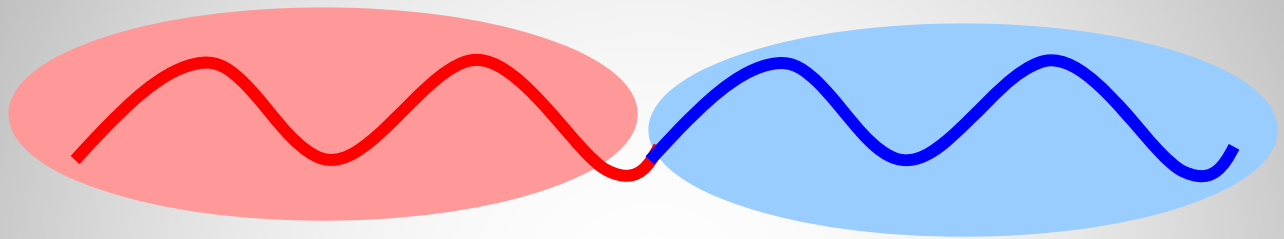
Block Copolymers
Materials with a Split Personality

Carmen Scholz

Chemistry

Block Copolymers

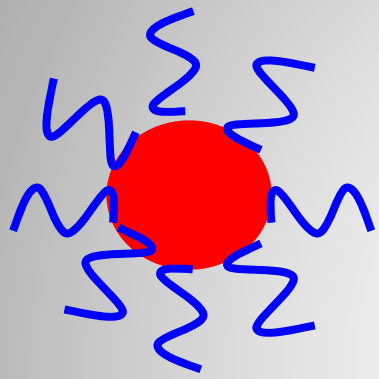


Hydrophobic **Hydrophilic**

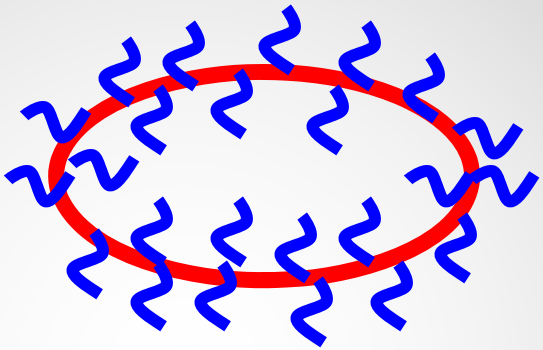
Crystalline **Amorphous**

Charged **Uncharged**

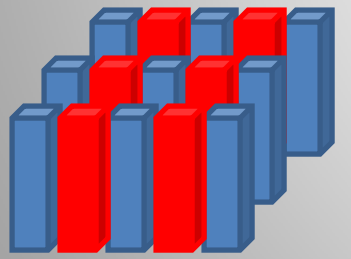
Self-Assembled Structures



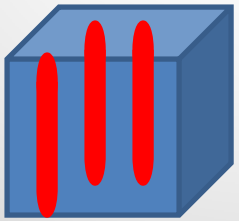
Micelles



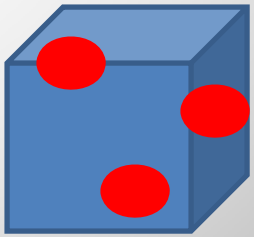
Vesicles



Lamellae



Cylinders



Nanodomains

Two Polymers

Polymer Blends:

Polymers immiscible

→ **Phase separation**

→ **Inhomogeneity**

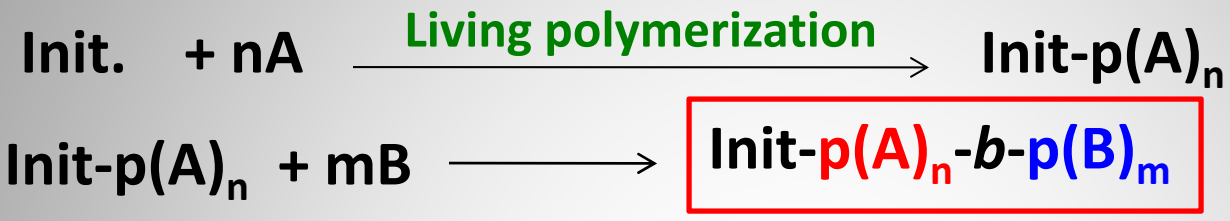
Block copolymers:

Forced Mixing of antagonist properties

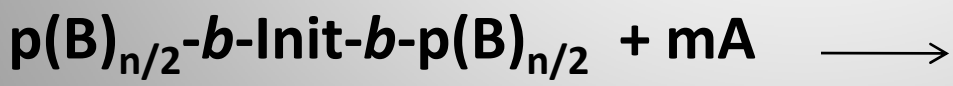
→ **Self-assembly**

→ **homogeneity on nanoscale level**

Synthesis



AB Diblock copolymer



ABA Terblock copolymer

Synthesis cont'd

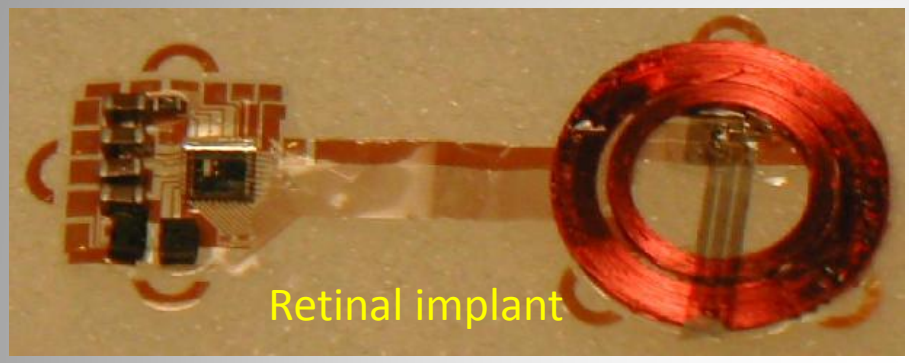
$p(A)_{m/2}$-*b*-$p(B)_{n/2}$-*b*-Init-*b*-$p(B)_{n/2}$ -*b*-$p(A)_{m/2}$

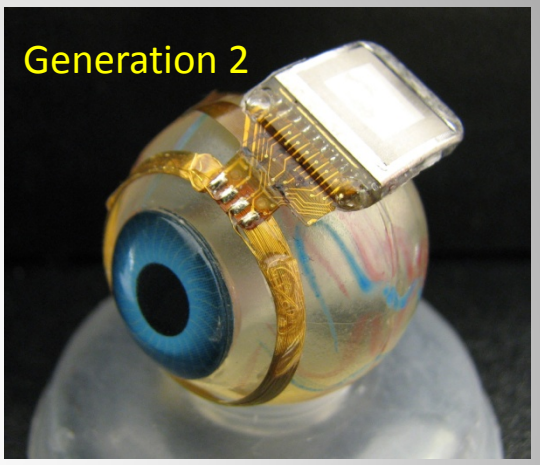
If Init. = Macroinitiator:

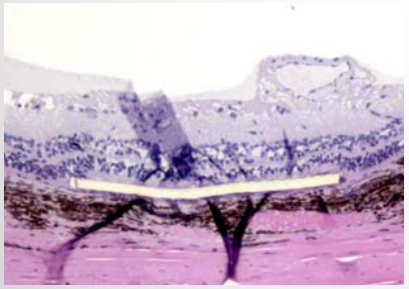
ABCBA Pentablock copolymer

Three Polymers with potentially three different physical (and chemical) properties

Surface Modification of Retinal Implants



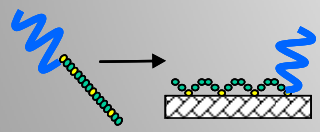




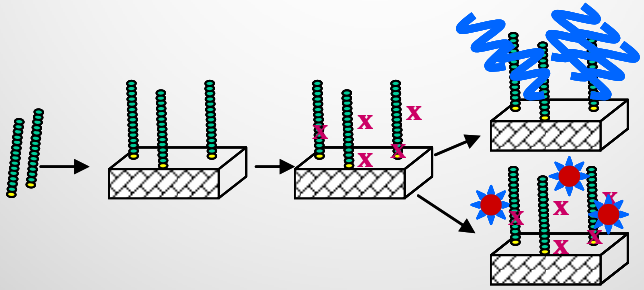
PI strip coated by physical adhesion with PEG implanted into the subretinal space of Yucatan pigs

How to attach PEG COVALENTLY to implant?

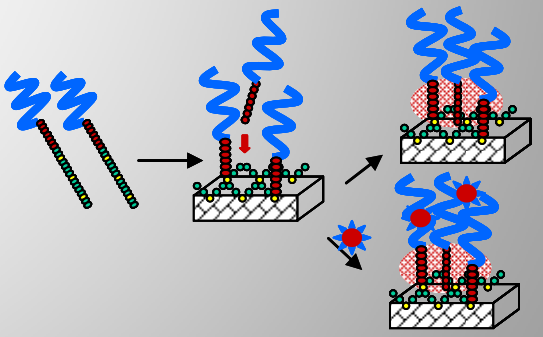
PEGylated poly(amino acids) for the surface coating of biomedical implants



PEG-paa block copolymer single chain attachment with multiple anchoring sites

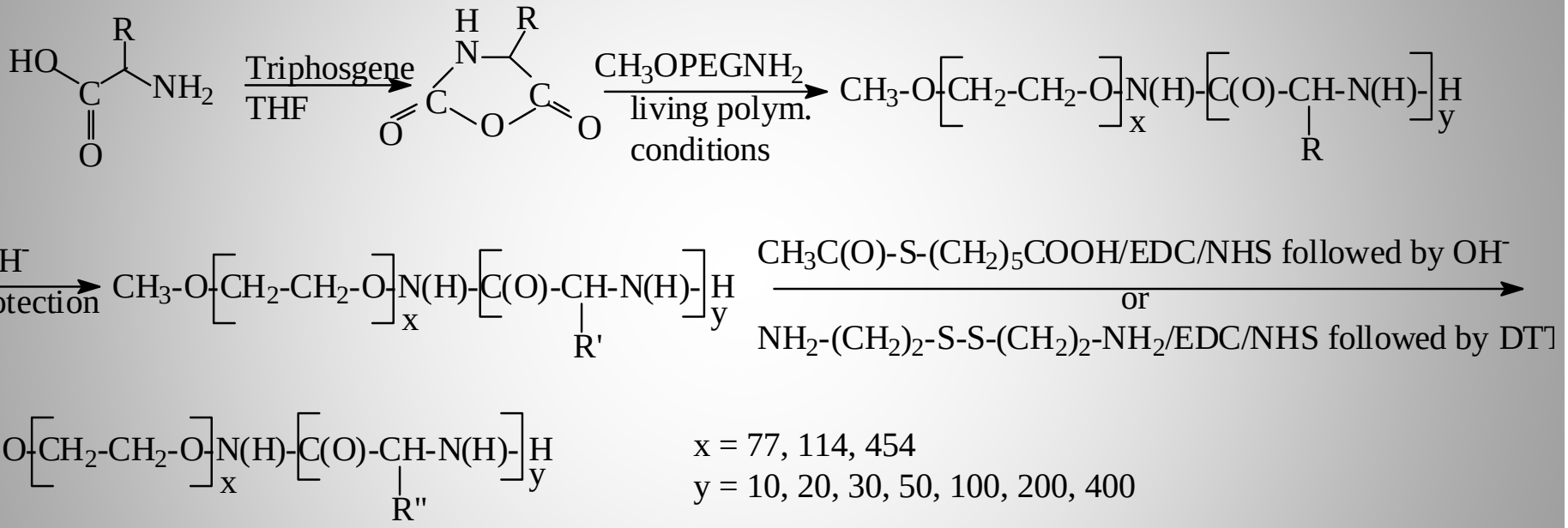


Deposition of paa-trunks and subsequent decoration with PEG or PEG-paa micelles



Deposition of PEG-paa block copolymers and subsequent decoration or densification

The Chemistry



x = 77, 114, 454

y = 10, 20, 30, 50, 100, 200, 400

R= $-CH_2-C(O)-O-CH_2-$ 

$-(CH_2)_2-C(O)-O-CH_2-$ 

$-(CH_2)_4-N(H)C(O)-CF_3$

R'= $-CH_2-C(O)-OH$

$-(CH_2)_2-C(O)-OH$

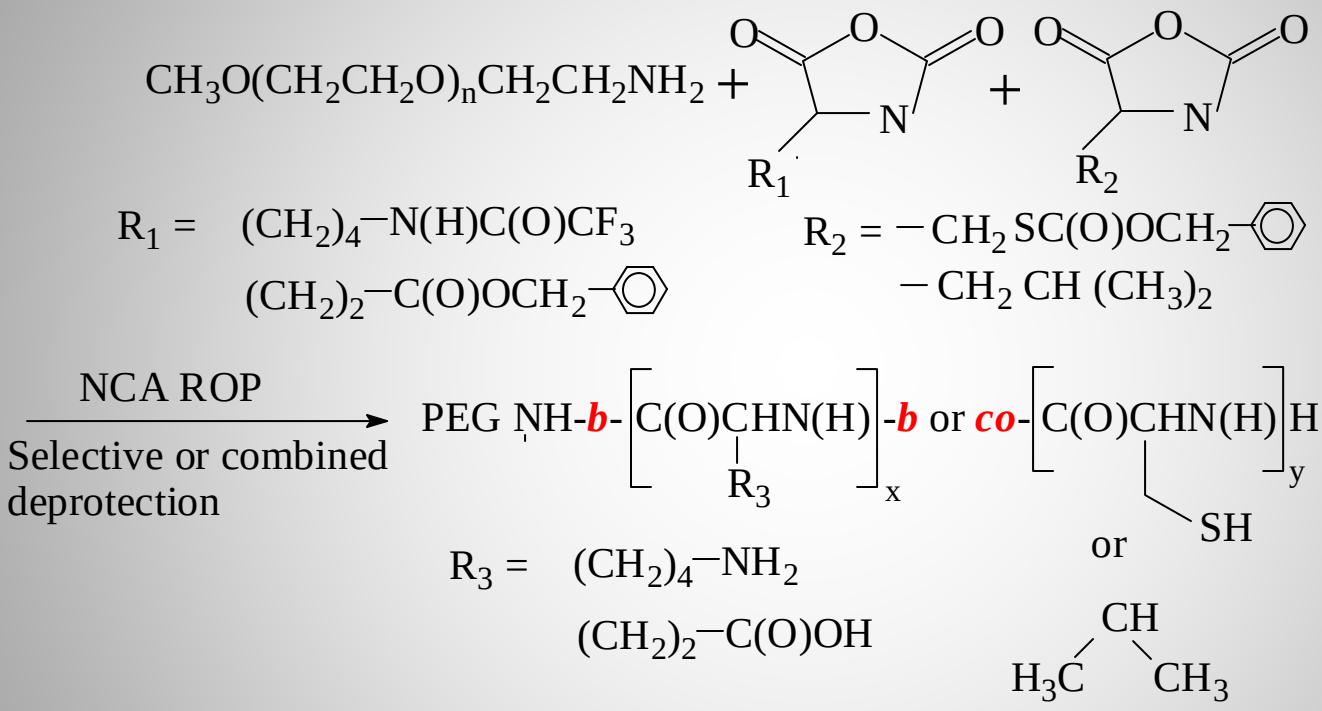
$-(CH_2)_4-NH_2$

R''= $-CH_2-C(O)-N(H)-(CH_2)_2-SH$

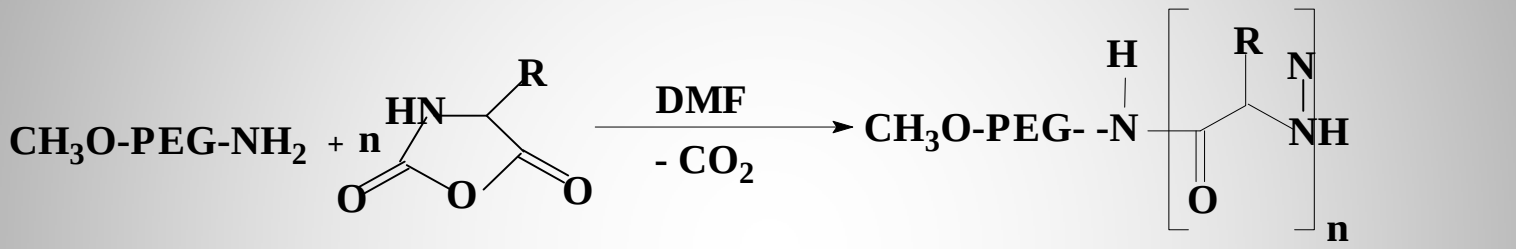
R''= $-(CH_2)_2-C(O)-N(H)-(CH_2)_2-SH$

$-(CH_2)_4-N(H)C(O)-(CH_2)_5-SH$

The Chemistry after commercially available protected *L*-Cysteine



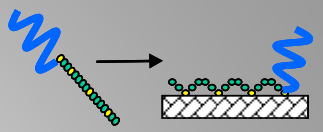
The Chemistry
The Take-home Message

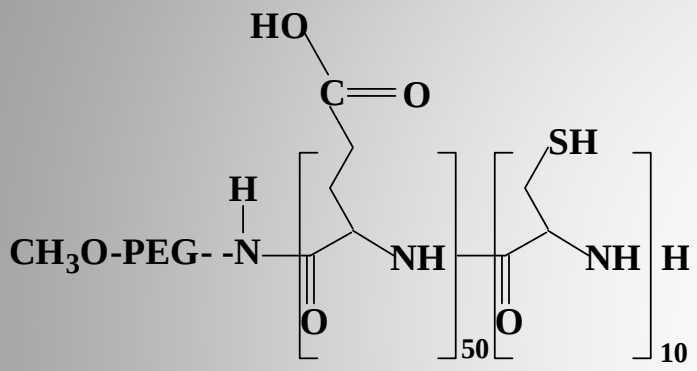


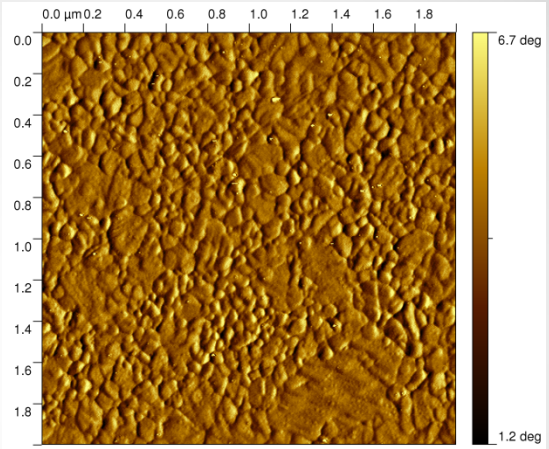
PEG-p(amino acid) diblock

no metal catalysts
strictly controlled molecular weight
low polydispersity

Results

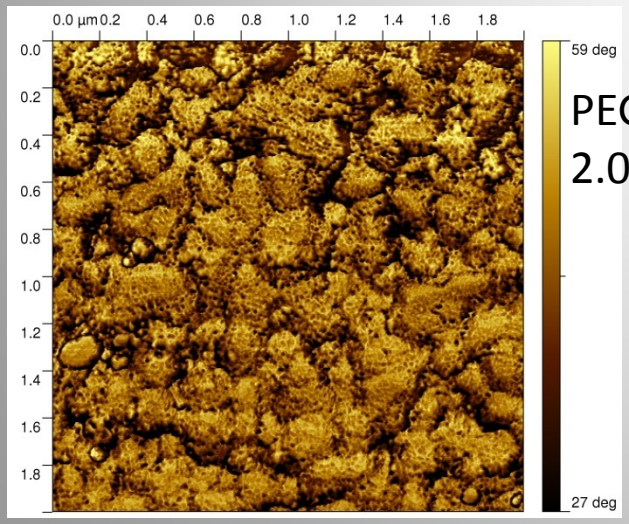






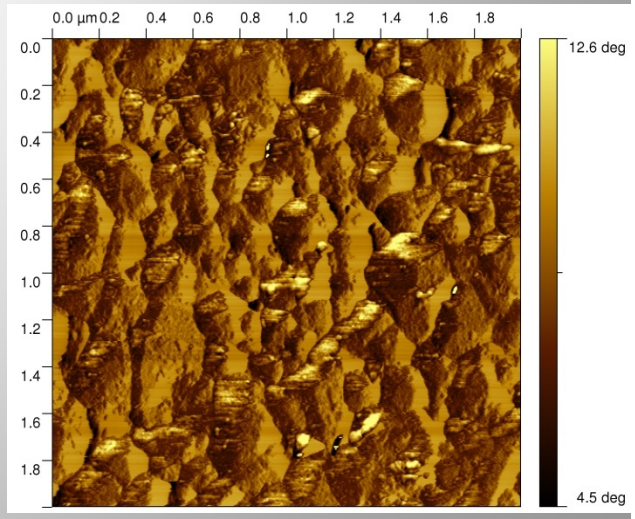
Phase Images

Au 2.0x2.0 µm

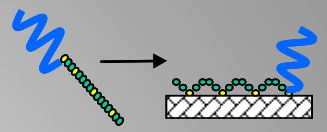


PEG-*b*-p(Glu_{110}-*block*-Cys_{10})
2.0x2.0 µm

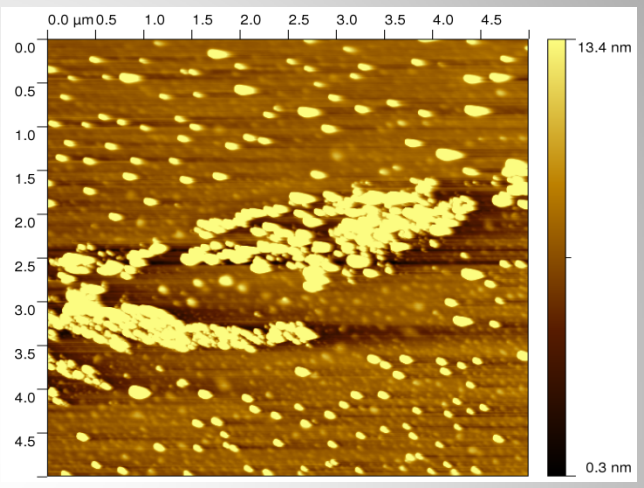
PEG-b-p(Glu_{110}-*co*-Cys_{10})
2.0x2.0 µm

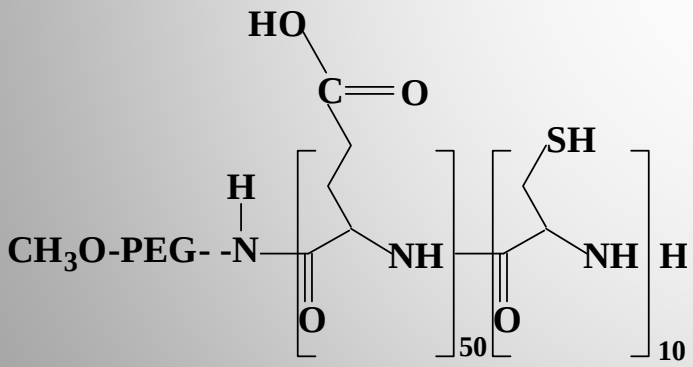


Proud Results

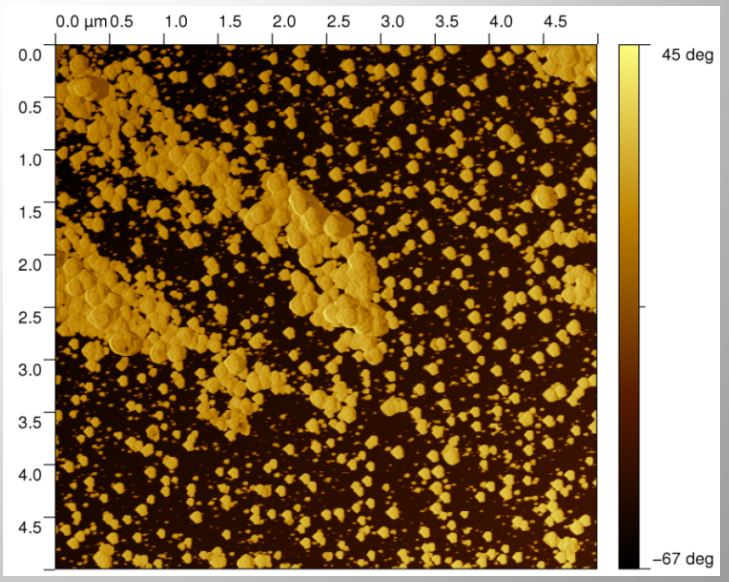


Au nanoparticles:
Double population (200-400 nm and 10-50 nm)
By wet-chemical deposition

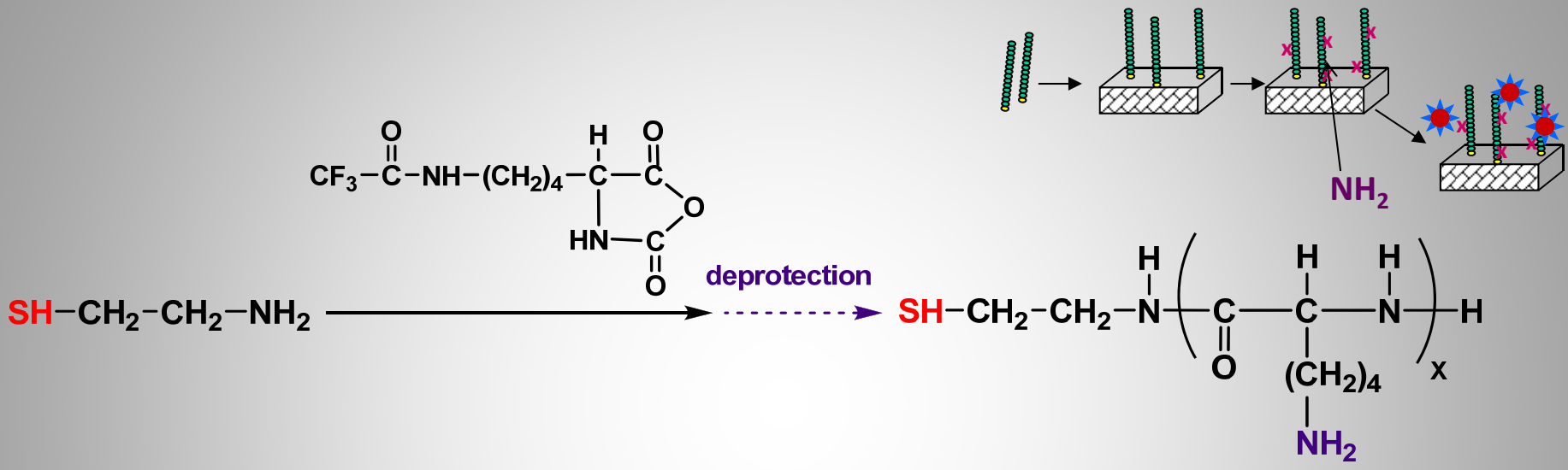


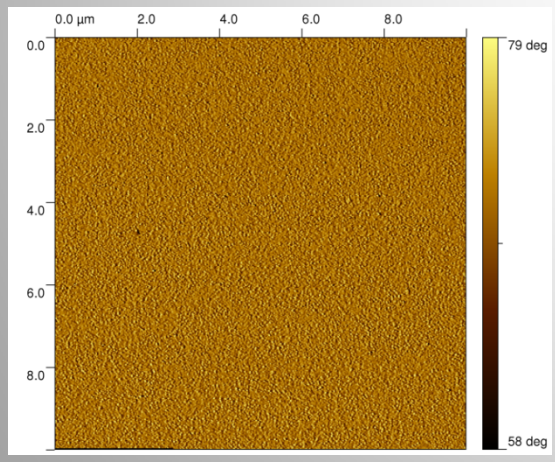


PEG-b-p(Glu$_{50}$-*co*-Cys$_{10}$)
2.0x2.0 µm

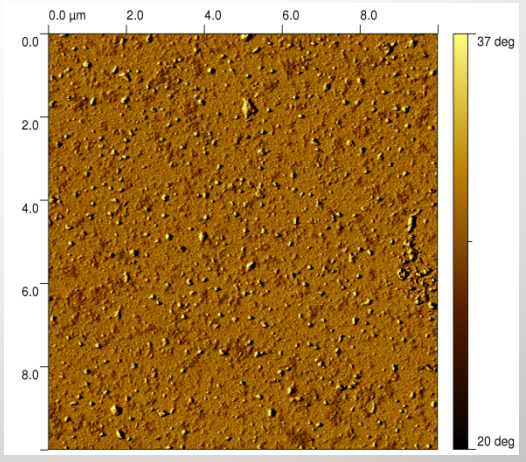


Poly(amino acid) Micelles

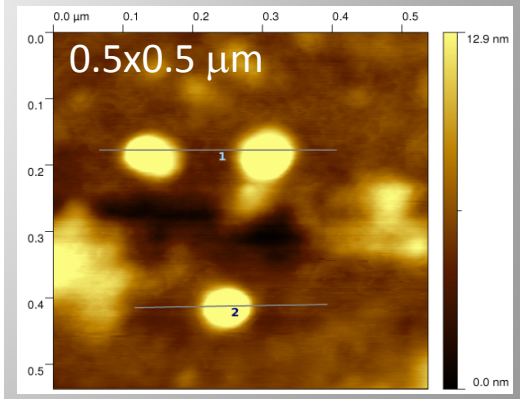




HS-p-(*L*-Lys) on Au

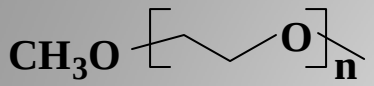


HS-p-(*L*-Lys) on Au + HOOC-PEG-b-p(L-Glu) micelles

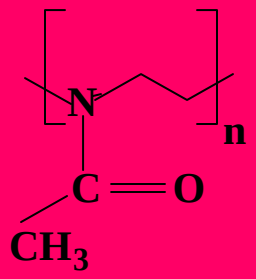


Individual micelles

Is PEG the Miracle Polymer?



- PEG is the biocompatible polymer of choice for almost all biomedical applications
- PEG is now in use in drug delivery systems
- More clinical data become available about PEG and some suggest: Renal Tubular Vacuolation (Bendele et al. Toxicological Sci. 1998, 42, 152)

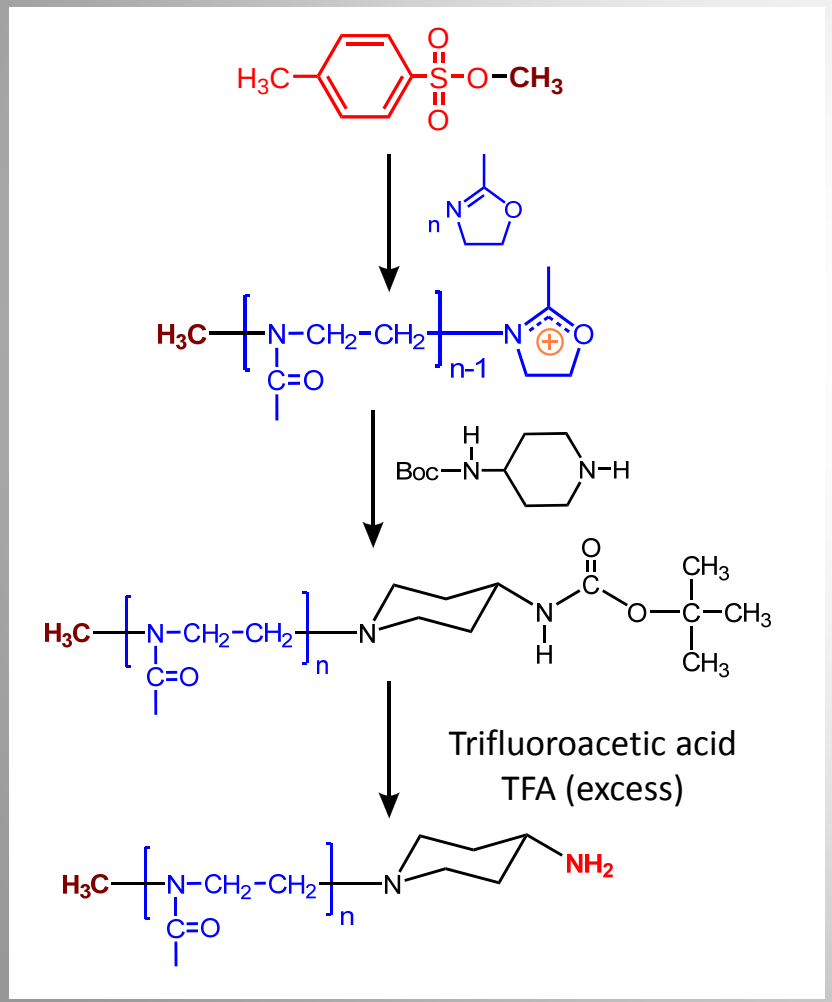


POX

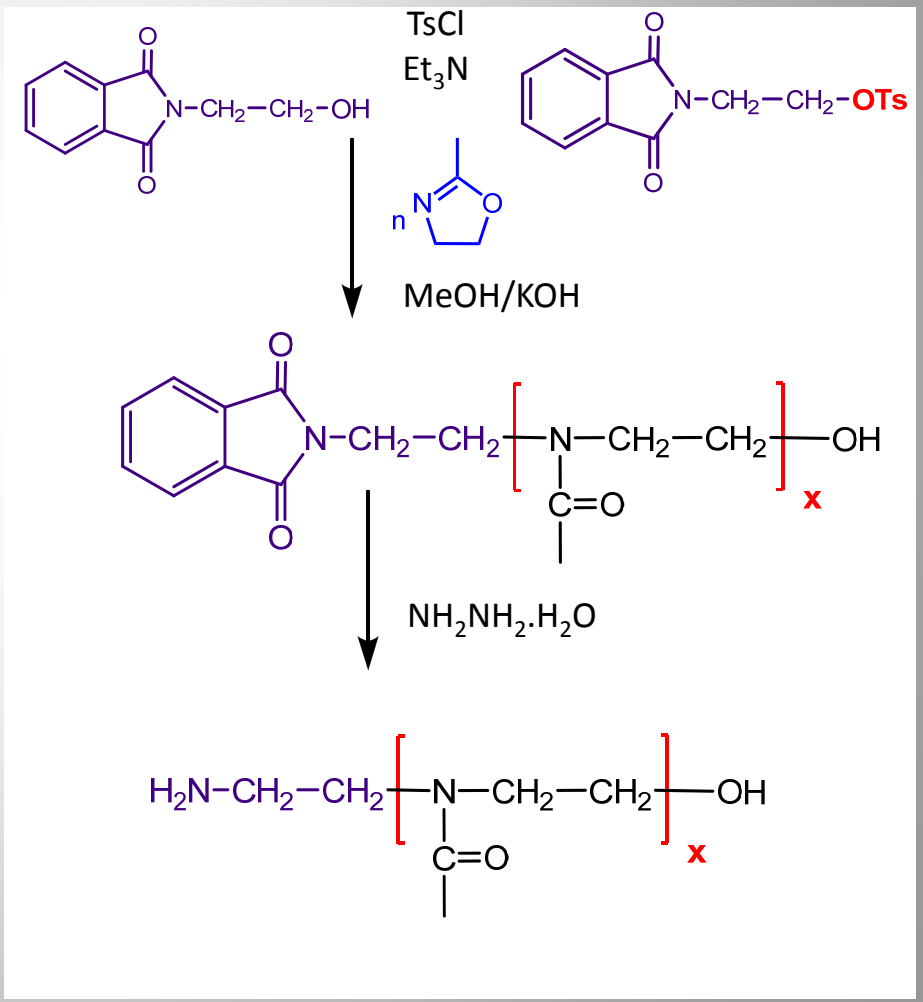
biocompatible
protein-like structure
prone to protease attack and degradation?

More Chemistry?

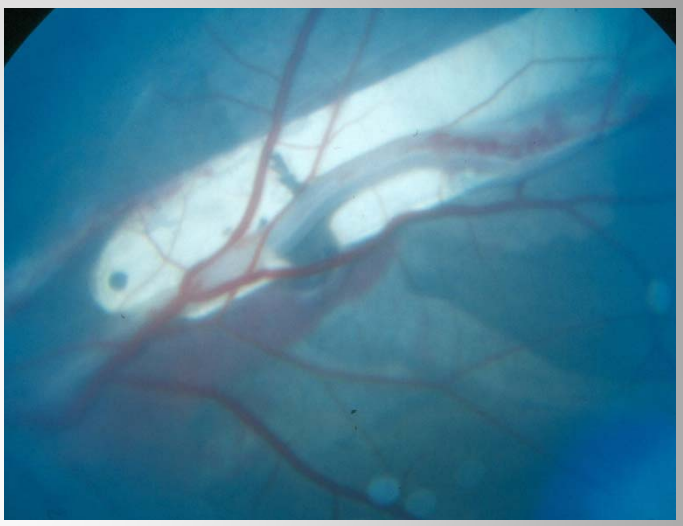
Boc-activation of p(oxazoline)

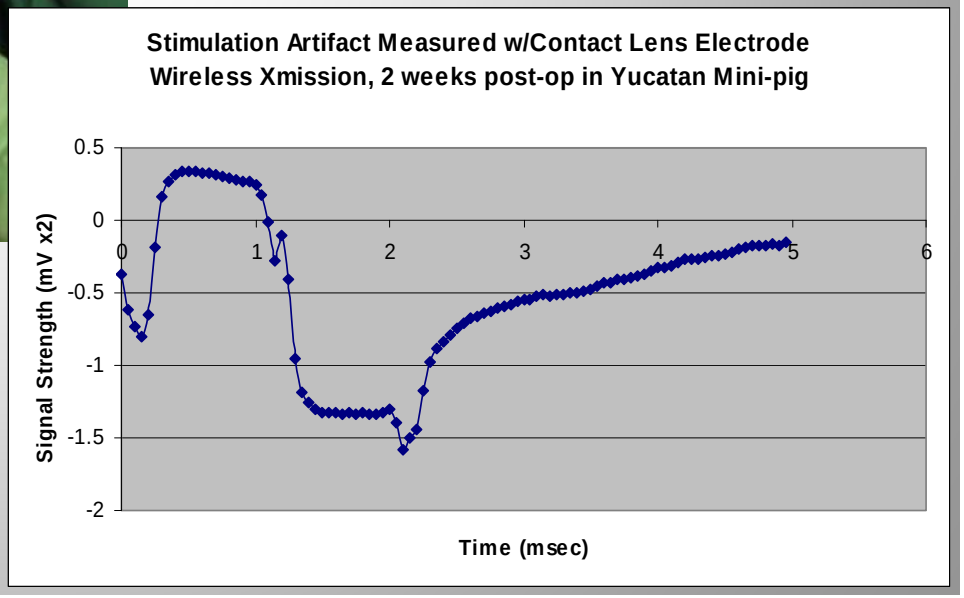


Synthesize our own, NH_2-terminated p(ox) macroinitiator



Our First Patient was a Real Pig





Thank you for your attention