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Chemically Functional Nanostructured Antifouling Coatings

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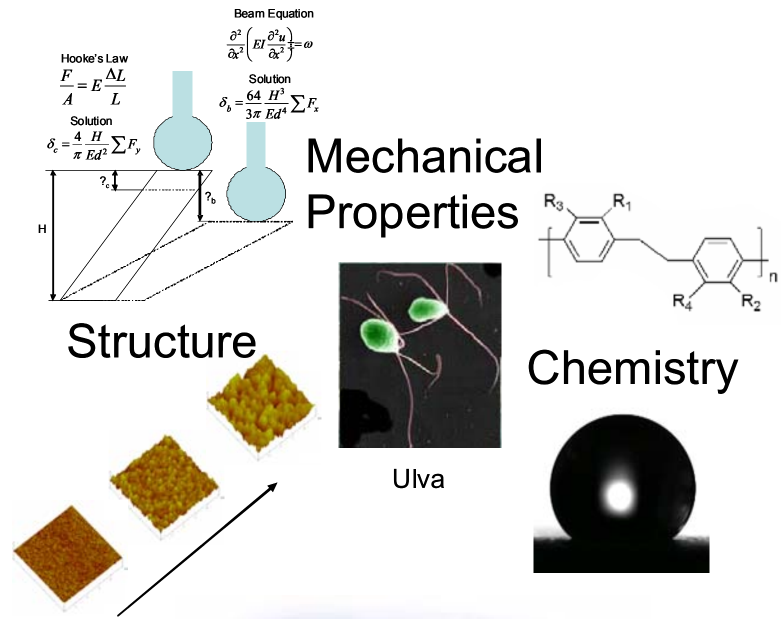
Outline

- Objective
- Film Preparation and Properties
- Antifouling Performance
- Conclusions

Objective

- To prepare nanostructured polymers using a complete bottom-up approach with controlled physicochemical properties, such as ***mechanical properties, structure (morphology) and chemistry*** for applications in the area of antifouling coatings

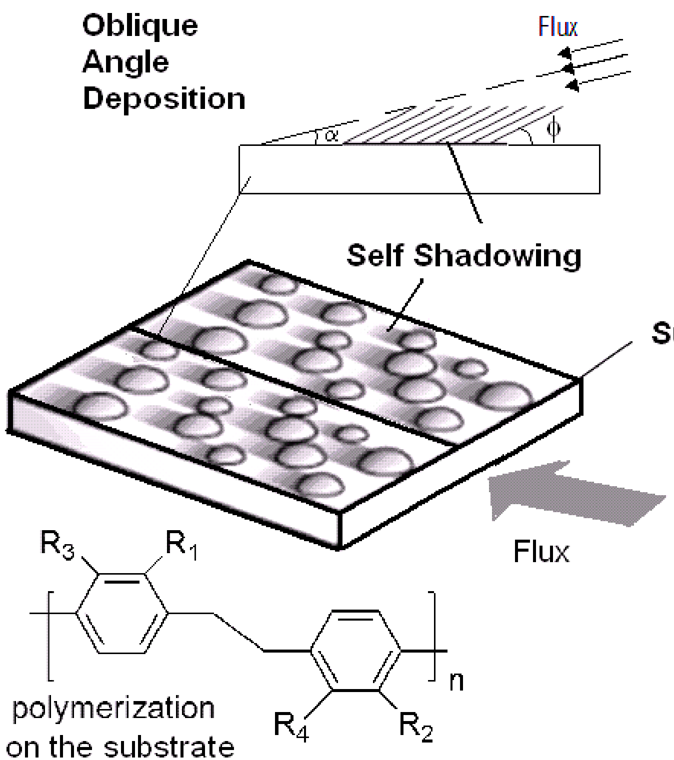
- Funding: Office of Naval Research, USA

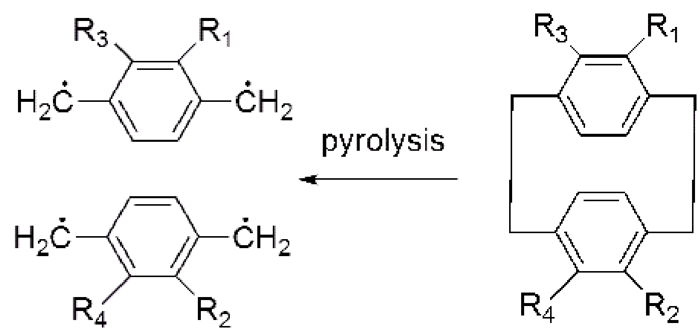


Oblique Angle Polymerization

Using substrate tilt and rotation – Simultaneous control of:

- Surface roughness
- Lateral morphology
- Mechanical Properties





Boduroglu, S., Cetinkaya, M., Dressick, W. J., Singh, A. & Demirel, M. C. *Langmuir* **23**, 11391-11395 (2007).

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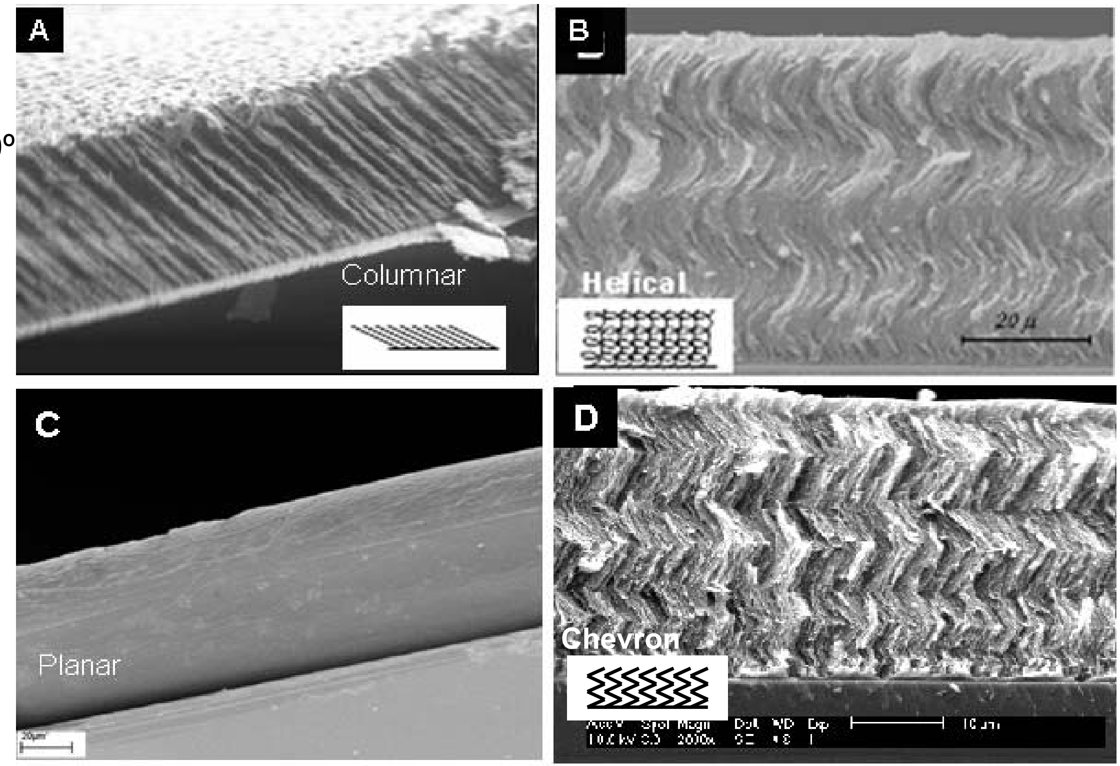
Different Lateral Morphologies

Tilt angle = 10º

No rotation



Tilt angle = 10º

Continuous +ve rotation

No Tilt (no nozzle)

No rotation

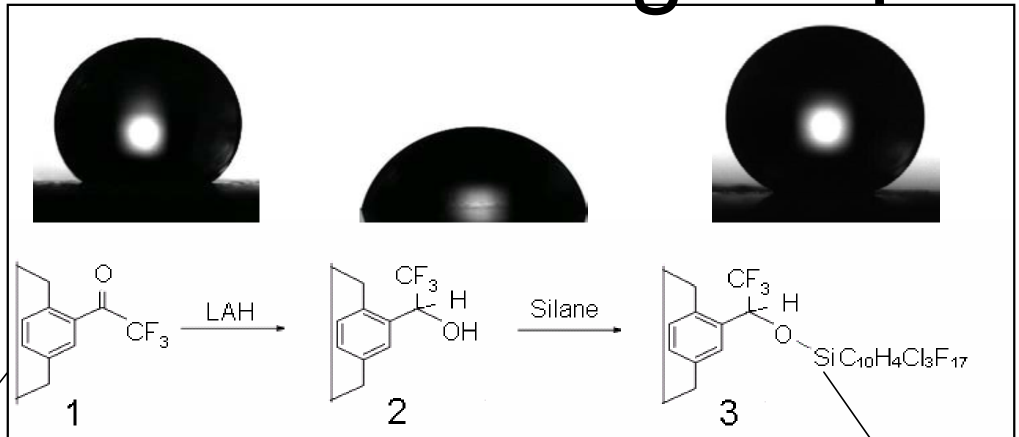
Tilt angle = 10º

Time bound +ve and -ve rotation

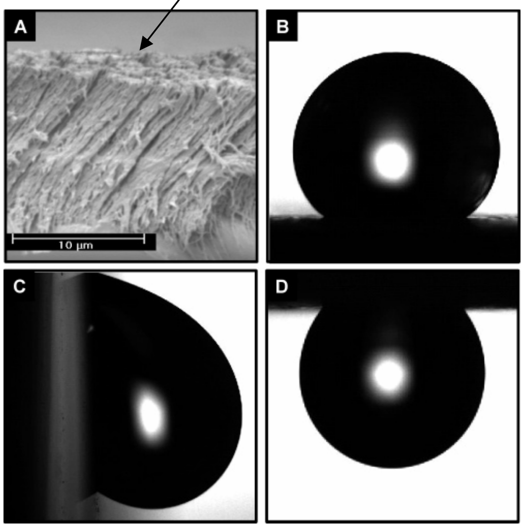
Tunable Wetting Property

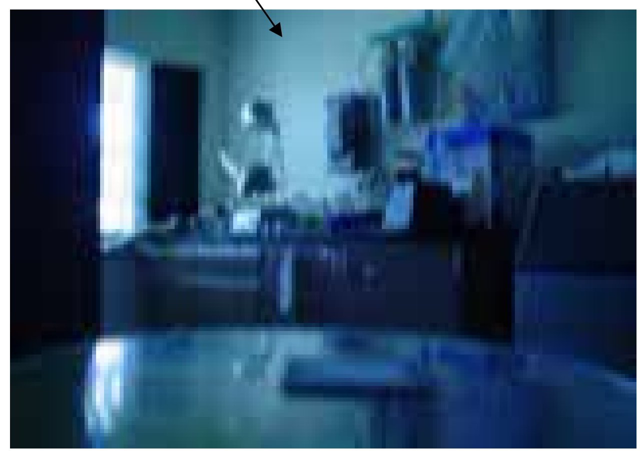
Adhesive and

Hydrophobic



Non-Adhesive and Hydrophobic
Roll off angle < 5 degrees





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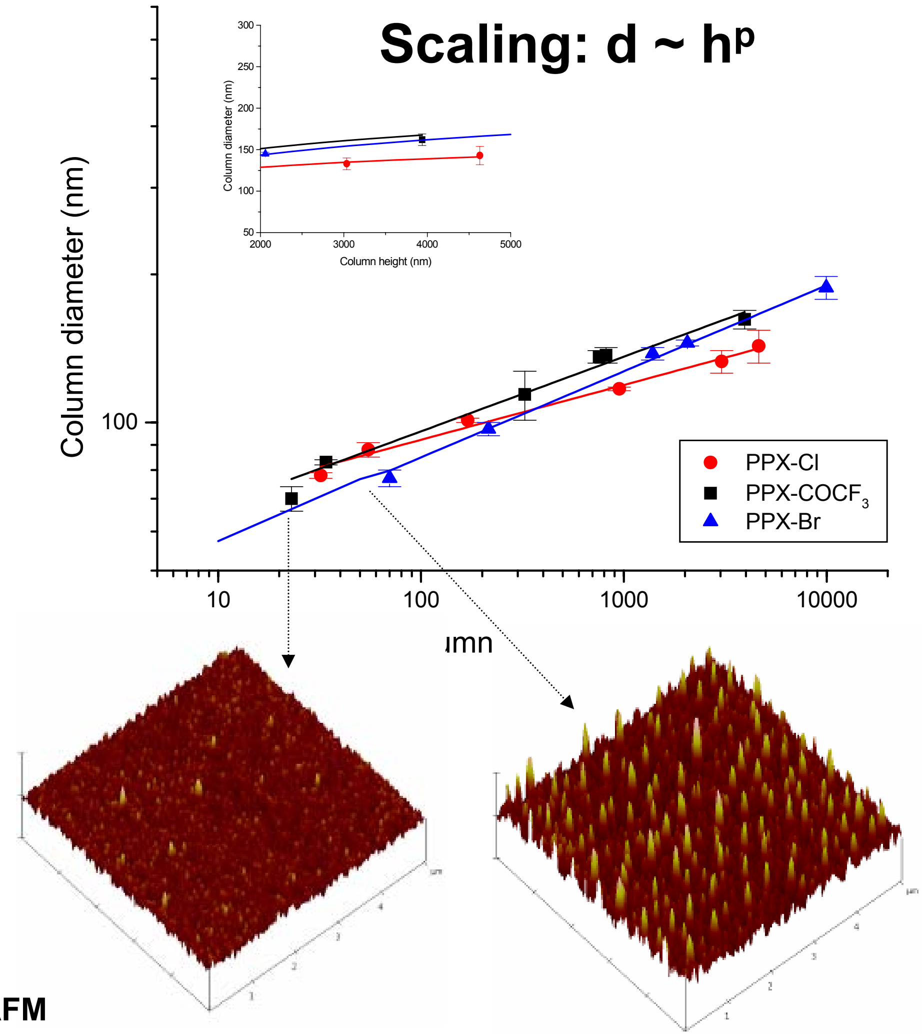
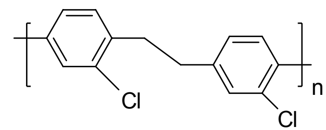
Evolution and Growth



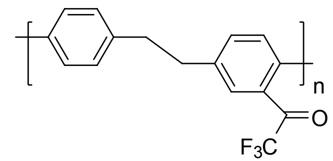
AFM

0<p<0.3 high diffusion

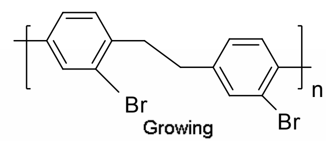
PPX-C ----- p= 0.12

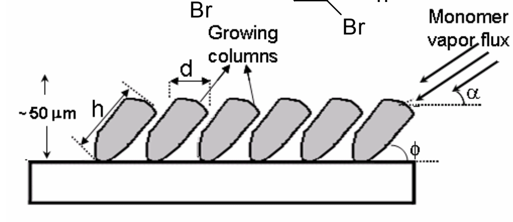


PPX-Br ----- p= 0.17



PPX-COCF3 ---- p= 0.20





Cetinkaya, M., Malvadkar, N., Demirel, M.C. *Journal of Polymer Science Part B: Polymer Physics* **46**, 640-648 (2008).

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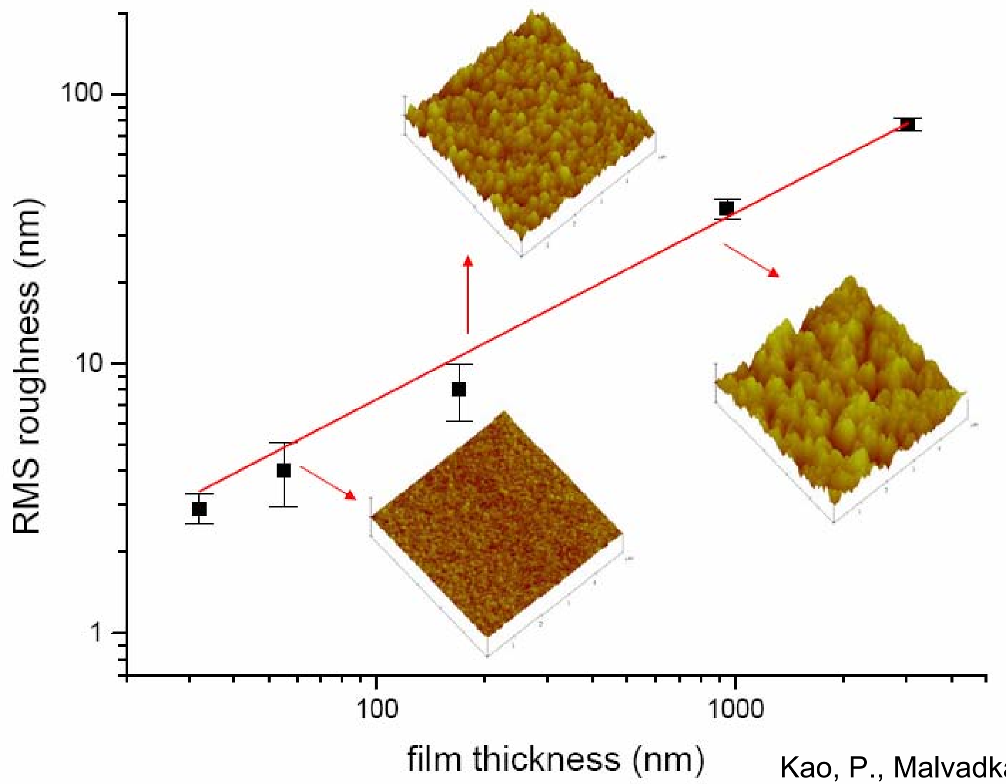
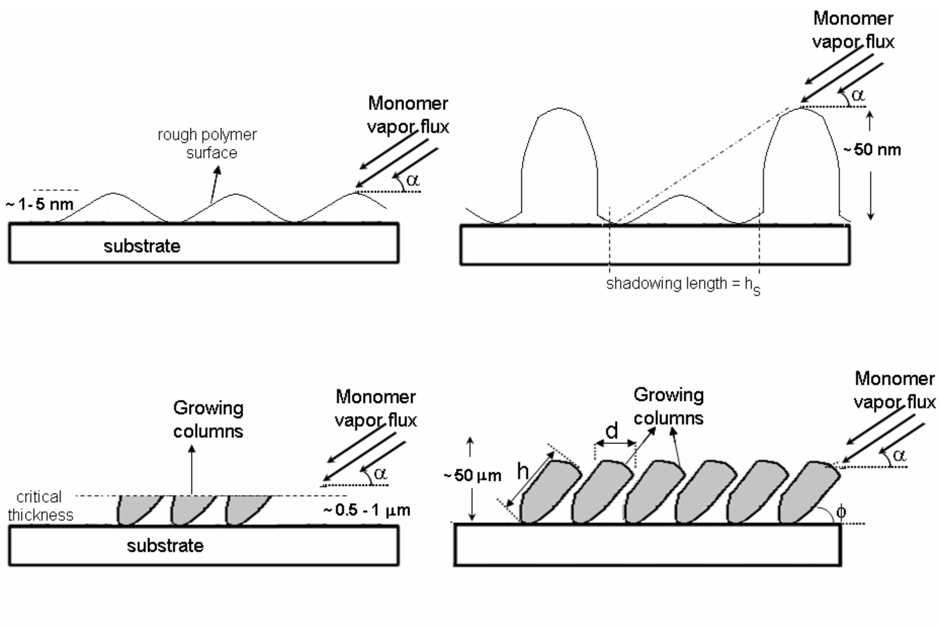
Power-Law Scaling



Kao, P., Malvadkar N., Allara, D., Demirel, M.C. *Advanced Materials*, In Press (2008).

Growth Model



Ballistic Monte Carlo Method

Cetinkaya, M., Malvadkar, N., Demirel, M.C. *Journal of Polymer Science Part B: Polymer Physics* **46**, 640-648 (2008).

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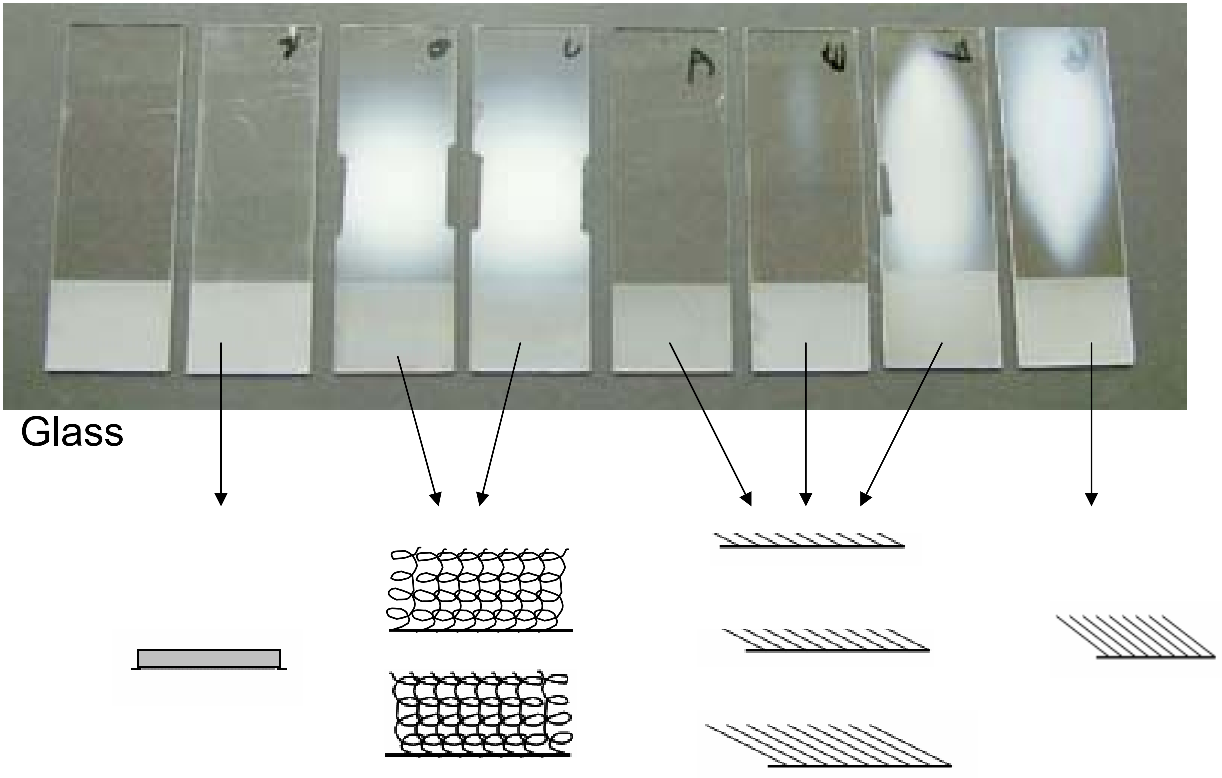
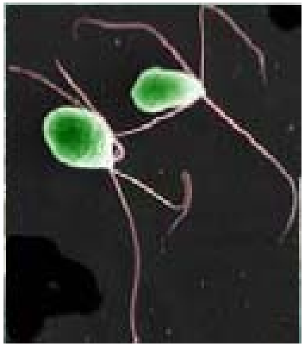
Samples to Test Antifouling Performance



Planar Helical Thickness Tilt Angle

Antifouling Test are conducted in collaboration with Prof. Callow’s group

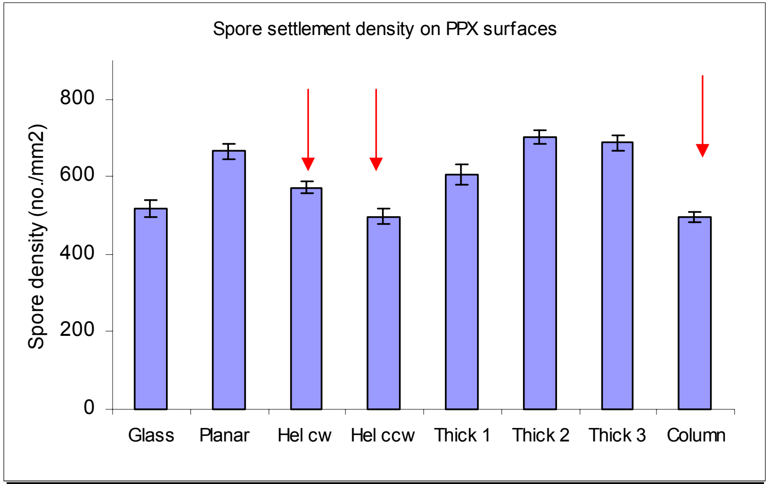
Effect of Nanotopography

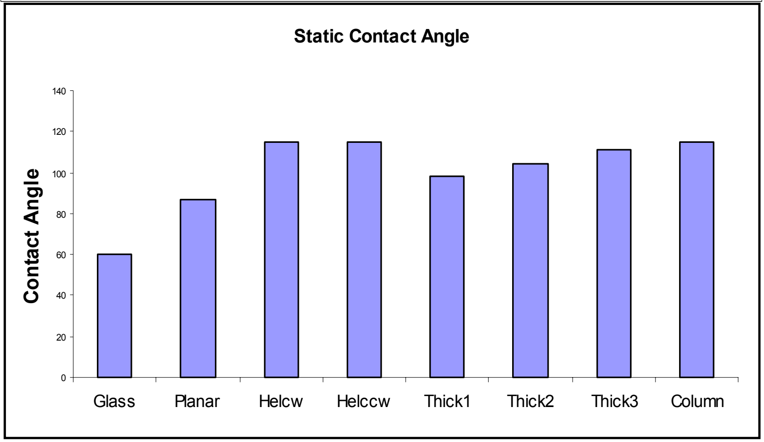


Different morphologies but similar settlement results. (~10% variation)

Zoospore suspension (1.5 x10^6 ml^{-1}) at 20 ºC

Simulated shear stress of 52 Pa in a water channel





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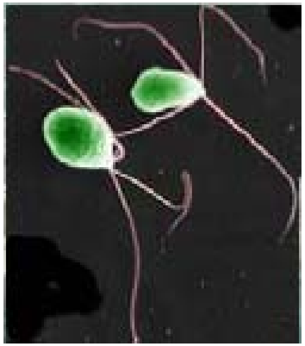
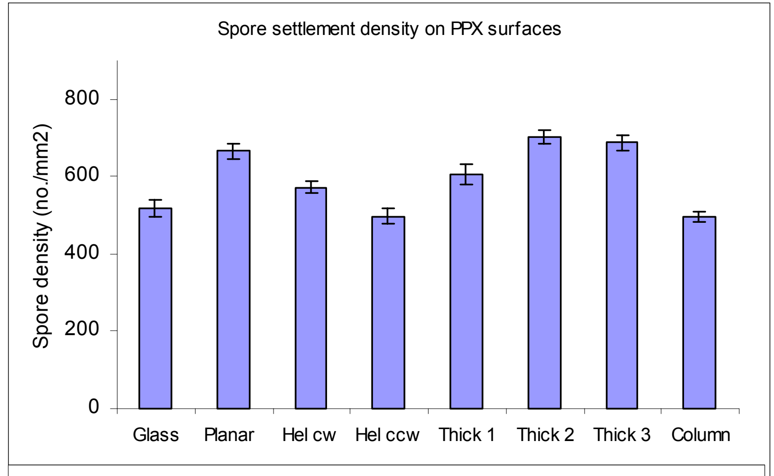
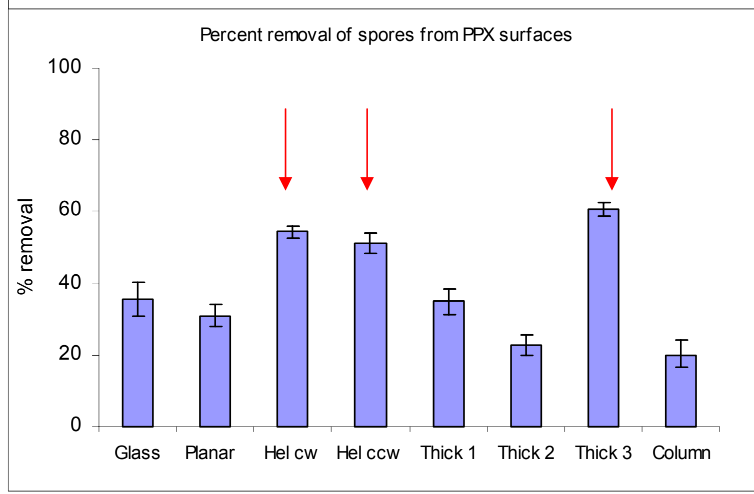
Lateral Morphology Effects







Nanostructured polymer morphology (***without chemical modification***) produced an increase amount of removal (40%) for Ulva

Thickness dependence shows that **mechanical properties** are important!.

Conclusions

- A complete bottom approach to create nanostructured polymers for application as antifouling coatings
- Tunable physicochemical properties: morphology, topology, surface chemistry, mechanical properties.
- The surface wetting properties can be tuned hydrophobic adhesive ⇔ hydrophobic non-adhesive
- Nanostructured polymer morphology produced an increase amount of removal (40%) compared to planar films with exactly same chemistry. (importance of nanotopography on antifouling)

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Acknowledgements

Demirel Lab:

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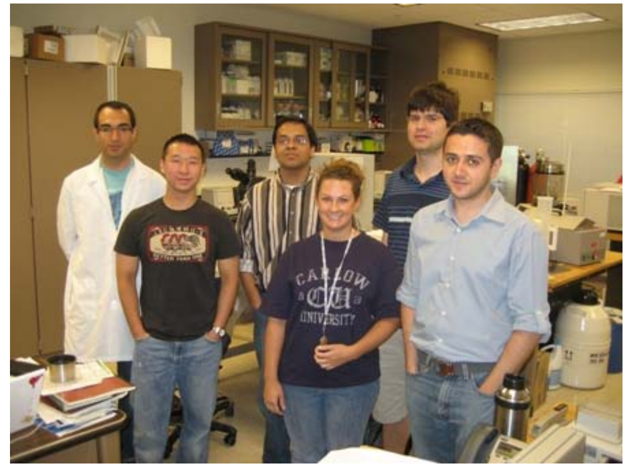
•**Undergraduates:** Ashlee Mangan, Tomas Marko, Brendon Purcell, Mike Anderson

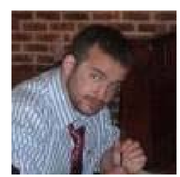
Outside (Active Collaborators):

•Walter Dressick(NRL): Metallization
•David Allara(Penn State): SERS
•Kathy Wahl (NRL): Mechanical Properties
•Callows' group (Birmingham, UK): Antifouling-John Finlay, Maureen Callow





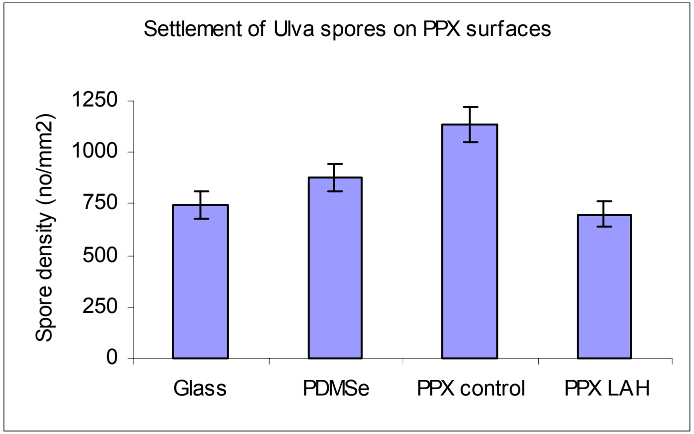




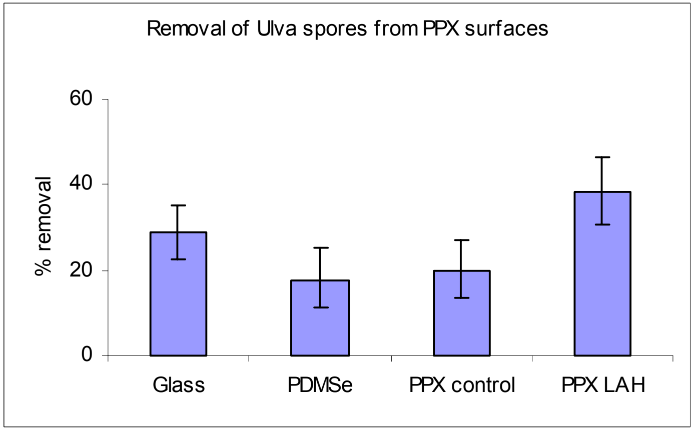

Appendix Slides

Antifouling Studies Using *Ulva* Spores

Comparative study with PDMSe antifouling coating

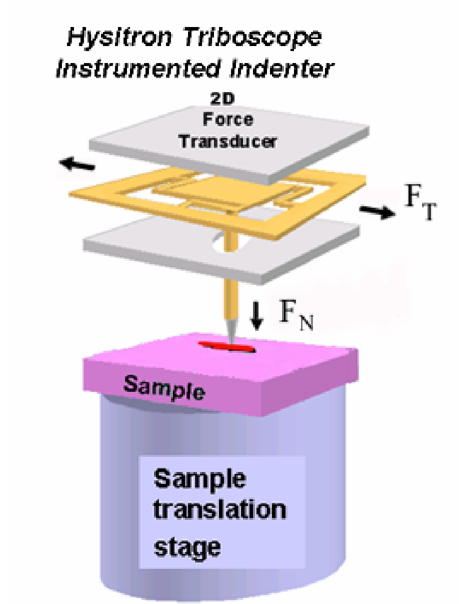


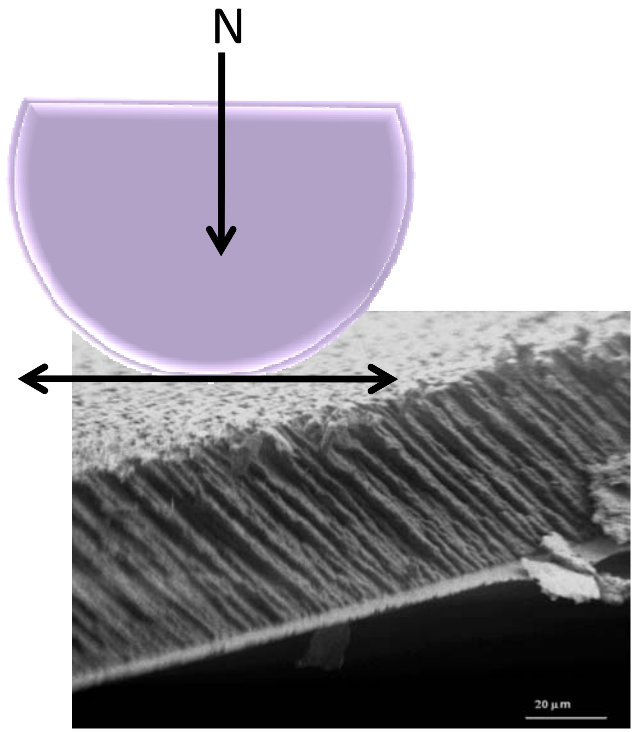
Zoospore suspension (1.5 x10^6 ml^{-1}) at 20 ºC



Simulated shear stress of 52 Pa in a water channel

Mechanical Properties





Do material anisotropies influence friction, deformation processes?

In collaboration with Kathy Wahl (Naval Research Lab)

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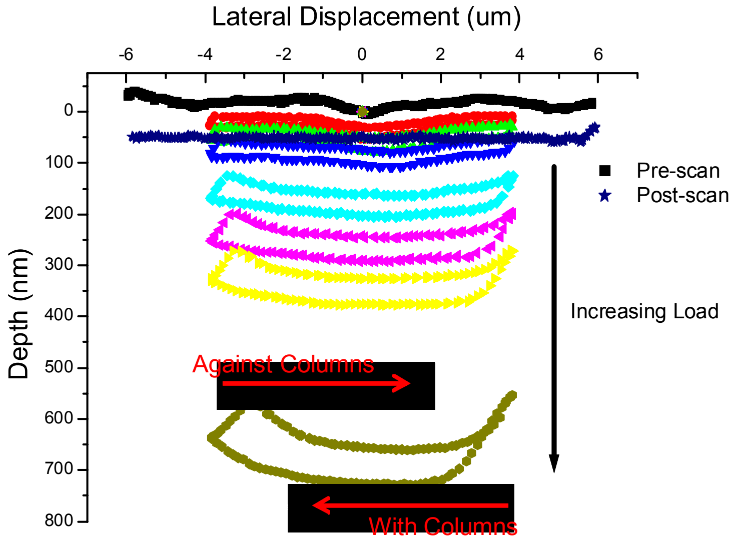
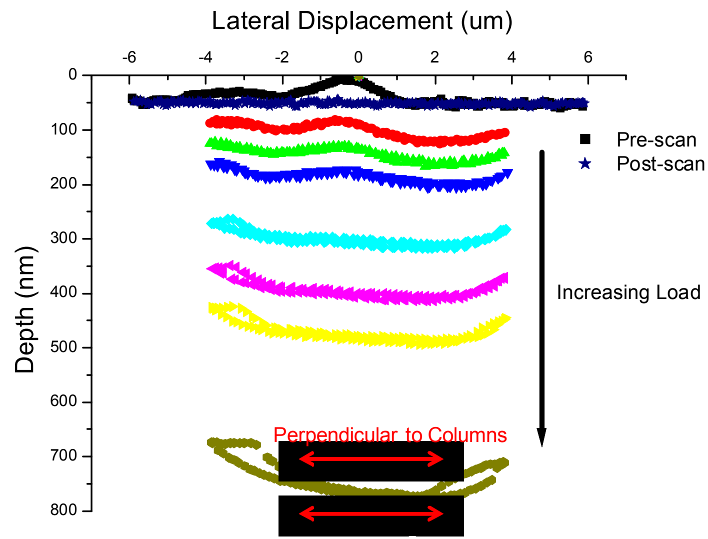
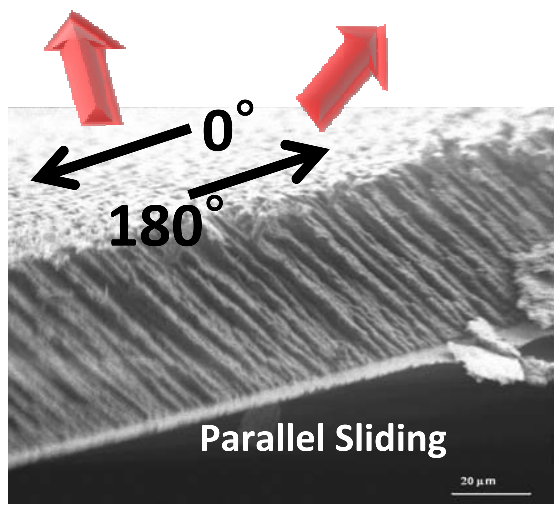
Contact Depths During Sliding





Anisotropy? YES

Tip penetrates deeper into film when sliding with column tilt



Arrows indicate the sliding direction

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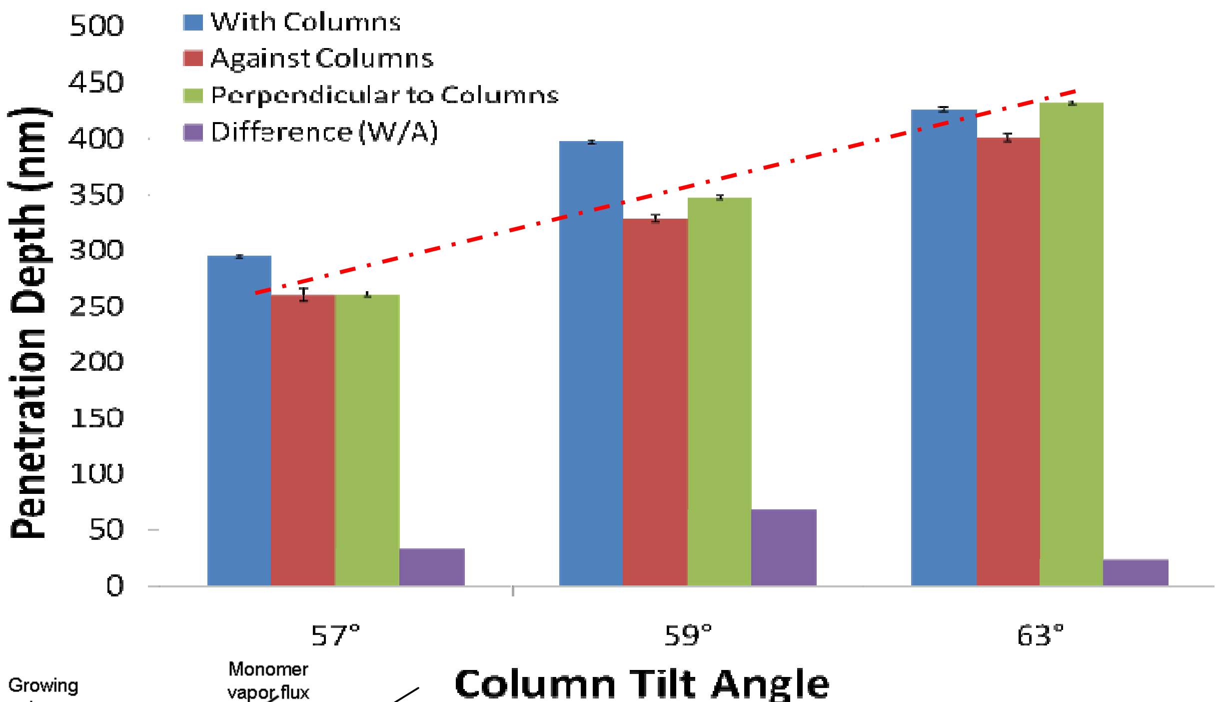
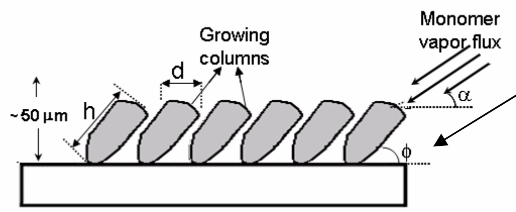
Penetration Depth vs. Load





Highly confident statistics demonstrating depth anisotropy

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Mechanical Deformation Hysteresis

Beam Equation

$$\frac{\partial^2}{\partial x^2}\left(EI\frac{\partial^2 u}{\partial x^2}\right) = \omega$$

Solution

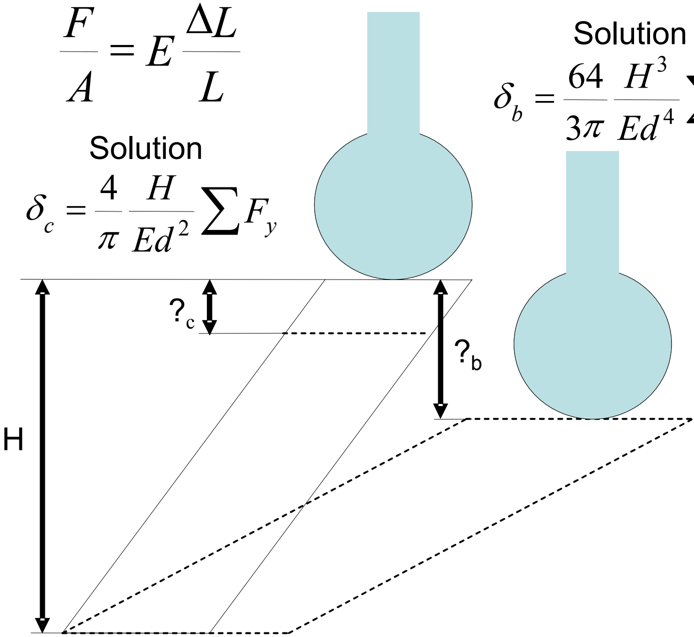
$$\delta_b = \frac{64}{3\pi}\frac{H^3}{Ed^4}\sum F_x$$

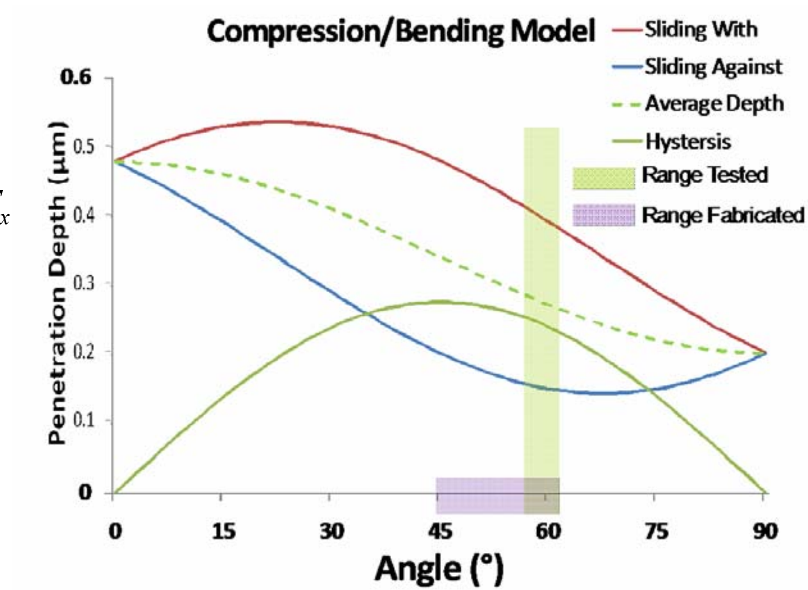
Hooke's Law

$$\frac{F}{A} = E\frac{\Delta L}{L}$$

Solution

$$\delta_c = \frac{4}{\pi}\frac{H}{Ed^2}\sum F_y$$





- Variations in total penetration depth may be more strongly correlated to film density, modulus
- Model does not include density, inter-column contact or friction

$$Depth = \delta_b\cos(\alpha) + \delta_c\sin(\alpha) = \frac{4H}{\pi E d^2}\left[\frac{16H^2}{3d^2}\sum F_x\cos(\alpha) + \sum F_y\sin(\alpha)\right]$$

Sliding perpendicular to film results in no hysteresis, predicted depths between with/against