Use of Hard X-Ray Photoemission Spectroscopy: Applications to Industrial R&D

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Important Uses of HAXPES for Characterization of Materials

- Non-destructive depth probe
  - Superior to angle resolved XPS for rough surfaces -- see e.g. Merzlikin et al. SS, 602 (2008) 755.
- Analyze deeper than lab based (Al k$\alpha = 1486.7$ eV) XPS
  - Provide more “bulk-like” data
- Access characteristic lines unavailable at lower energy
  - Note this can sometimes result in shallower analysis depths to give more surface sensitive information

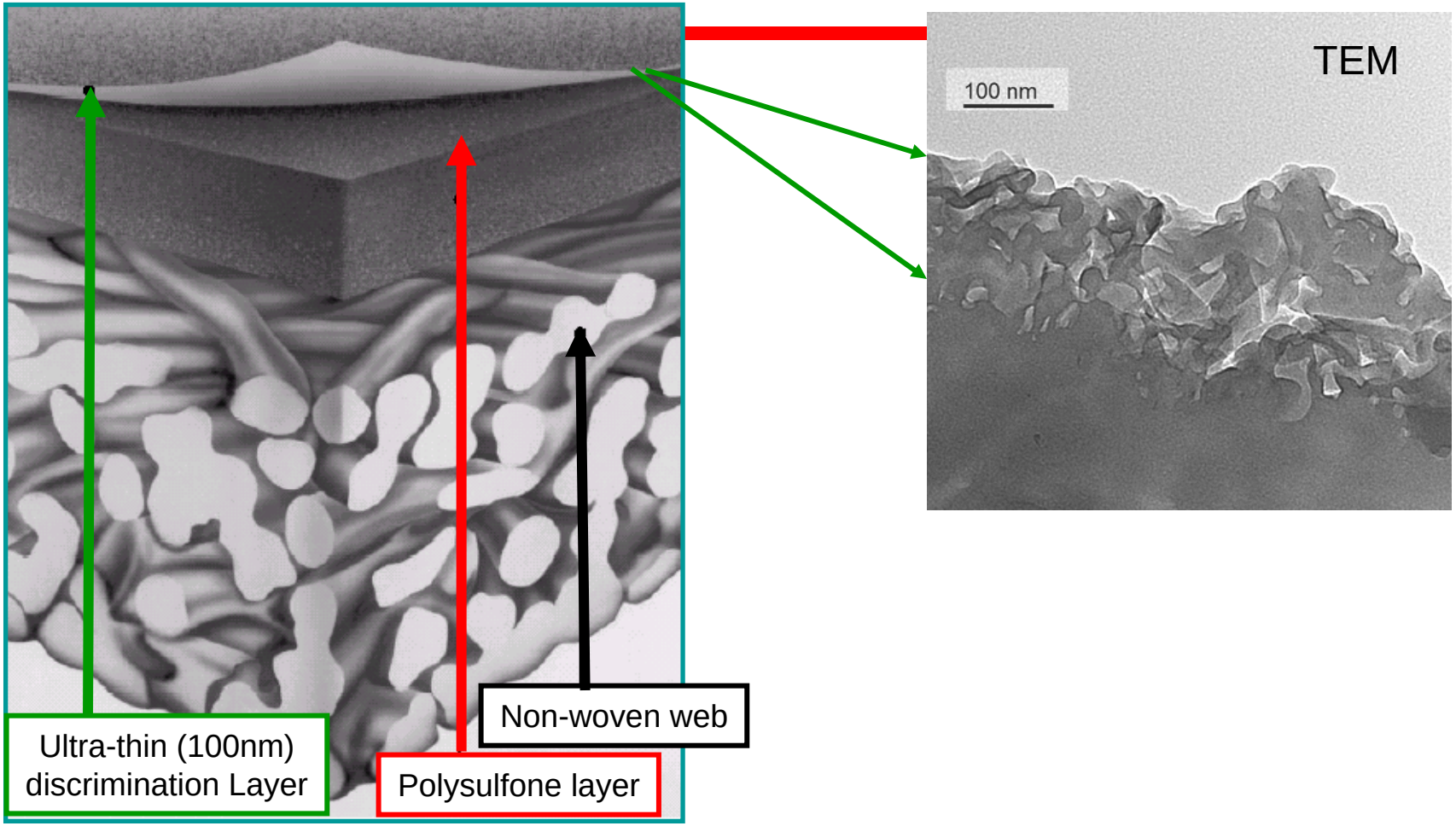
Potential Application Areas

- Reverse Osmosis Membranes
- Characterization of intermixing in inorganic thin films
- Surface derivatization for understanding surface functionality
- Automotive adhesive applications
- Grafted polymers to modify adhesion for foot ware and laminated films
- Coatings with surface polarized release functionality for anti-adhesive applications
- Characterization of composition vs. depth for powdered materials: Heterogeneous catalyst characterization
  - “seeing” into Porous catalysts (zeolites etc.)
    - Pt / zeolite want most Pt in pore not on exterior of particle where it is non-shape selectable
  - Thin film oxides supported on oxide catalysts

Reverse Osmosis

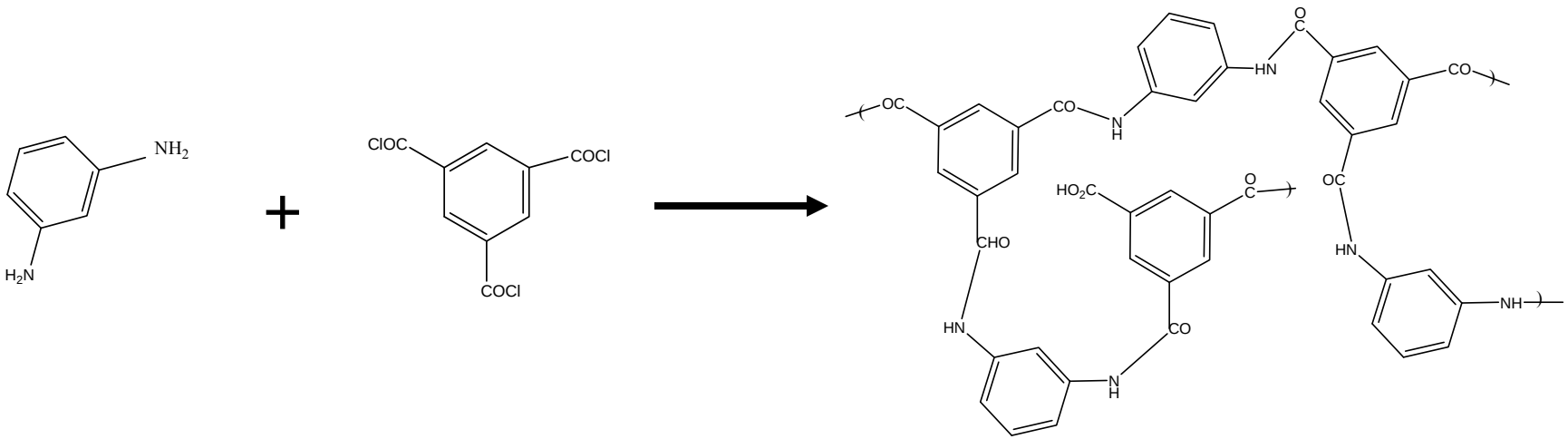
- Water purification
  - Seawater and brackish water desalination
  - Removal of ionic impurities
  - Removes biological contamination
- FT30 membrane consists of 3 layers:
  - Polyester support layer
  - Porous polysulfone transition layer
  - Semi-permeable ultrathin polyamide discrimination layer

Membrane Composite Structure



Polyamide Discrimination Layer Chemistry

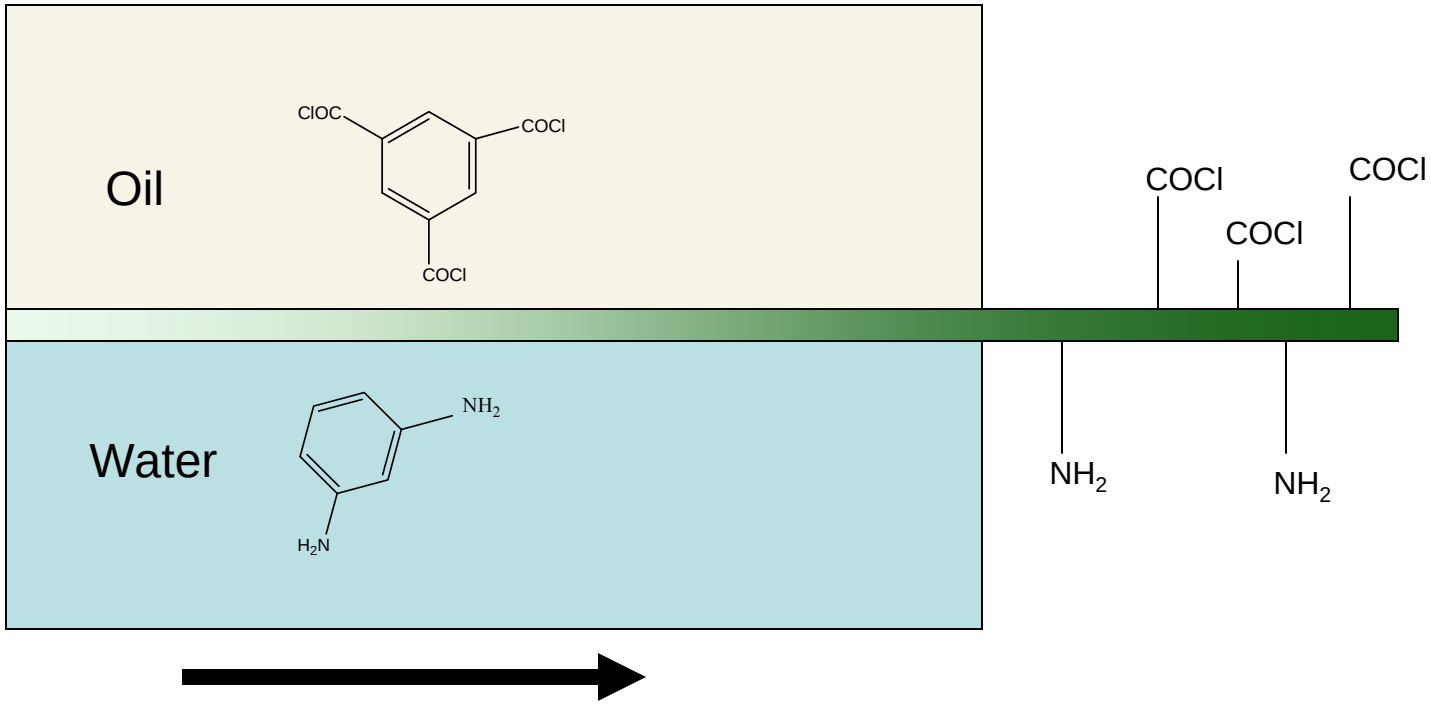
FT 30 = Interfacially polymerized copolymer of meta phenylene diamine (MPD) + Trimesic acid chloride (TMC):



Any excess acid chloride hydrolyzes readily in water

Aramide, Amine, carboxylic acid groups all possible

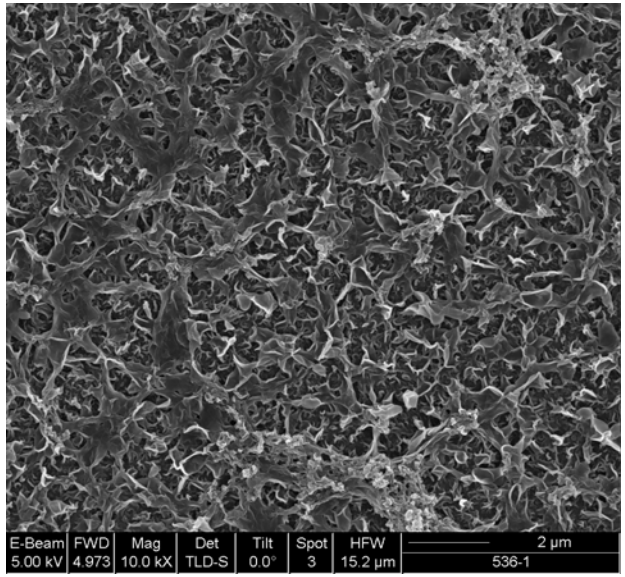
Interfacial polymerization of Discriminating Ultra-thin Polyamide

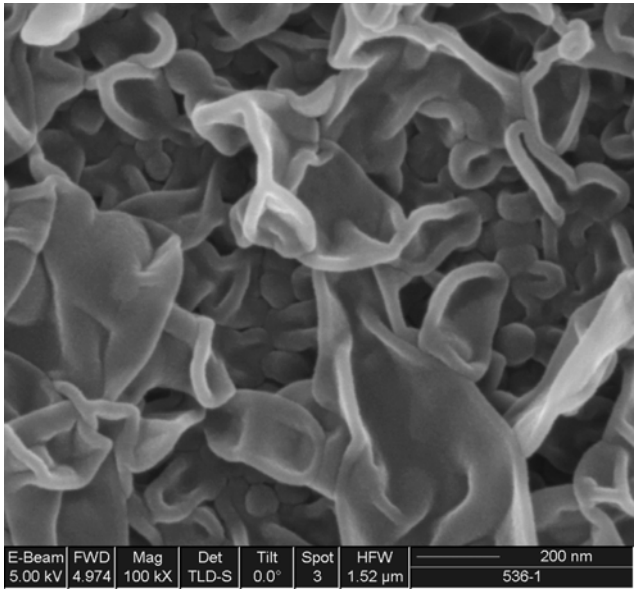


Target Information for HAXPES

- End group location for interfacially polymerized films
- Characterization of coatings that enhance Membrane properties
  - Adjust hydrophobicity
  - Enhance rejection of particular ions

SEM Image of FT30 Membrane





SEM images highlight the complex physical structure of the surface of the discrimination layer

Derivatization / XPS for Determining Surface Functionality

Applications for HAXPES:

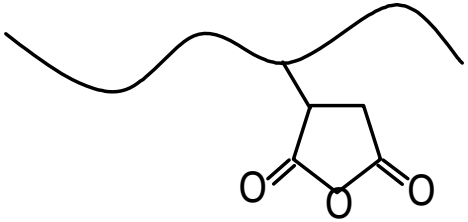
- How deep is a surface derivatized?
- Variation of functional groups with depth?

Enhancing adhesion to polyolefin surfaces

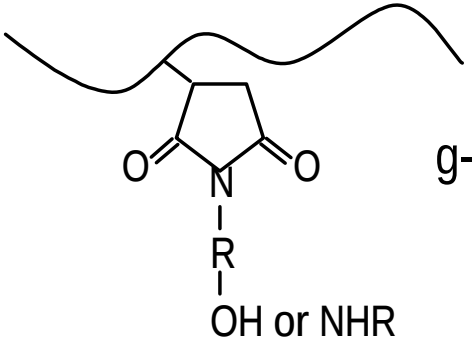
<u>Polyolefins have low energy surfaces</u>

- Poor adhesion
- Paintability

Solution ⇒ Grafting reactive moieties to polyolefin chain

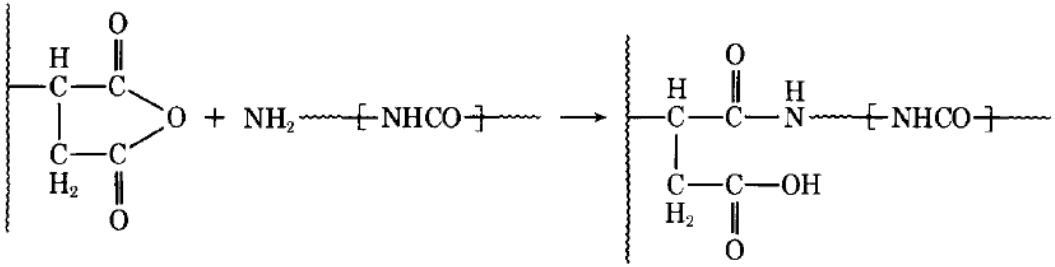


g-MAH



g-OH, g-NH

Chemical bond at interface



Macromolecules, 1996, *29*, 774

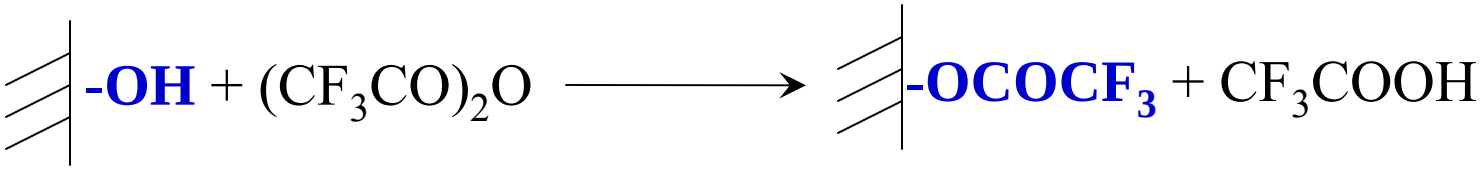
Surface Chemistry of Grafted Polyolefins

XPS (X-ray Photoelectron Spectroscopy)

- Elemental analysis (~10nm surface layer)
- Molecular specificity?

Chemical Derivatization + XPS

❖ Surface functionality ❖ Introducing F atoms



Chemical Derivatization + XPS + VKE-HAXPES

❖ Depth of surface functionality

Gas-Phase Chemical Derivatization

Enhance detection of g-MAH, g-OH, g-NH

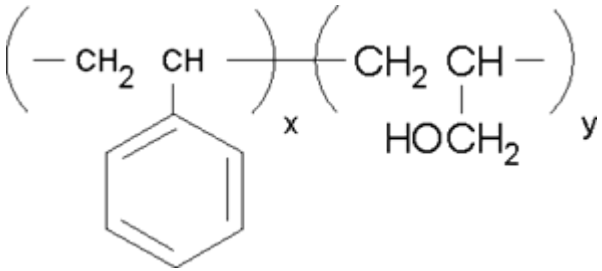
- Grafted in low concentration: 1.5 - 0.15 wt% bulk
- Molar concentration: ~ 0.17 - 0.017% (LOD XPS ~ 0.2 atomic %)

Use fluorinated molecule to enhance detection

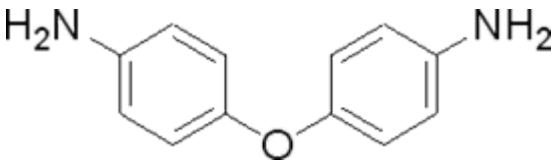
- Gas-phase
- Should not cause surface swelling / conformational changes
- Few interferences
- Fluorine increases XPS sensitivity

Applied to multiple chemical functionalities

Derivatization Reactions

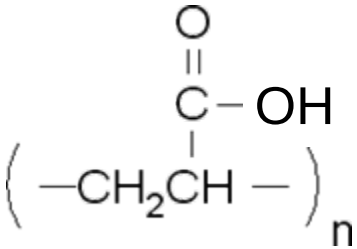


-OH



-NH_2

-NH-



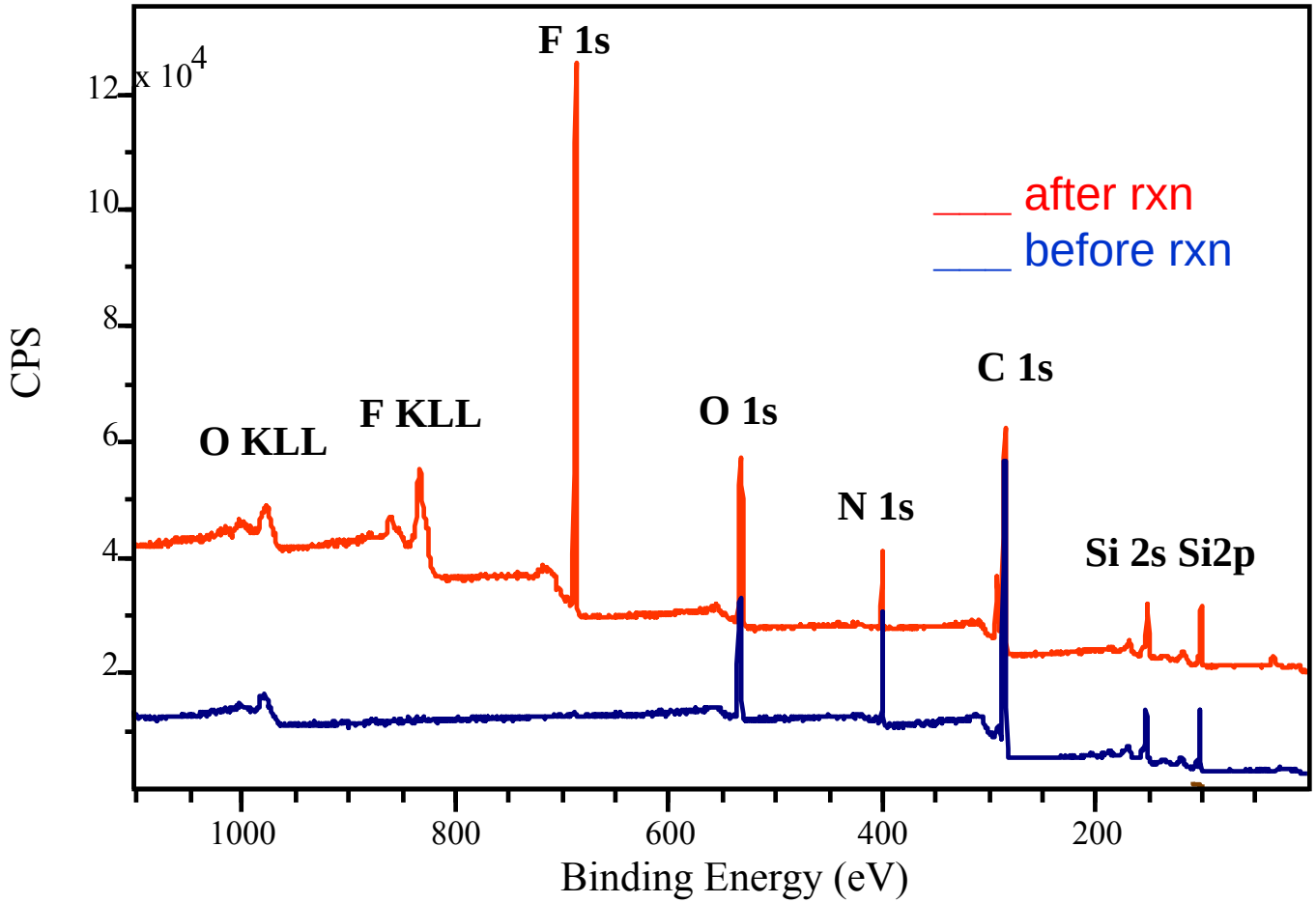
-COOH, anhydrides

$(CF_3CO)_2O$

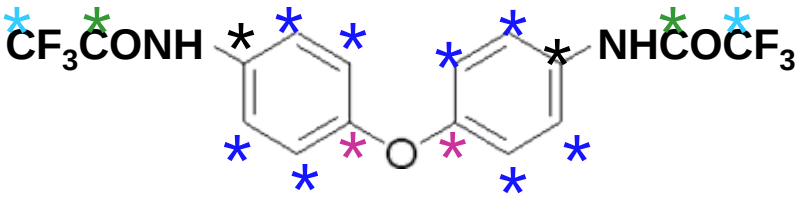
C_6F_5CHO

CF_3CH_2OH

XPS survey
bis-phenol-A-diamine with TFAA



C 1s spectrum --- diamine with TFAA

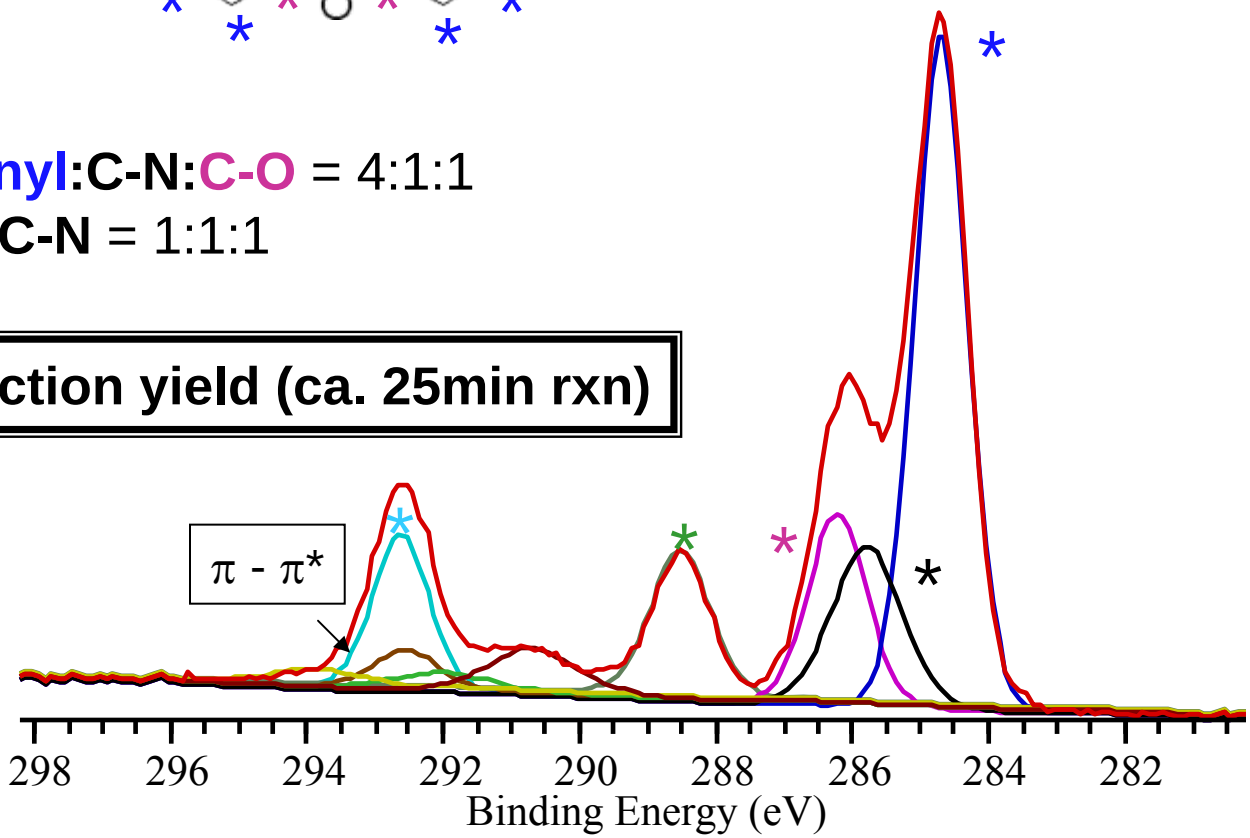


C ratios:

✓**C in phenyl:C-N:C-O** = 4:1:1

✓**CF3:CO:C-N** = 1:1:1

~100% reaction yield (ca. 25min rxn)



NH_2% quantification from F%

Data source	N conc. in mol%
F 1s	7.4
Theoretical ($C_{16}F_6N_2O_3$)	7.4

Question: what is the surface conc. before the derivatization?

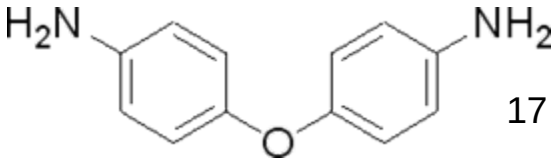
$NH_2 \rightarrow NHCOCF_3$

$X\%$ $\quad 7X\%$

So N% after the reaction is:

$$\frac{X\%}{(1-X\%)+7X\%} = F\%/3$$

$X\%$ = 13.3%, consistent with $C_{12}N_2O$



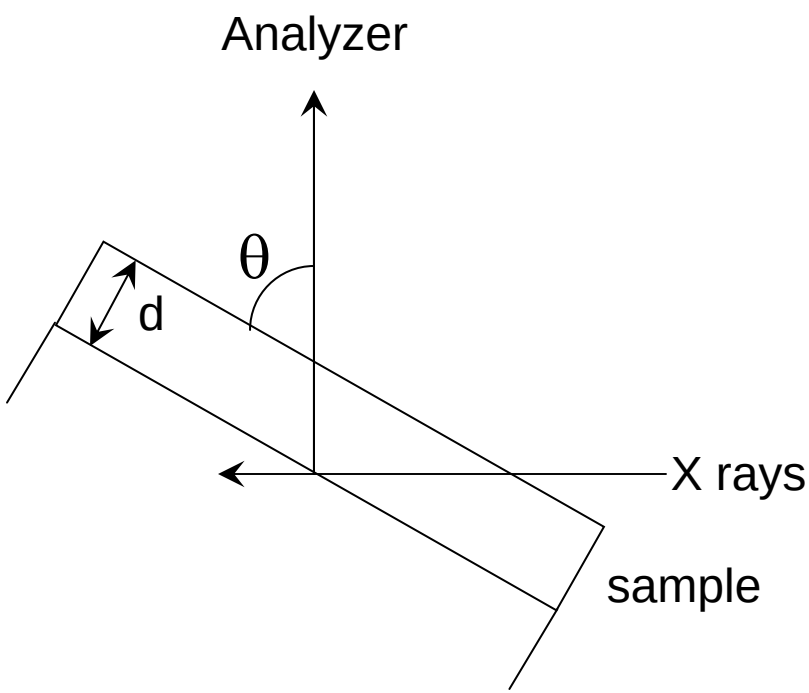
Penetration depth --- take-off angle study

PS/allyl alcohol reacted with TFAA	90°	45°	30°
depth ratio	1	0.7	0.5
depth in nm*	9	6.3	4.5
F%	10.6%	9.4%	9.5%
O%	6.3%	6.4%	6.2%
F/O	1.69	1.46	1.53
C%	83.2%	84.2%	84.3%

*Estimated based F1s photoelectrons; reference: Seah MP, Dench WA, *Surf. Interface Anal.*, 1, 2, 1979.

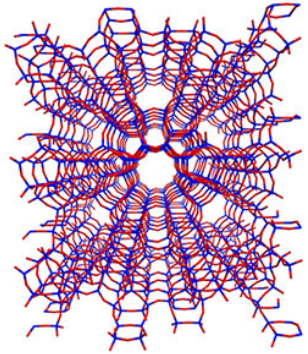
Penetration depth

$$d \propto \sin\theta$$



Heterogeneous Catalysts

- Zeolites provide shape selective catalysis
  - Active sites (usually Lewis acid metal atoms) must be within pore – not on surface
  - Higher kinetic energy required to probe internal structure
  - Energy variation to determine surface vs. inside pores



Acknowledgements

- Bill Mickols -- Dow Water & Process Solutions
- Kevin Sikkema -- Dow Water & Process Solutions
- Josh Chen -- Dow Analytical Sciences
- Paul O'Connor -- Dow Analytical Sciences
- Sandeep Dhingra -- Dow Analytical Sciences
- Ashish Batra -- Dow Elastomers
- Joe Woicik -- NIST
- Dan Fischer -- NIST