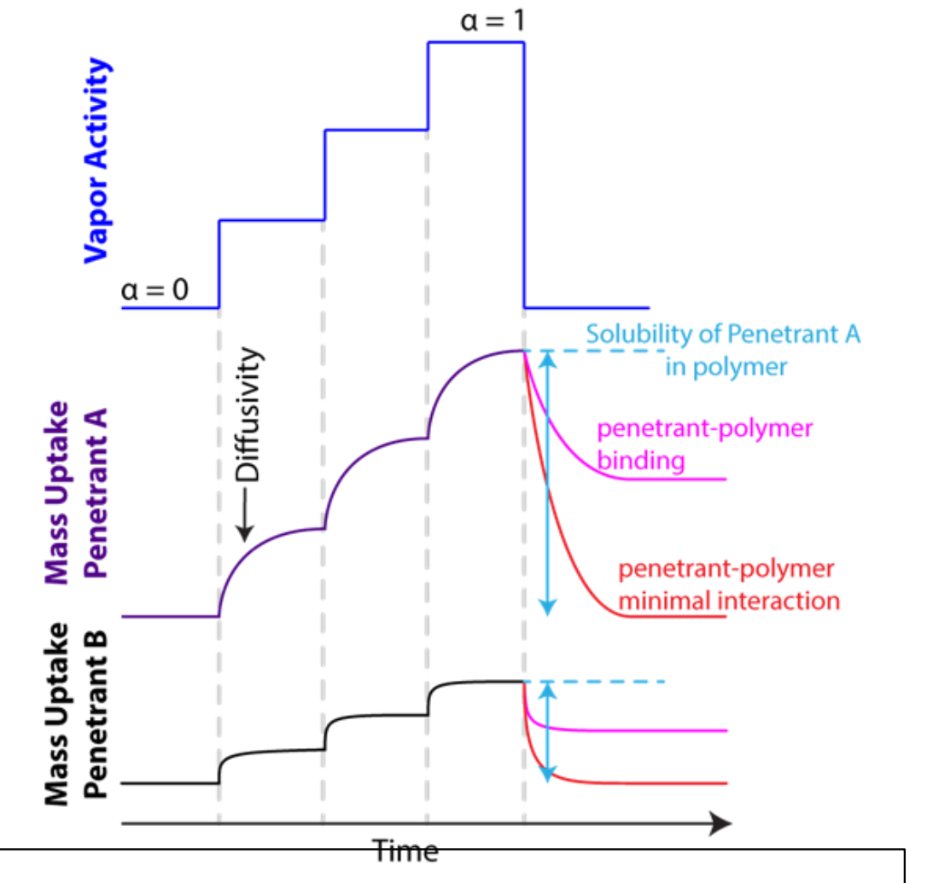
- Quantifies the **degree of chemical interaction** between chemical penetrant and polymer matrix as function of polymer chemical structure.
- Here: χ > 0 indicates a lack of attraction between CEES and nMUS.

Instrumentation Validation



Polymer: PMMA
Thickness: ~300 nm
Solvent/Penetrant: Chloroform
Temperature: 20 ° C
Single activity step (a = 1)
Calculated density: 1.80 g/cm^3
Published density: 1.80 g/cm^3
Calculated X: 0.43
Published X: 0.43

Next Steps



Objectives to evaluate:

- Speed of penetrant transport through polymer (e.g., physical properties such as molecular weight or molar volume)
- Mass of penetrant into polymer film (e.g, penetrant solubility via Hansen solubility parameters, chemistries, etc.)

Which factors drive penetrant transport into the coating?
Goal is to understand what impacts transport into the polymer, as well as the changes imparted by probe molecule penetration.
Goal of down-selection is to identify the fewest chemicals to provide a sufficient answer to the transport questions.
If we can understand the properties that drive toxic chemicals, can we predict what will happen with other penetrants?

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