Polymeerverwerking: een complex (coacervaat) verhaal

Marleen Kamperman

rijksuniversiteit groningen

06.2018


NATIONAL GEOGRAPHIC
PLANET OR PLASTIC?
18 billion pounds of plastic ends up in the ocean each year. And that's just the tip of the iceberg.

Plastic Revanche: ik kom altijd terug

Veelgebruikte plastics breken nauwelijks af in de natuur

- Recycling
- Afbreekbare plastics
- Biobased en biopolymeren

Judith Hofland

Biomimicry

‘Biomimicry, innovation inspired by nature’
Janine Benyus (1997)

- De natuur als model.

Biomimicry is een wetenschap die de voorbeelden uit de natuur bestudeert en imiteert of als inspiratie gebruikt om problemen in het mensdomein (geïndustrialiseerde samenlevingen) op de te lossen.

- De natuur als maatstaf.

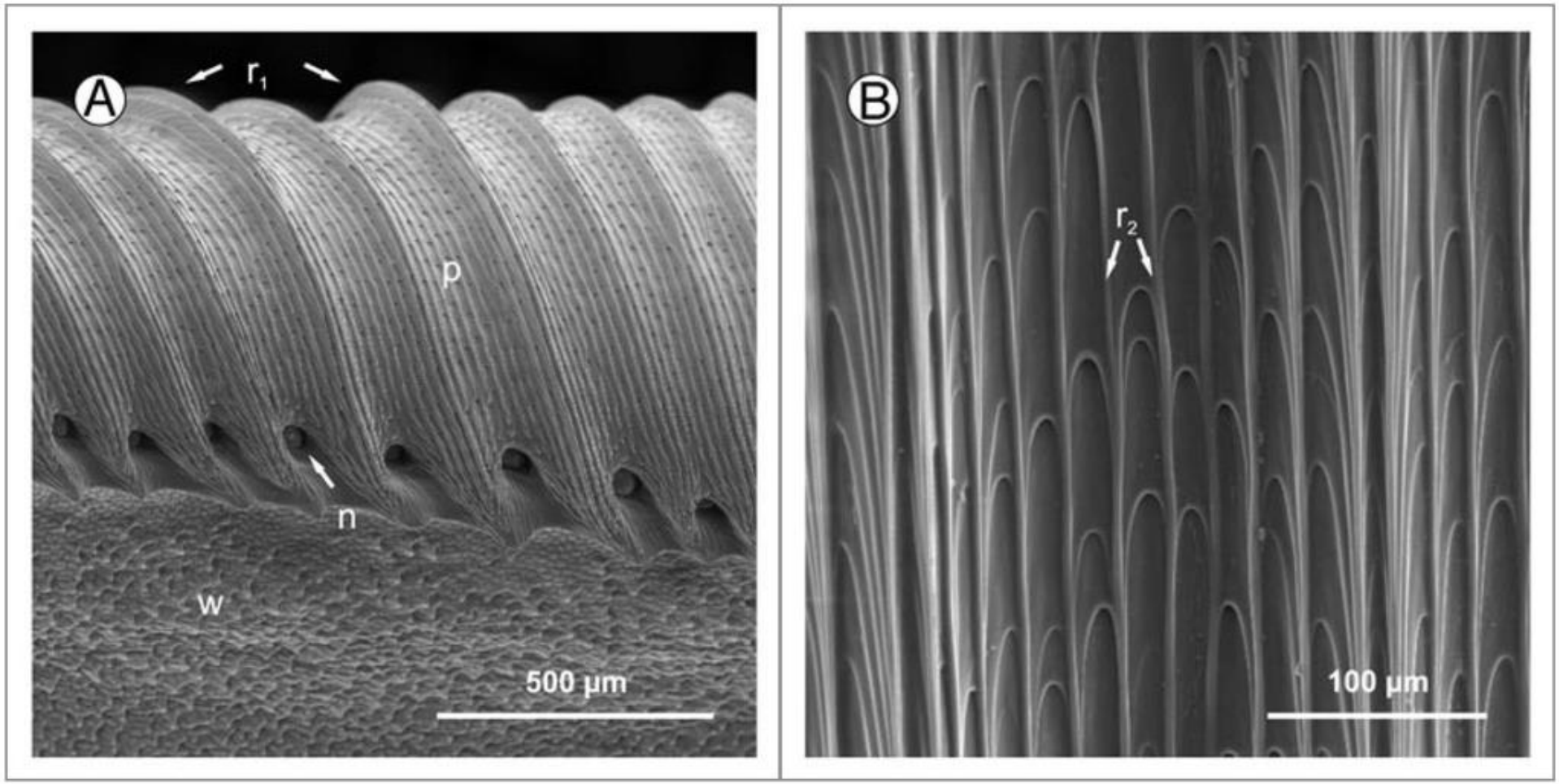
Biomimicry past ecologische maatstaven toe om de ‘passendheid’/ ‘juistheid’ van innovaties te bepalen. Na 3,8 miljard jaar evolutie heeft de natuur geleerd: Wat werkt. Wat geschikt is. Wat blijvend is.

- De natuur als mentor.

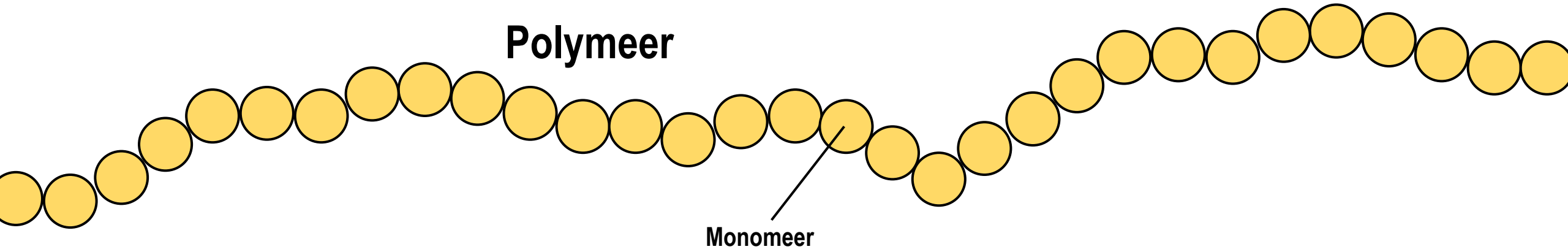
Biomimicry is een nieuwe manier van kijken naar en waarderen van de natuur. Het introduceert een tijdperk dat niet gebaseerd is op wat we uit de natuur kunnen halen, maar wat we van de natuur kunnen leren.

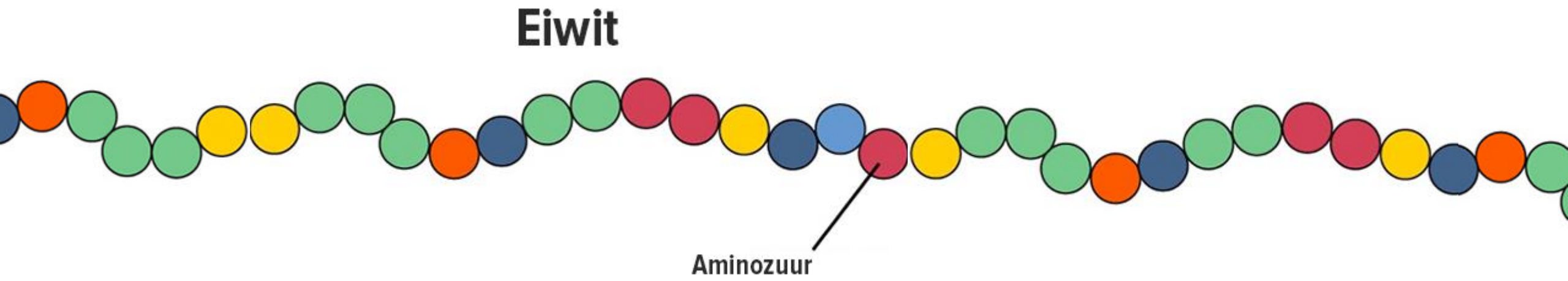
biomimicry NL


dry


A
r1
p
n
w
500 µm
B
r2
100 µm

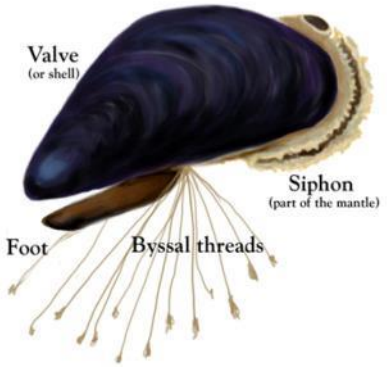

SLIPS Polypropylene Bottles
Ketchup

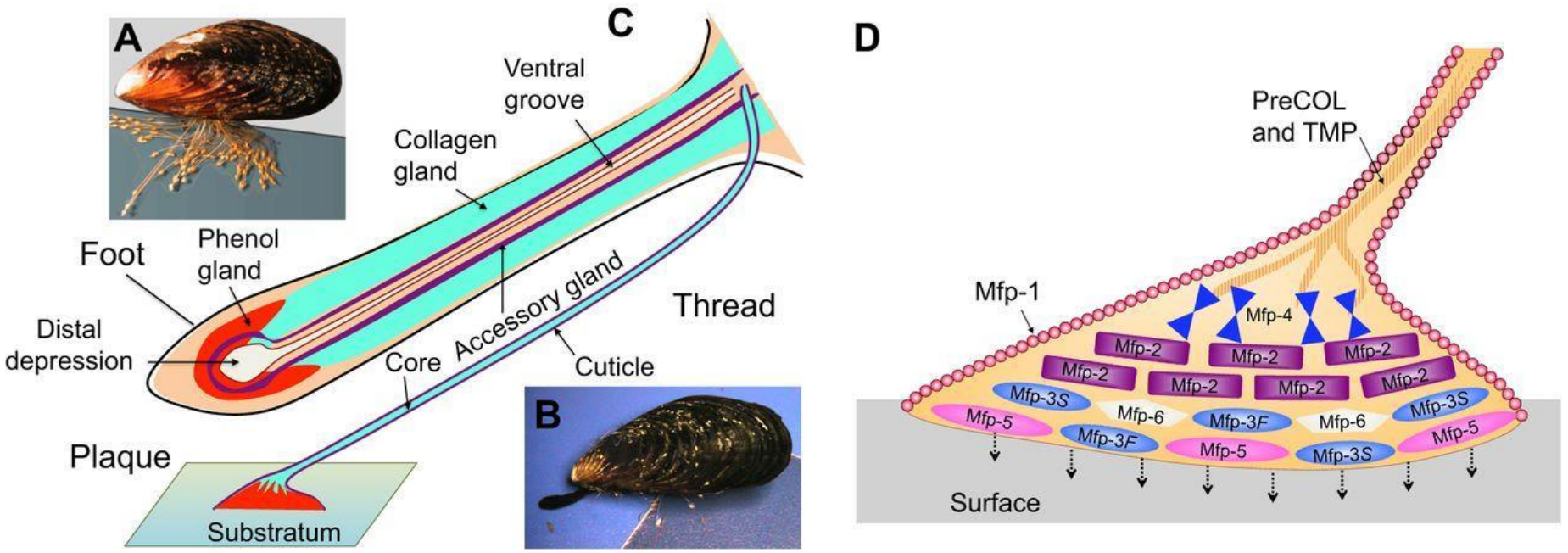

Polymeer
Monomeer


Eiwit
Aminozuur

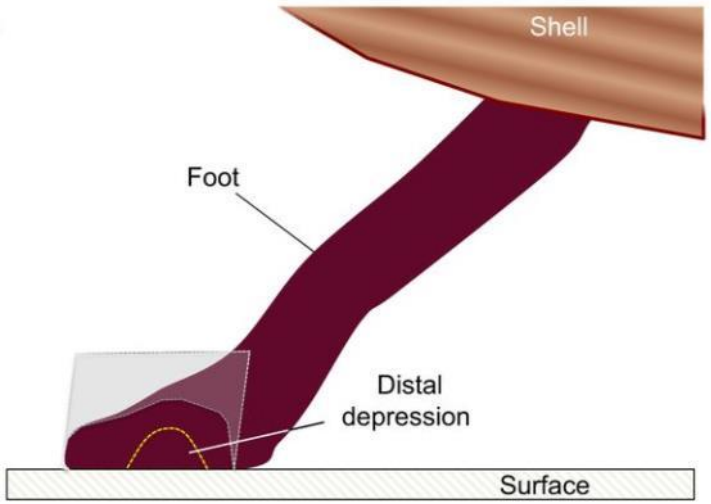
Smithsonian
CHANNEL

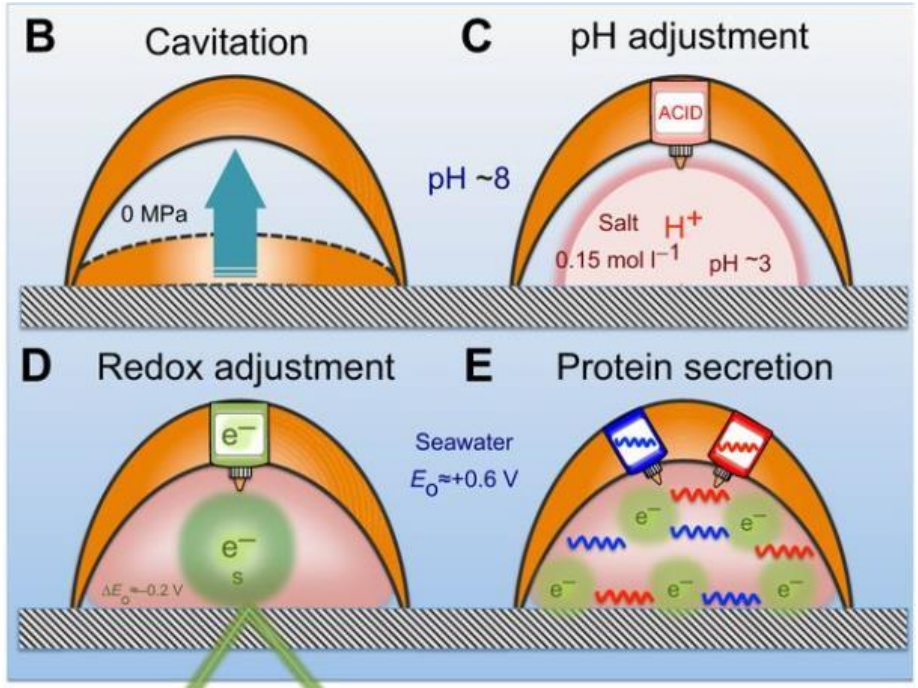
Mosseldraden

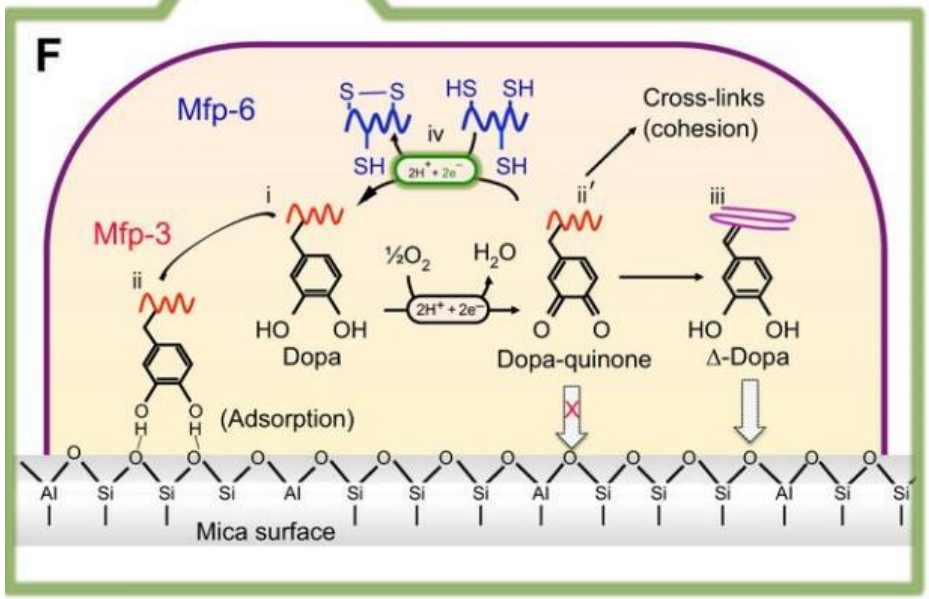


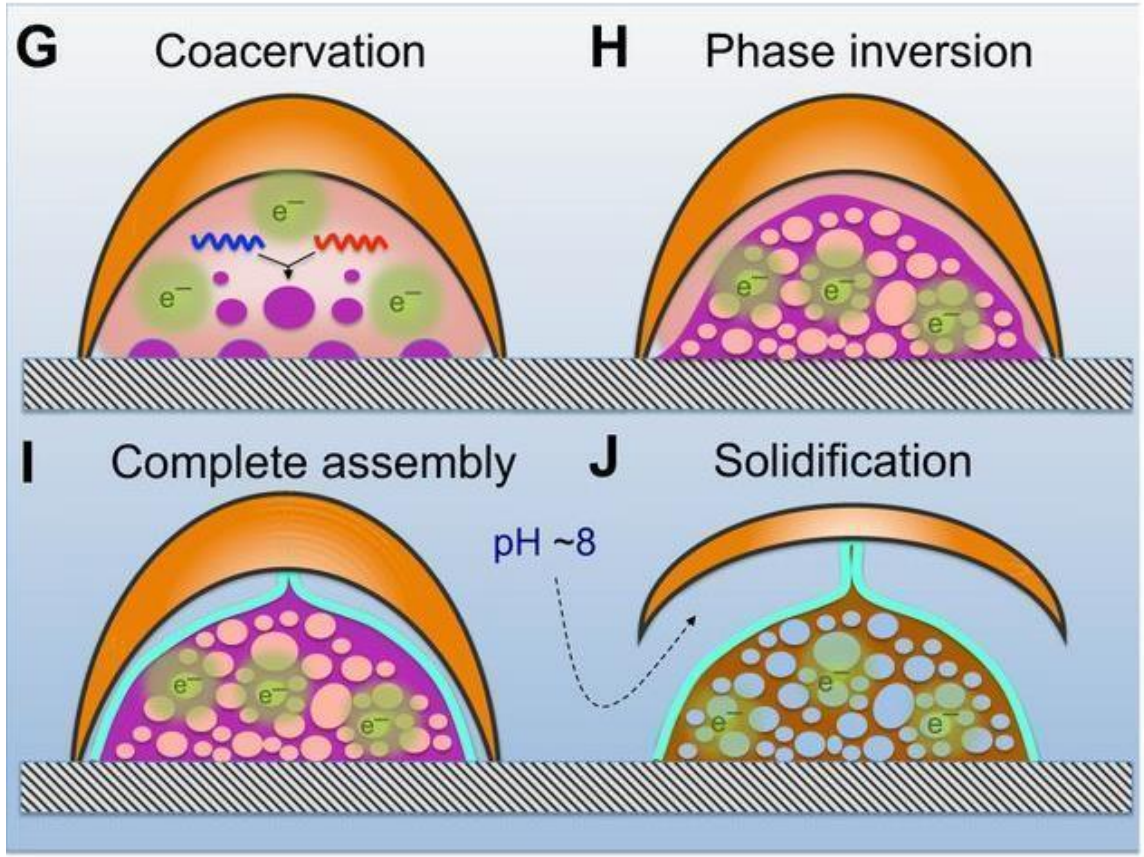


Herbert Waite *Journal of Experimental Biology* (2017) 220, 517

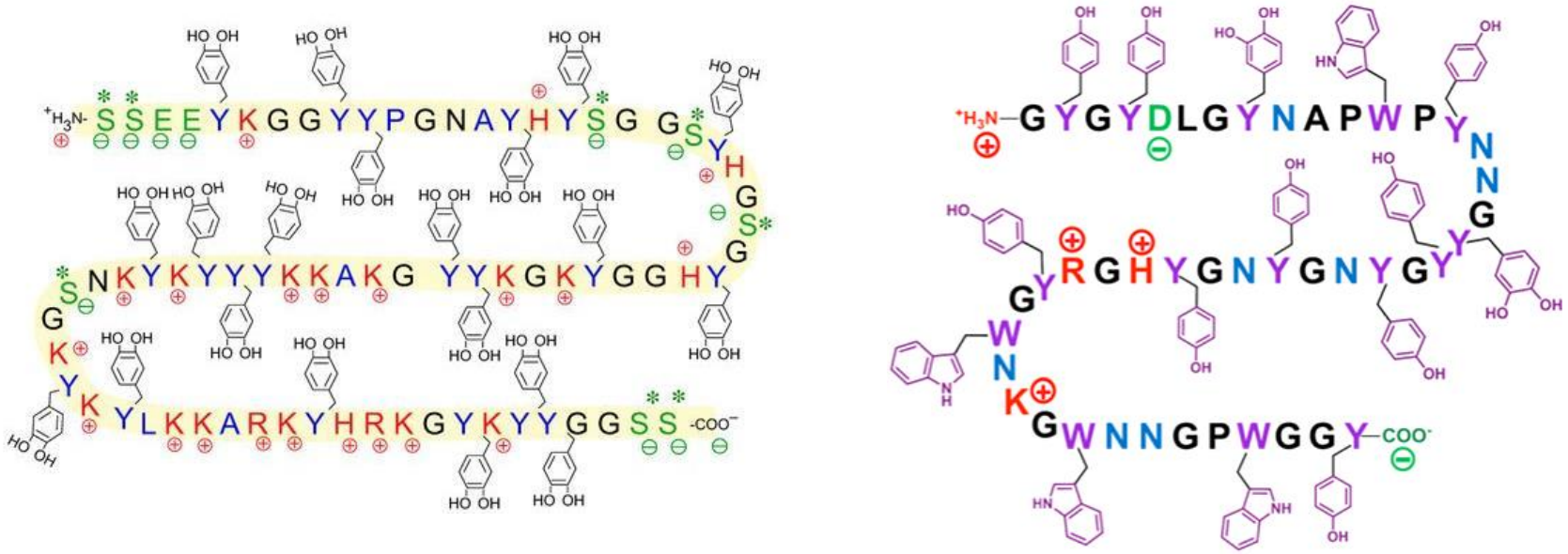

Shell
Foot
Distal
depression
Surface


B
Cavitation
0 MPa
C
pH adjustment
ACID
pH ~8
Salt
0.15 mol l−1
H+
pH ~3
D
Redox adjustment
e−
e−
s
ΔE0 ≈−0.2 V
E
Protein secretion
Seawater
E0≈+0.6 V
e−


F
Mfp-6
S—S
HS
SH
iv
SH
2H+ + 2e−
SH
Cross-links
(cohesion)
i
ii′
iii
Mfp-3
ii
½O2
H2O
2H+ + 2e−
HO
OH
Dopa
O
O
Dopa-quinone
HO
OH
Δ-Dopa
(Adsorption)
Al
Si
Mica surface



Herbert Waite *Journal of Experimental Biology* (2017) 220, 517



Aminozuur: L-3,4-dihydroxyphenylalanine (DOPA)

Herbert Waite *Journal of Experimental Biology* (2017) 220, 517

Uitdaging voor coating producenten

Alkydverf: bindmiddel in organisch oplosmiddel

- ✓ Uitstekende dekking en glad resultaat
- x Gezondheidsrisico's door schadelijke dampen

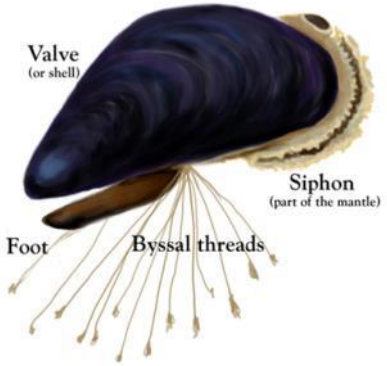
Acrylverf/latexverf: dispersie van deeltjes in water

- ✓ Minder schadelijke dampen
- x Smeert minder goed

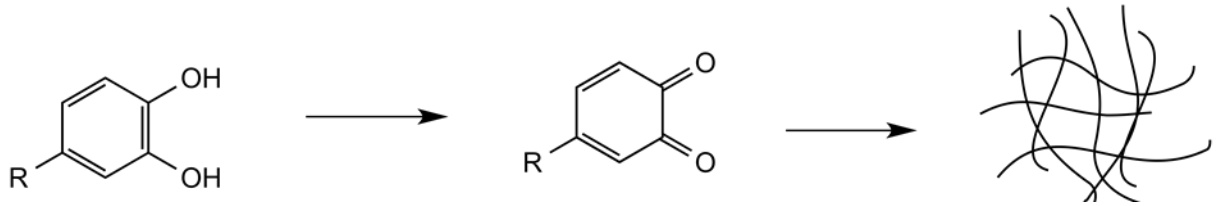
Alternatief

Vereisten:

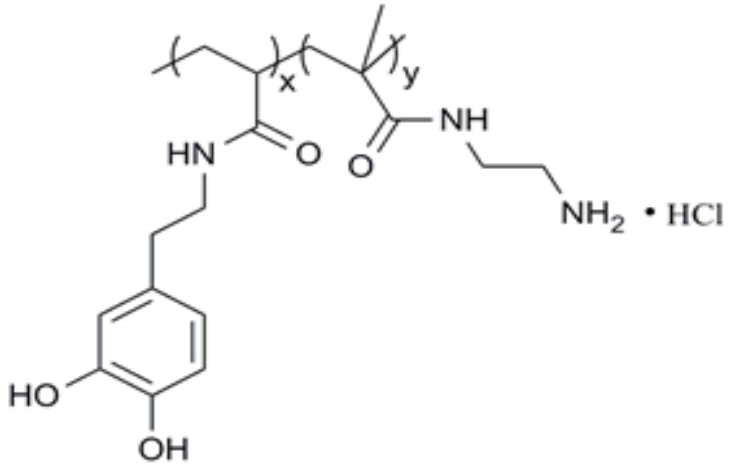
1. Wateroplosbaar bindmiddel
2. Oplosbaarheid sterk veranderd met zuurgraad
3. Uihardingsproces



1. Eiwitproductie (pH < 5)
2. Solidificatie en uitharding na uitscheiding (pH 8)



Sterk afhankelijk van pH



poly(dopamine acrylamide-co-2-aminoethyl methacrylamide)

1. Wateroplosbaar
2. Onoplosbaar bij pH verhoging

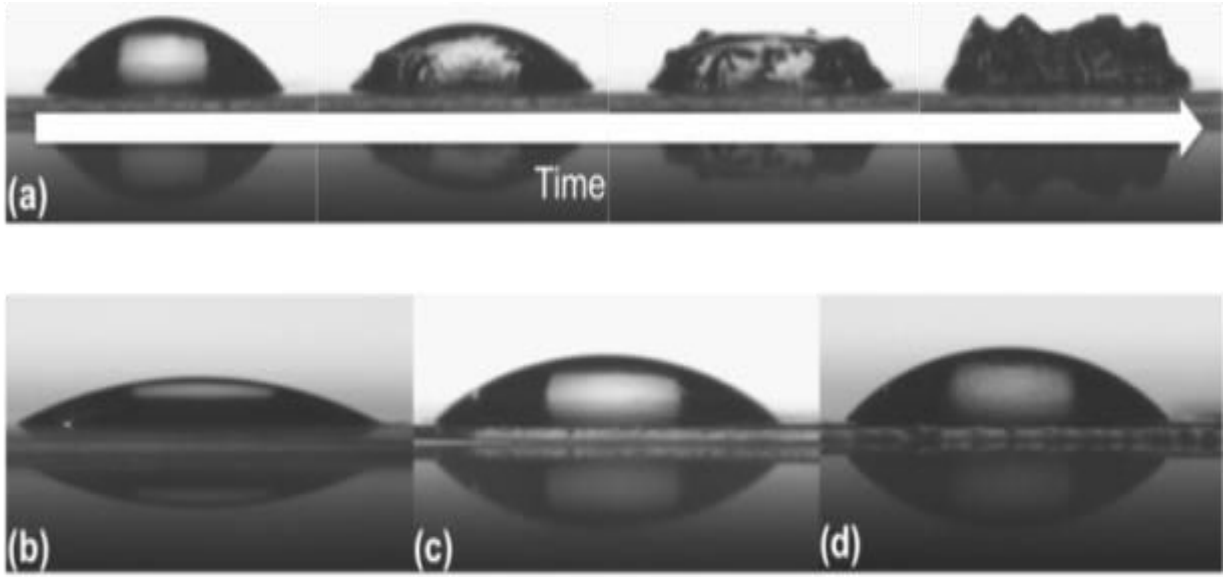
Low pH

High pH

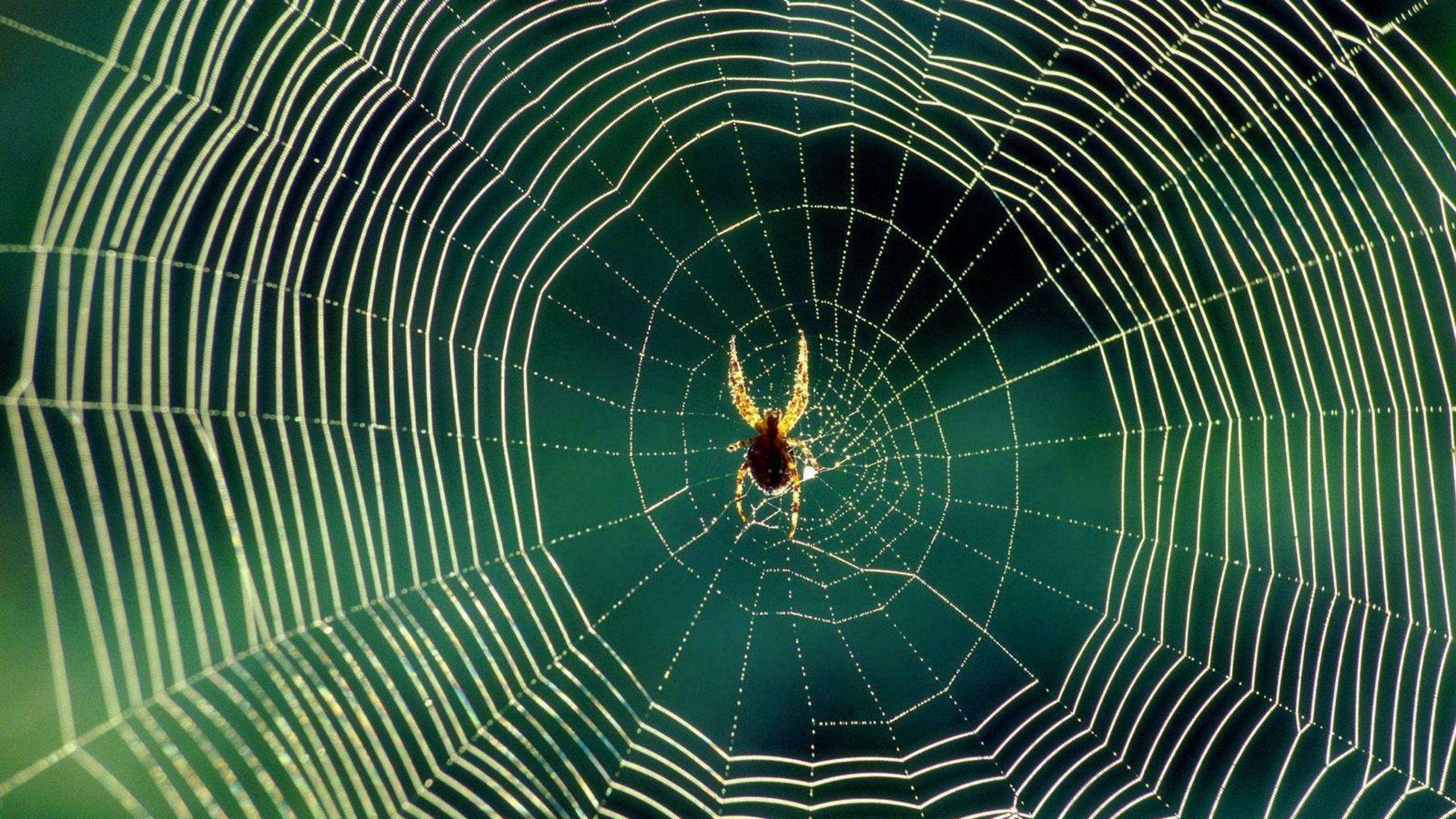
3. Uitharding

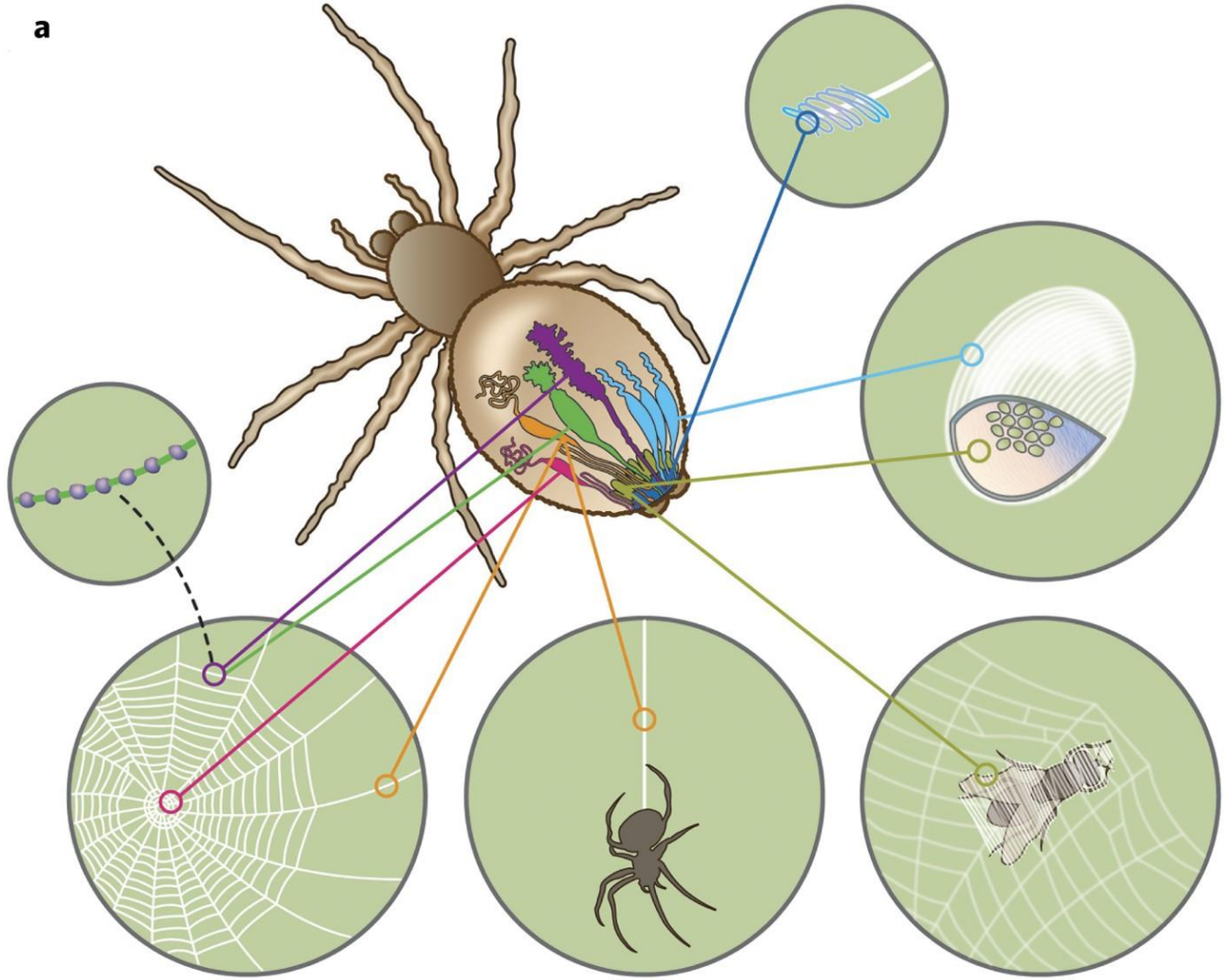
Lage pH

Hoge pH

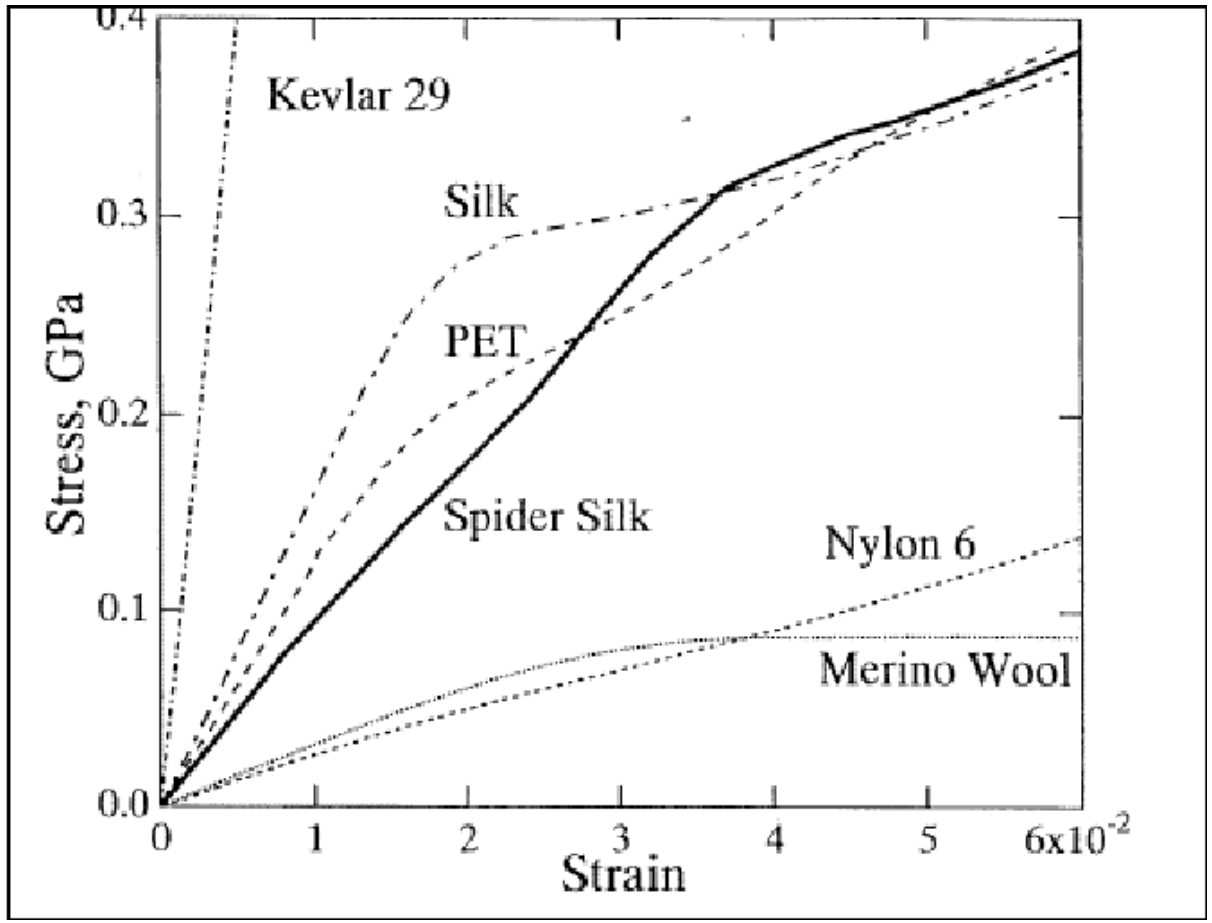


- Coating op polystyreen, roestvrijstaal, glas
- Uitstekende hechting





- Cylindrical glands; outer silk of egg sac
- Aggregate gland; aqueous coating of capture spiral
- Flagelliform gland; core fibers of capture spiral
- Major ampullate gland; dragline and structural silk
- Minor ampullate gland; auxiliary spiral
- Aciniform gland; soft inner silk of egg sac and silk for swathing prey
- Pyriform gland; cement for joints and attachments


Kevlar 29
Silk
PET
Spider Silk
Nylon 6
Merino Wool
Stress, GPa
Strain
0.0
0.1
0.2
0.3
0.4
0
1
2
3
4
5
6x10-2

nature chemical biology

PERSPECTIVE

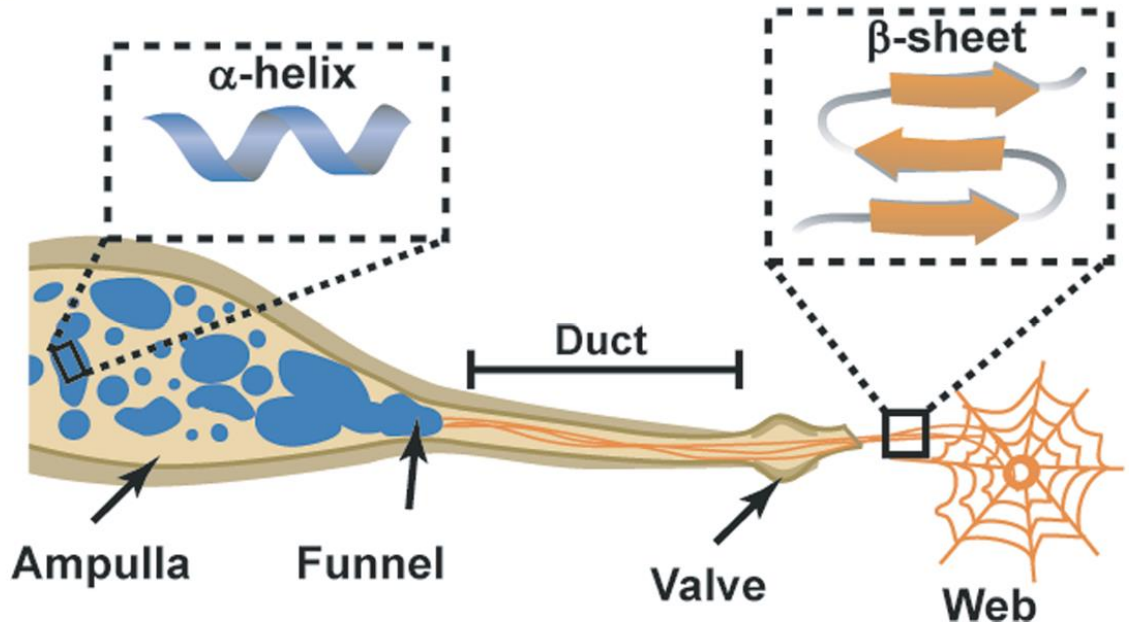
PUBLISHED ONLINE: 17 APRIL 2015 | DOI: 10.1038/NCHEMBIO.1789

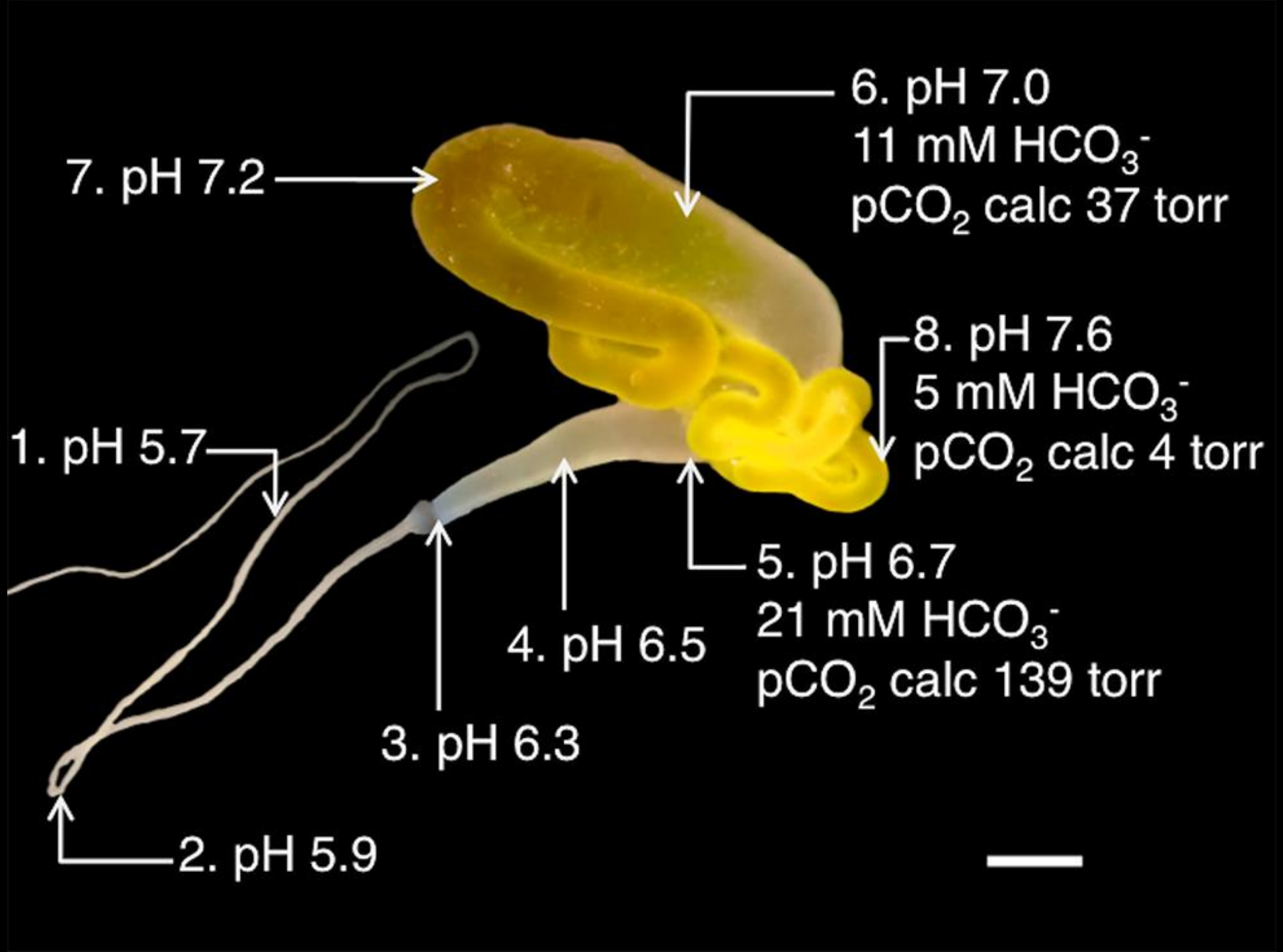
Toward spinning artificial spider silk

Anna Rising[1,2*] & Jan Johansson[1,2*]

"Despite the spidroins **being able to assemble into a solid fiber within a fraction of a second**, the spider manages to keep them **soluble at very high concentrations** (30–50%, w/v) for long-term storage."

How to transition from a polymer that is highly water-soluble into a water-insoluble fiber?


α-helix
β-sheet
Duct
Ampulla
Funnel
Valve
Web


6. pH 7.0
11 mM HCO_3^-
pCO_2 calc 37 torr
7. pH 7.2
8. pH 7.6
5 mM HCO_3^-
pCO_2 calc 4 torr
1. pH 5.7
5. pH 6.7
21 mM HCO_3^-
pCO_2 calc 139 torr
4. pH 6.5
3. pH 6.3
2. pH 5.9

SCIENCE ADVANCES | RESEARCH ARTICLE

MATERIALS SCIENCE

Spider silk self-assembly via modular liquid-liquid phase separation and nanofibrillation

Ali D. Malay[1]*, Takehiro Suzuki[2], Takuya Katashima[1†], Nobuaki Kono[3], Kazuharu Arakawa[3], Keiji Numata[1,4]*

Spider silk fiber rapidly assembles from spidroin protein in soluble state via an incompletely understood mechanism. Here, we present an integrated model for silk formation that incorporates the effects of multiple chemical and physical gradients on the different spidroin functional domains. Central to the process is liquid-liquid phase separation (LLPS) that occurs in response to multivalent anions such as phosphate, mediated by the carboxyl-terminal and repetitive domains. Acidification coupled with LLPS triggers the swift self-assembly of nanofibril networks, facilitated by dimerization of the amino-terminal domain, and leads to a liquid-to-solid phase transition. Mechanical stress applied to the fibril structures yields macroscopic fibers with hierarchical organization and enriched for β-sheet conformations. Studies using native silk gland material corroborate our findings on spidroin phase separation. Our results suggest an intriguing parallel between silk assembly and other LLPS-mediated mechanisms, such as found in intracellular membraneless organelles and protein aggregation disorders.

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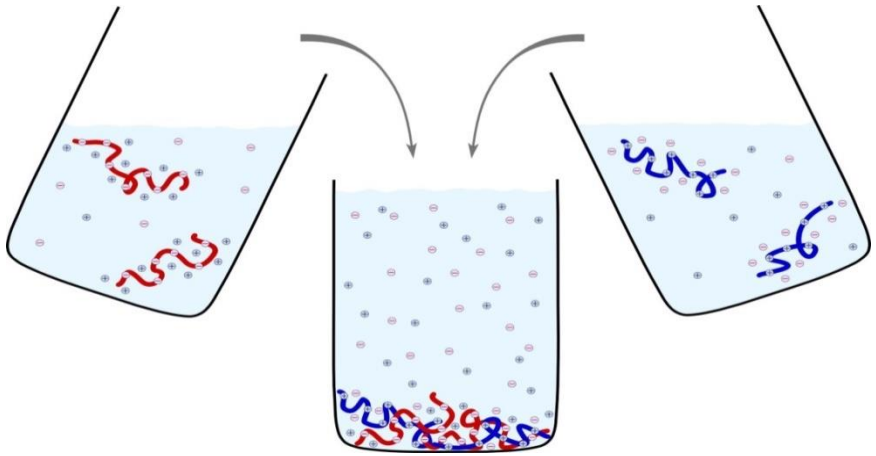
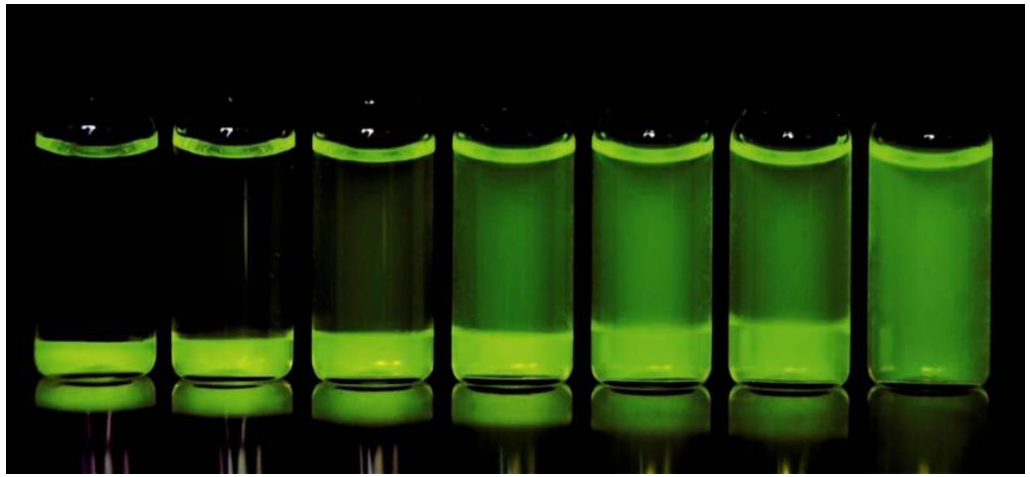
November 2020

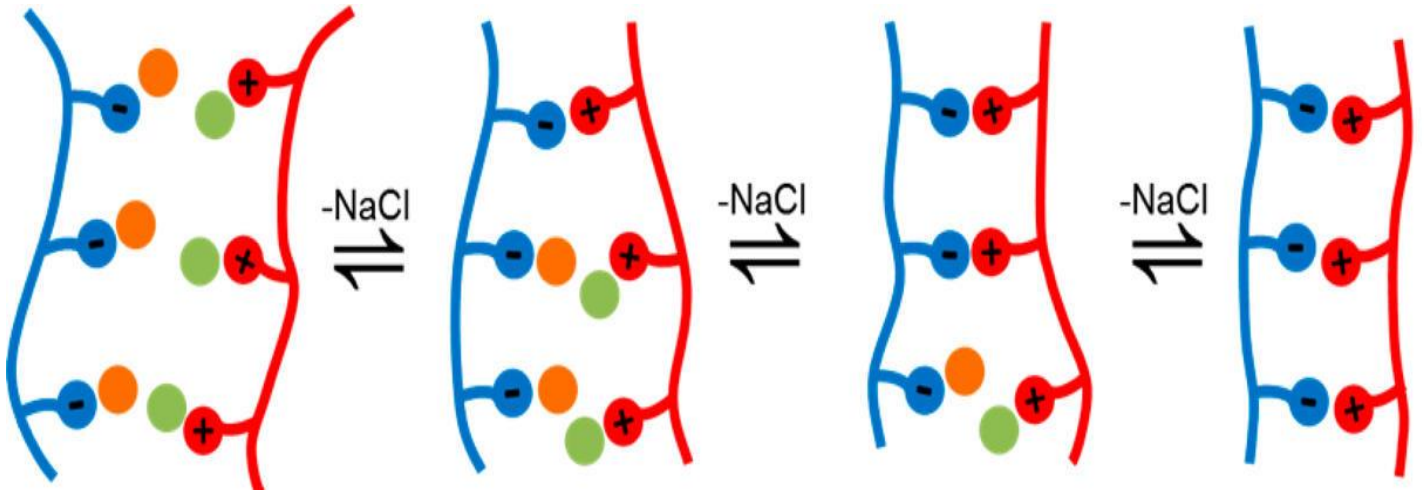
Wat is liquid liquid phase separation (LLPS) of coacervatie?





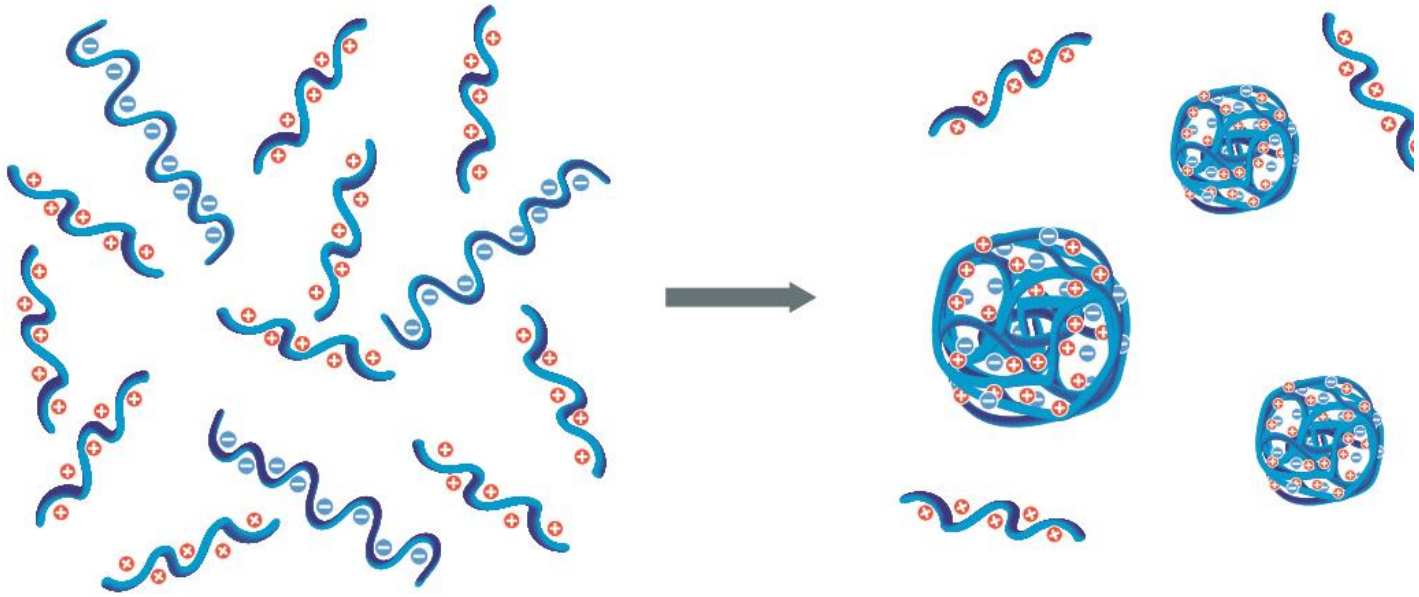
E. Spruijt, “Strength, structure and stability of polyelectrolyte complex coacervates,” 2012.

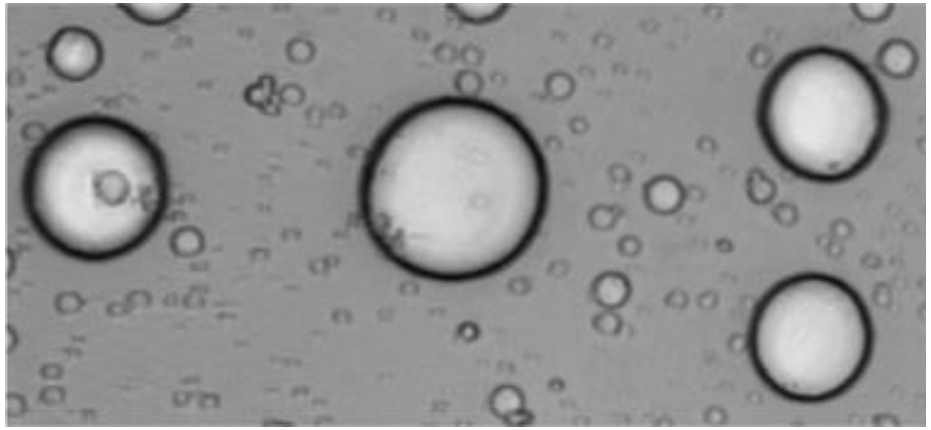
Tegenionen



J. Fu and J. B. Schlenoff, “Driving Forces for Oppositely Charged Polyion Association in Aqueous Solutions: Enthalpic, Entropic, but Not Electrostatic,” J. Am. Chem. Soc., vol. 138, no. 3, pp. 980–990, Jan. 2016.

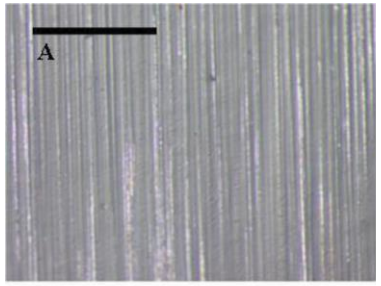
Coacervatie

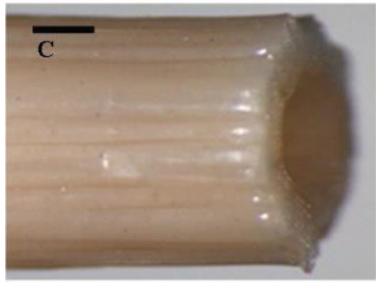


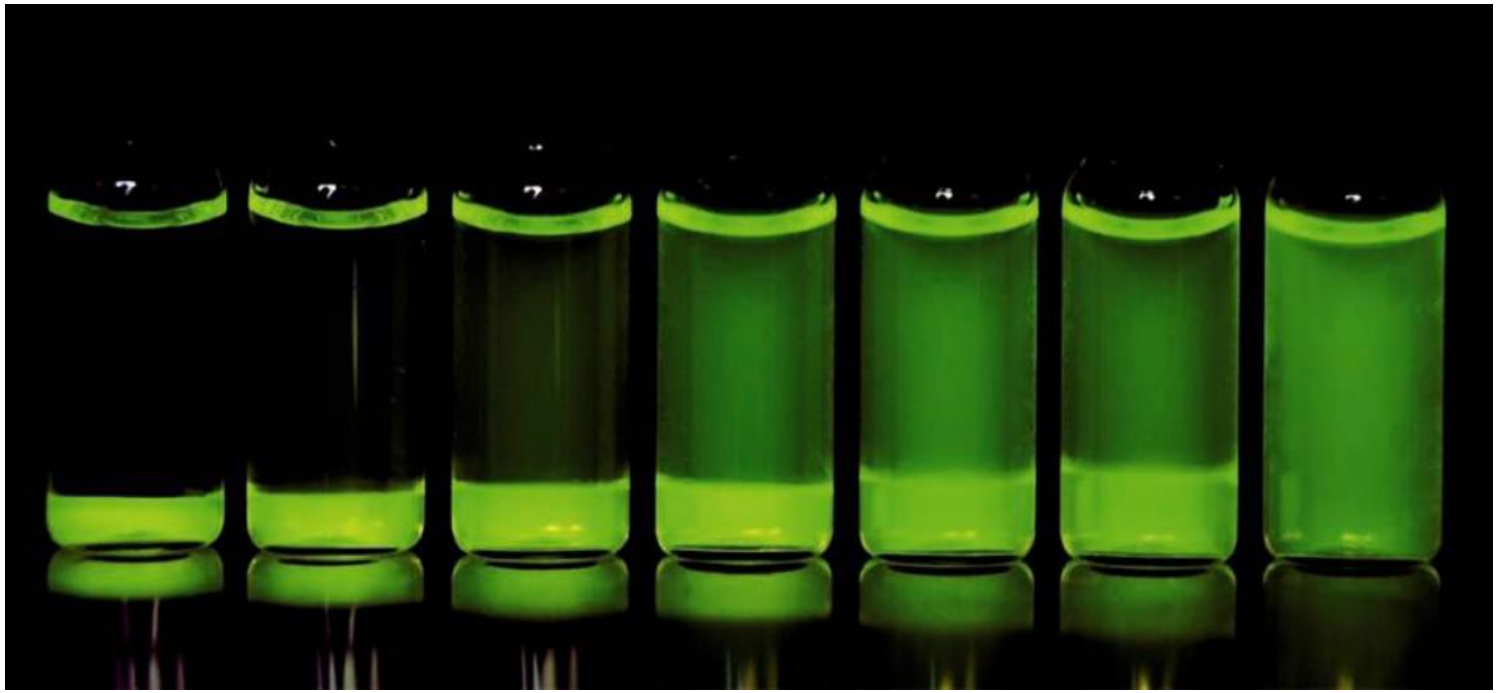


gradient in ionic strength

gradient in pH



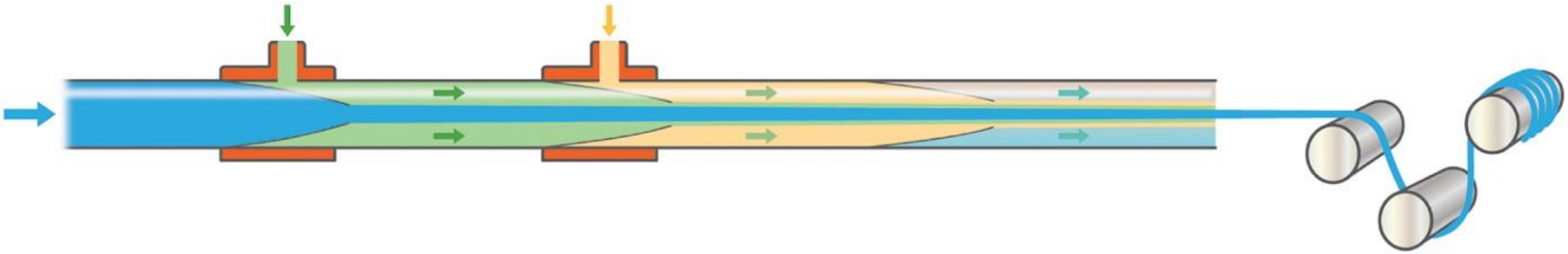


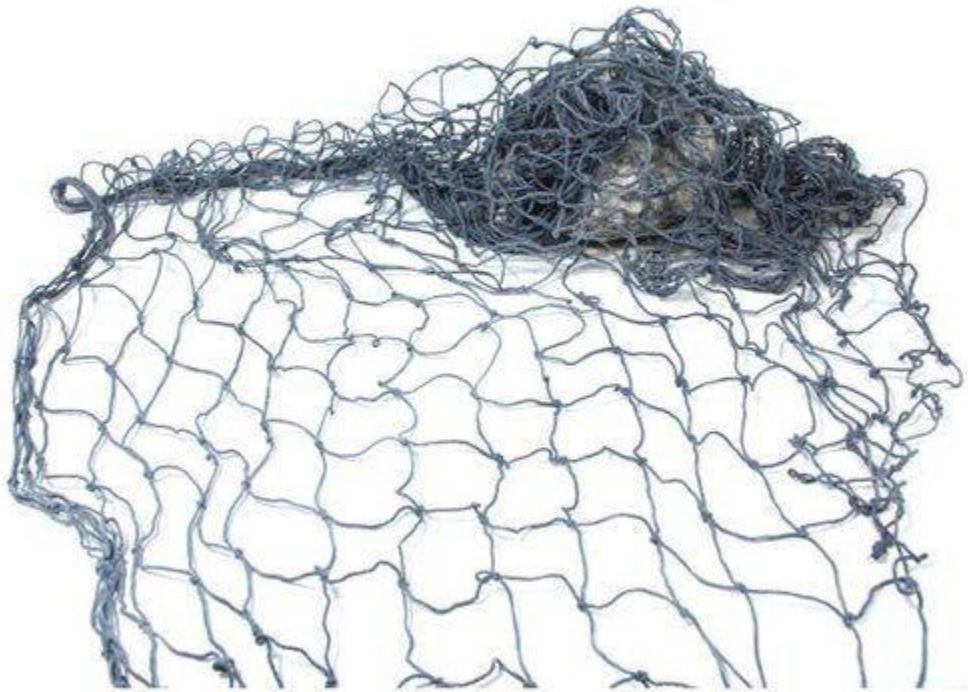


E. Spruijt, “Strength, structure and stability of polyelectrolyte complex coacervates,” 2012.

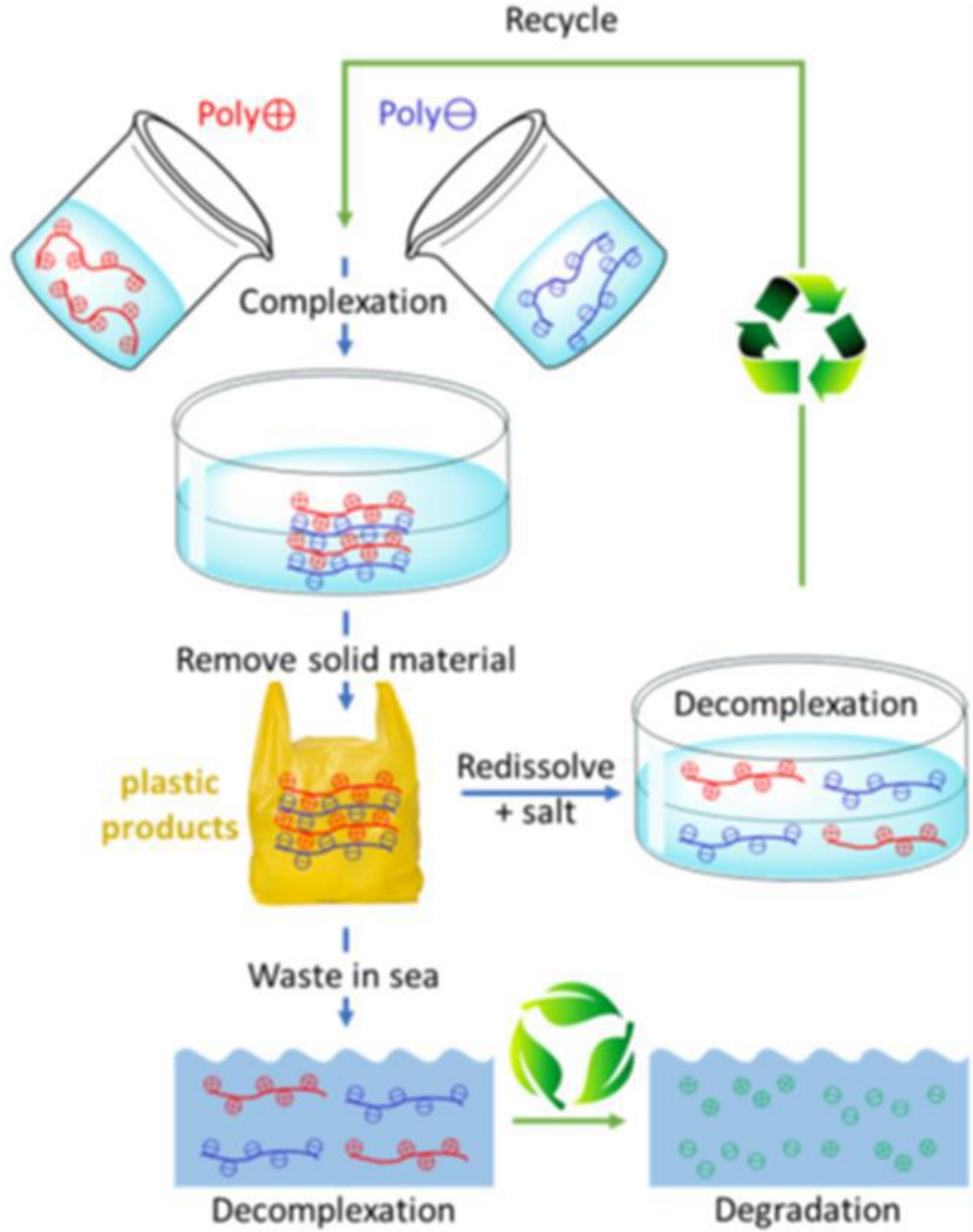
gradient in specific ions or temperature

Gradient coagulation

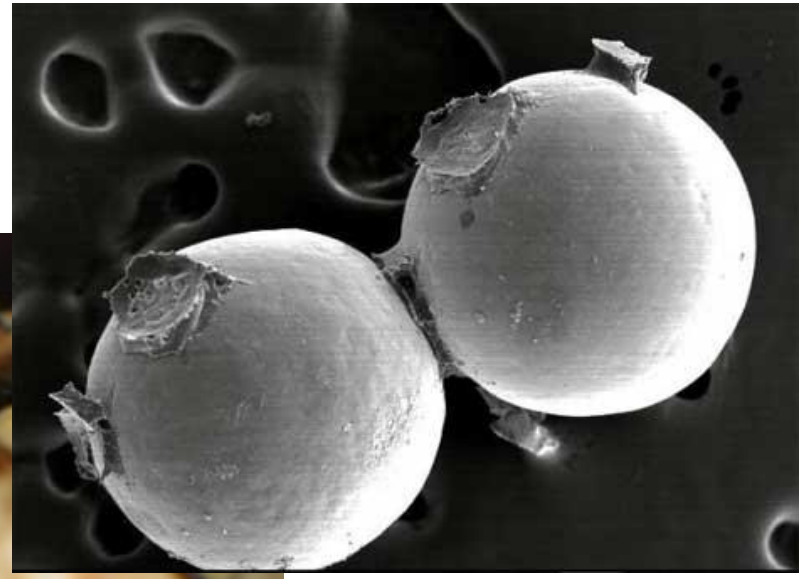




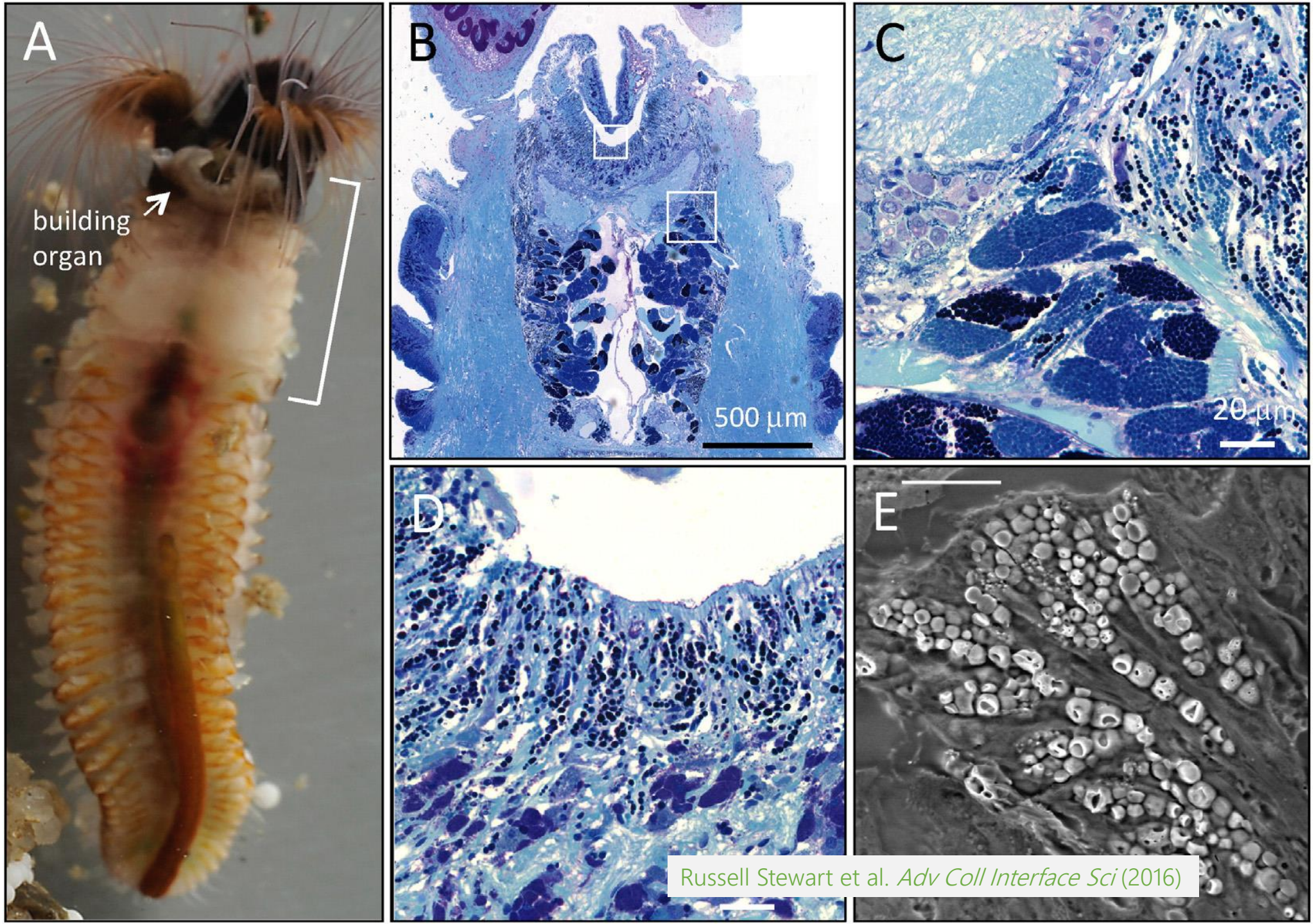

Aardbeien 400g
Blauwe bessen 400g
Rode bessen 300g
Frambozen 250g
Bramen 250g


Recycle
Poly⊕
Poly⊖
Complexation
Remove solid material
plastic products
Redissolve + salt
Decomplexation
Waste in sea
Decomplexation
Degradation

Russell Stewart
University of Utah



Russell Stewart
University of Utah

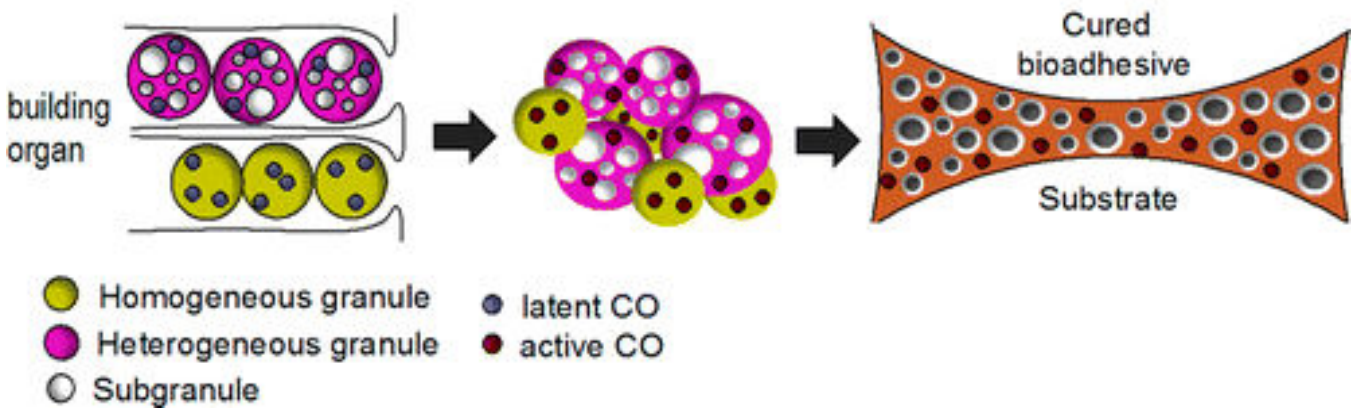


Russell Stewart et al. *Adv Coll Interface Sci* (2016)

Table 1
Sandcastle glue components.

Homogeneous granules	Heterogeneous granules
Sulfated polysaccharides	Polyphosphate proteins (Pc3B)
Polybasic proteins (Pc2, Pc5)	Polyampholytic proteins (Pc3A)
Catechol oxidase	Polybasic proteins (Pc1, Pc4)
	Mg^{2+}
	Catechol oxidase

Blue: polyanions, Purple: polycation and polyanion blocks,
Red: polycations



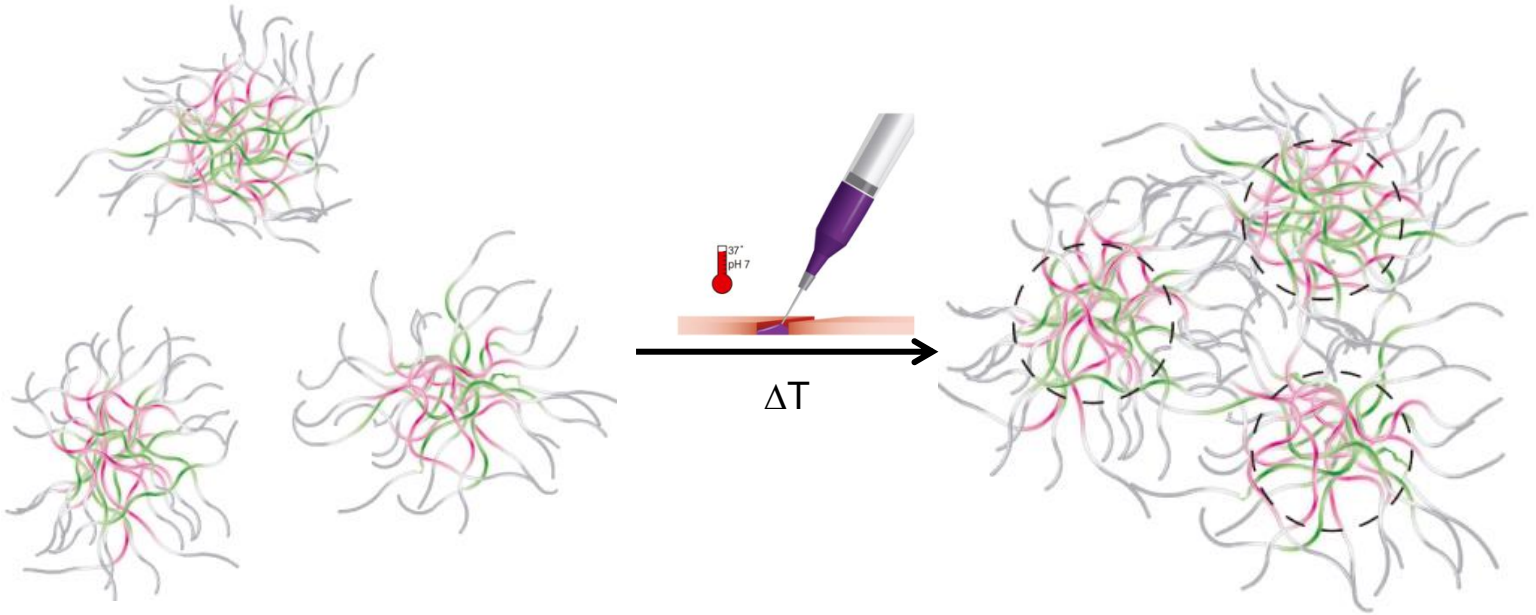
Russell Stewart et al. *Adv Coll Interface Sci* (2016)

Waarom coacervatie?

Voordelen van coacervatie voor lijmtoepassingen:

1. Onmengbaar met water
2. Goede bevochtiging van oppervlakken
3. Uitharden door externe trigger
4. Controleerbare mechanische eigenschappen

Uitharding door opwarmen



PNIPAM-*b*-PAA-*b*-PNIPAM

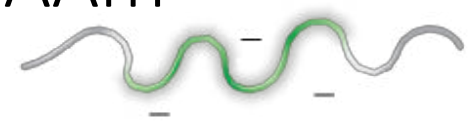
PNIPAM-*b*-PDMAEMA-*b*-PNIPAM

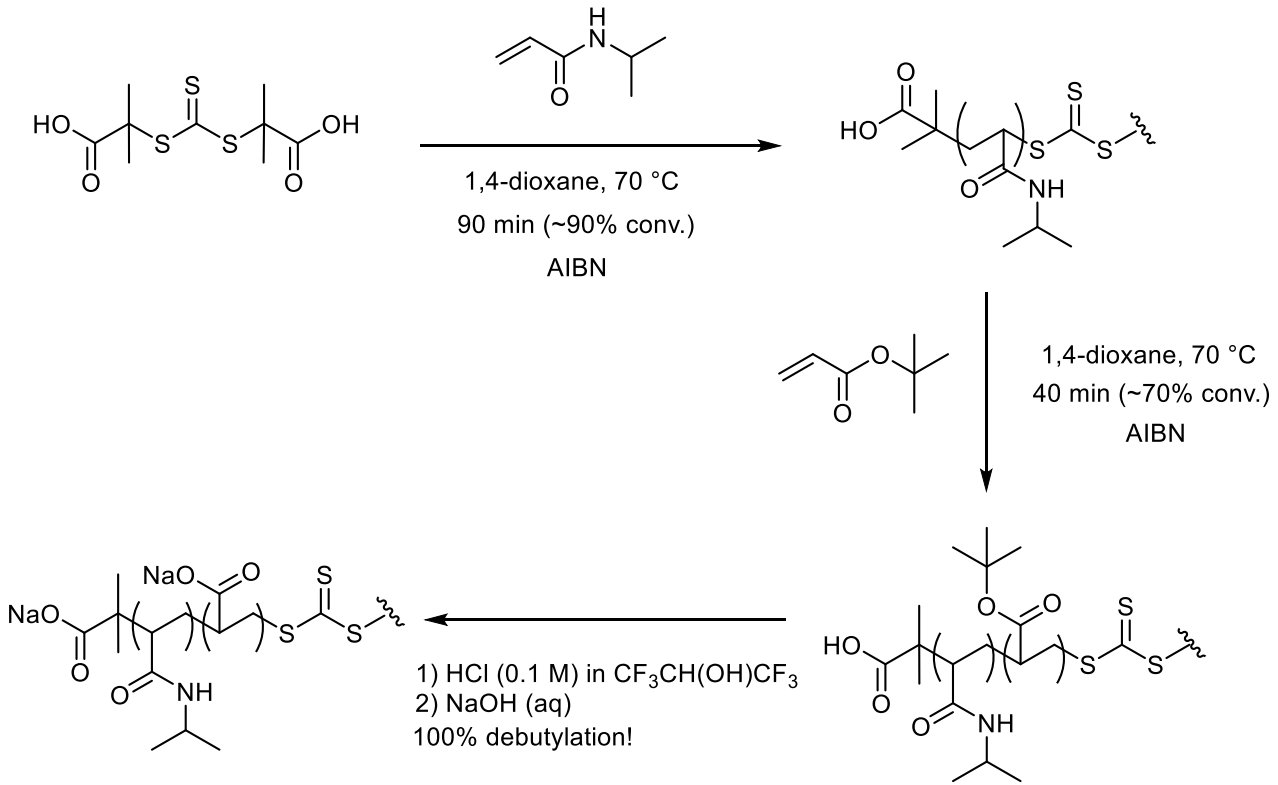
Underwater adhesion of complex coacervates

temperature increase

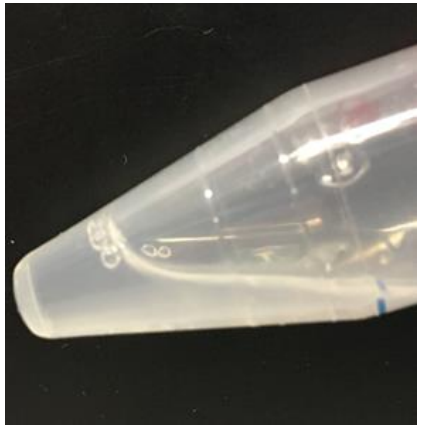
university of

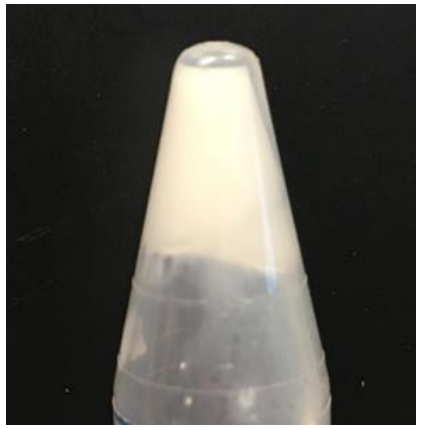
Synthesis of pNIPAAm-*b*-pAA-*b*-pNIPAAm

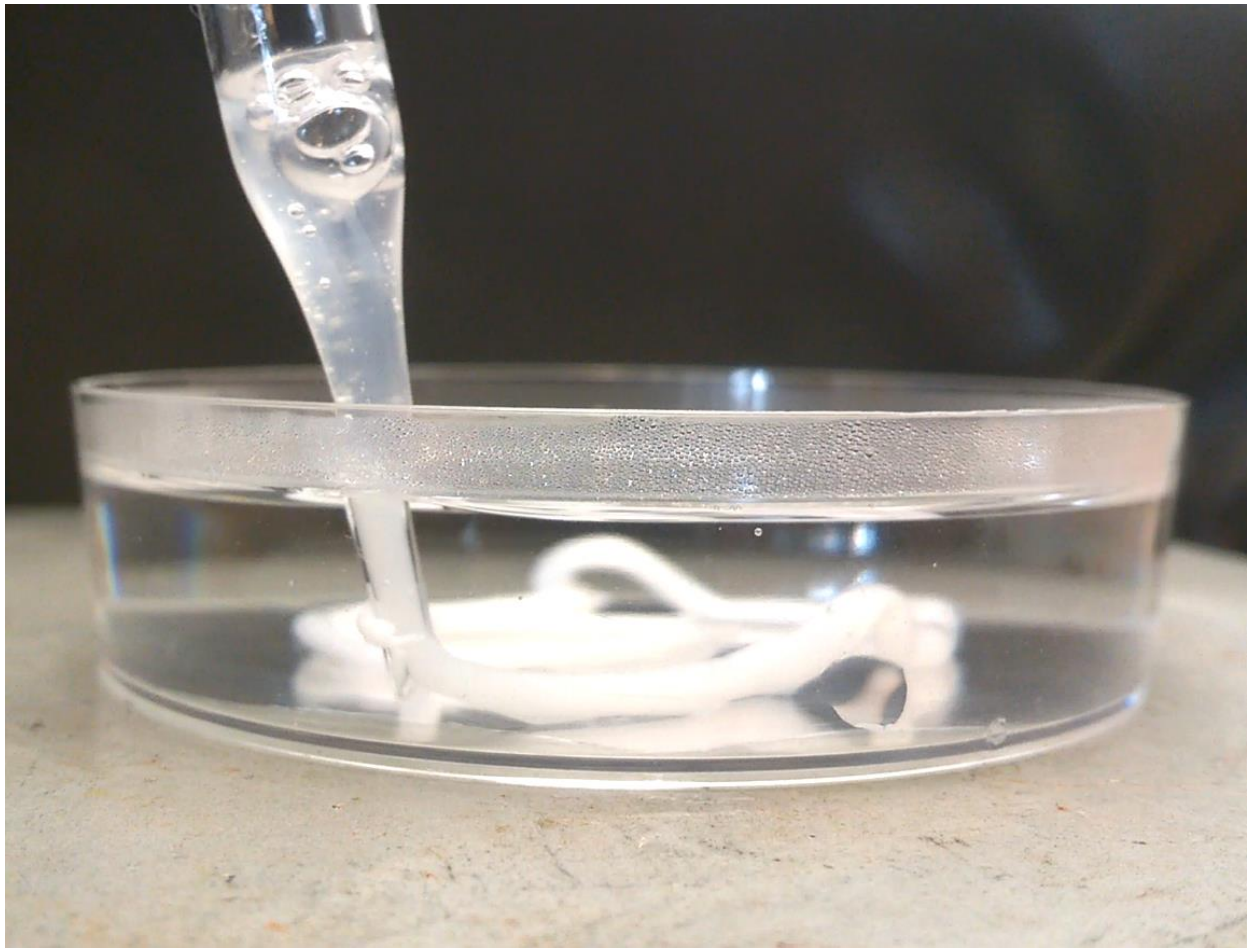




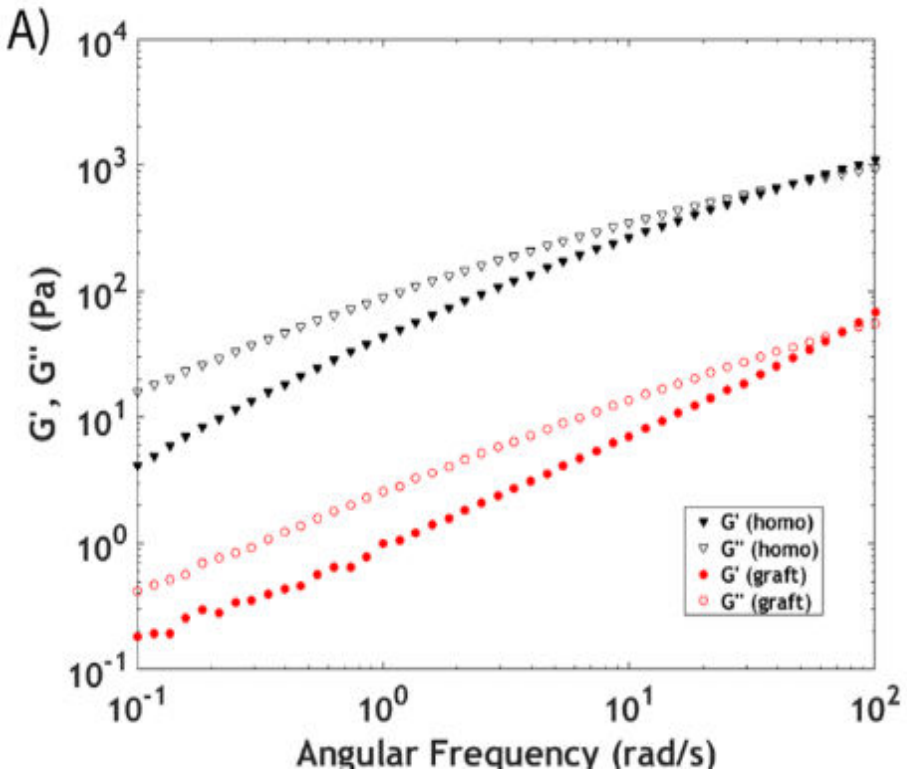
M_w up to 40 kDa
Đ < 1.4



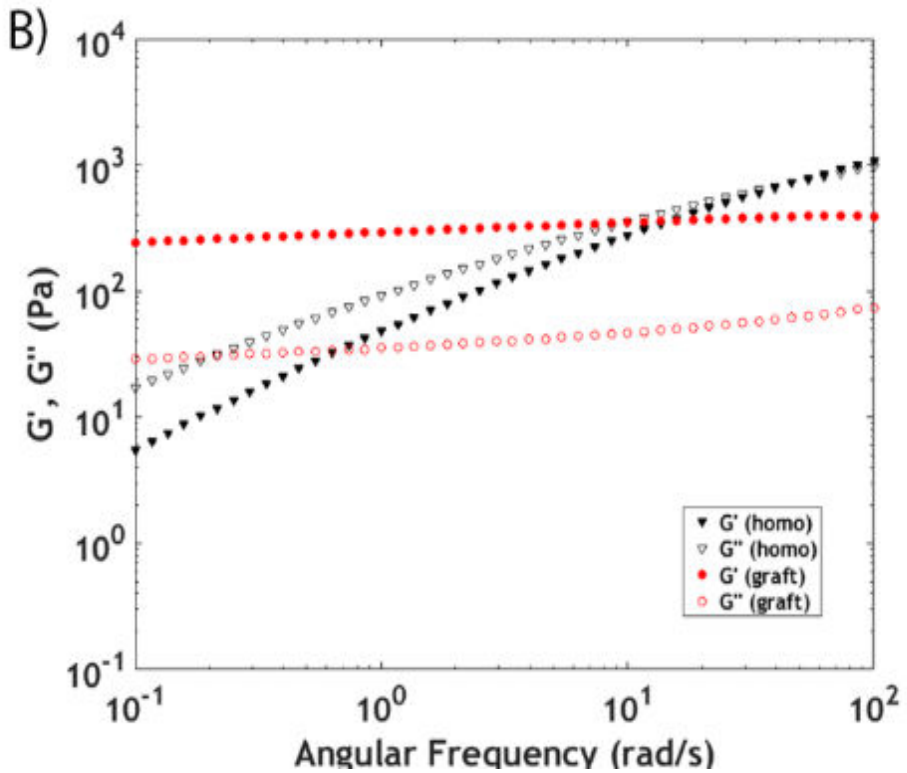




Rheologie

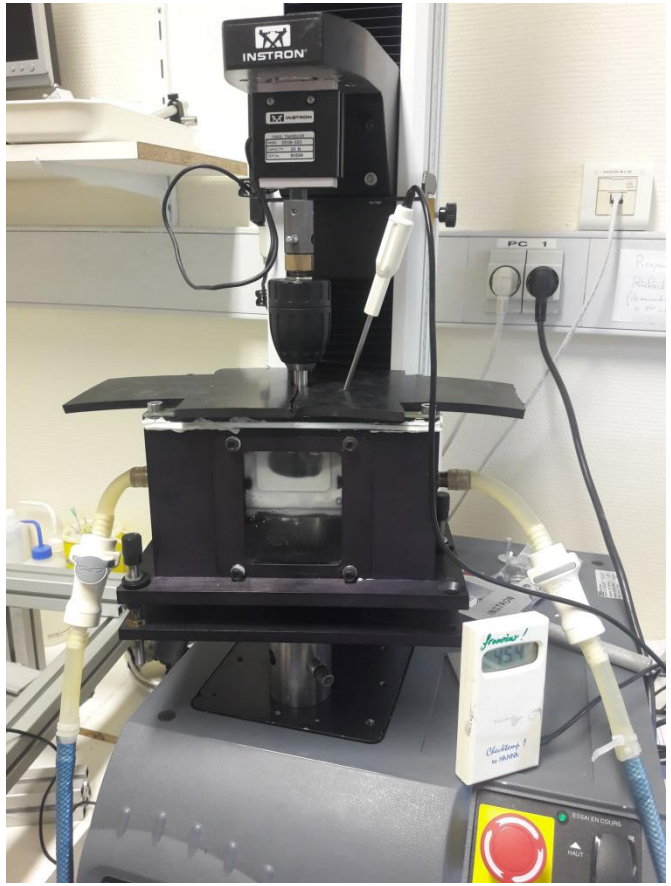


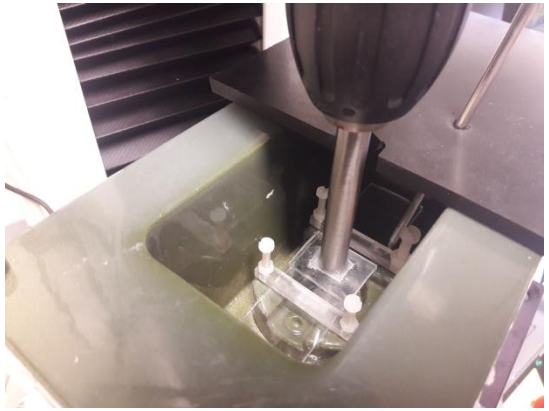
RT, 0.75 M NaCl

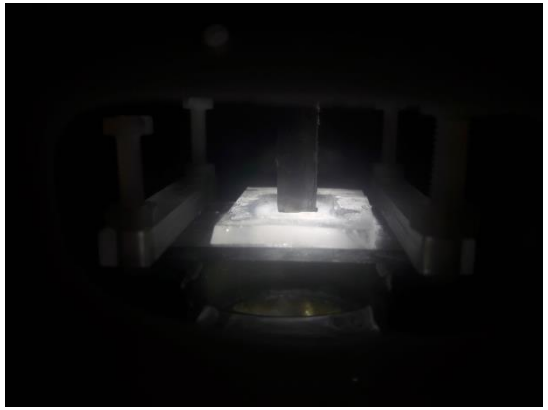


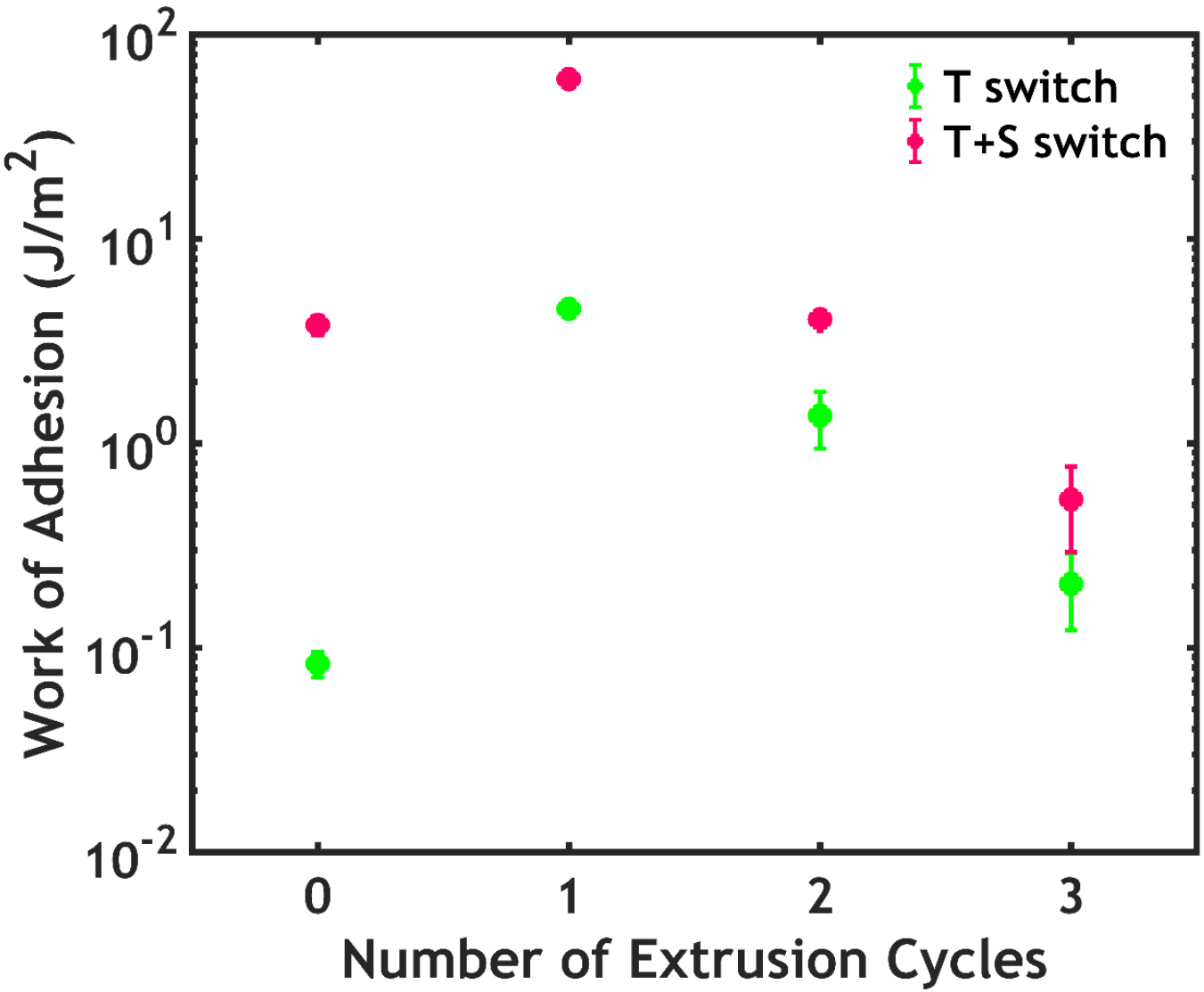
50°C, 0.75 M NaCl

Adhesiemetingen

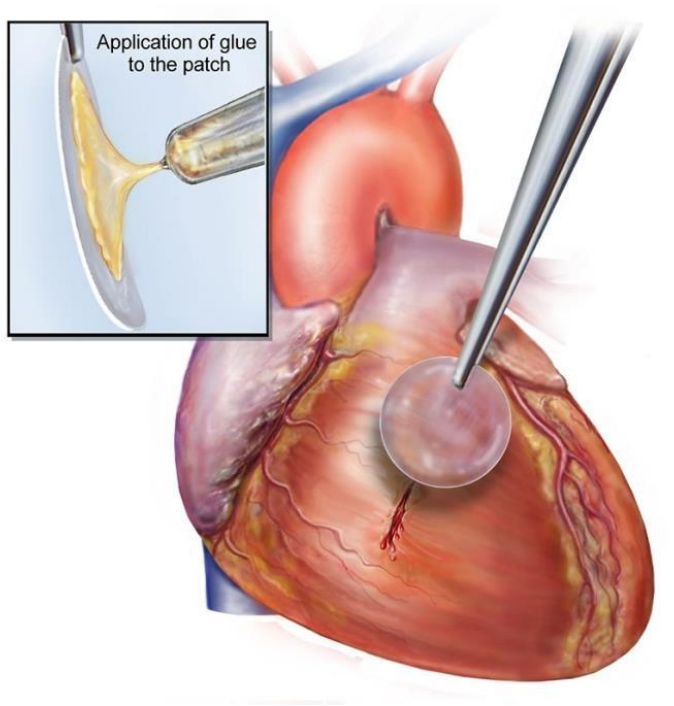







10^2
10^1
10^0
10^{-1}
10^{-2}
Work of Adhesion (J/m^2)
0
1
2
3
Number of Extrusion Cycles
T switch
T+S switch


O+
O+
O+
O+
O CCD.se

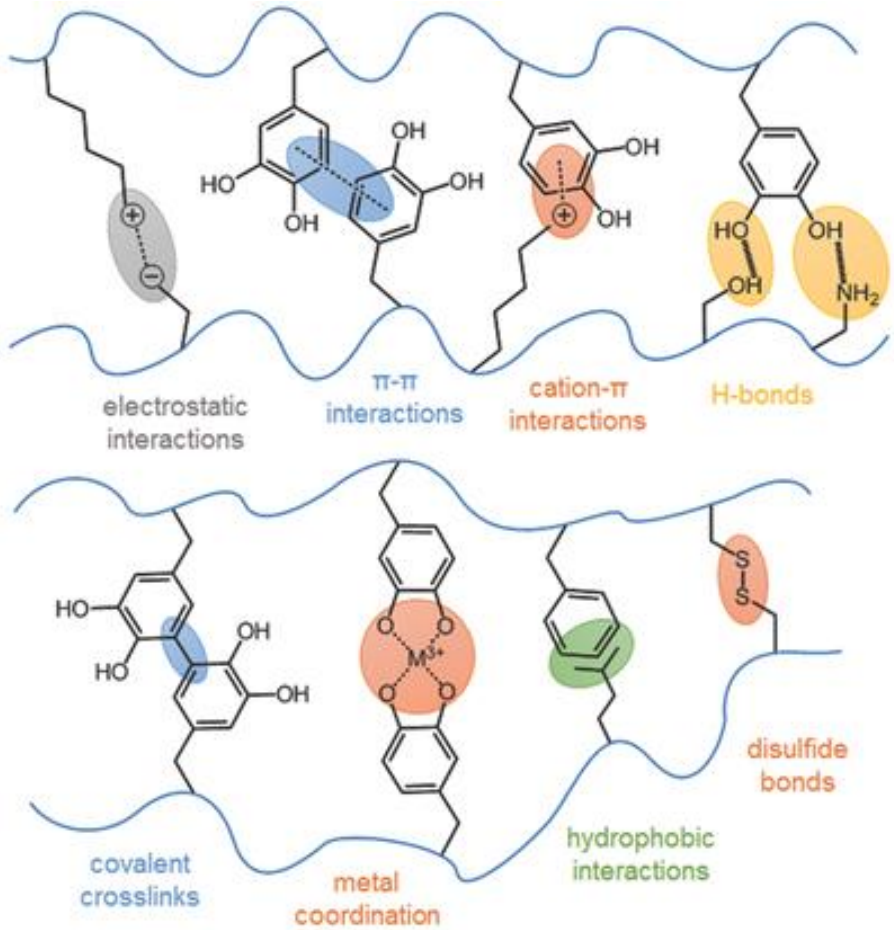

Application of glue
to the patch

Dank!

erc

nationale wetenschaps agenda

NWO


HO
OH
OH
OH
OH
OH
HO
OH
OH
NH2
electrostatic interactions
π-π interactions
cation-π interactions
H-bonds
HO
OH
HO
OH
M3+
S
S
covalent crosslinks
metal coordination
hydrophobic interactions
disulfide bonds


MYLIUM
Soft touch. Strong story.