Changing Polymer and Fiber Surfaces for Basic Properties, and Those Specifically Oriented to Medical Uses

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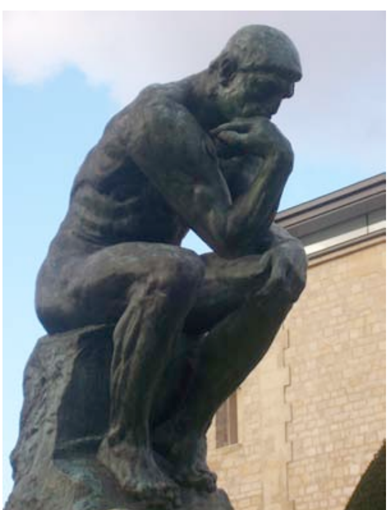
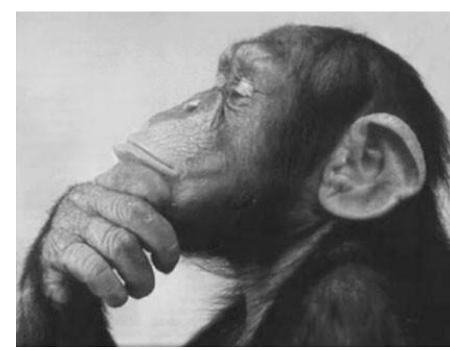




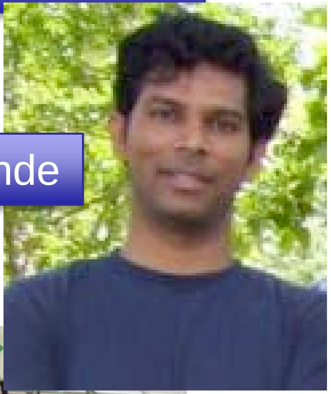
Outline

- Introduction to Coatings that respond to stimuli

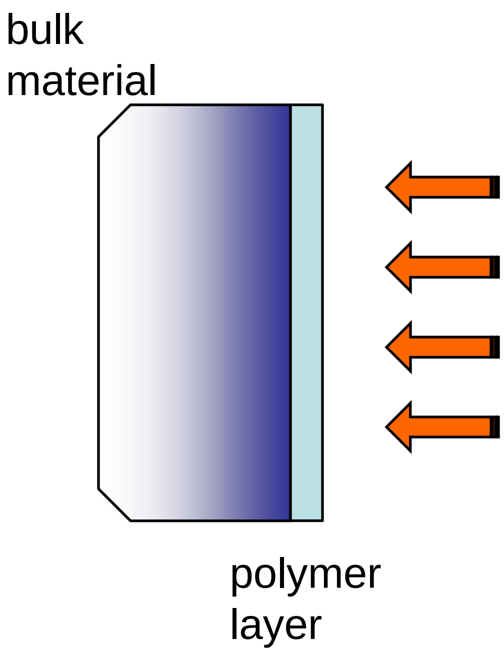
- Light Driven Actuation
  - Design of spiropyran based polymer brushes
  - Wettability changes
  - Reversible Ion Sensors

Polymers that kill bacteria on contact

Surface-Initiated Polymerization of Conjugated Polymers
  - Polymer Electrodes
  - “Wiring Molecules”



Ultrathin Films



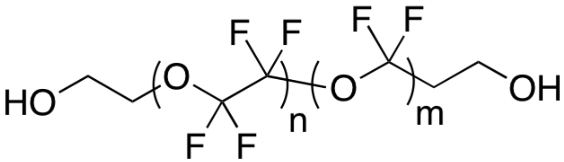
<u>Control the interaction between material and environment</u>

- protection against corrosion
- friction
- adhesion
- adsorption of molecules
- wetting with water or other liquids

A thin coating (few angstroms) can influence nature of material so strongly that the bulk material is completely hidden and interaction of whole system is governed by the coating

The Importance of Coatings

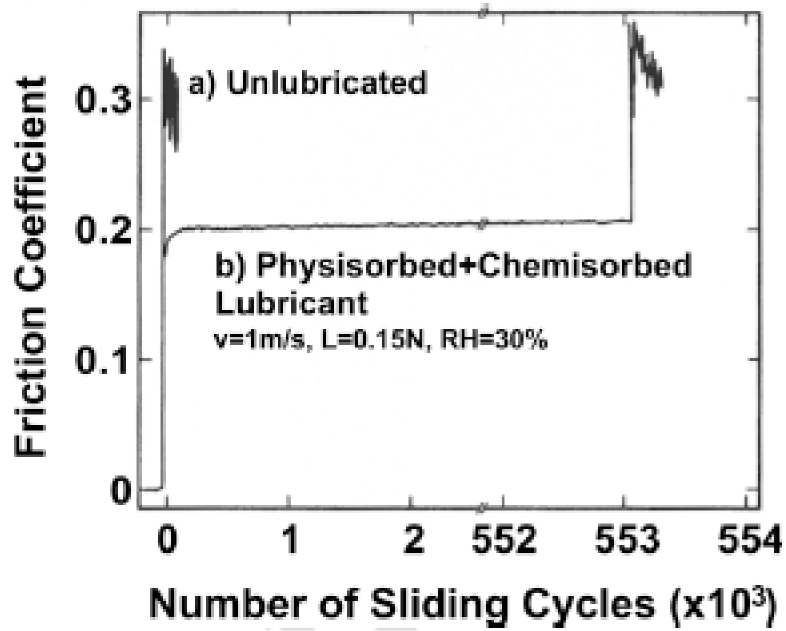
Example from the microelectronics industry



2-4 nm coating

computer hard drive

Accelerated wear test



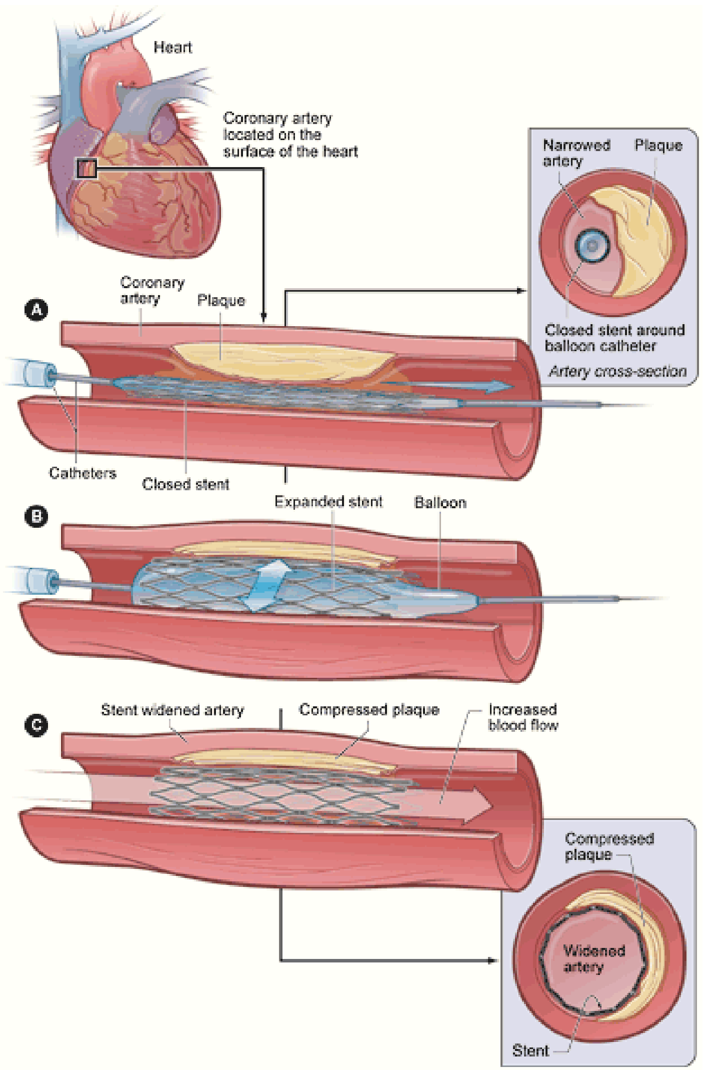
(a) unlubricated
(b) 1.5 nm chemisorbed, 1 nm physisorbed perfluoropolymer

High friction and noise is strong stick-slip behavior, which is beginning of catastrophic behavior

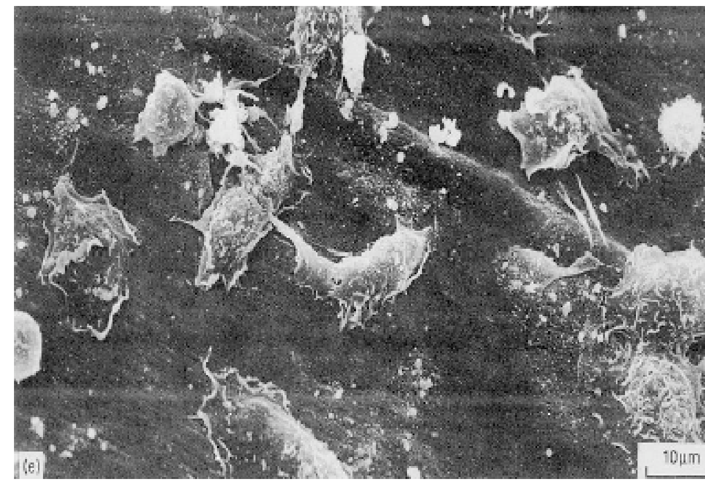
Rühe *et al. J. Tribol. Trans. ASME* **1996**, *118*, 663

Blood-implant interface

Stents are often used in the treatment of coronary heart disease to hold open blood vessels that have become blocked



deposition of blood clots on surface of implant

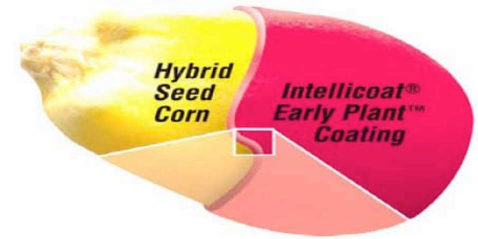


Blood proteins like fibrinogen adsorb rapidly to the surfaces of implant, followed by adhesion of blood cells to the protein layers

blood clots become attached
can break off into bloodstream

Seed Coatings: Temperature activated polymer coatings!

It knows when to grow !

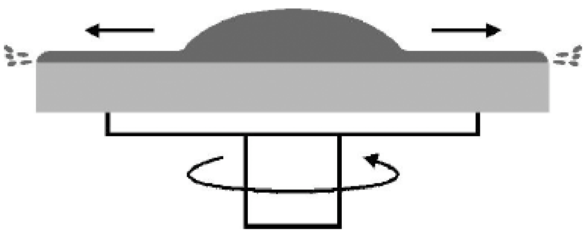


planting up to 4 weeks early
only active when soil reaches optimum temperature

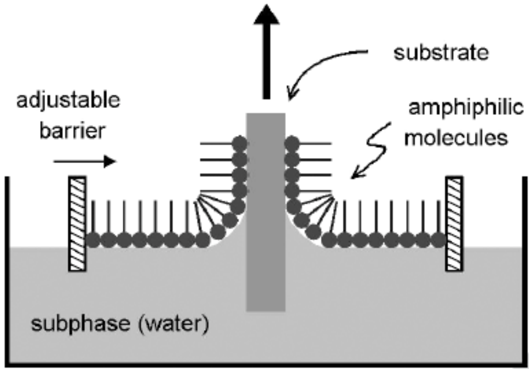
LANDEC Ag Inc
Seeds of Innovation

www.landec.com

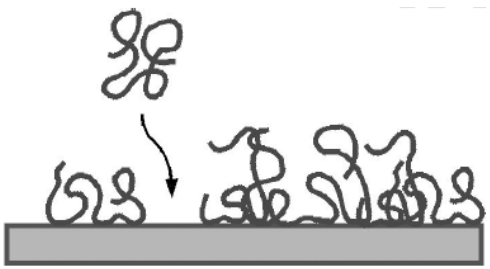
Different deposition processes



spin-coating



Langmuir-Blodgett-Kuhn



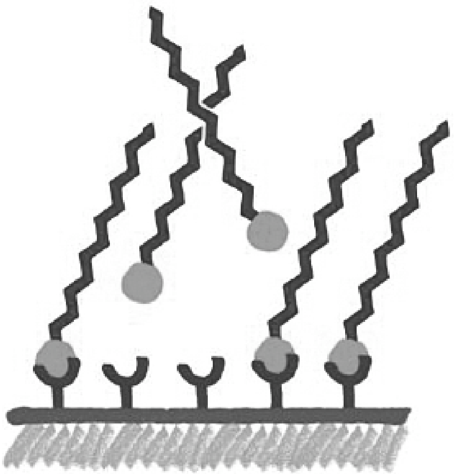
adsorption from solution

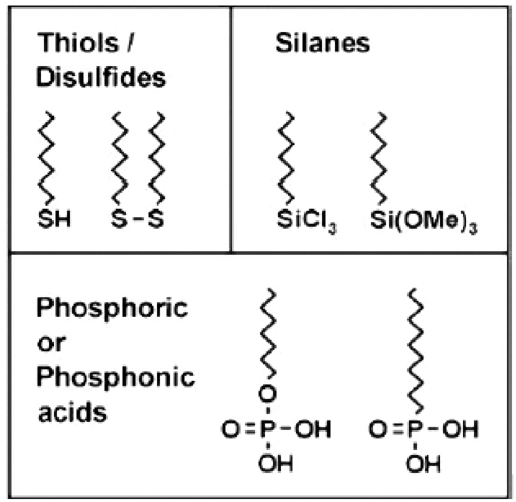
physical interactions: consequence: weak forces holding them on surfaces

The 4 Ds

1. Desorption during solvent exposure
2. Displacement by molecules which have stronger interaction with the surface
3. Dewetting (for films above Tg)
4. Delamination (films below Tg)

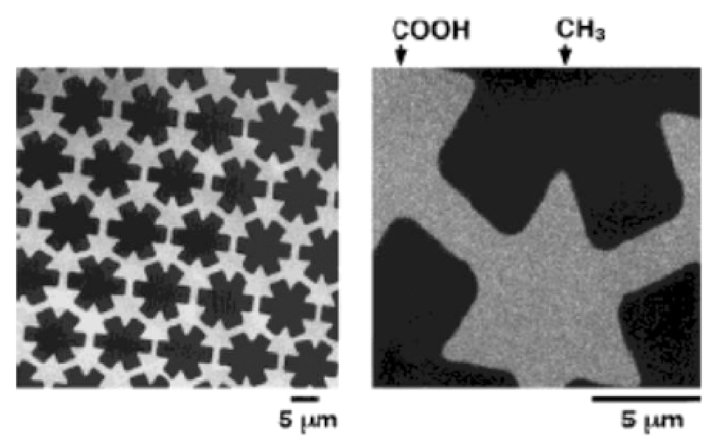
Spontaneous Self-assembly



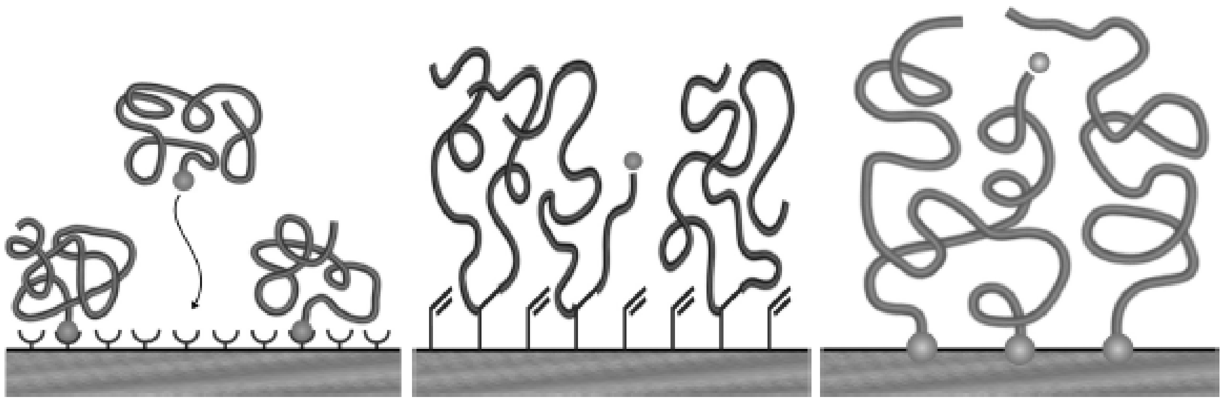


stable
strong degree of positional and orientational order
crystalline (in some cases)

silanes on oxides
phosphate or phosphonate on metal(oxide)
thiols or disulfides on noble metals



Grafting Methods for Polymer Brushes

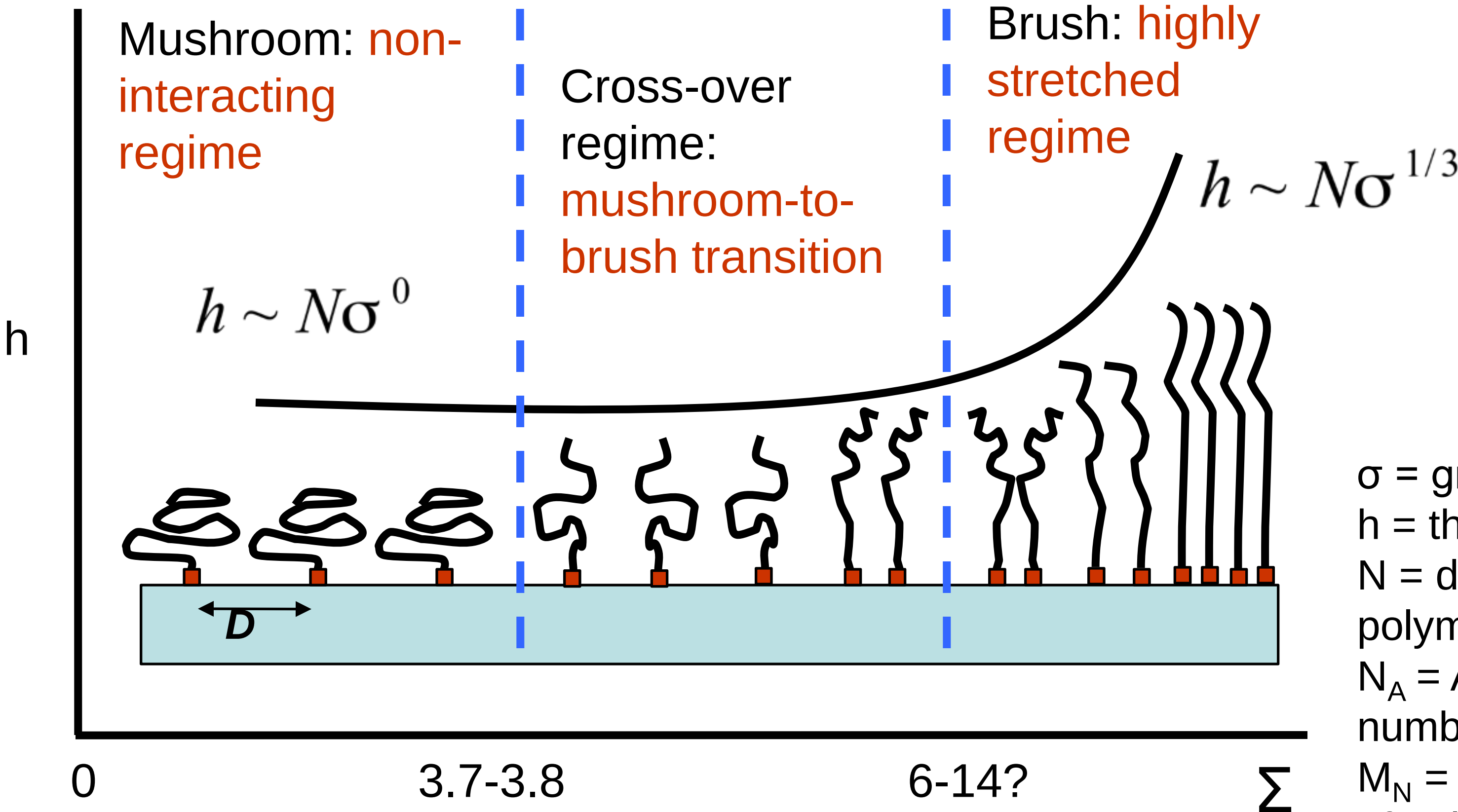


“grafting to”   **surface bound monomer**   **“grafting from” or SIP**

Why Surface Initiated Polymerization (SIP)?

- High brush density: average distance b/w grafting points < radius of gyration (*Rg*).
- Functionalized surfaces, controlled surface energies, controlled surface chemistry
- different methods of initiation: free-radical, ATRP, cationic, anionic, ROMP, etc.
- Model polymerization studies in confined environments
- Novel and advanced materials, colloidal particle stabilizers, polymeric surfactants, nanotechnology

Surface-Bound Polymer Chains



$$\sigma = \frac{h\rho N_A}{M_N}$$

$$\Sigma = \sigma\pi R_g^2$$

σ = grafting density
h = thickness
N = degree of polymerization
N_A = Avogadro's number
M_N = molecular weight of polymer

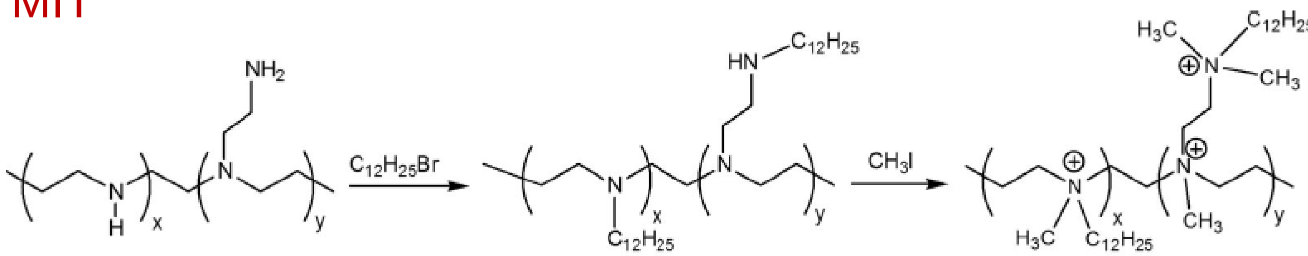
Σ = reduced tethering (or surface) density

- Ignores interaction between tethered chains and substrate
- Independent of molecular weight and type of solvent

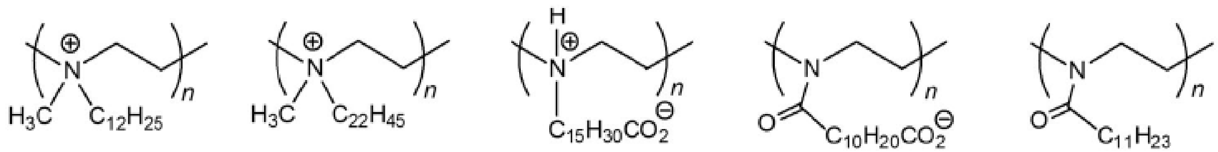
Macromol. Rapid Commun. **2000**, *21*, 243
JACS **2002**, *124*, 9394
Phys. Rev. Lett. **2004**, 93, 028301

Hydrophobic PEI derivatives

Alexander Klibanov, MIT



1a-c



2a-c **3** **4** **5** **6**

Kills bacteria and viruses on contact!

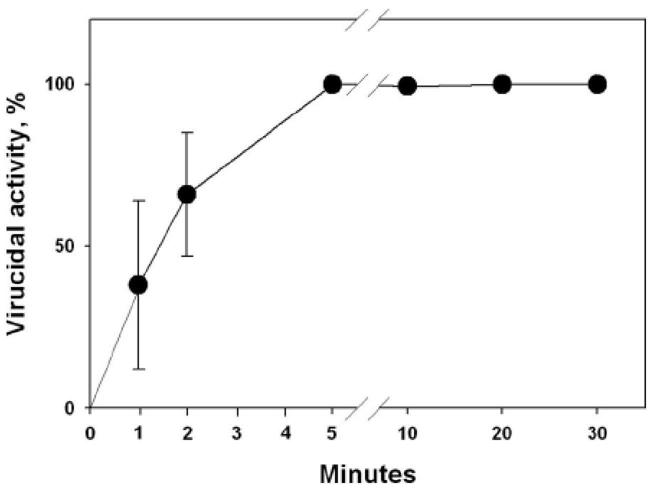


Fig. 2. The time course of inactivation of influenza virus (WSN strain) by a glass slide painted with **2a** at r.t. See *Materials and Methods* for details.

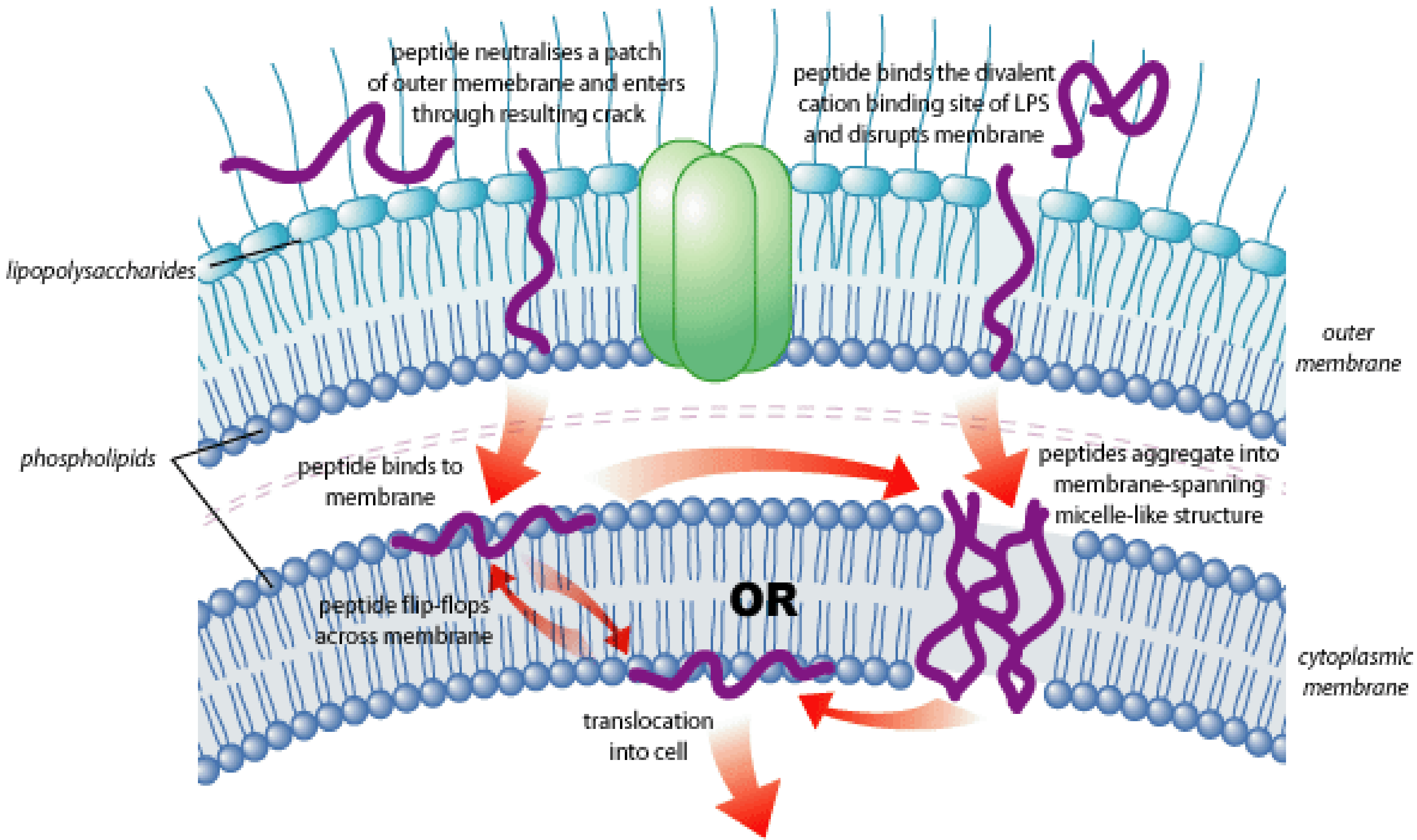
Table 1. Microbicidal activity of glass slides painted with 1a, 2a, 4, 5, and 6

PEI derivative	Virucidal activity* after 30 min, %	Bactericidal activity, %	
		S. aureus	*E. coli*
1a	100	99 ± 1	99 ± 1
2a	100	100	100
4	100	26 ± 4	14 ± 2
5	66 ± 3	21 ± 1	22 ± 3
6	6 ± 6	34 ± 1	14 ± 2

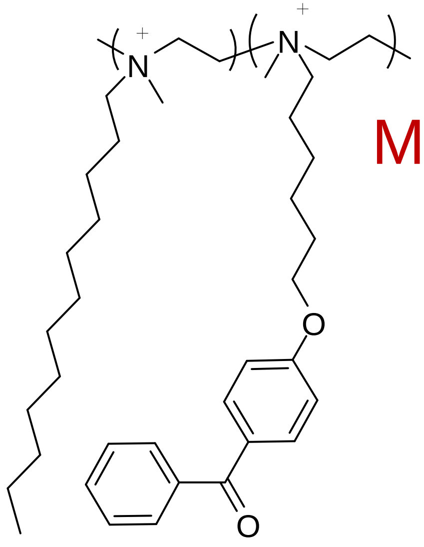
Haldar *et al. PNAS* **2006**, *103*, 17667-17671

Mechanism of Cell Death Has Not Been Completely Elucidated

Similar to antimicrobial peptides: disrupt cell membranes, causing breakdown of the transmembrane potential, leakage of cytoplasmic contents, and ultimately cell death.

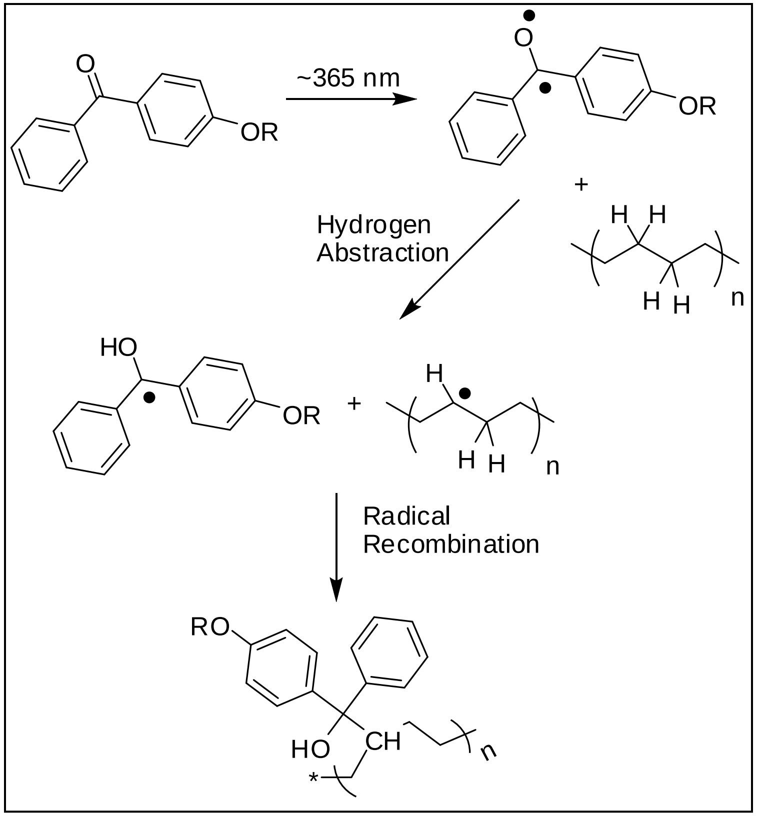


Some Simple Modifications to Create Reactive Polymers



Mn = 125,000 (30% BP)

Synthetic design is straightforward and scalable



Linear polymer more effective than branched

Solubility of BP-PEI is higher in acetone, $CHCl_3$ and longer chain alcohols

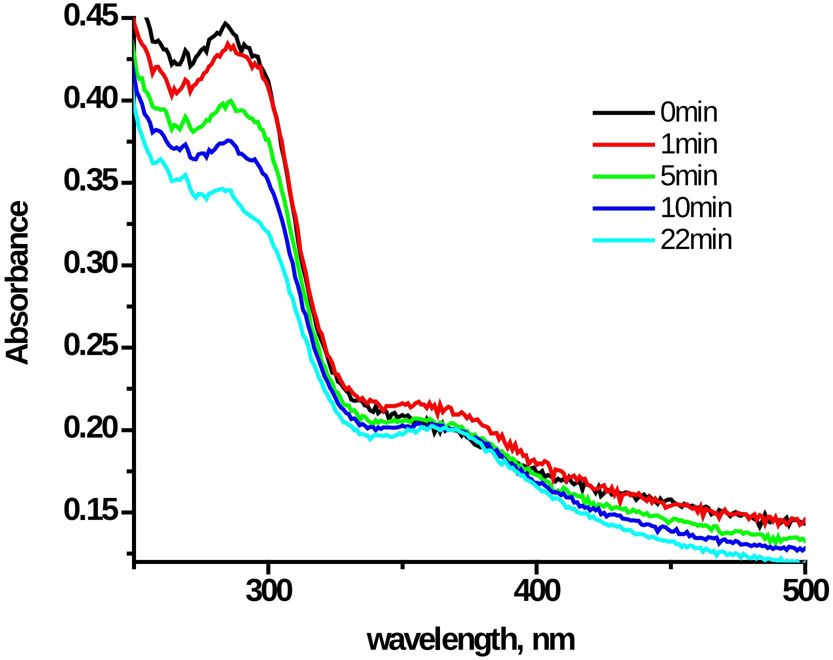
•Upon irradiation, benzophenone groups will abstract hydrogen from any alkyl species providing covalent attachment

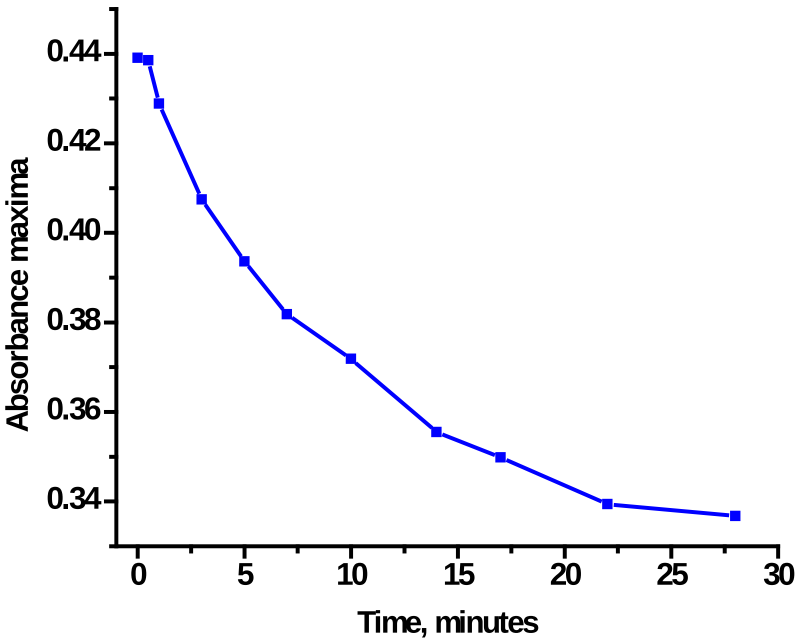
•Can attach to ANY substrate with C-H bond

Patent Pending: University of Georgia Research Foundation, Inc

Cross-linking Rate

- Decrease in absorbance of benzophenone carbonyl can be used to monitor the crosslinking
- Reaction complete within 25 minutes at very low intensity under mild conditions





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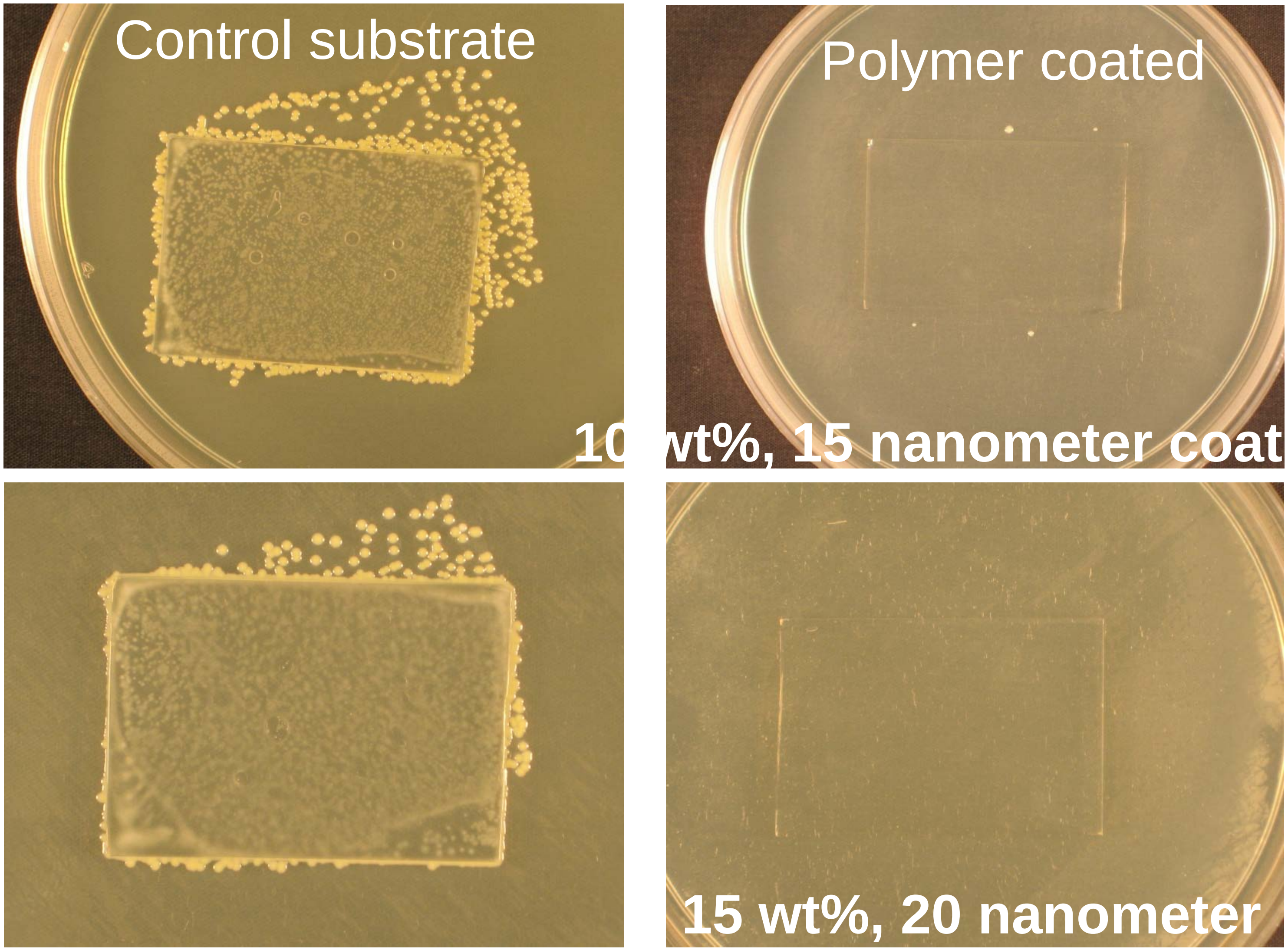
Sprayed Bacteria Tests on Glass Substrates Coated with Organic SAMs

Staphylococcus aureus spray test (~150 cells per cm^2), 12-15 hour incubation



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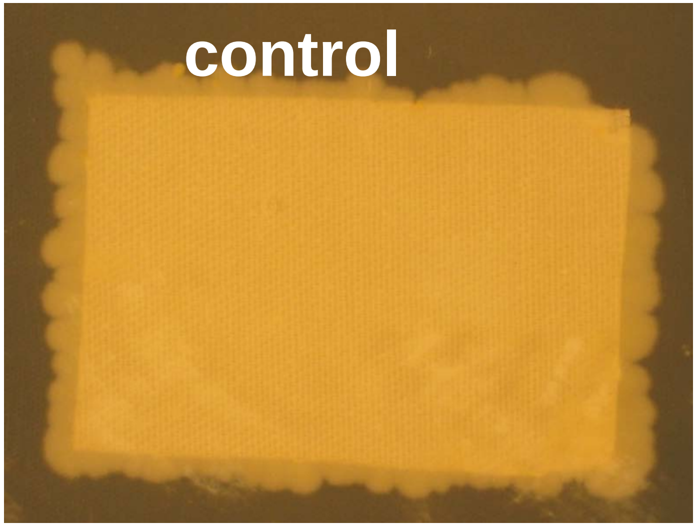
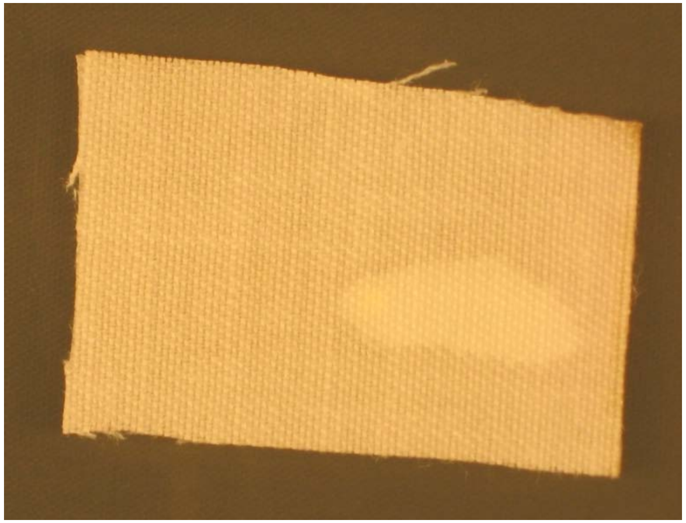
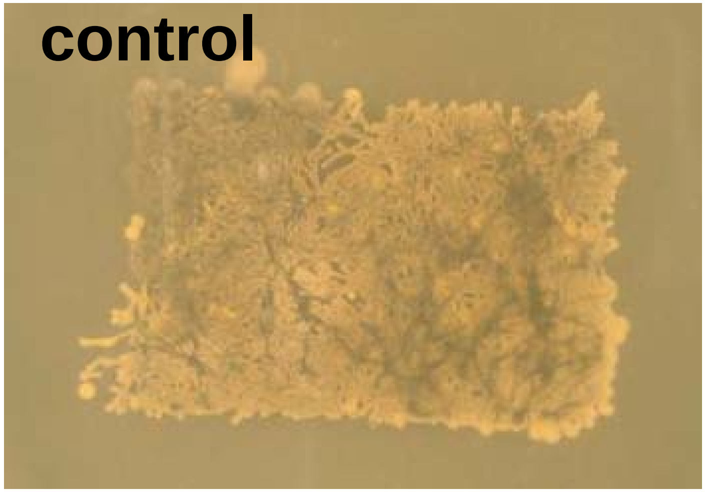
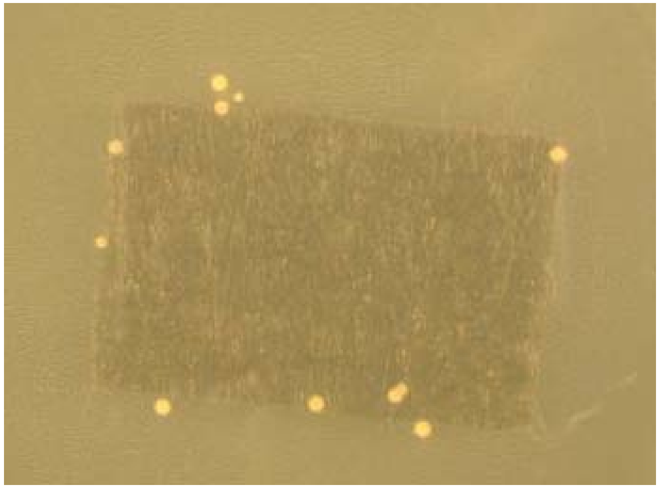
Coating is Effective on Various Polymer Substrates

Cotton with 15 nm sprayed coating:









polypropylene geotextile

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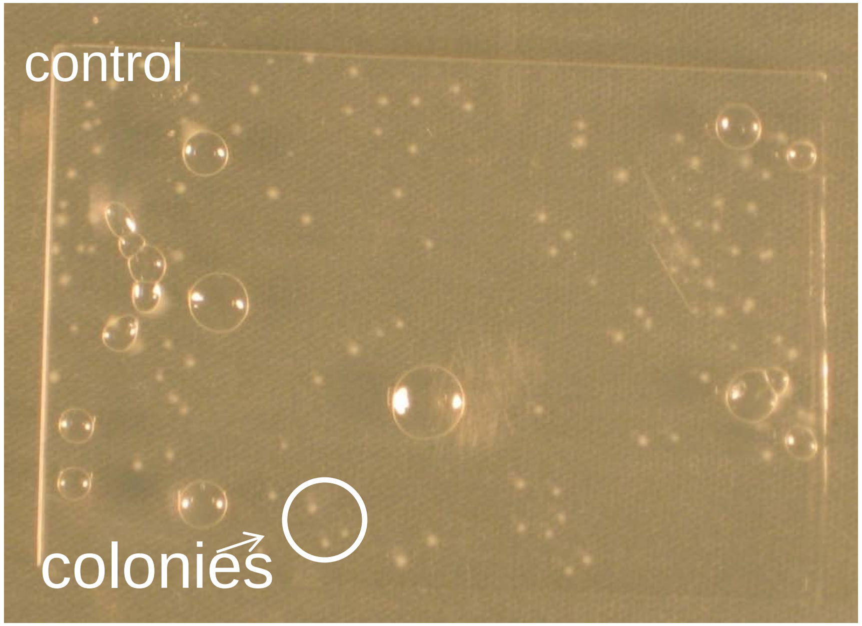
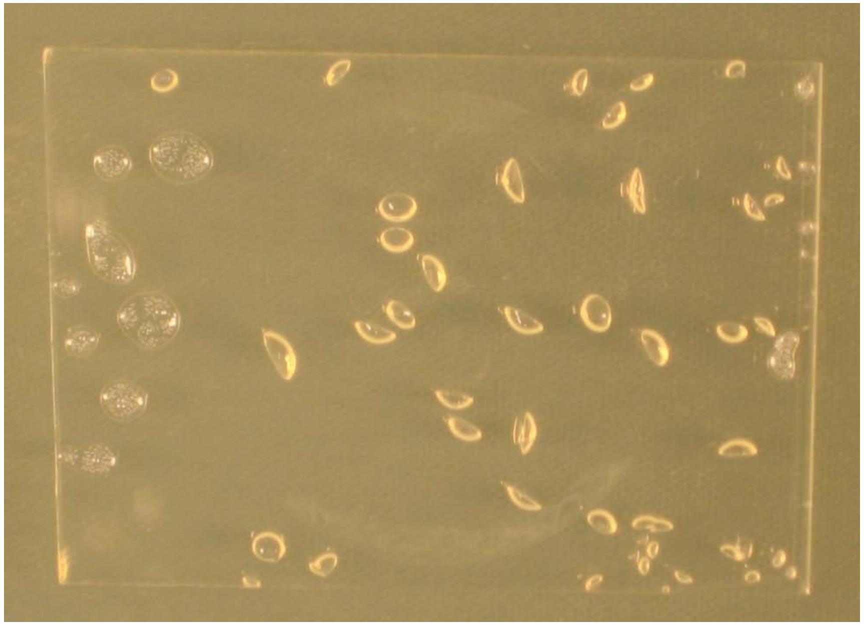
Coatings also Effective Against Gram Negative Bacteria

E. Coli spray test, 24 hours incubation





In coated substrates: bubbles are just trapped air, no colonies are present

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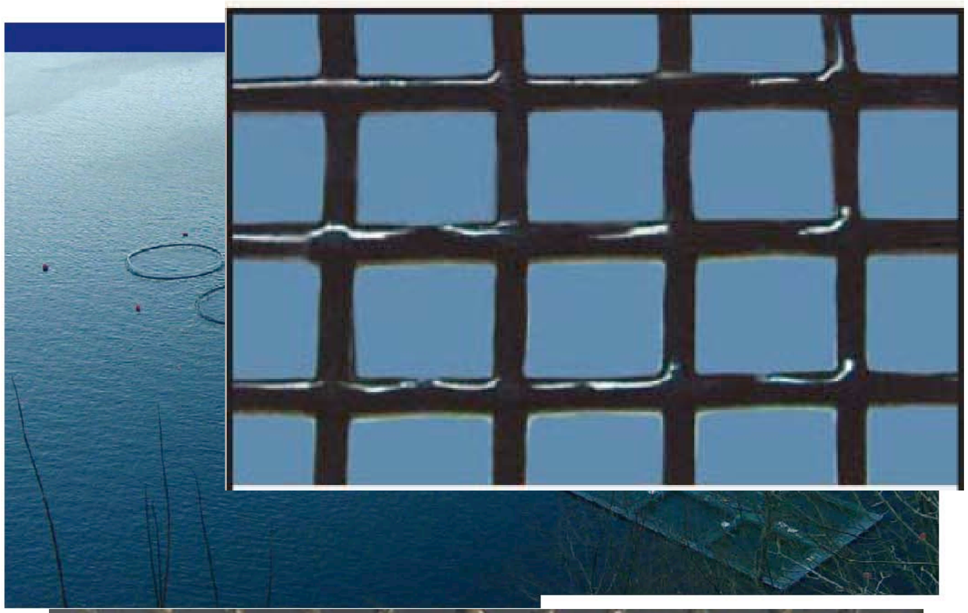
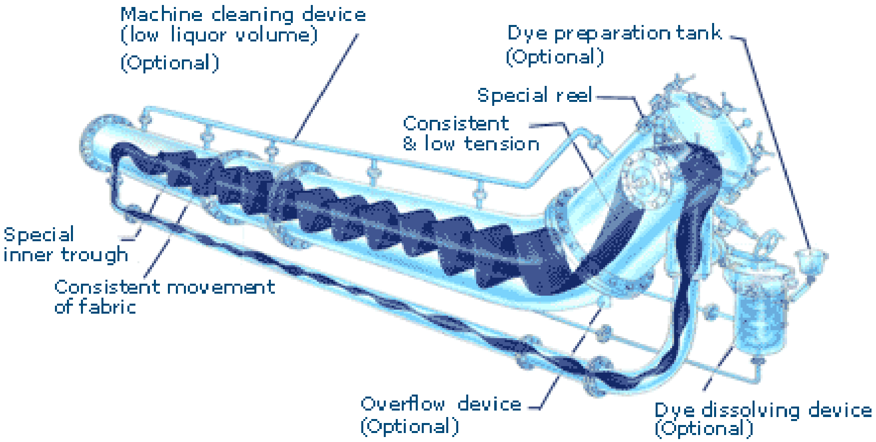
Aquaculture


control

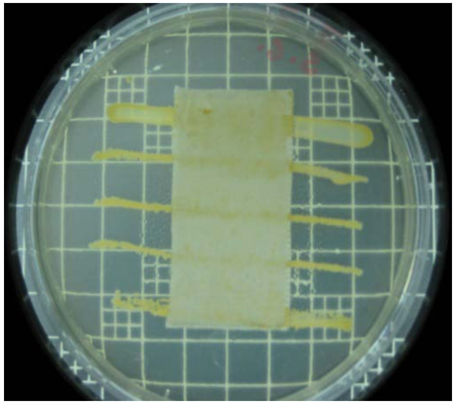


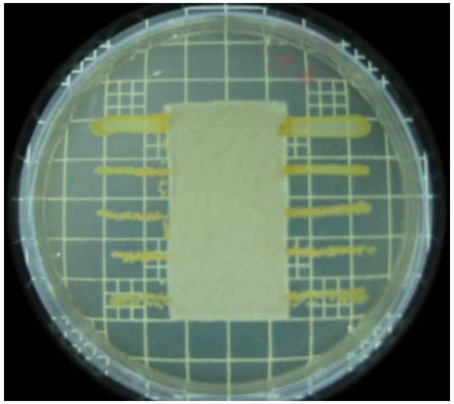

coated

Taking a Page From Reactive Dye Chemistry



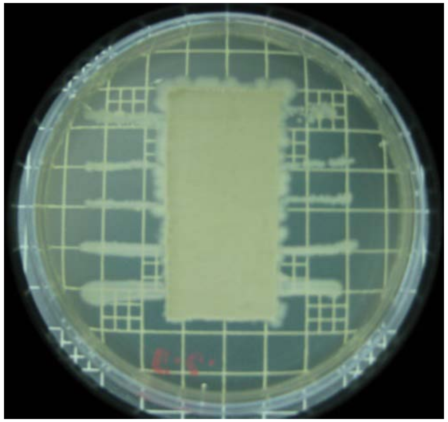
"Vinyl sulfone" quaternary PEI (SQ-PEI)

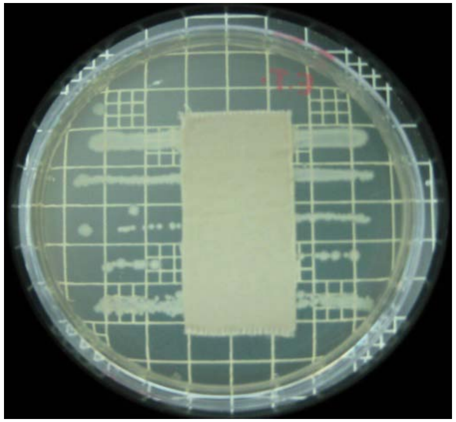




Control: *S. aureus*   SQ-PEI : *S. aureus*

Gram positive bacteria





Control: *E. coli*   SQ-PEI : *E. coli*

Gram negative bacteria

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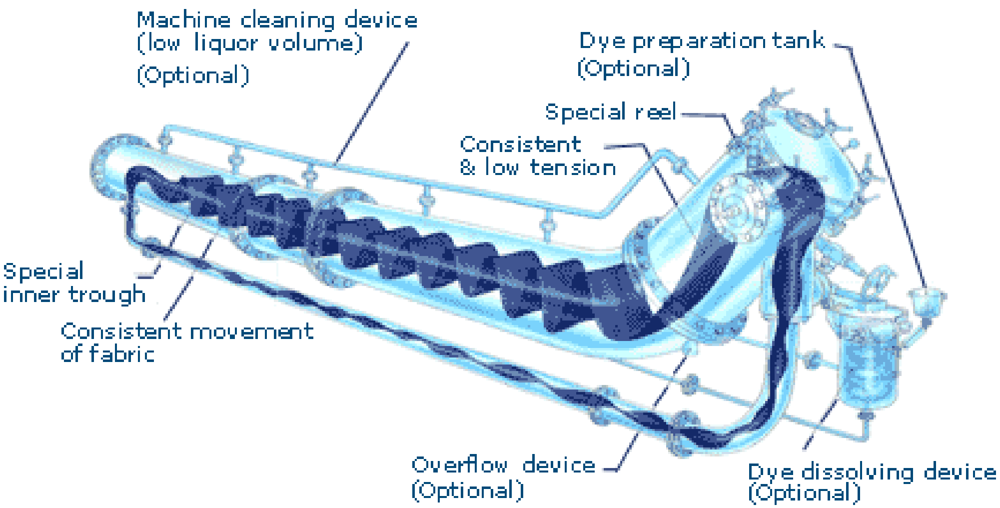
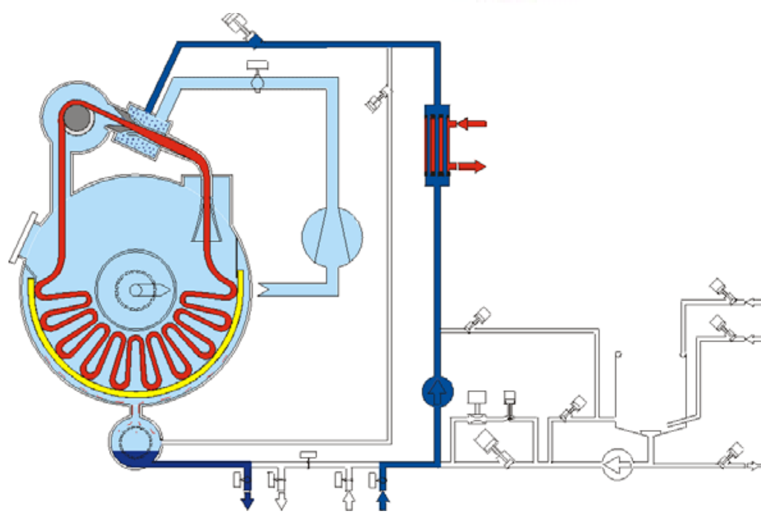
Reactive Dyes





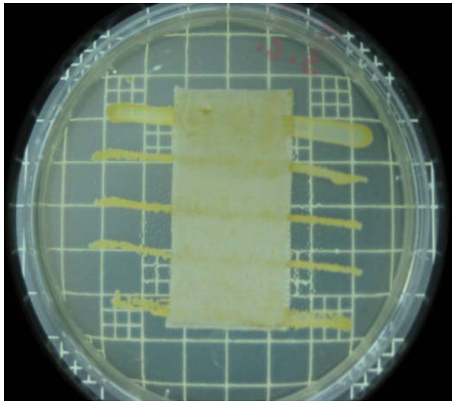
http://textileinfo.com/en/it/hisaka/img/p1_02.gif
http://www.anjaniindustries.com/images/innerimg/photo2.jpg

Polymer backbone

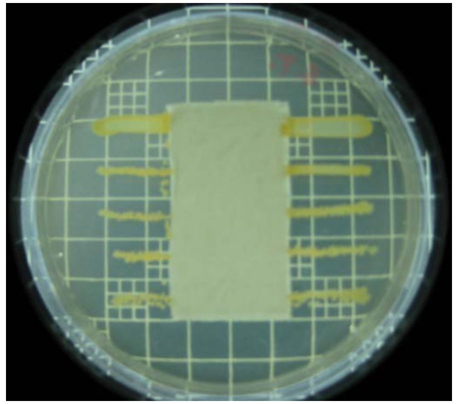
Synthesis of pendant group

Sulfated quaternary PEI (SQ-PEI)

Application on substrate



Control: *S. aureus*



SQ-PEI : *S. aureus*

Fabric: 5 ×2.5 cm

Finishing agent: 2% owf

Treatment time: 1 hour

Temperature: 45-50°C

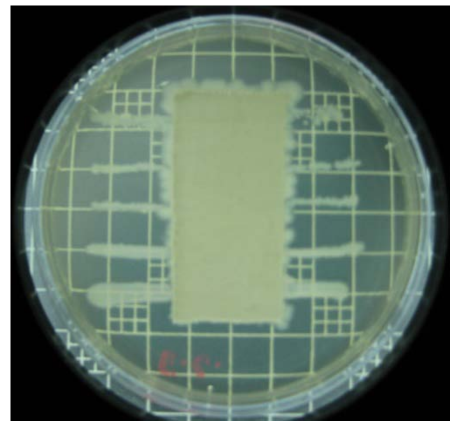
Material to liquor ration : 1:40

pH: 9-10

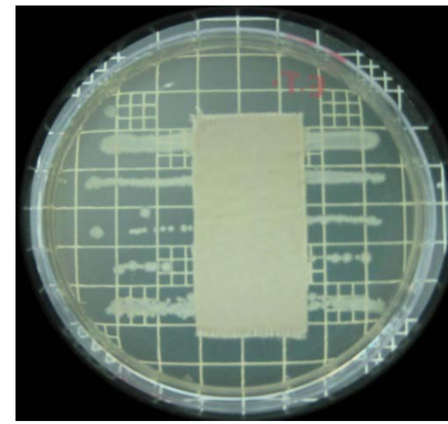
Substrate: Cotton

Gram positive bacteria

AATCC Test Method 147



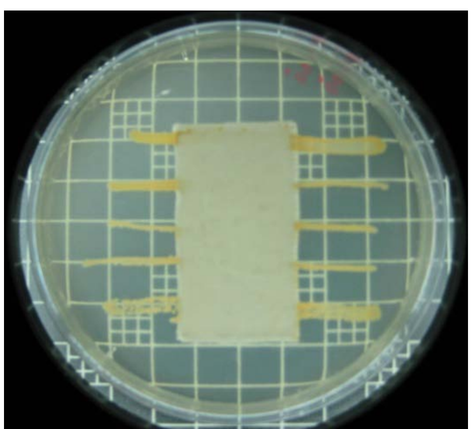
Control: *E. coli*



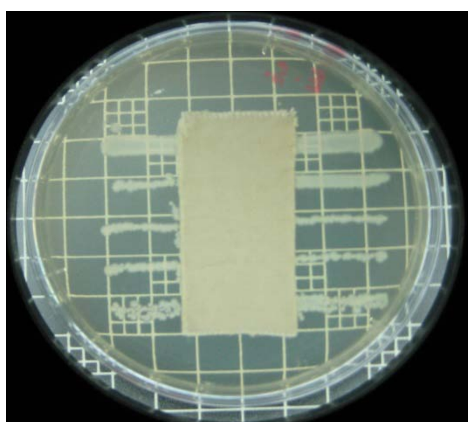
SQ-PEI : *E. coli*

Gram negative bacteria

Sonicated samples



SQ-PEI: *S. aureus*



SQ-PEI : *E. coli*

Final Comments

- Continuing work on synthesis of reactive links to our PEI-based antimicrobials
- Working with our Infectious Disease Center on the UGA campus
- Working on testing of durability of polymeric finishes
- Question of "shielding" of anti-microbial effect
- Collaboration opportunities are always welcomed

- Thank you and "Xie Xie"!