# WATER AT POLYMER INTERFACES

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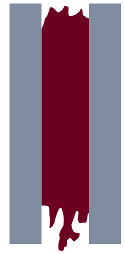
# Environment impacts adhesive strength

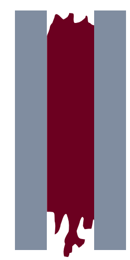


Adhesive Joint

RH = 78 %

Joint failure

RH = 19 %



No problems

What are the origins of this adhesion failure at a molecular level?

Can we engineer strategies to overcome this?

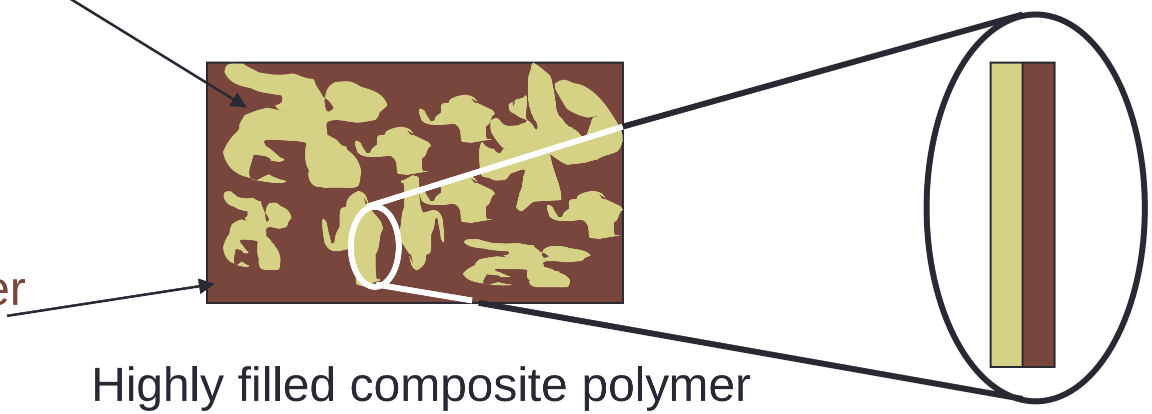
# Why worry about adhesives?


- More than 50,000 rivets to hold together
- Reduce rivets by replacing with adhesive
- Decrease maintenance costs!
- Changing environmental conditions – how does this effect the adhesive strength?

# Interfaces and composite systems

Problem: disordered system with multiple length scales

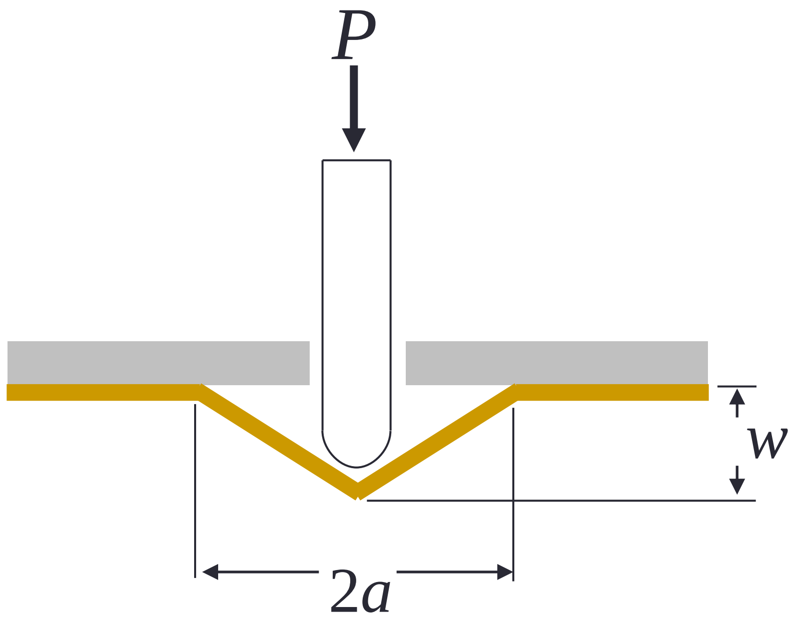
How to obtain fundamental understanding of moisture in these systems?

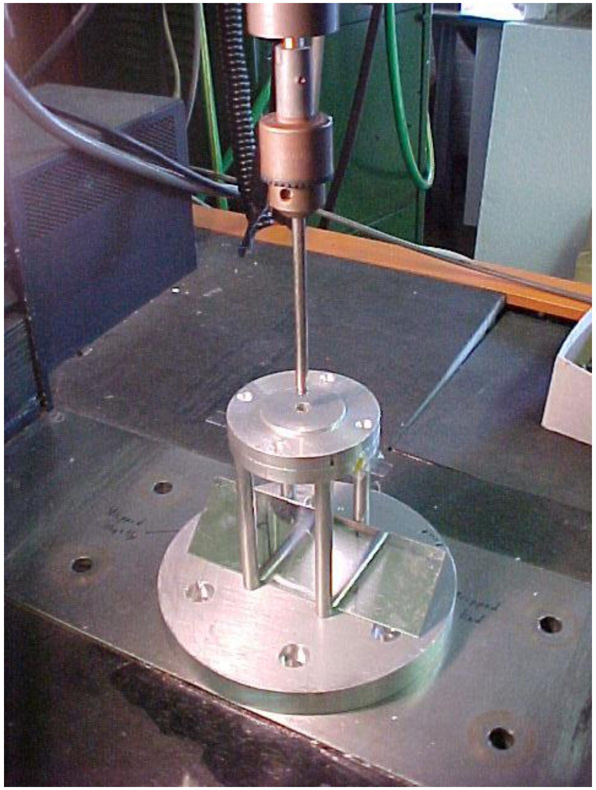



Highly filled composite polymer systems intrinsically high interfacial area

Idealized interface = thin film

# Adhesion measurements using shaft loaded blister test



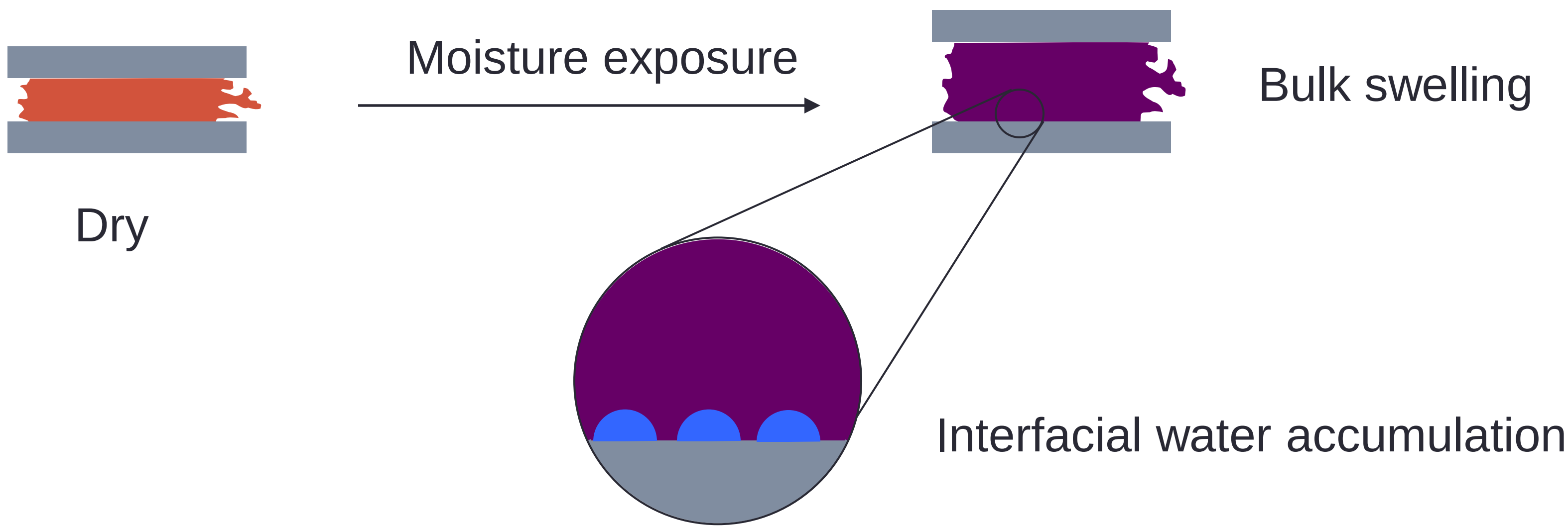
displacement-based equation ($w$)

$$\mathcal{G} = \frac{Eh}{16}\left(\frac{w}{a}\right)^4$$

*Eh*: Film Stiffness (modulus, *E*, · thickness, *h*)

But this is a bulk measurement, how to understand mechanisms?

# Moisture influence: Bulk versus interface contributions




<u>Bulk swelling</u>
Decreased cohesive strength
Stress development in polymer

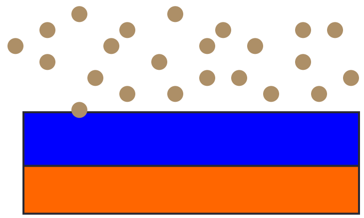
<u>Interfacial moisture</u>
Decreased contact area
Stress development in polymer

**Which effect controls adhesive failure?**

# Contrast control through isotopic substitution

## X-ray Reflectivity (XR)

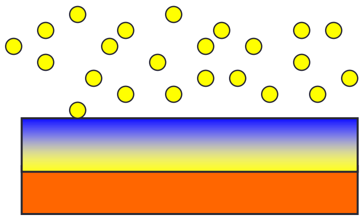
Water ‘looks’ like polymer
(similar density)



- Measure thickness change due to moisture absorption
- Mass density profile

## Neutron Reflectivity (NR)

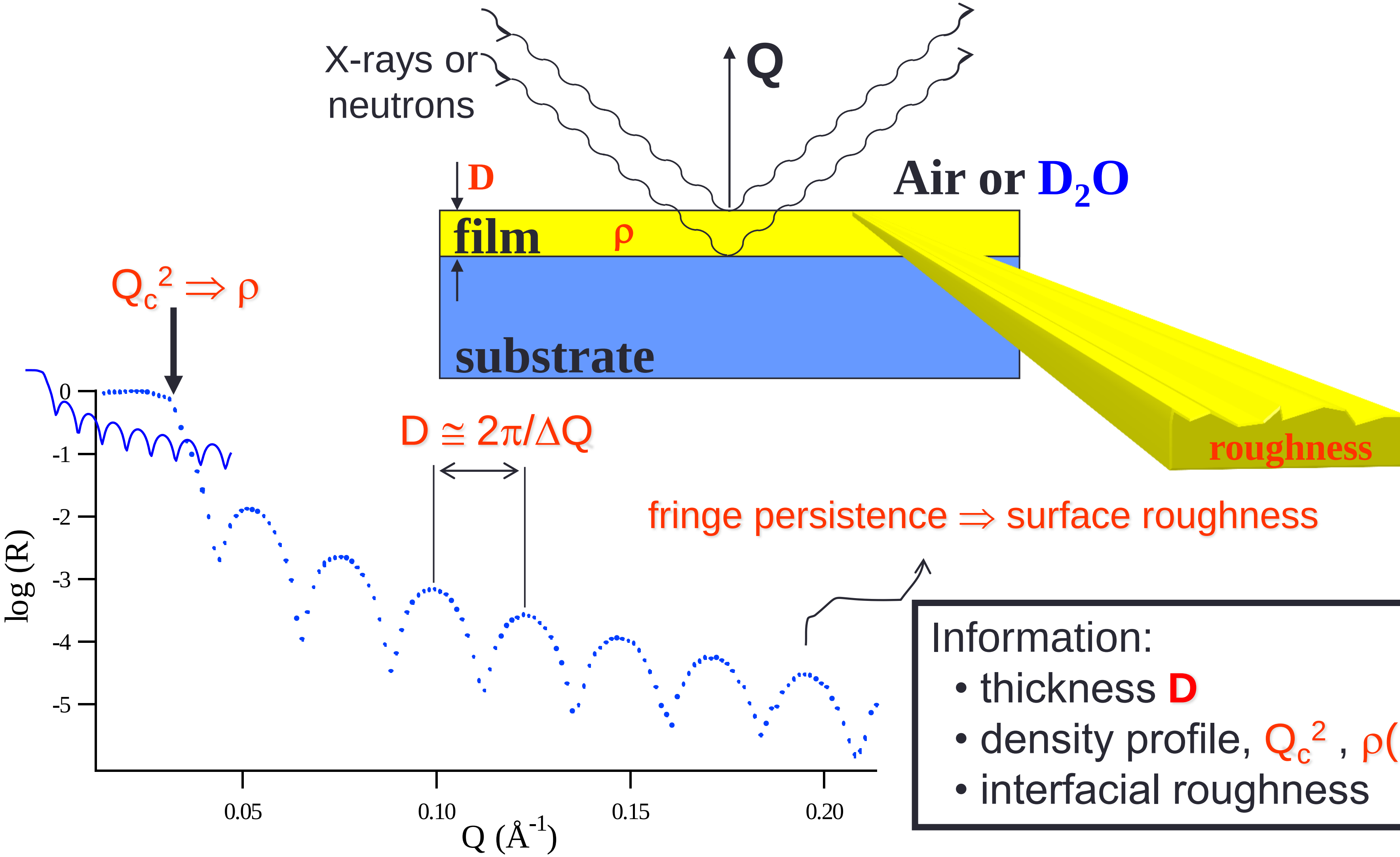
Water visible
(Heavy water, $D_2O$)



- Isotopic sensitivity ($^1H$ vs $^2H$)
- Measure water distribution within film

Use NR to directly observe water distribution in film

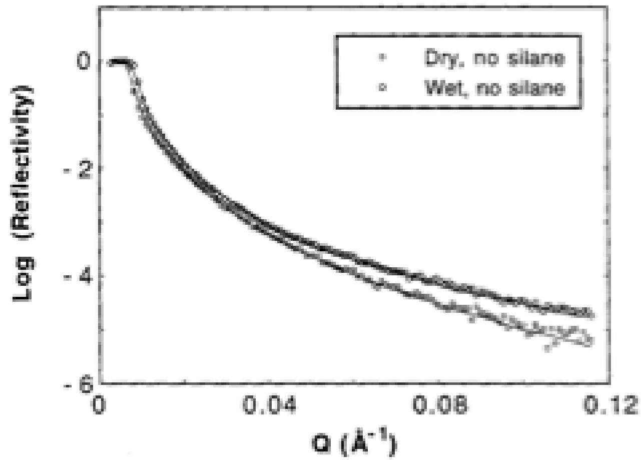
# Quantifying moisture distribution: X-ray and neutron reflectivity

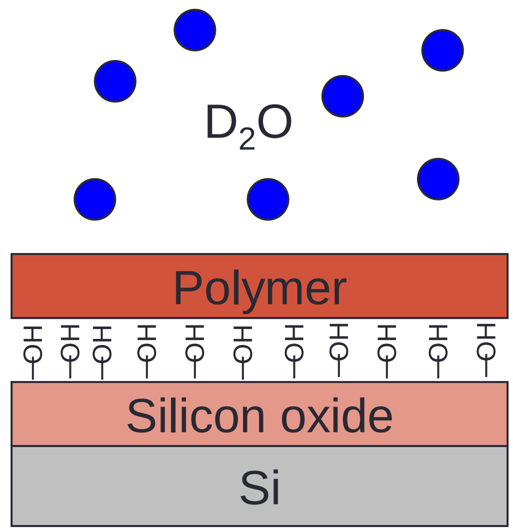



Information:
- thickness **D**
- density profile, $Q_c^2$, $\rho(z)$
- interfacial roughness

# Examining water at polymer interface

Thick polyimide on silicon wafer




$Q_c^2 = 3.21 \times 10^{-4}$ Å$^{-2}$

$Q_c^2 = 1.57 \times 10^{-4}$ Å$^{-2}$
h = 2 μm

$Q_c^2 \cong 1.5 \times 10^{-4}$ Å$^{-2}$
h = 2 nm

$Q_c^2 = 1.06 \times 10^{-4}$ Å$^{-2}$
h= 2 mm

*Wen-Li Wu, William J. Orts, Charl*

from the interface, the $Q_c^2$ value and thickness of an intermediate layer which might be present, and the thickness of both transition zones, i.e. between PI and the intermediate layer, and between Si and the intermediate layer. The resulting potential energy profiles, expressed in $Q_c^2$ vs. distance from the Si surface for both the dry (lower curve) and the wet (upper curve) samples are given in *Fig. 3*. The origin on the dis-

silicon

polymer

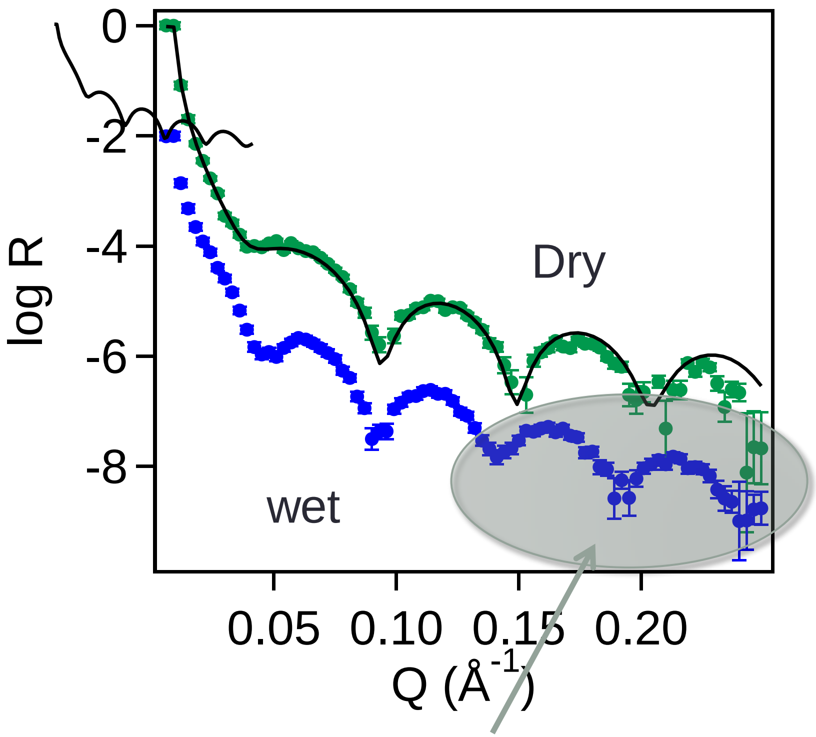
Wu et al. *Polymer Engineering and Science*, **1995**, 35, 1000.

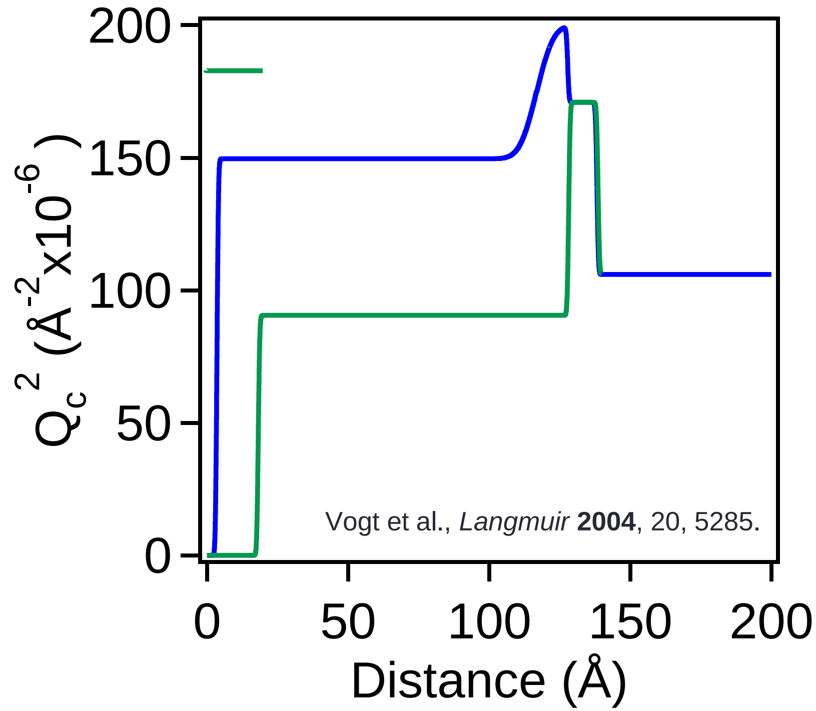
No well defined interferences due to relative thicknesses

Shift in critical edge and change in decay only differences

Fit suggests $D_2O$ accumulates at interface

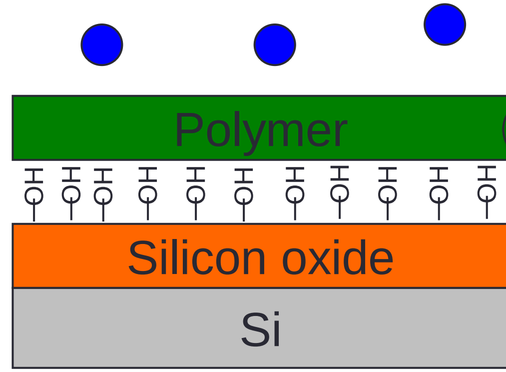
# Polyhydroxystryrene on silicon wafer




Minima in reflectivity not fit without excess at interface

Improved sensitivity to interface by decreasing film thickness

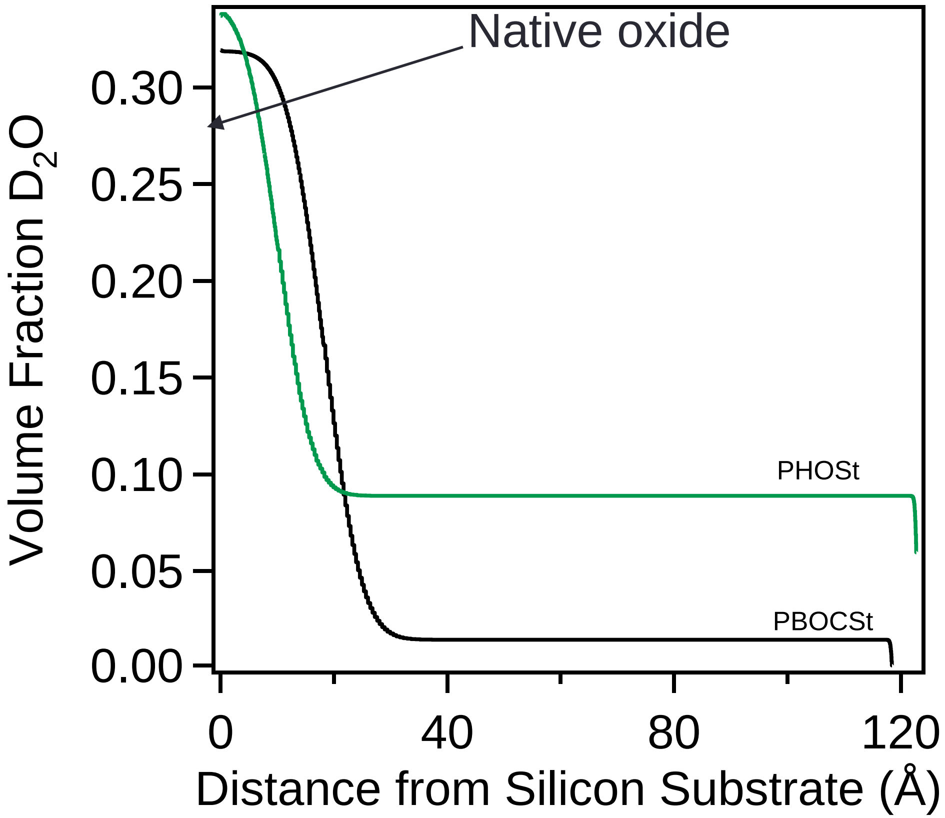



$Q_c^2$ = 0.79 x 10$^{-4}$ Å$^{-2}$
h = 80 nm

$Q_c^2$ = 1.6 x 10$^{-4}$ Å$^{-2}$
h = 2 nm

$Q_c^2$ = 1.06 x 10$^{-4}$ Å$^{-2}$
h= 2 mm

# Effect of polymer on interfacial concentration




Vogt et al., *Langmuir* **2004**, 20, 5285.

Convert SLD profile to vol. frac.

$$\varphi_w(x) = \frac{Q_c^2(x) - Q_c^2{}_{(poly)}}{Q_c^2{}_{(D_2O)} - Q_c^2{}_{(poly)}}$$

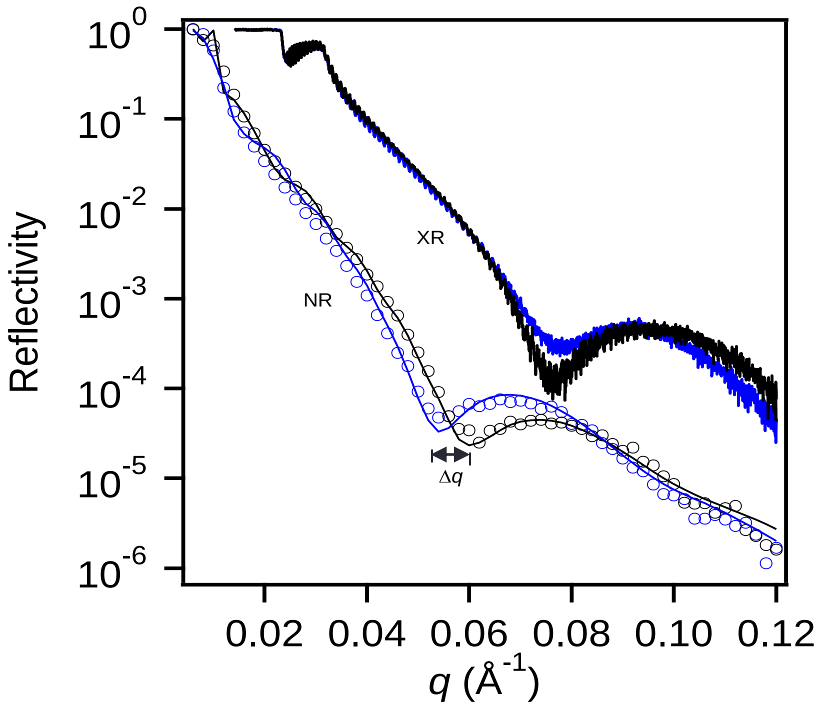
This can be extended to multiple phase systems

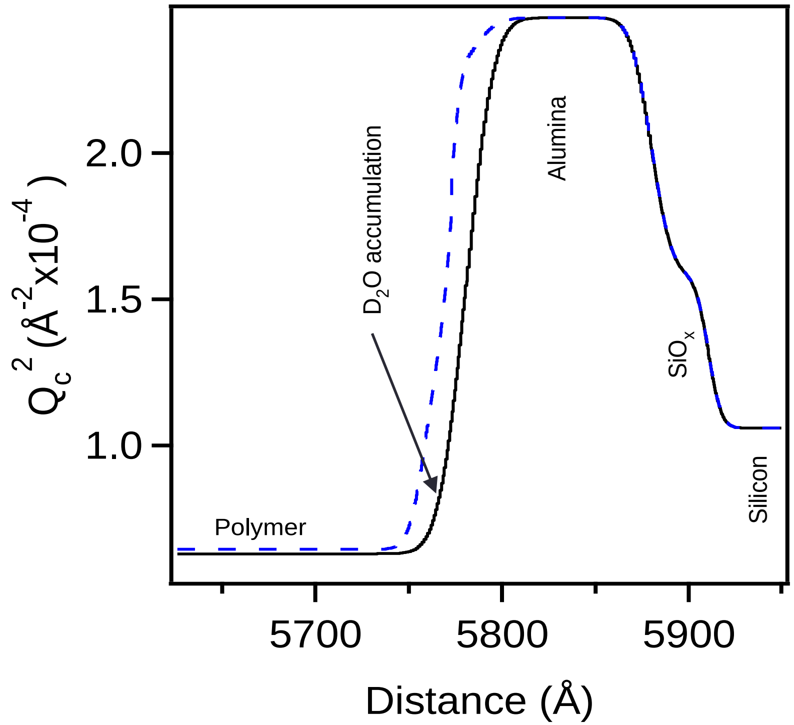
Concentration profile near substrate *independent* of polymer

*J. Mater. Sci.* **1996** 31 927-927
*Langmuir* **2004** 20(4) 1453-1458
*J. Microlitho. Microfab.* **2005** 4(1) 013003

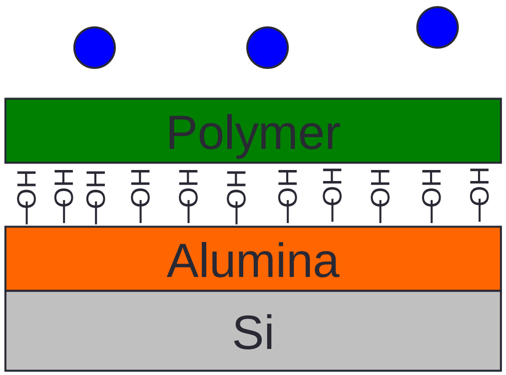
Can we further increase sensitivity?

# Crosslinked polyacrylate on sputtered alumina




Vogt et al., *J. Appl. Phys.* **2005**, 97, 114509




$Q_c^2$ = 3.21 x $10^{-4}$ $Å^{-2}$

$Q_c^2$ = 0.79 x $10^{-4}$ $Å^{-2}$
h = 1.5 μm

$Q_c^2$ = 2.4 x $10^{-4}$ $Å^{-2}$
h = 35 nm

$Q_c^2$ = 1.06 x $10^{-4}$ $Å^{-2}$
h= 2 mm

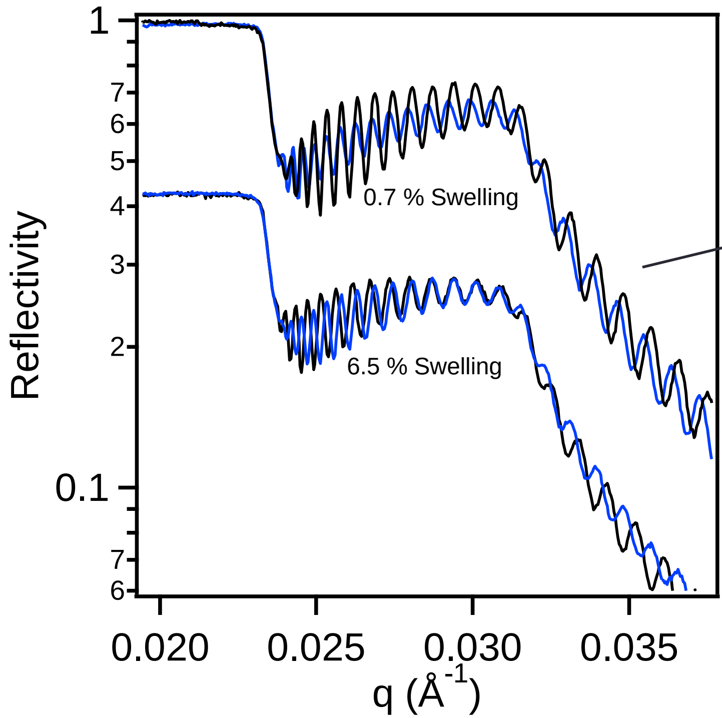
Interference fringes from thin alumina

Shift due to contrast change from $D_2O$ sorption

Improved sensitivity to interface

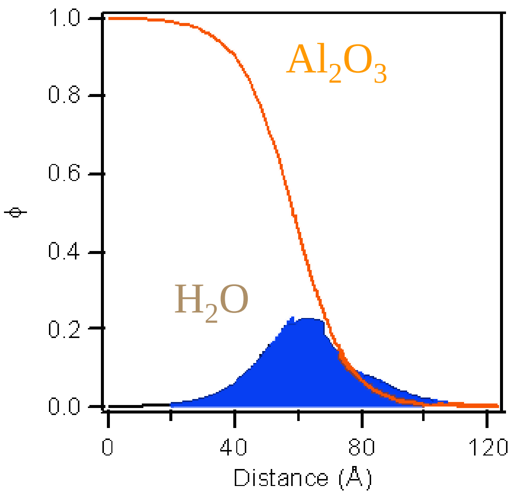
# Moisture accumulation for polyacrylate on alumina

XR – measure film swelling



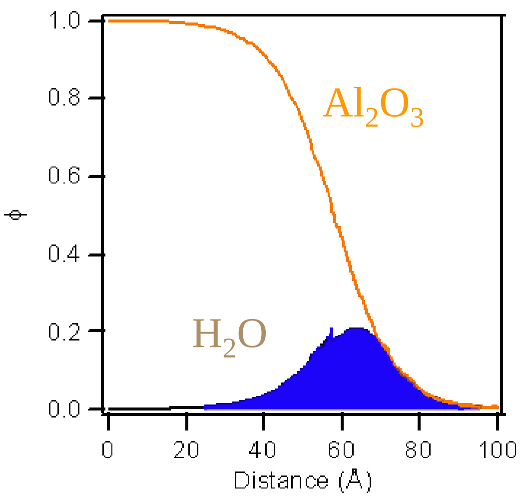

Vary cure condition to change $H_2O$ solubility

NR




Vogt et al., *J. Appl. Phys.* **2005**, 97, 114509

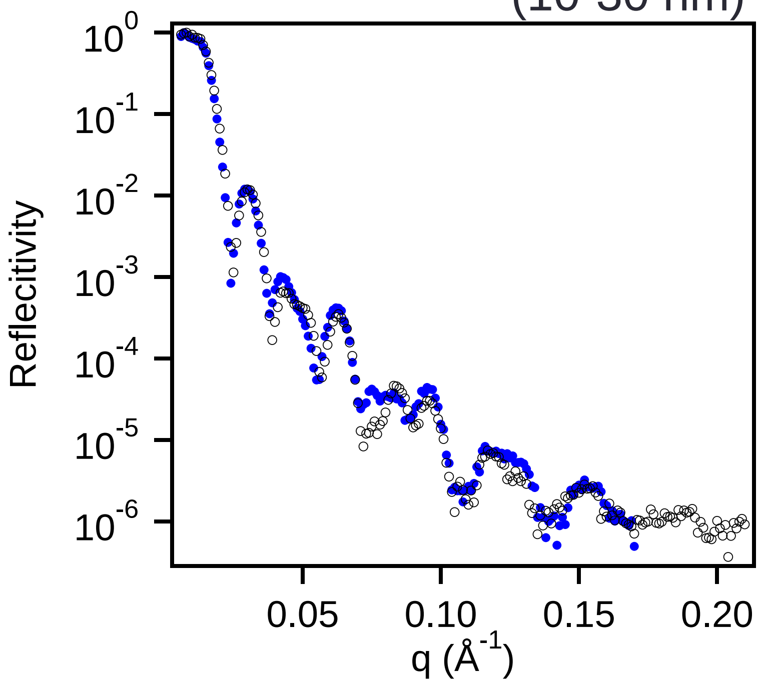
NR

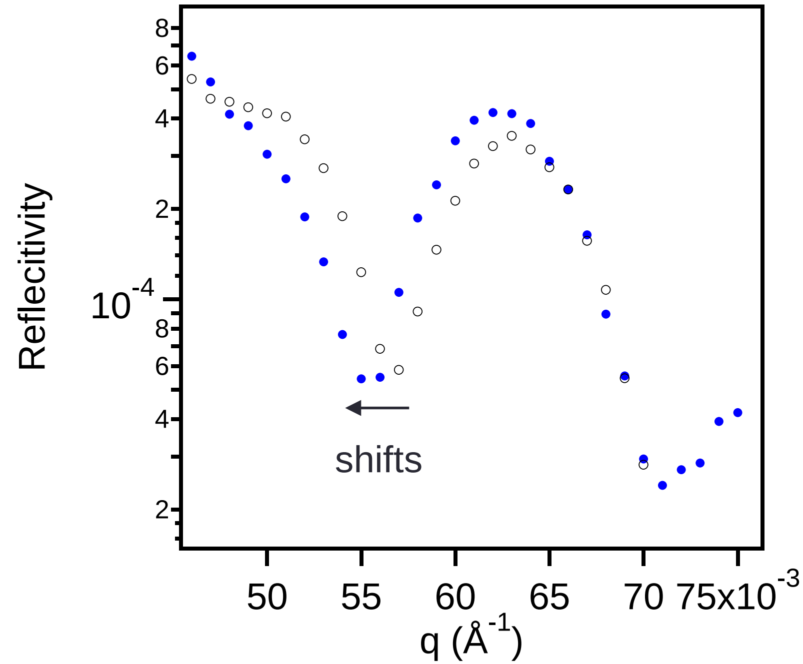


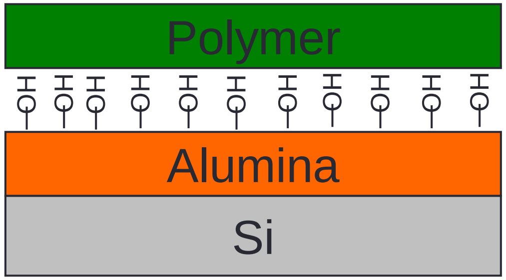

Bulk solubility does not influence moisture content at alumina / polymer interface

# Design of system to maximize sensitivity

★ Relatively thin polymer coating (< 150 nm) ★ High contrast oxide layer (10-30 nm) ★ $D_2O$ as probe ★




$Q_c^2 = 0.79 \times 10^{-4}$ Å$^{-2}$
h = 85 nm

$Q_c^2 = 2.4 \times 10^{-4}$ Å$^{-2}$
h = 35 nm

$Q_c^2 = 1.06 \times 10^{-4}$ Å$^{-2}$
h= 2 mm

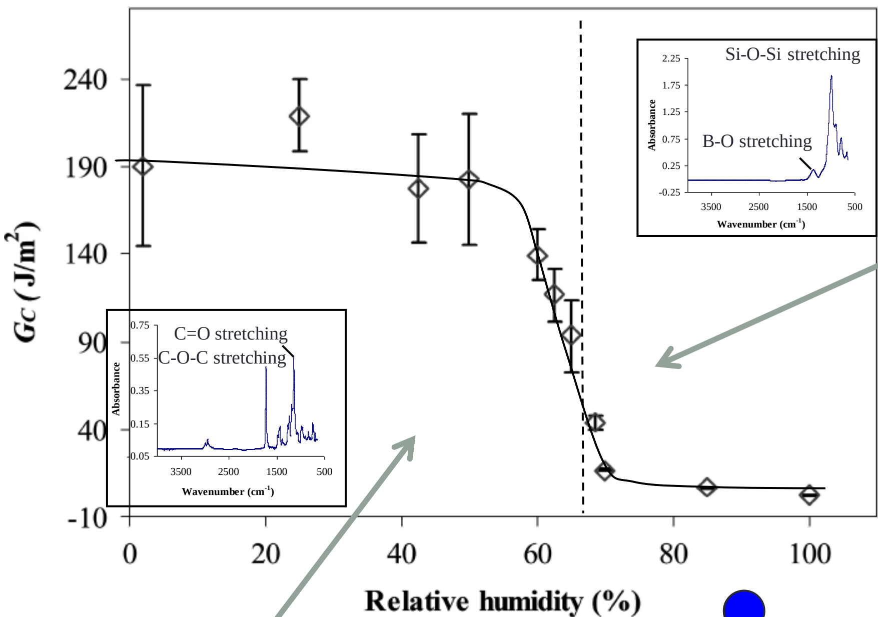
Vogt et al., *Langmuir* **2005**, 21, 2460

Multiple interferences yields added sensitivity to buried interface contrast

# Water accumulates at interface

- Does this accumulation directly impact adhesion?
- Can this accumulation be controlled?
- What are critical factors?

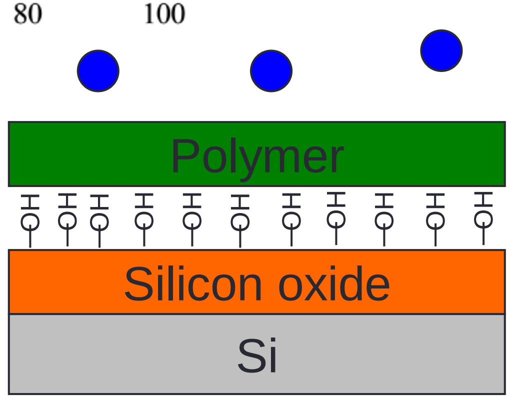
# Critical relative humidity




Adhesive failure

Is the interface to blame for failure at high humidity?

Cohesive failure



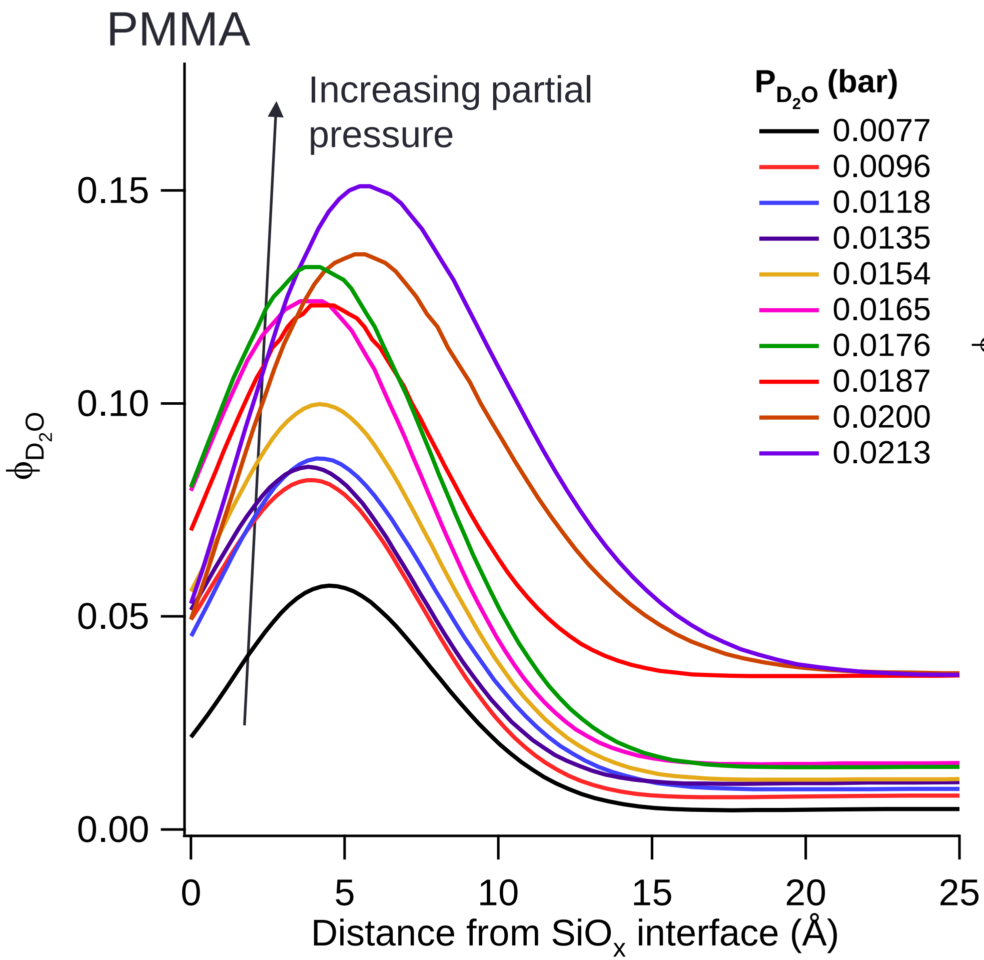

$Q_c^2 = 0.79 \times 10^{-4}$ Å$^{-2}$
h = 85 nm

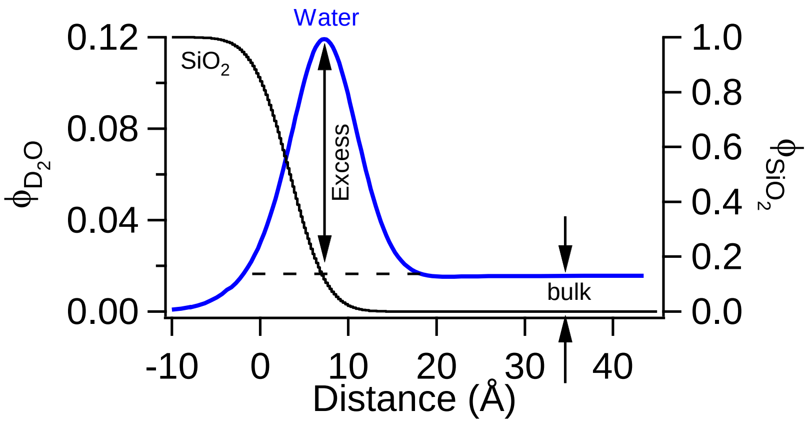
$Q_c^2 = 1.6 \times 10^{-4}$ Å$^{-2}$
h = 15 nm

$Q_c^2 = 1.06 \times 10^{-4}$ Å$^{-2}$
h= 2 mm

Tan et al., *Langmuir* **2008**, 24, 9189

# Impact of humidity on interfacial properties

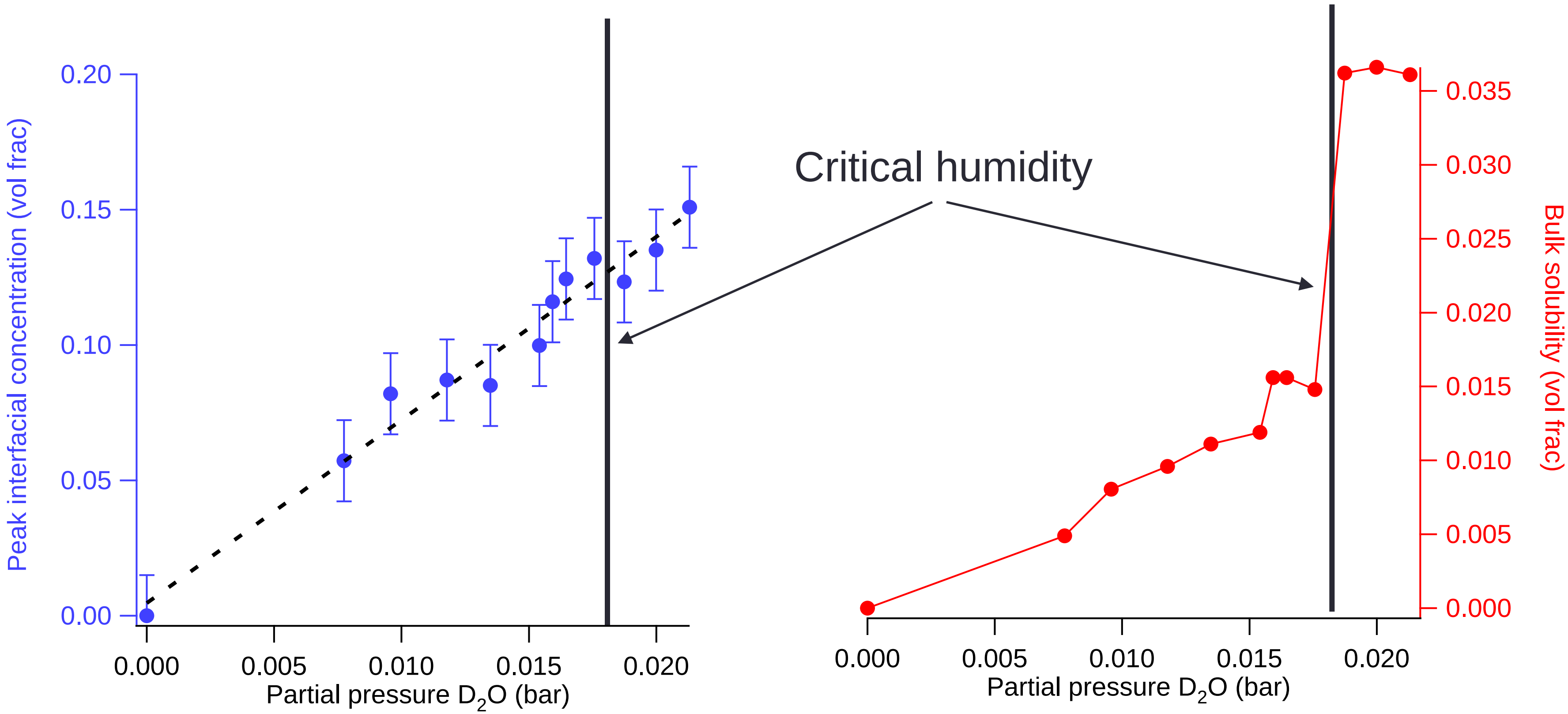



What's driving the failure?

Tan et al., *Langmuir* **2008**, 24, 9189

# Comparison of interface and bulk

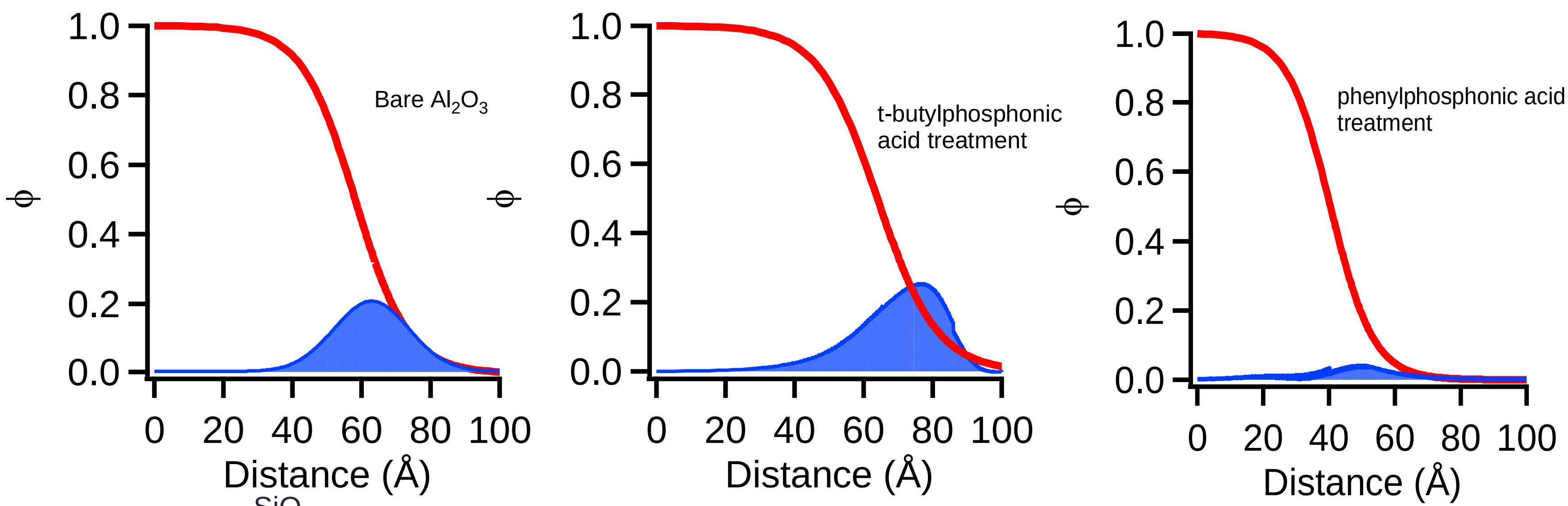


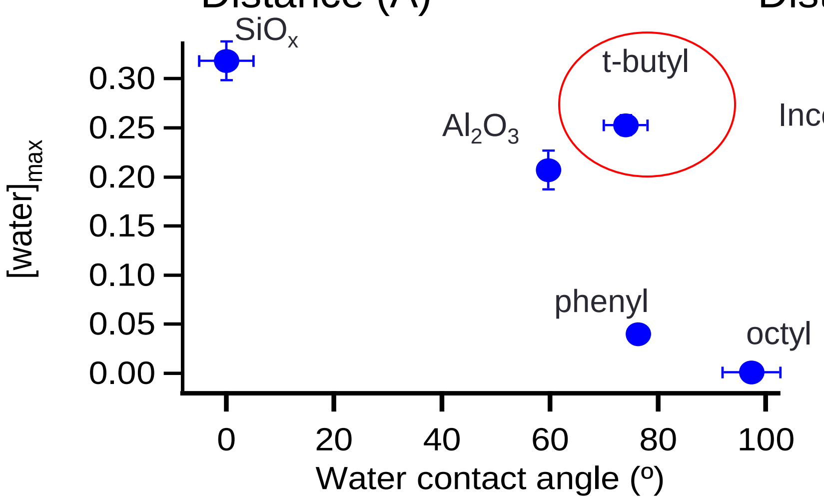

No discontinuity at interface

So is moisture at interface important?

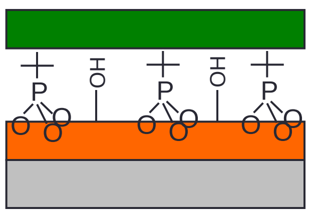
Tan et al., *Langmuir* **2008**, 24, 9189

# Influence of substrate on moisture accumulation



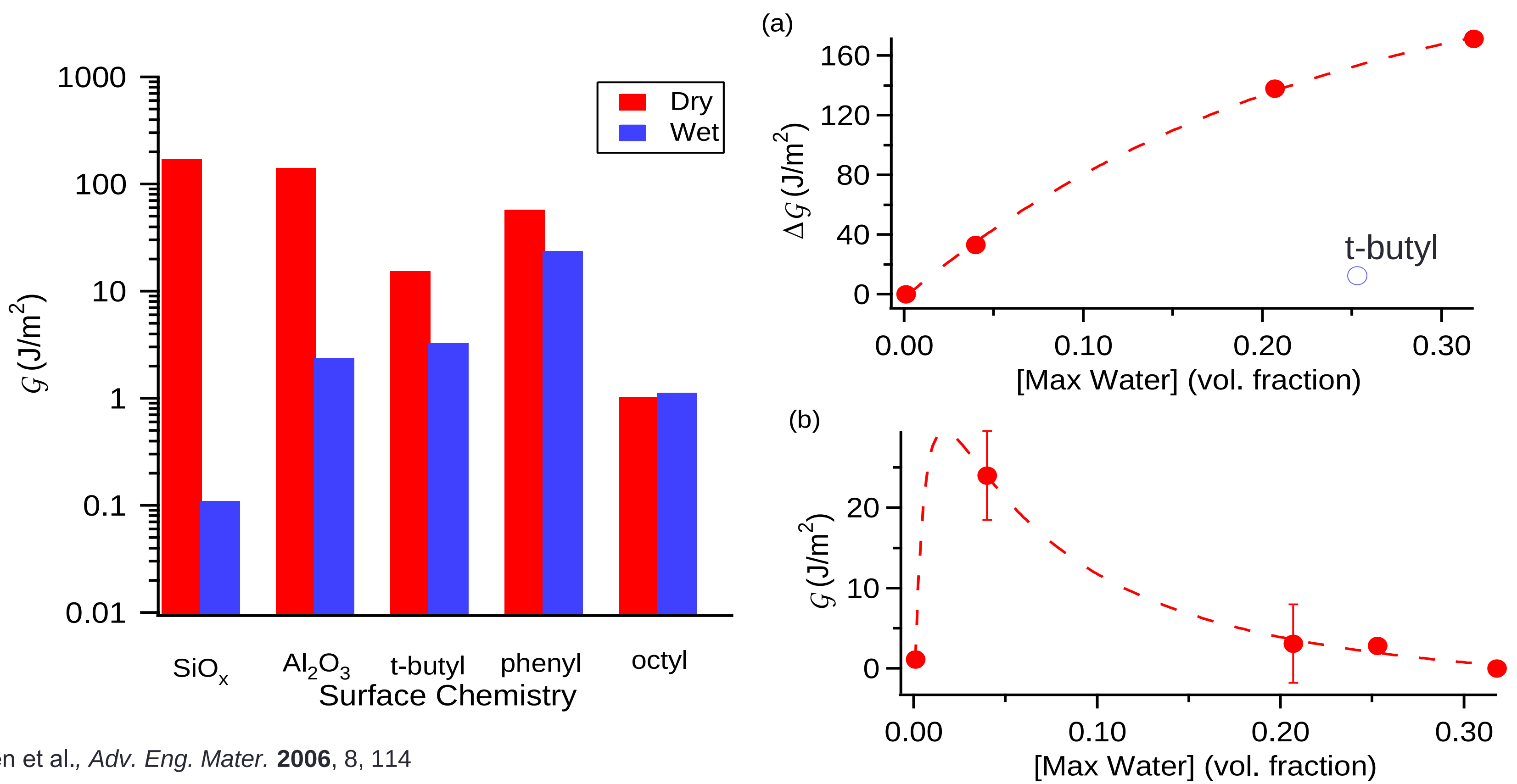

Incomplete coverage (74°)
90° for monolayer




Moisture accumulation at interface dependent upon surface chemistry

O’Brien et al., *Adv. Eng. Mater.* **2006**, 8, 114

# Correlating interfacial moisture and adhesion for PMMA



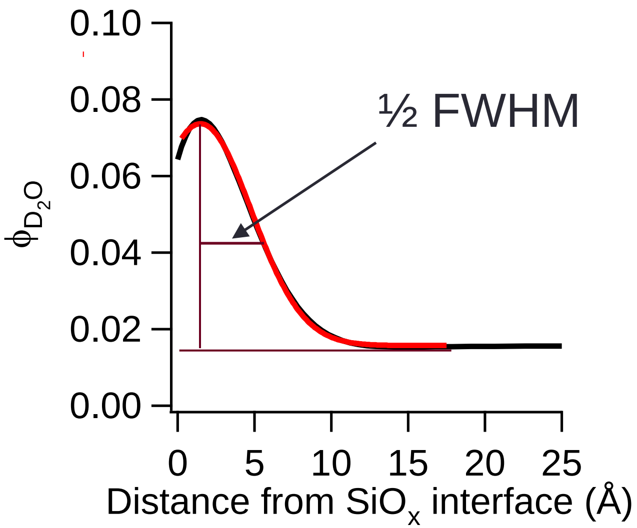

O'Brien et al., *Adv. Eng. Mater.* **2006**, 8, 114

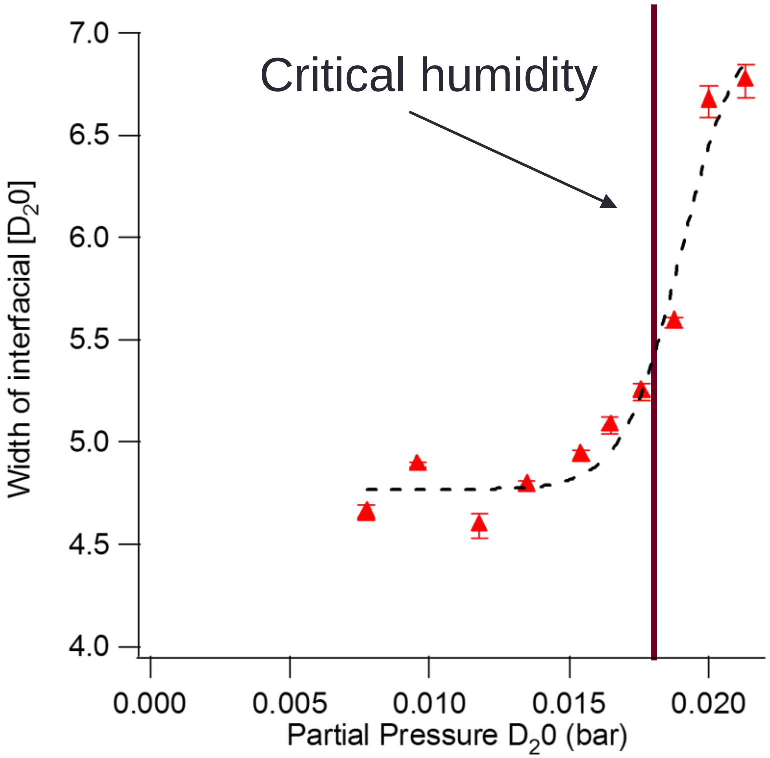
Interplay between dry adhesion and moisture accumulation

Intermediate surface energy for best wet adhesion

Interfacial water matters!

# Change in the interface at the critical humidity




Tan et al., *Langmuir* **2008**, 24, 9189

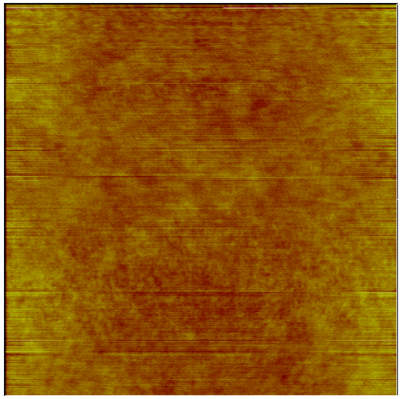
Interfacial moisture broadens at the critical humidity

Is this responsible for the failure?

# How could this change in the profile impact adhesion?

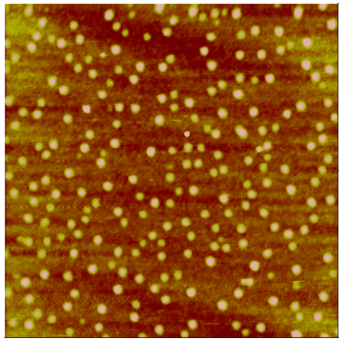
Only the average in plane distribution of water is determined from neutron reflectivity
Distribution is not uniform!

Dry surface

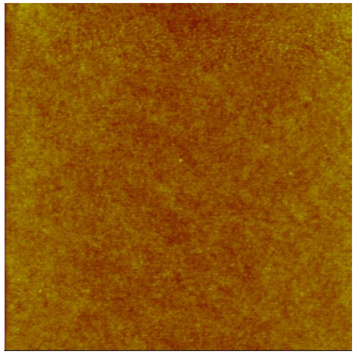


Ultrathin film (15 nm)

Water drop on surface

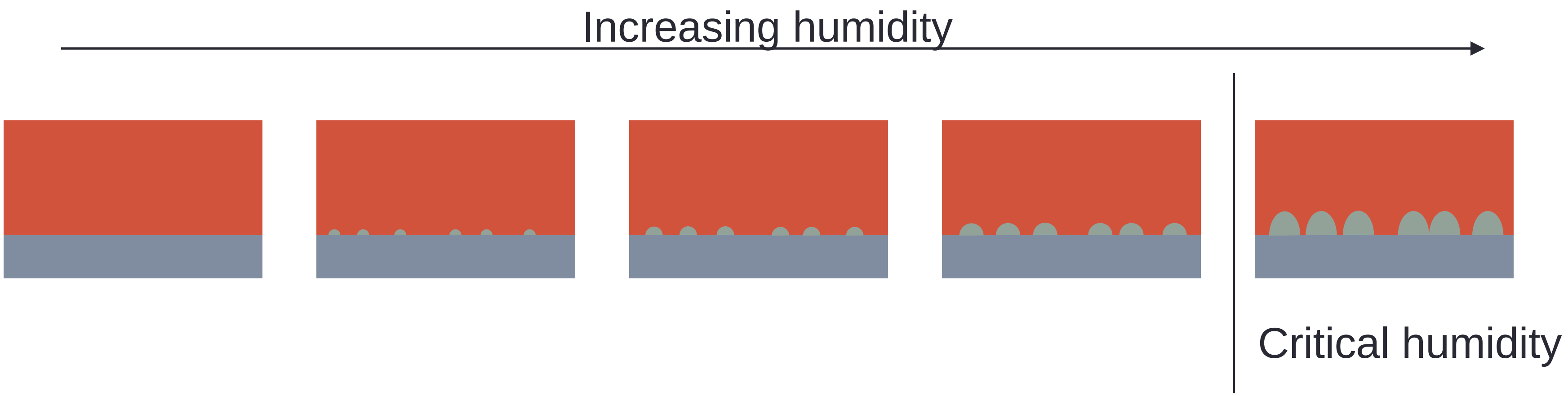


Hydrophilic interface
(catastrophic adhesion loss)



Hydrophobic interface
(minimal adhesion loss)

# Proposed model for critical relative humidity

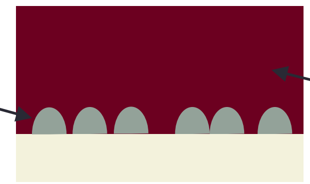



1. Initial accumulation at the interface only mildly perturbs the contact area – adhesive energy still greater than cohesive energy
2. This grows, but does not significantly stress the interface
3. When the bulk concentration increases significantly at the critical humidity, it causes shear stress accumulation near the interface due to the decreased contact area
4. This stress forces the additional water accumulating at the interface to be pushed into the film
5. This additional water at the interface causes a large stress normal to the film surface leading to adhesive failure

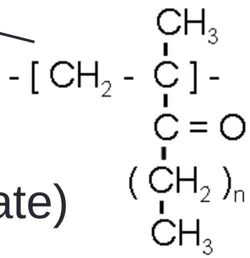
# How to test model?

- Stress accumulation should be important

Water causes normal stress in adhesive?



Model: poly(n-alkyl methacrylate)




| PMMA | PEMA | PnPMA | PnBMA |
|---|---|---|---|

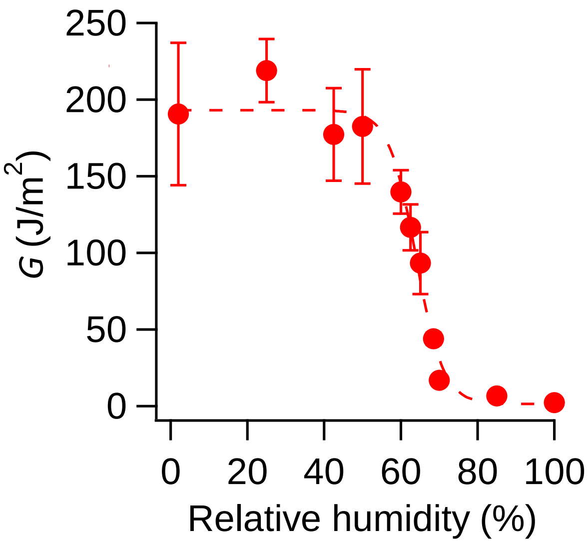
Increasing chain length

| | | | |
|---|---|---|---|
| $E_f$= 3.15 ± 0.07 GPa | $E_f$=1.91 ± 0.1 GPa | $E_f$=1.20 ± 0.06 GPa | $E_f$ < 100 MPa |
| $T_g$ = 105 ºC | $T_g$ = 65 ºC | $T_g$ = 36 ºC | $T_g$ = 15 ºC |
| n=0 | n=1 | n=2 | n=3 |

Torres et al., *ACS Nano* **2009**, 3, 2677

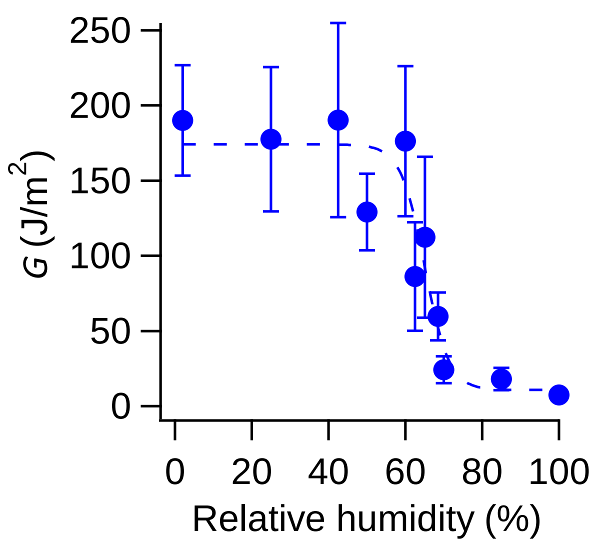
# Impact on changing the model adhesive

PMMA



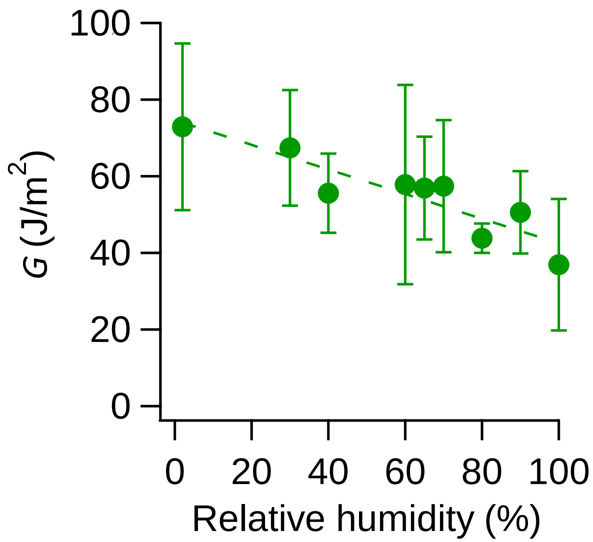

Glassy

PEMA




Glassy

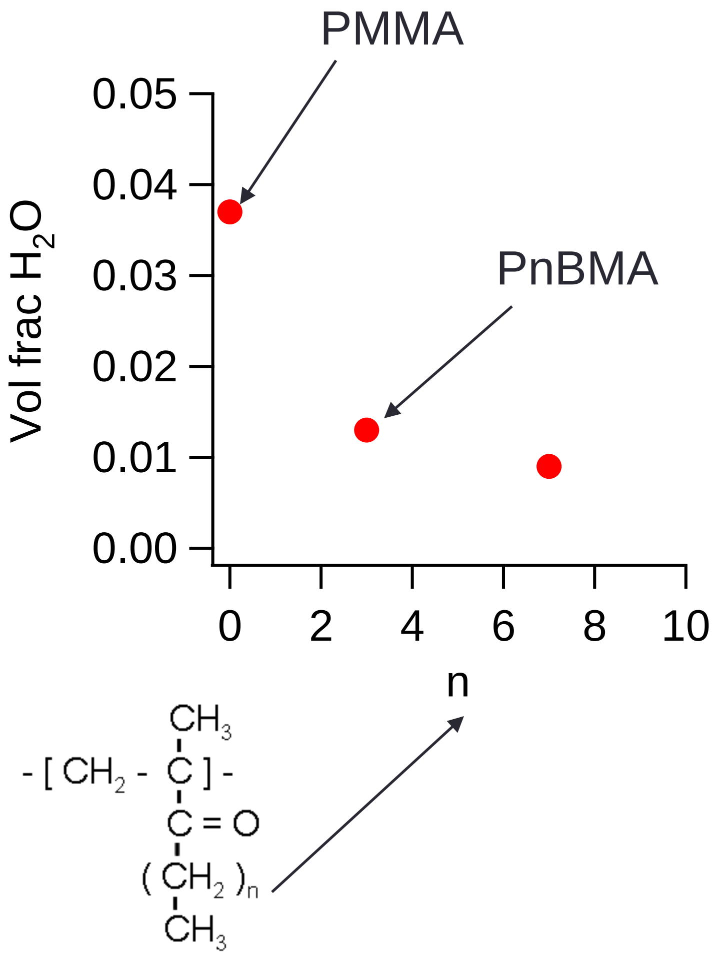
PnBMA




Rubbery

Low modulus PnBMA does not exhibit critical relative humidity

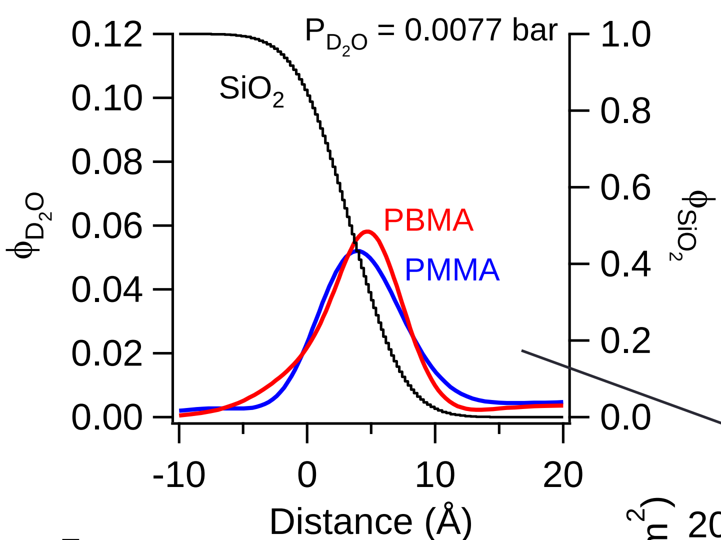
# What about moisture uptake?

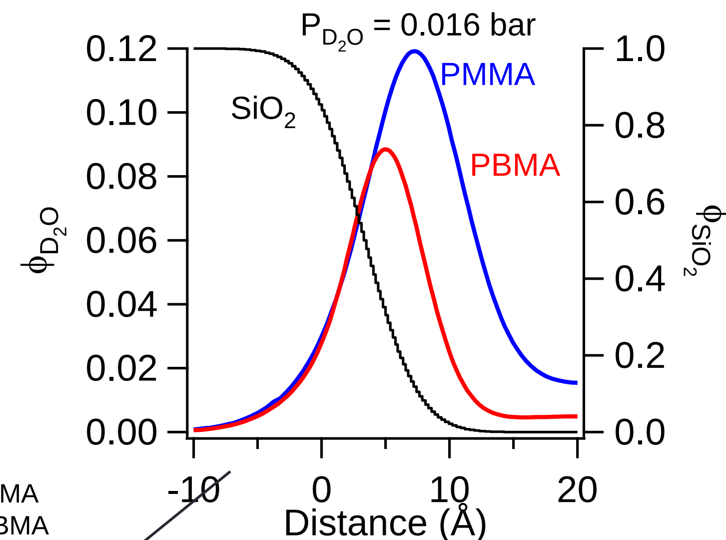


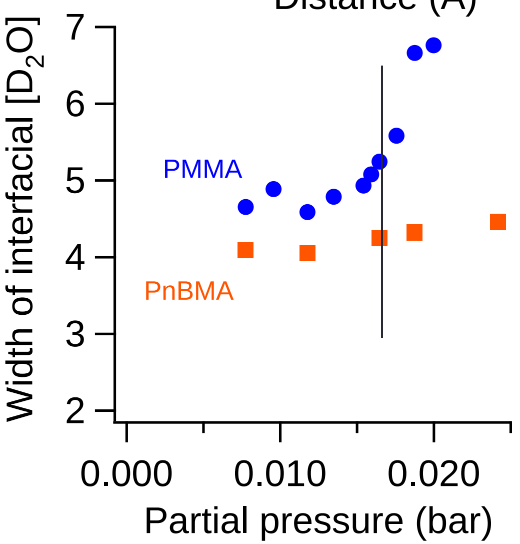

Near saturation – less water in PnBMA than PMMA

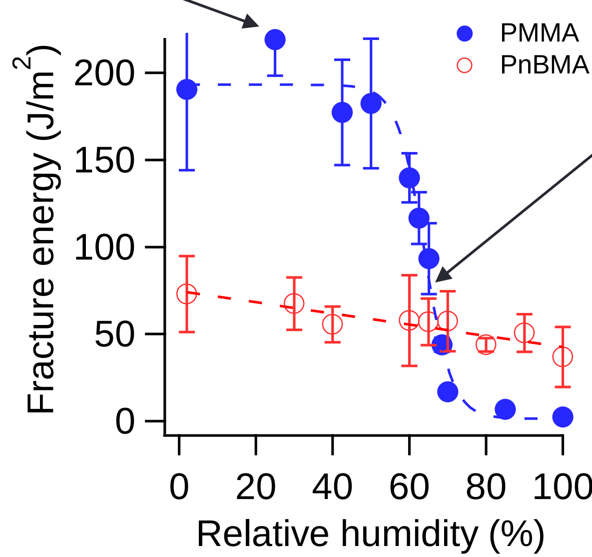
Longer alkyl chain leads to more hydrophobic model adhesive

# Is the interface impacted?



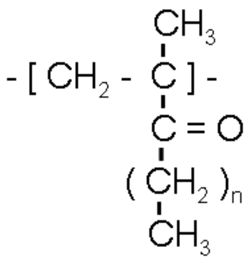



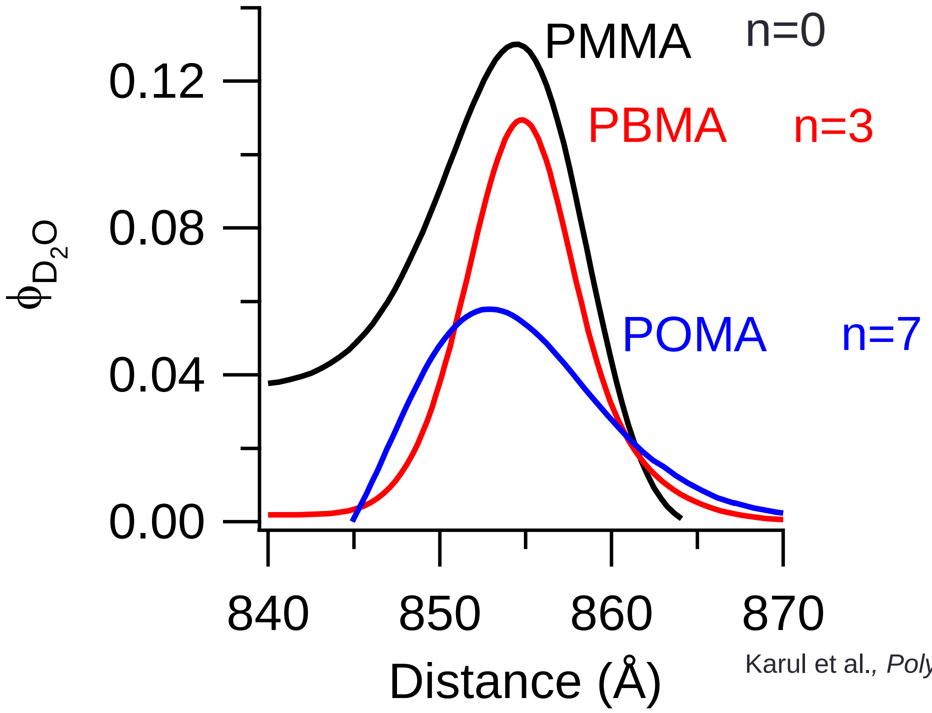




**Different at high humidity?**

# Does low modulus lead to decrease in moisture?



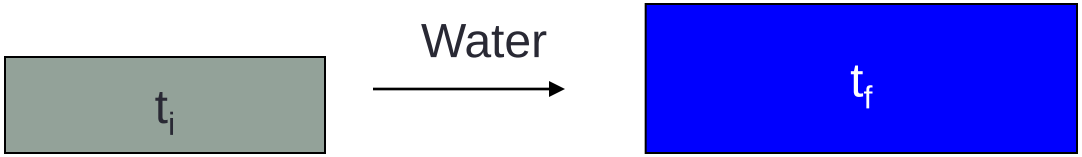




Karul et al., *Polymer* **2009**, 50, 3234

Low modulus appears to lead to suppression of moisture accumulation at interface (rubbery polymers)

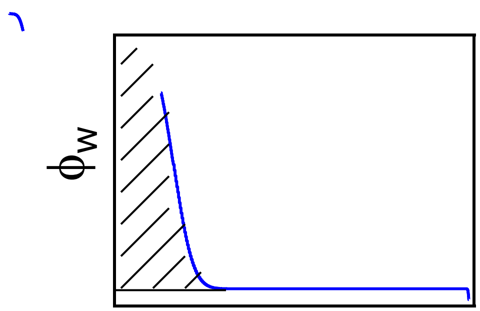
# Simple Model for Thickness Dependent Swelling

## Bulk Swelling




$$\phi_{eq} = \frac{t_f - t_i}{t_f}$$

## Excess Swelling



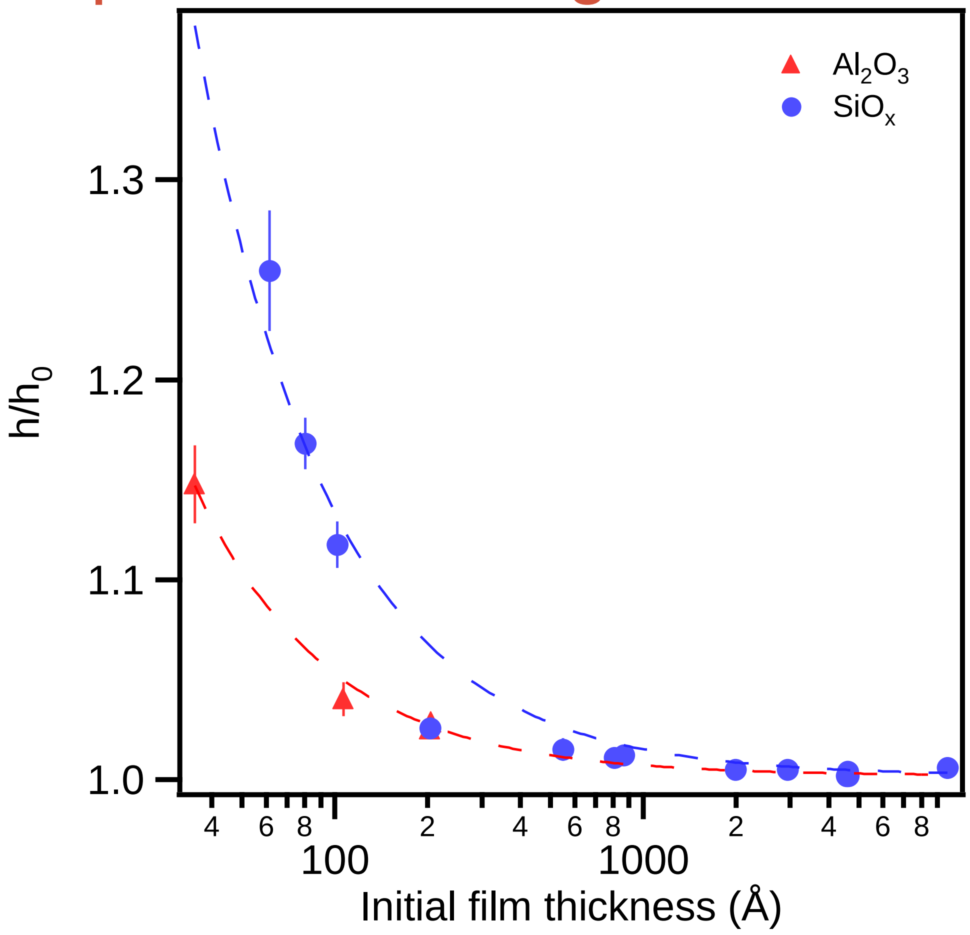

$$t_{excess} = \int_0^T \left(\phi_w(x) - \bar{\phi}\right) dx$$

Shaded area is excess thickness

$$\frac{h}{h_0} = 1 + \frac{\Delta t_{eq}(h_0) + t_{excess}}{h_0}$$

Vogt et al., *Langmuir* **2005**, 21, 2460

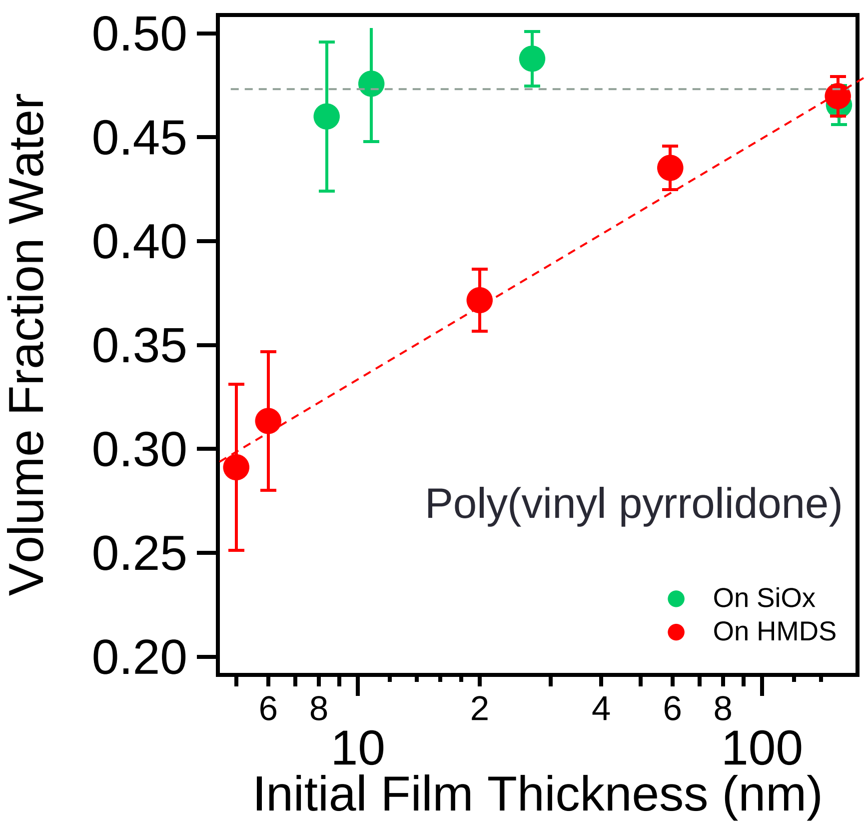
# Thickness dependent swelling




Model corresponds well with thickness dependent swelling

Vogt et al., *Langmuir* **2005**, 21, 2460

# Is there always an excess at the interface?

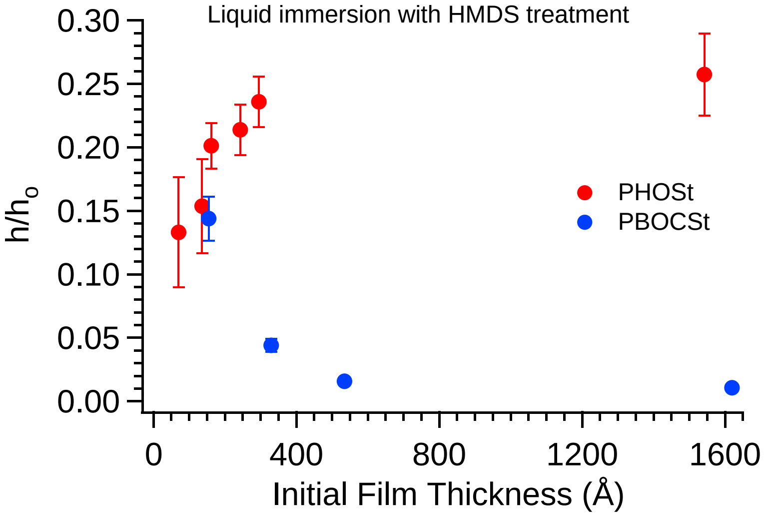



No thickness dependence for films on native oxide

HMDS treated substrate leads to decrease in absorption for thin films

Vogt et al., *Polymer* **2005**, 46, 1635

# What about aqueous solutions?

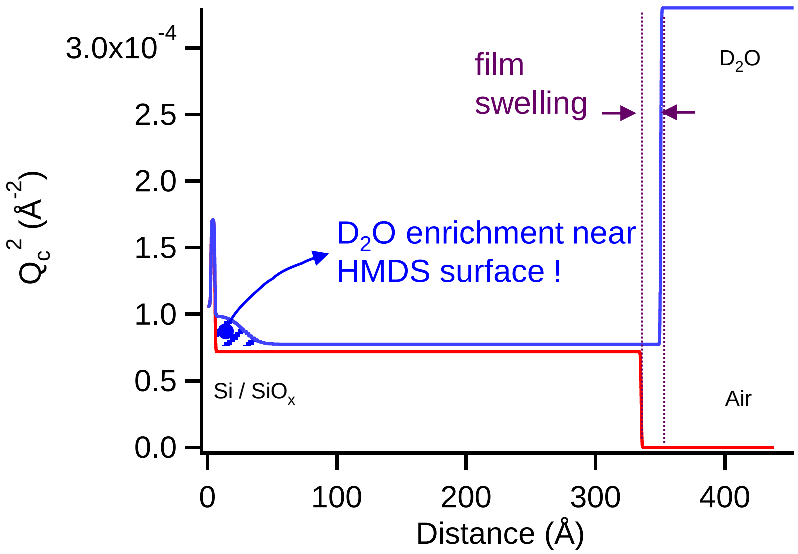


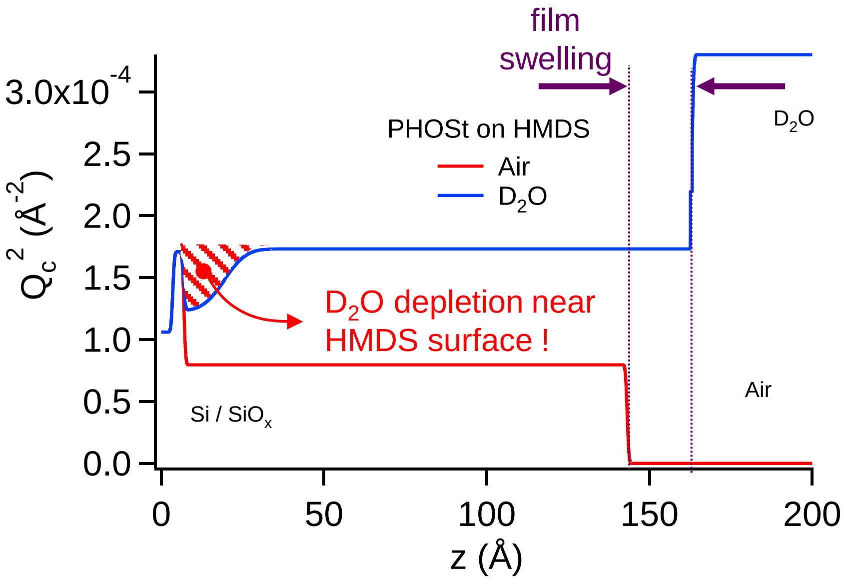

- Hydrophilic interface relative to bulk polymer

⇒ interfacial excess & enhanced thin film swelling

- Hydrophobic interface relative to bulk polymer

⇒ interfacial depletion & suppressed thin film swellin

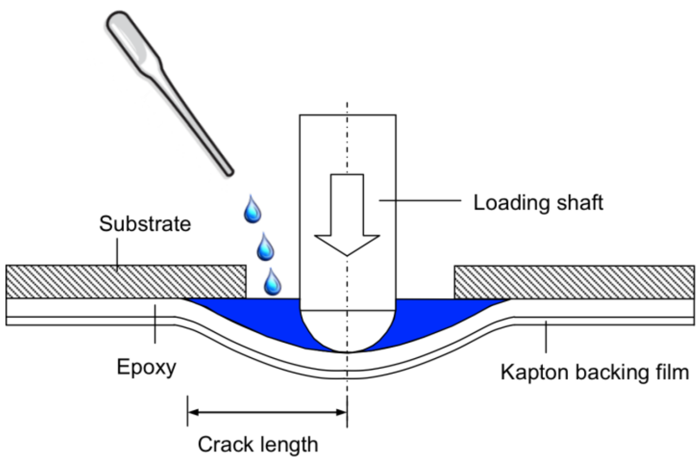


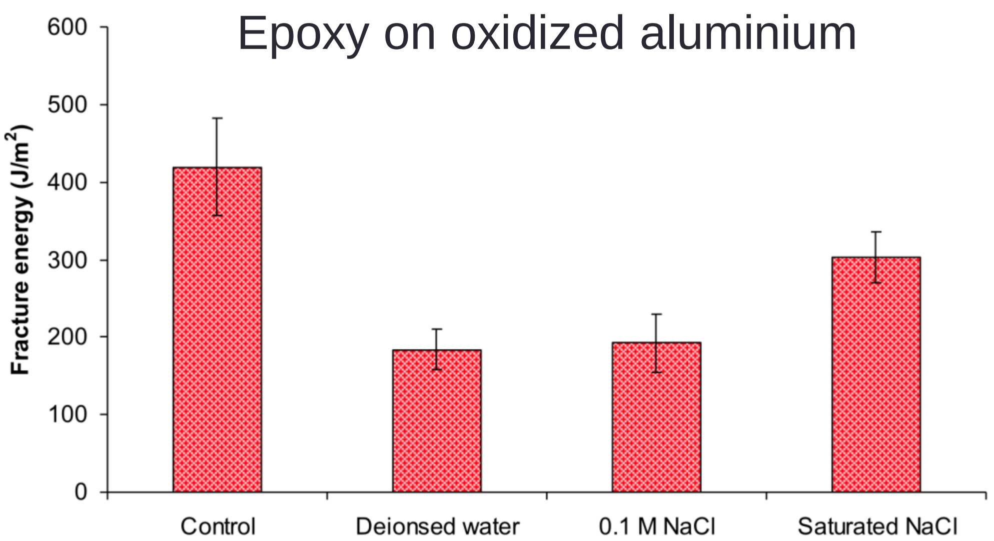




Vogt et al., *J. Microlith. Microfab. Microsys.* **2005**, 4, 013003

We obtain similar information about the interfaces immersed in $D_2O$

# What about salts?

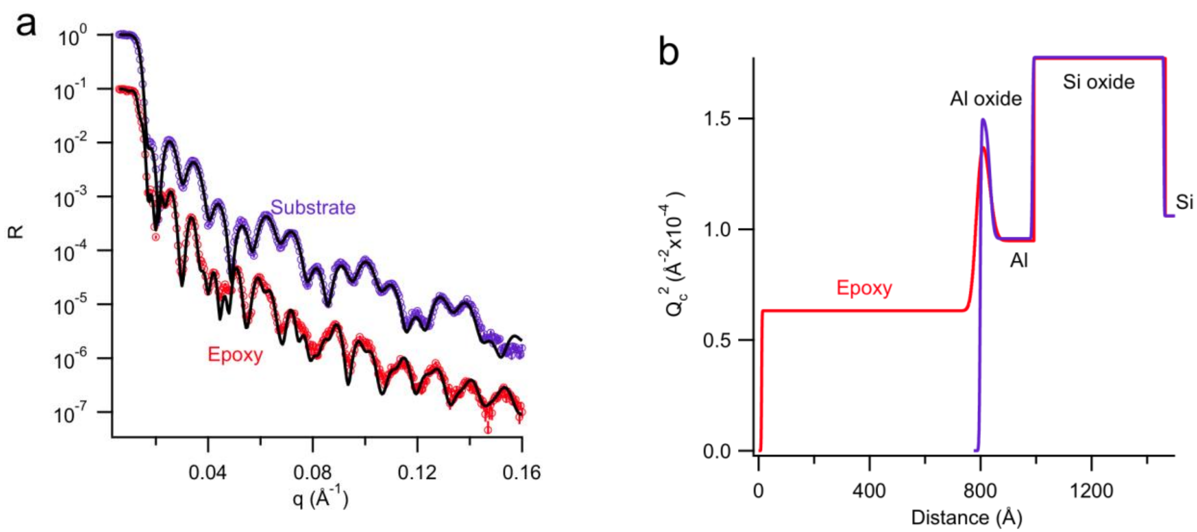



Addition of salt increases fracture energy for failure

Does this correlate with the interfacial water content?

# Developing system with high sensitivity

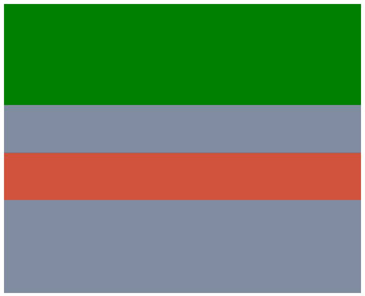



Epoxy $Q_c^2 = 0.59 \times 10^{-4}$ Å$^{-2}$ h = 80 nm

Aluminum $Q_c^2 = 0.95 \times 10^{-4}$ Å$^{-2}$ h= 18 nm

Silicon oxide $Q_c^2 = 1.68 \times 10^{-4}$ Å$^{-2}$ h = 25 nm

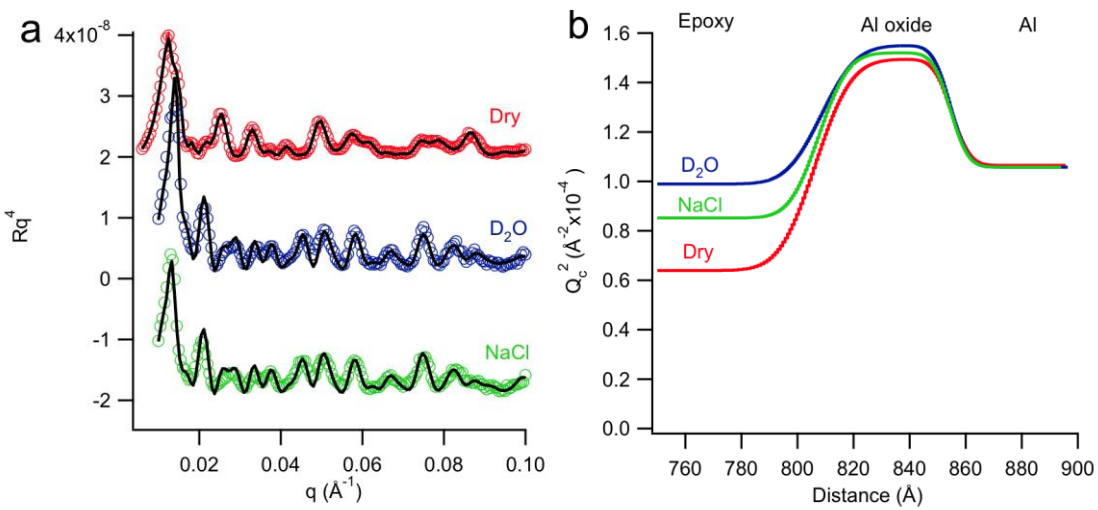
Silicon $Q_c^2 = 1.06 \times 10^{-4}$ Å$^{-2}$ h= 2 mm



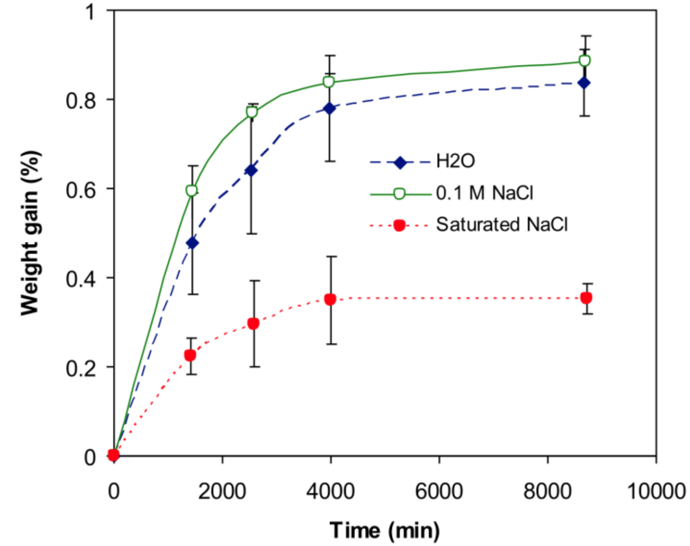
Note that SLD for aluminum is very close to silicon

# Impact of salt on water distribution

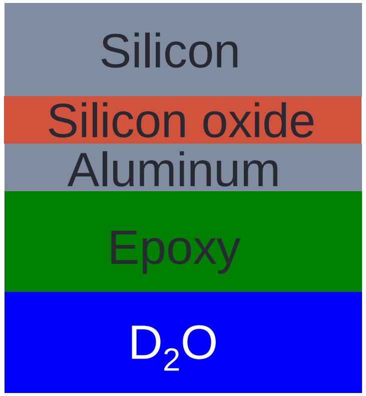
Comparison of profiles with saturated NaCl and $D_2O$




Bulk behavior




Sharper interface between epoxy and aluminum oxide in case of salt

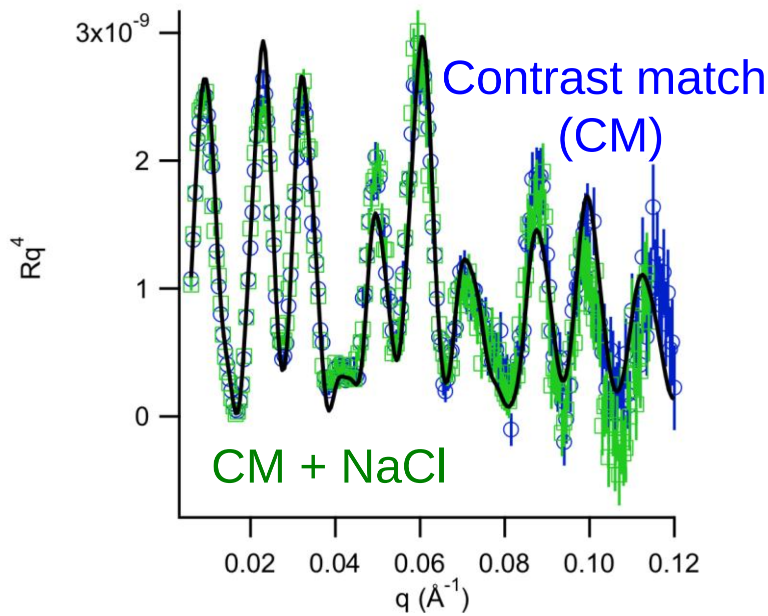



Less bulk swelling in case of salt as well

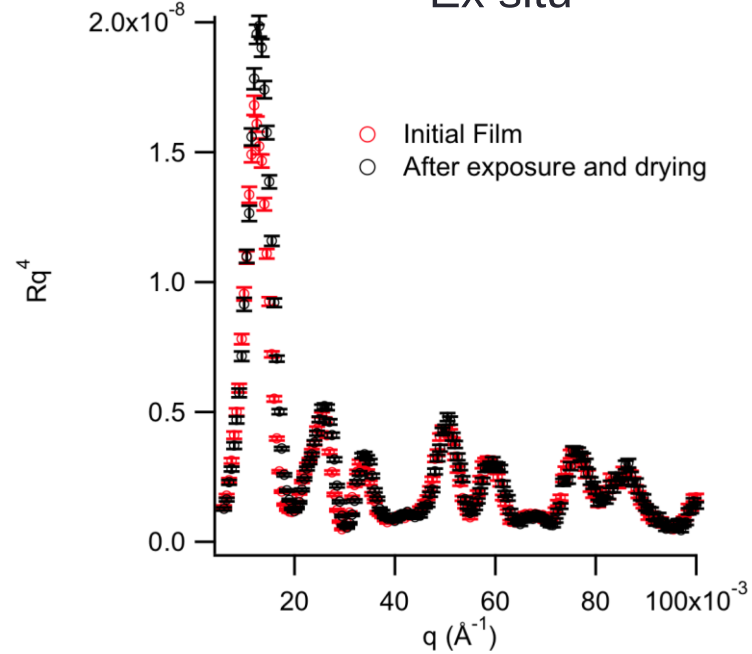
Is this due to salt incorporation into the film?

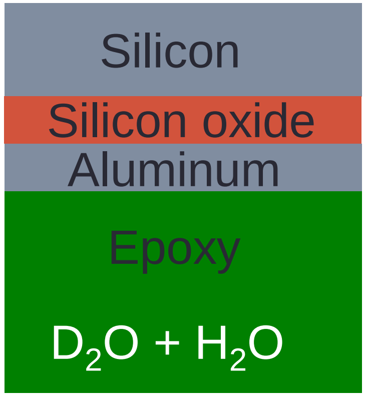
# Examination of NaCl in film

In situ




Ex situ



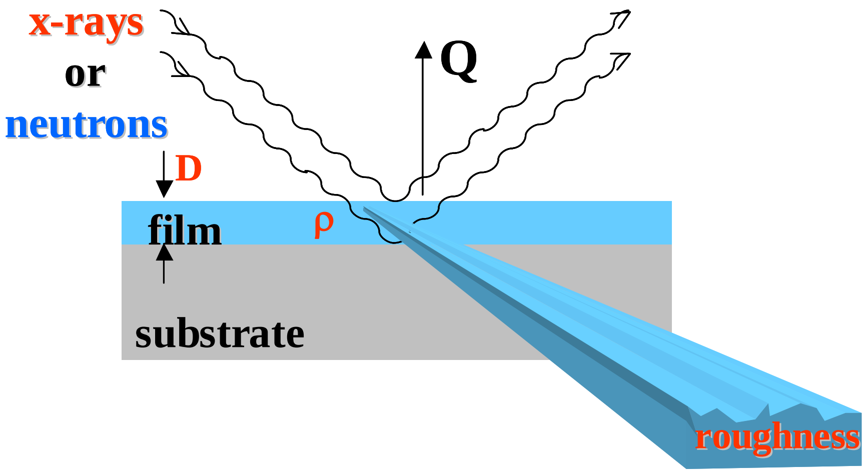



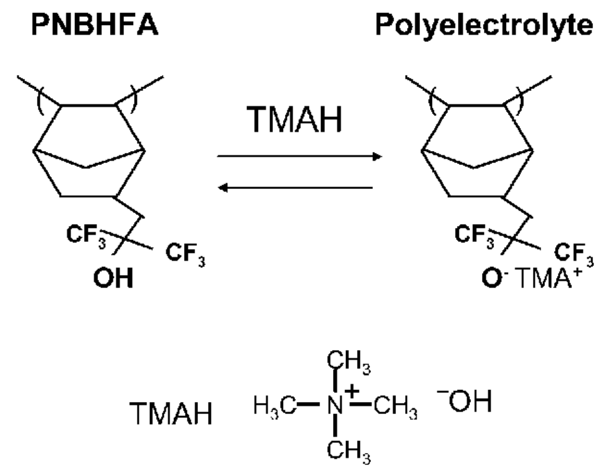

No evidence of salt accumulation within polymer

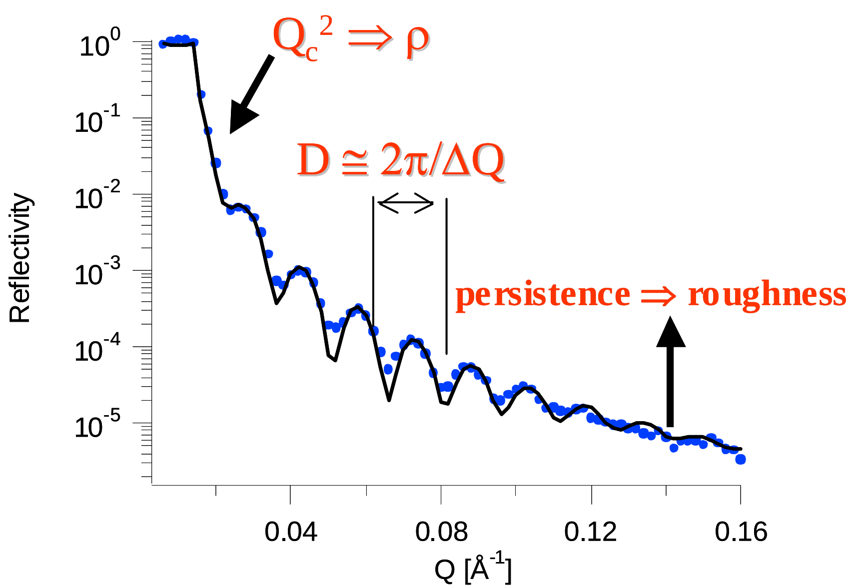
$Q_c^2 = 1.04 \times 10^{-4}$ Å$^{-2}$ for NaCl

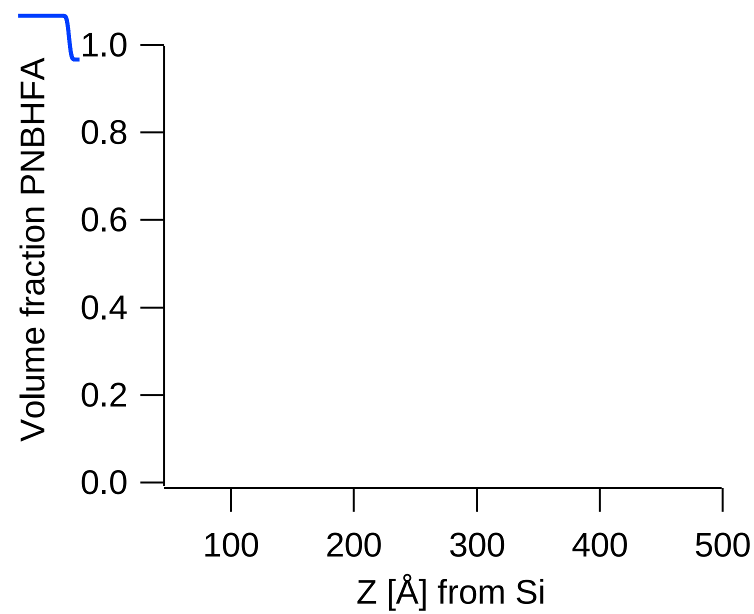
(Wang and Schaefer, *Langmuir* **2010**, 26, 234)

# Can we directly visualize salt ion distribution?



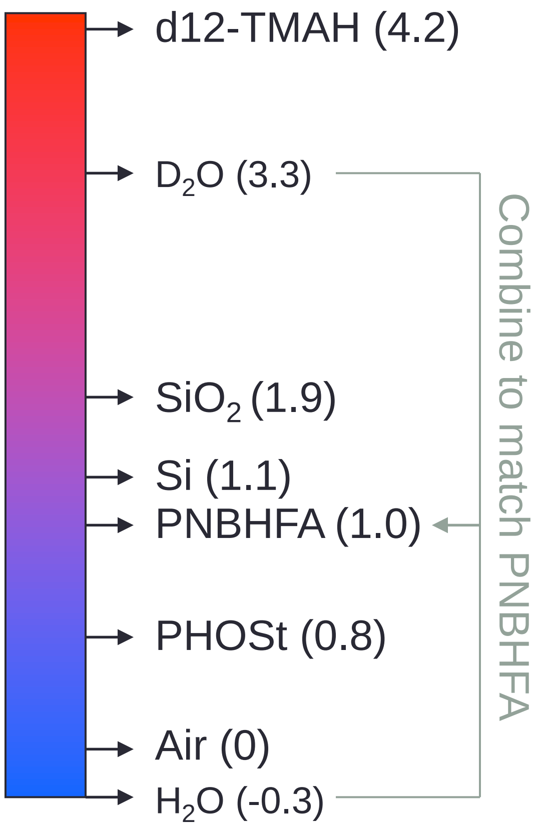



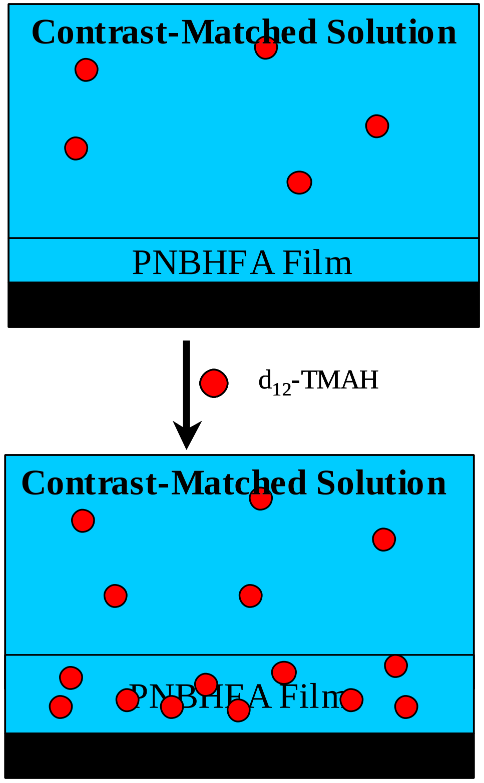



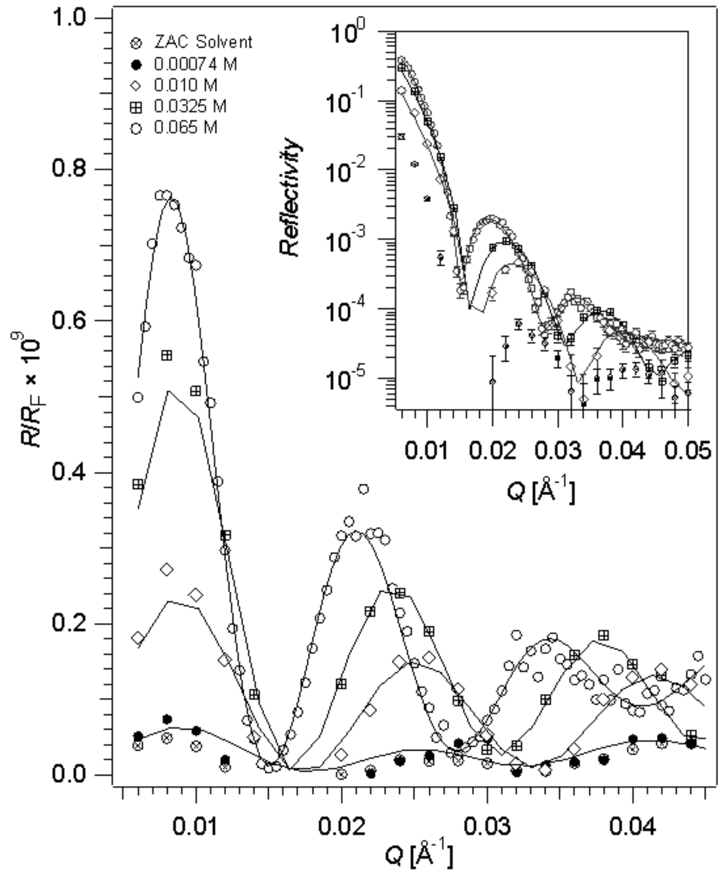




Prabhu et al., *Langmuir* **2005**, 21, 6647

# Direct measurement of Developer Profile

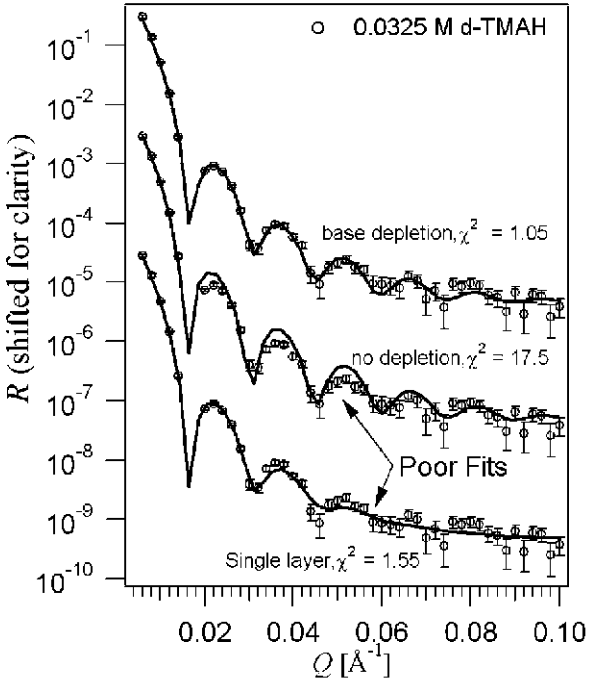


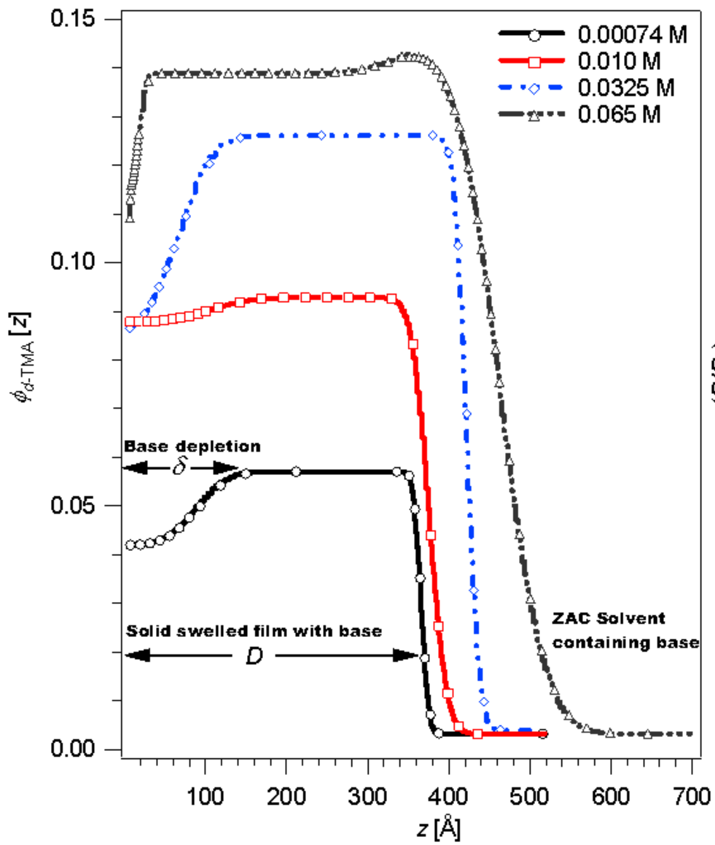



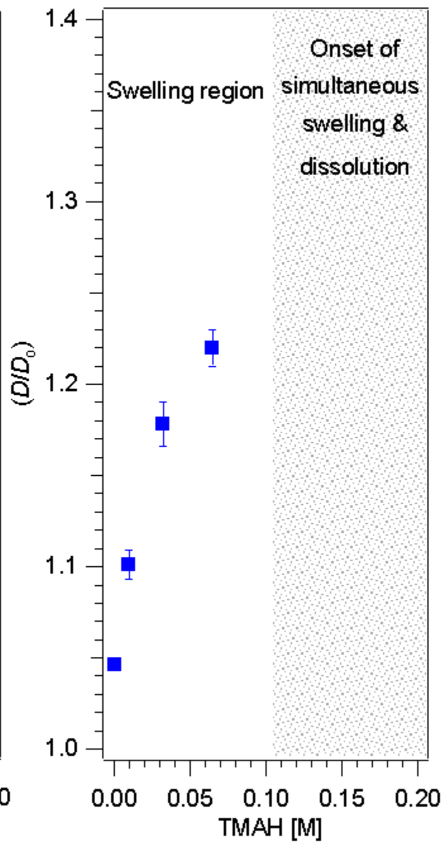

- Contrast match solvent to the dry film (not much reflectivity)
- $d_{12}$-TMA uptake increases contrast (more reflectivity)
- **Base uptake observed**

# $d_{12}$-TMA profile *within* ultrathin PNBHFA



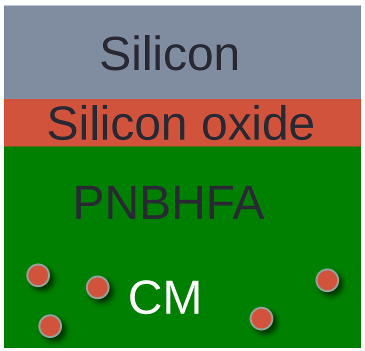

Prabhu et al., *Langmuir* **2005**, 21, 6647



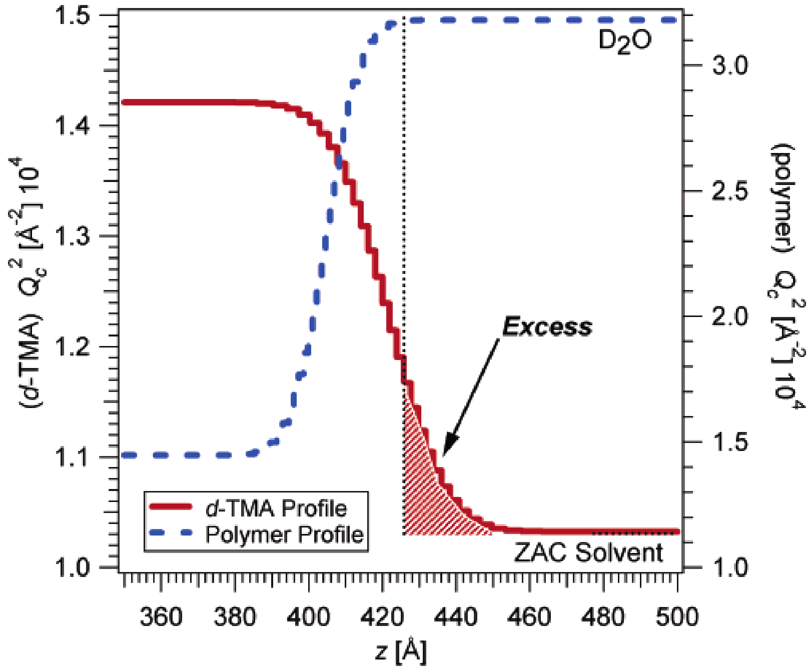

- **Direct measurement** of base profile within thin solid polyelectrolyte films
- TMA+ concentration within film enhanced with increasing base concentration
- Non-uniform profile within the film; reduced near the substrate
- Diffuse counterion profile at free surface

# Combining contrasts

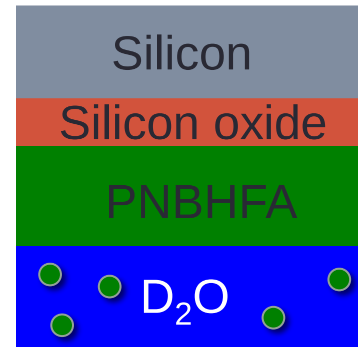



d-TMAH

Ions are visible




Prabhu et al., *Langmuir* **2005**, 21, 6647




h-TMAH

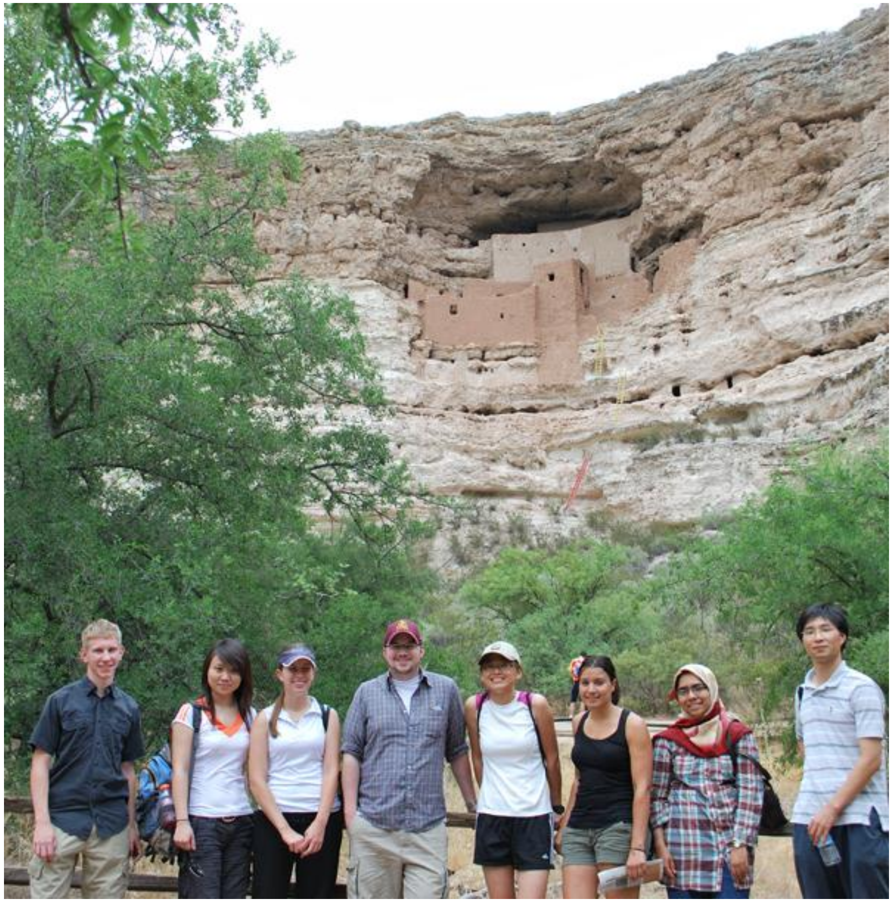
Polymer is visible

Can measure excess ion concentration that extends into solution from charging of polymer film

# Conclusions

- Water accumulates at polymer/substrate interface
- Concentration at interface
  - *Independent* of bulk solubility
  - Dependent on substrate chemistry
- Water accumulation correlates with adhesion loss
- Mechanism for critical relative humidity appears to be stress concentration due to moisture accumulation
- Salts can increase or decrease water uptake in films
- Contrast match provides facile route to visualize ion distribution

# Acknowledgements

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