Aqueous Nanodispersions of Biodegradable Polyesters for Nanofiber Preparation by Electrospinning

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From water processable to water stable

Biodegradable Polyesters

Water stable???

Nanomaterial

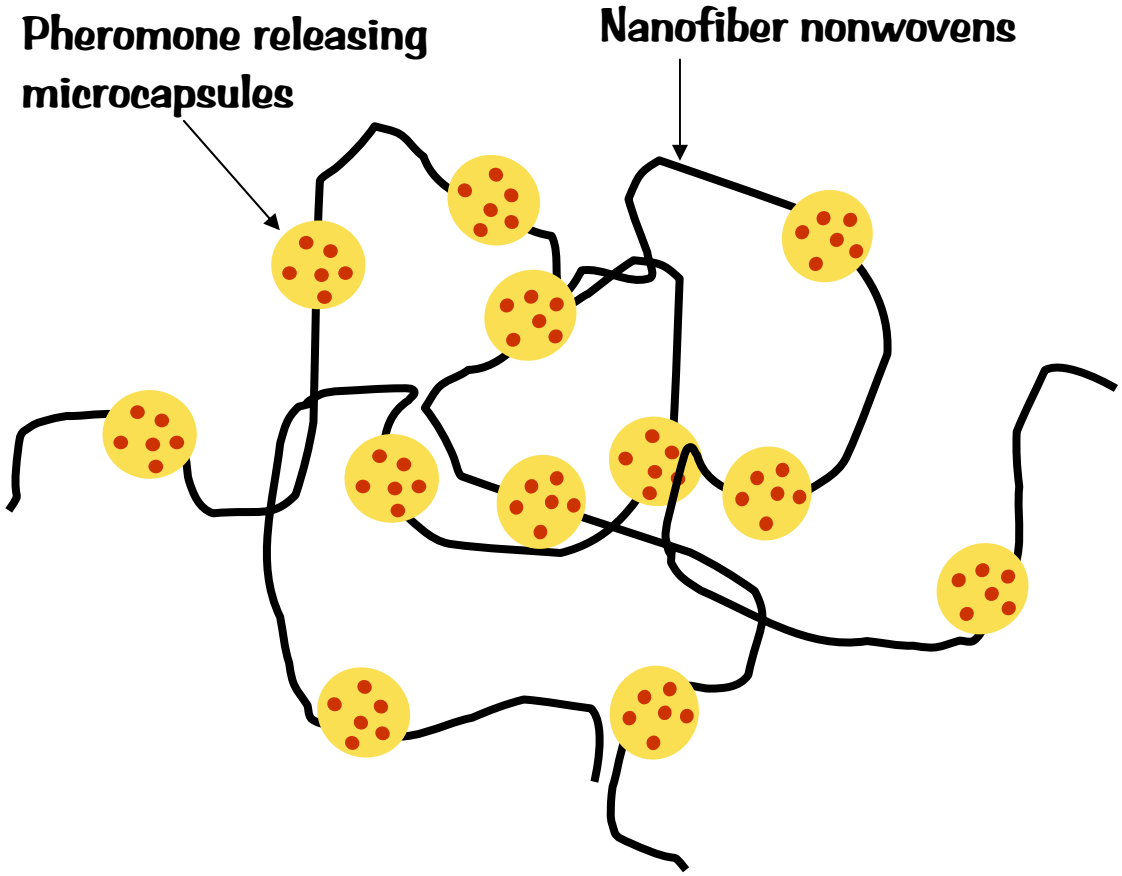
Processing from water

The vision
Protection by mating disruption with pheromones from artificial dispensers

Requirements

- Dispensers have to create homogenous phermone cloud
- Dispensers have to be biodegradable
- Dispensers have to be stable during release of pheromone – suspension electrospinning
- Dispensers have to release pheromone steadily

The concept
Use of electrospun pheromone releasing nonwovens

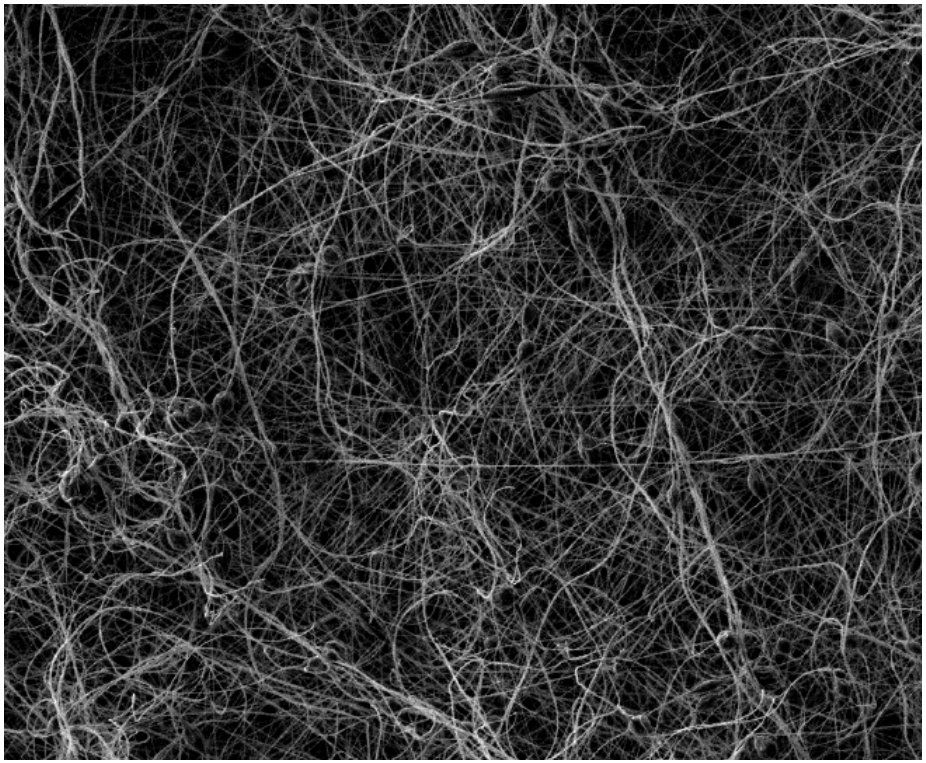


The green approach

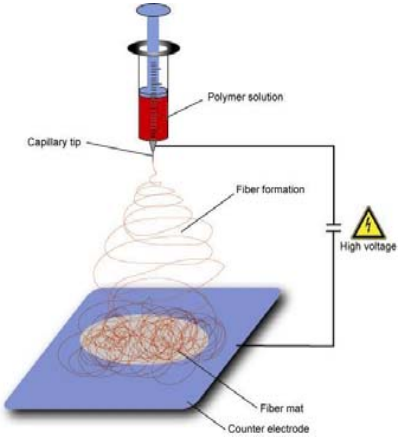
- Water based formulation
- Water stable nonwoven
- Degradable nonwoven
- Phermone release

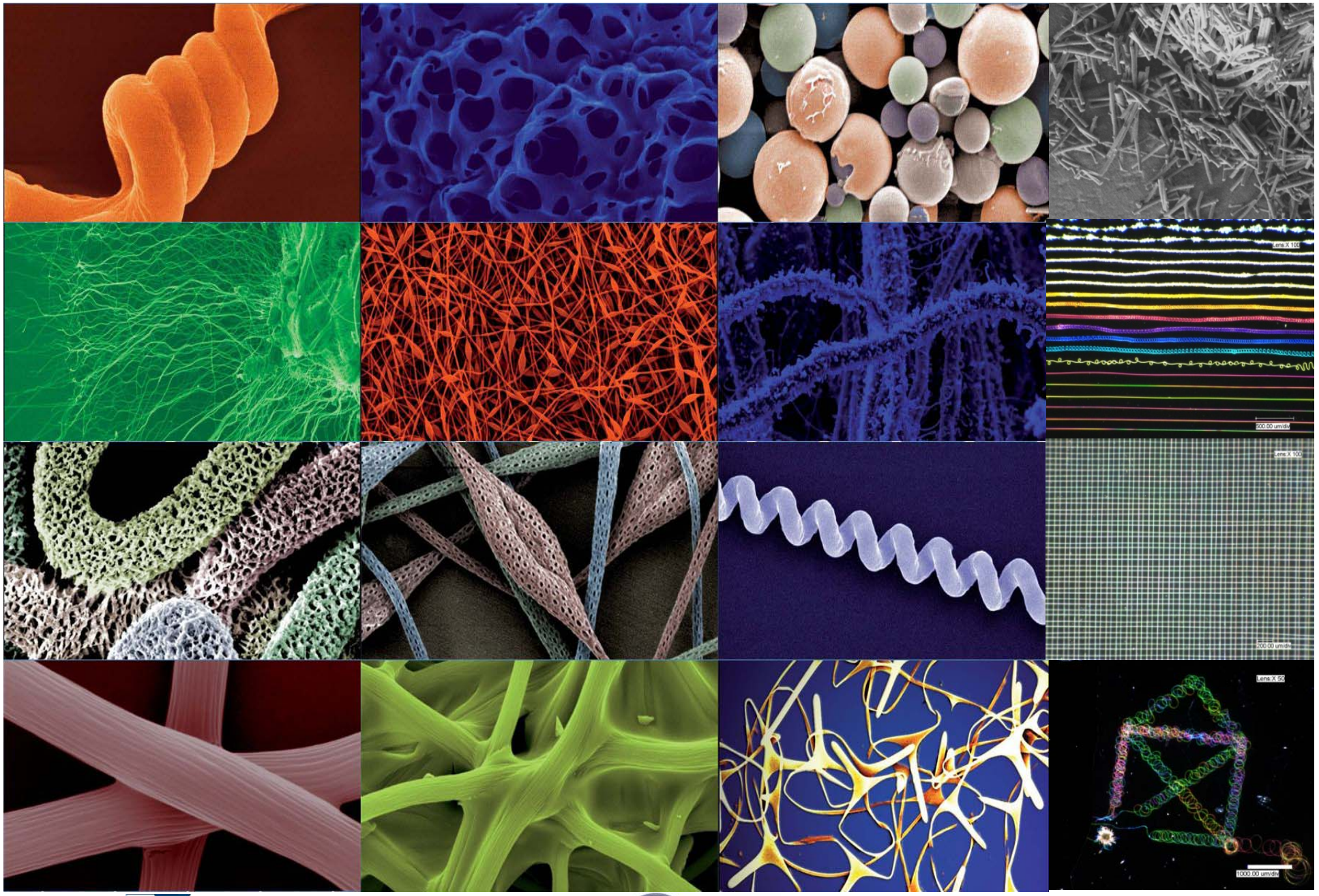
In brief about nonwovens by eletrospinning
A coating technique

Fiber diameters 1 – 10.000 nm



From lab scale to technical scale



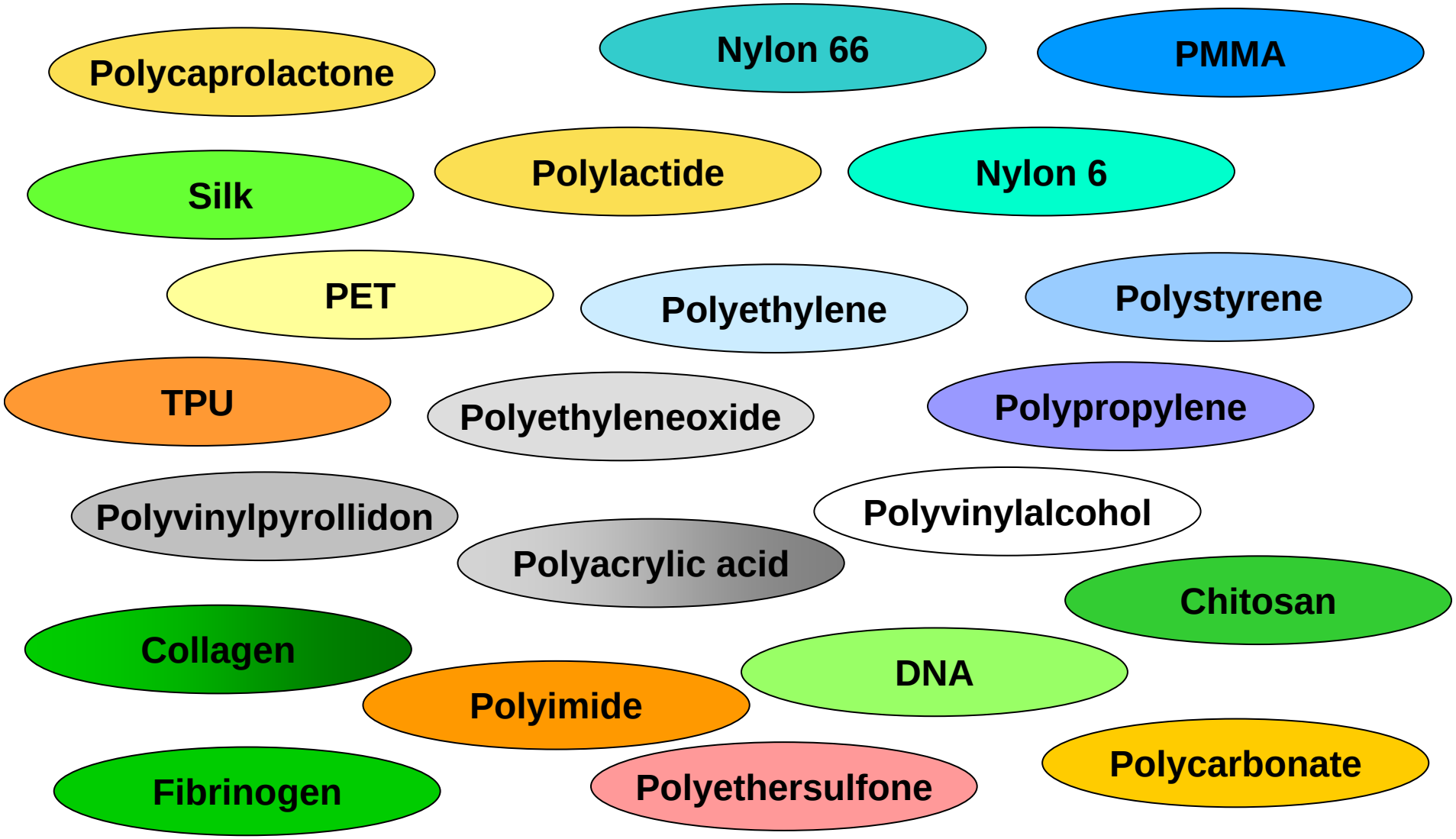


TransMIT
Gesellschaft für
Technologietransfer mbH

Philipps Universität Marburg

PNT PolyNanoTec

Polymers for electrospinning



Take home message

So many options by electrospinning for novel nanofiber nonwovens

Reviews:

Greiner, Wendorff, Angew. Chem. Int. Ed. 2007, 46, 5670

Agarwal, Wendorff, Greiner, Polymer 2008, 49, 5603 (Biomed.)

Agarwal, Greiner, Wendorff, Adv. Funct. Mater. 2009, 19, 1

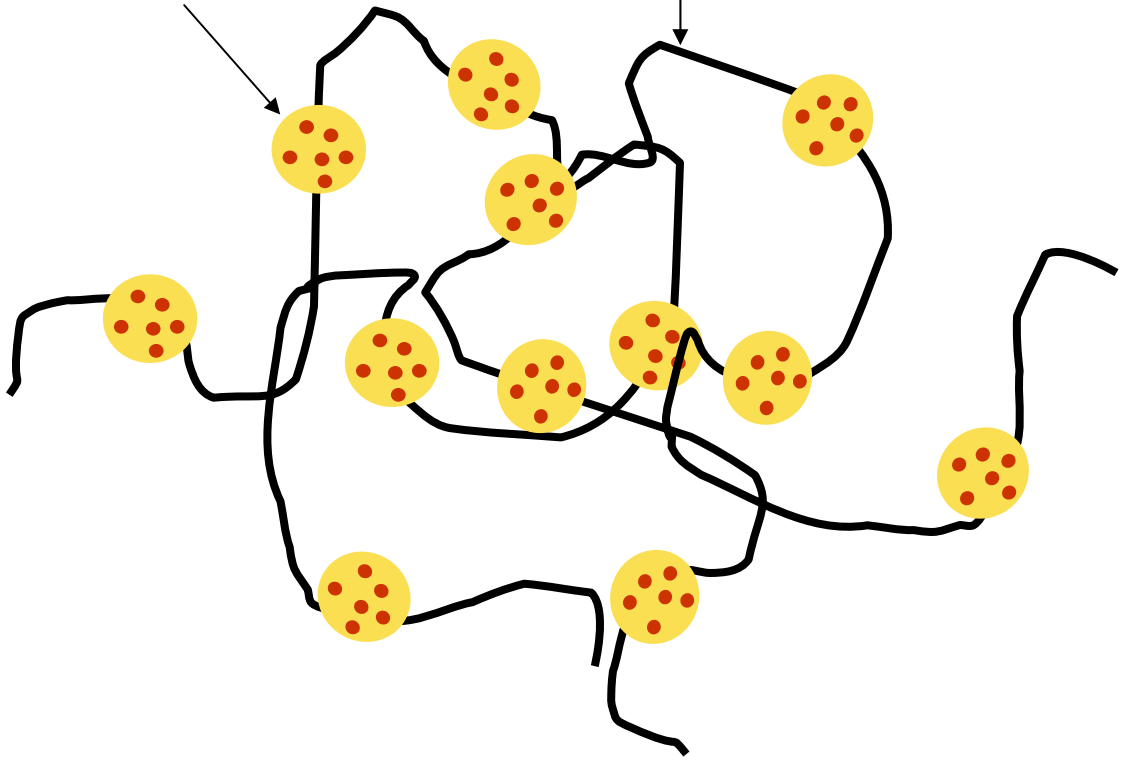
Agarwal, Greiner, Wendorff, Adv. Mater. 2009, 21, 1 (Tissue Eng.)

Agarwal, Wendorff, Greiner, Macromol. Chem. Rapid Commun. 2010, 31,

Agarwal, Greiner, Special Topic Issue on Eletrospinning, Polym. Adv. Techn., 2011

Pheromone releasing Microcapsules???

Nanofiber nonwovens ???



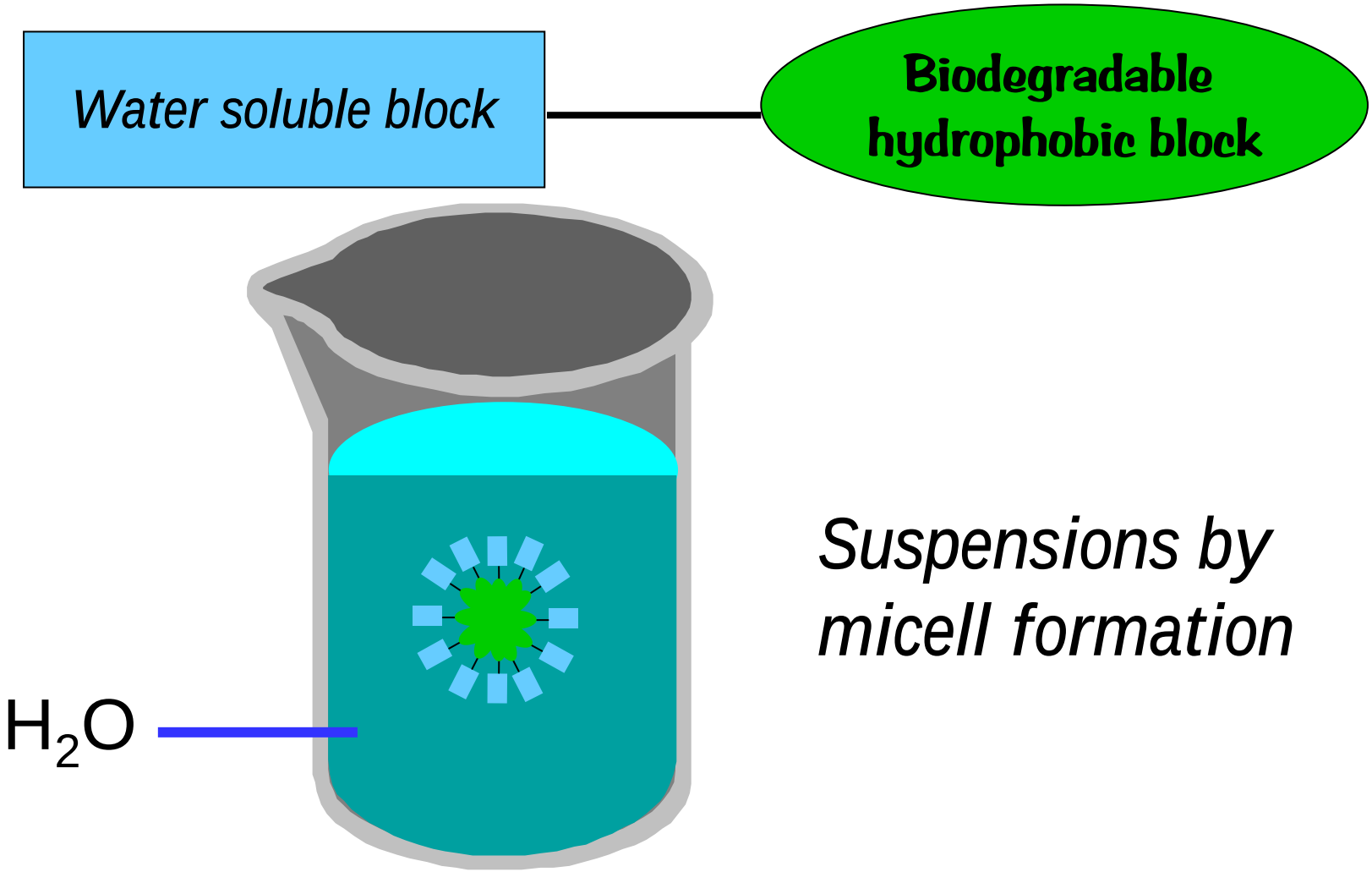
How to electrospin for water stable biodegradable polymers from water?

Well established biodegradable polymers:
Aliphatic polyesters (polylactide, PCL...)

Problem: soluble only in hazardous solvents
No electrospinning on fields possible

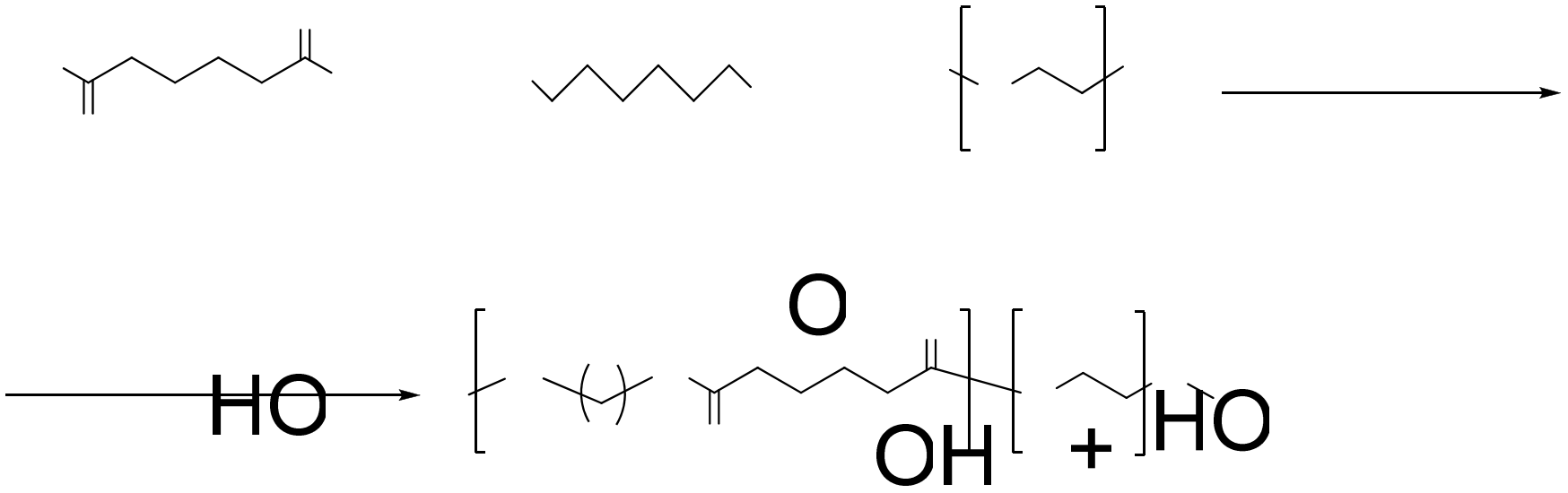
The possible solution:
Suspension electrospinning of secondary suspensions of biodegradable polyesters

How to get secondary suspensions of biodegradable polymers?



Suspensions by micell formation

Synthesis diblock copolyester



M_n = 6400 (GPC – PS standards M_w / M_n = 2.1

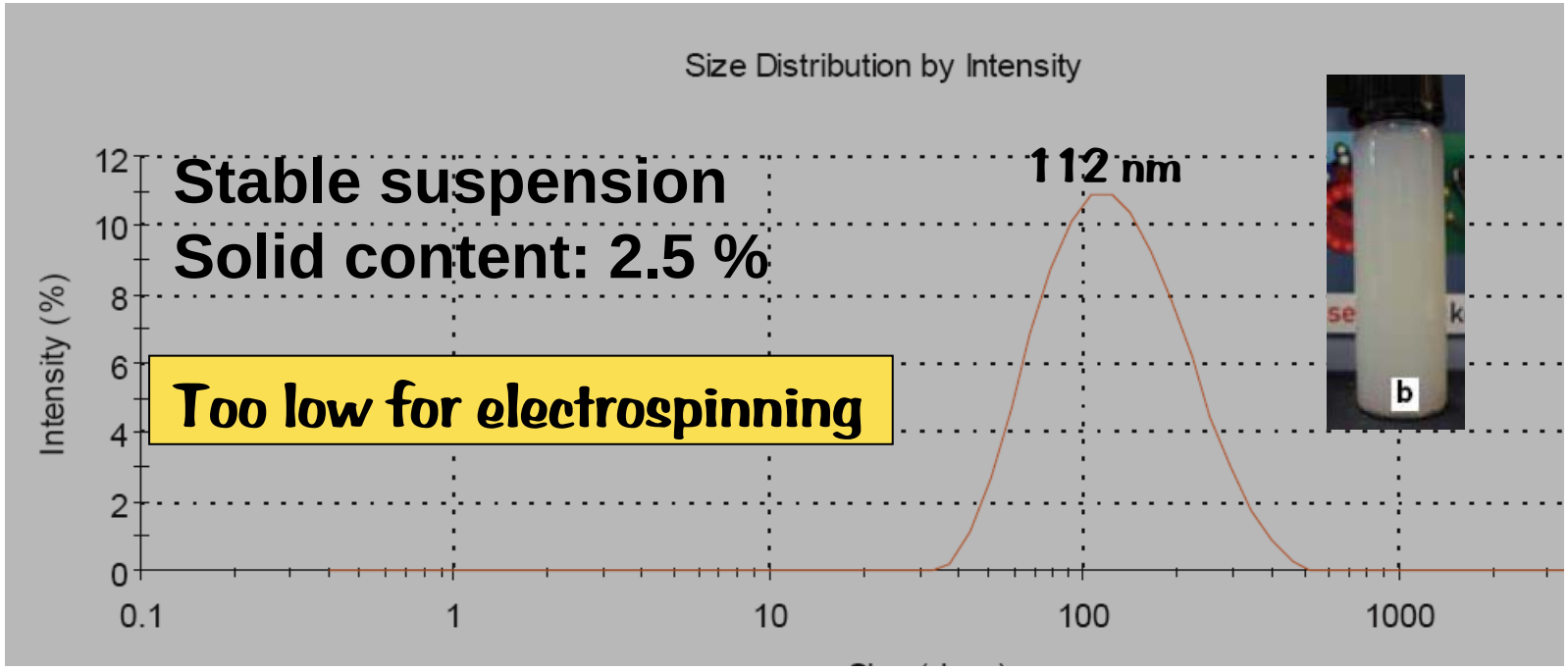
Insoluble in water

T_m = 58 °C

Secondary dispersion of the diblock copolyester in water

Follow protocol of solvent displacement method

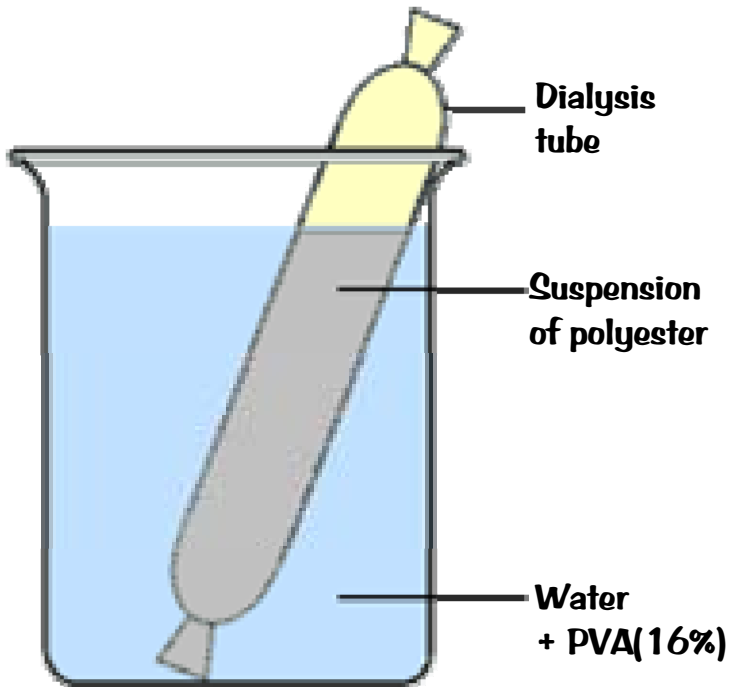
- Dissolve polyester and Brij78 (10%) in actone
- Add water
- Apply ultrasound



Up-concentration of the secondary dispersion

Dialysis of suspension

Set-up of dialysis

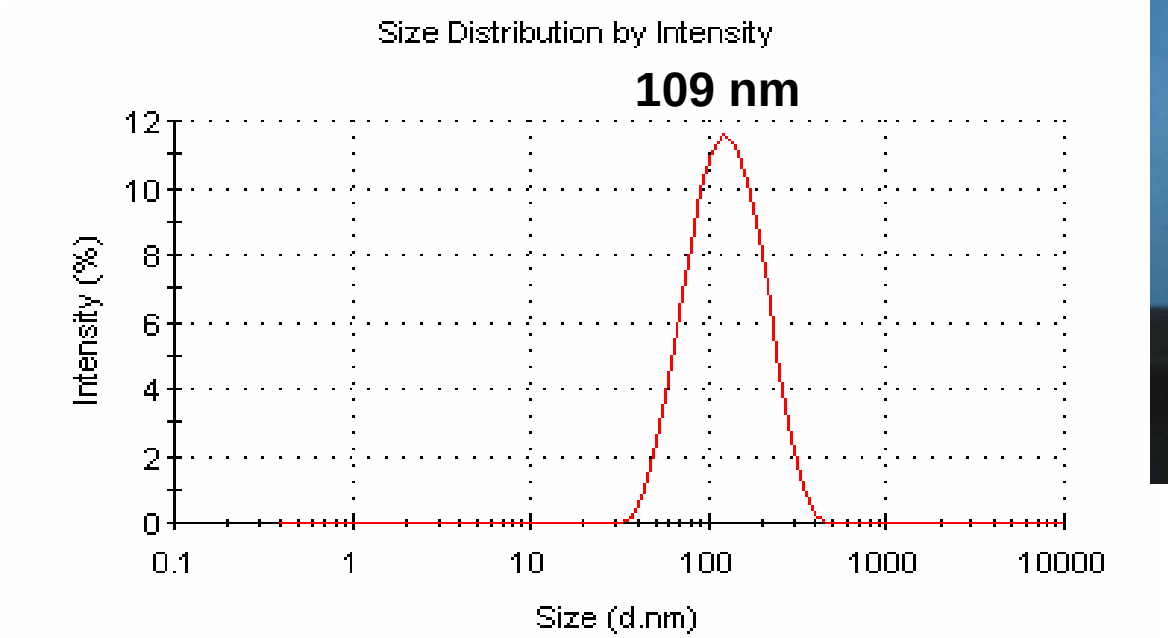


Up-concentration of the secondary dispersion

Dialysis of suspension

Stable suspension
Solid content: 16 %

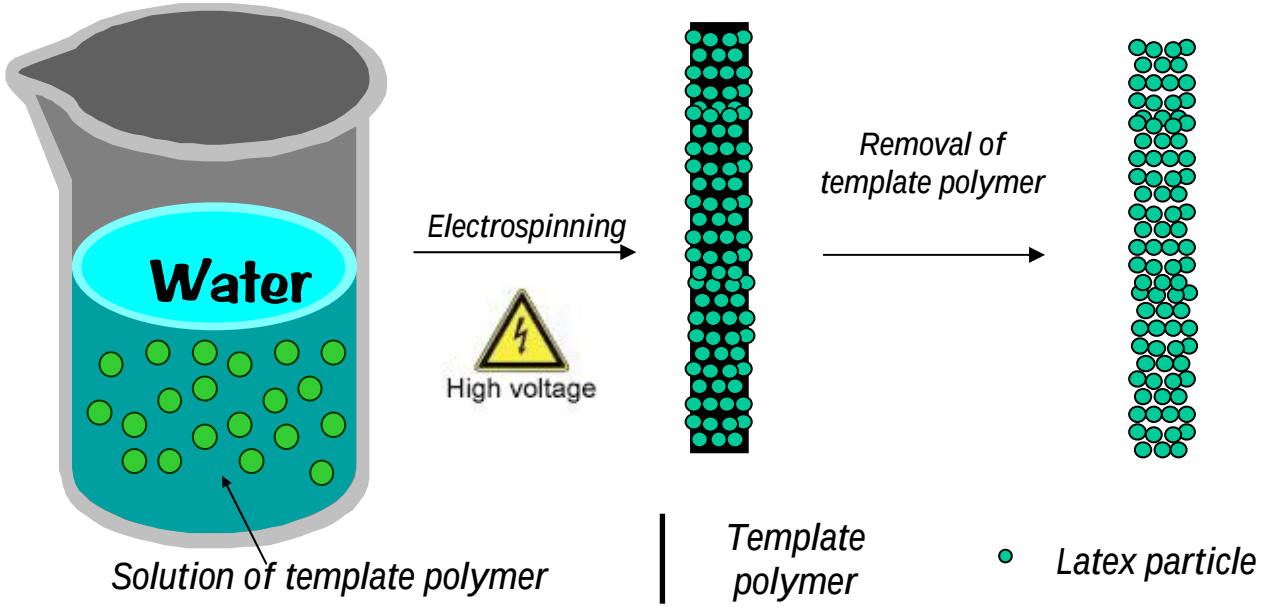
Good for electrospinning



Take home message

Aliphatic water insoluble polyesters can be dis-persed in water up to 20 %

Concept for submicron fibers by suspension electrospinning

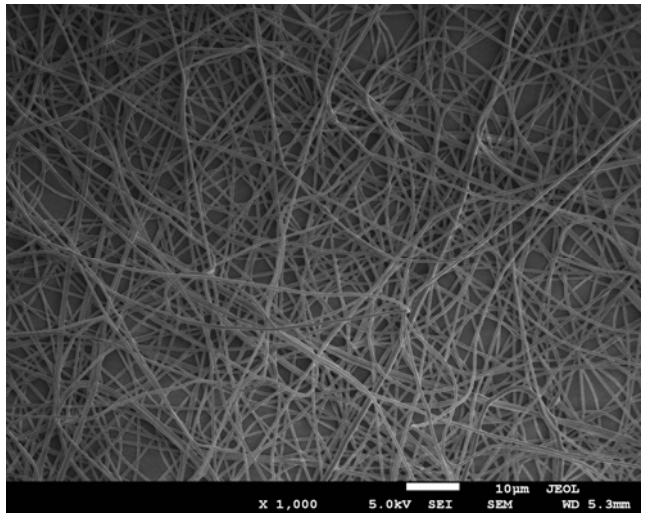


Stoiljkovic et al., Polymer **2007**, *48, 3974*
Stoiljkovic et al., Macromolecules **2009**, *42, 6147*
J. Sun et al., Macromol. Chem. Rapid Commun. **2010**, *31, 2077*
P. Bansal et al., in prep.

Electrospinning of up-concentrated secondary dispersions

+ 3 % PEO

Electrospinning



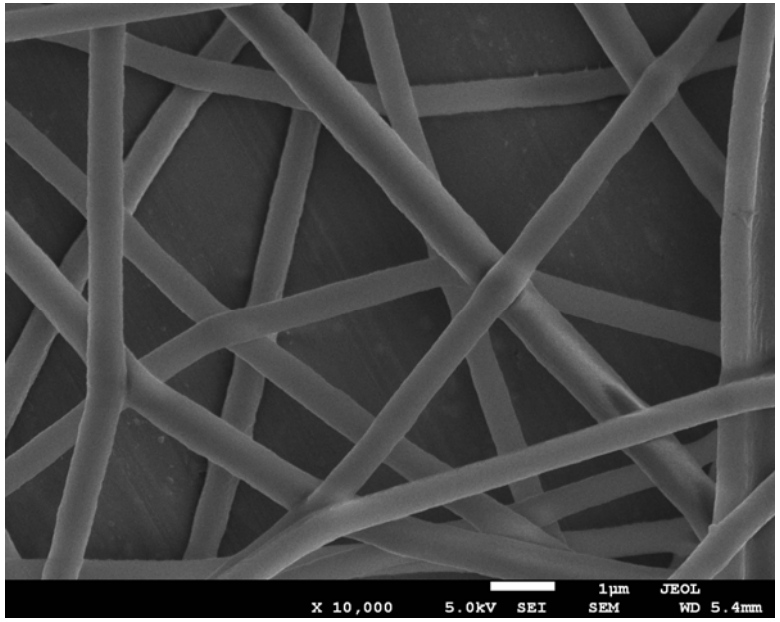
Fiber diameter
300 – 500 nm

J. Sun, K. Bubel, F. Chen, T. Kissel, S. Agarwal, A. Greiner, Macromol. Chem. Rapid Commun., 2010

Water treatment of electrospun fibers of secondary dispersions

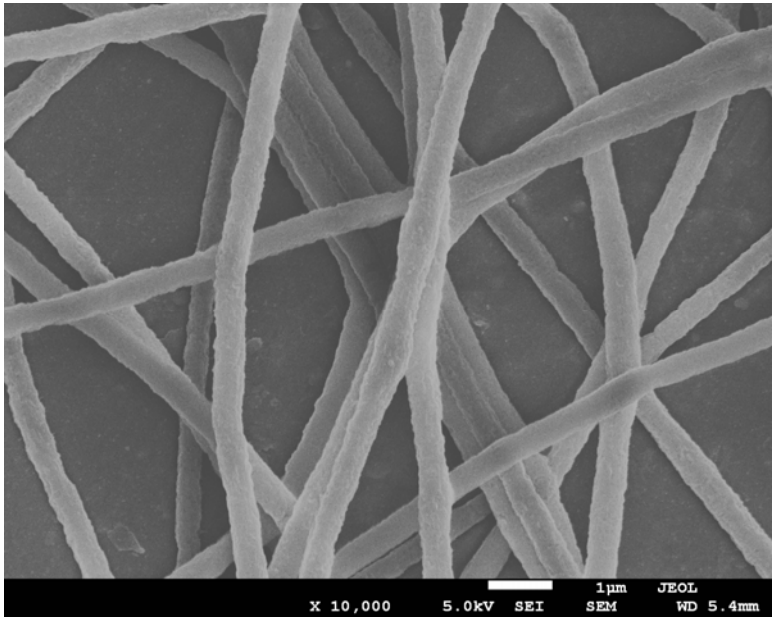
Water-stable electrospun biodegradable fibers from aqueous secondary dispersions

As-spun



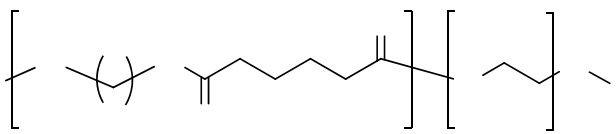
Polyester+PEO+Brij78
No suspension particles visible

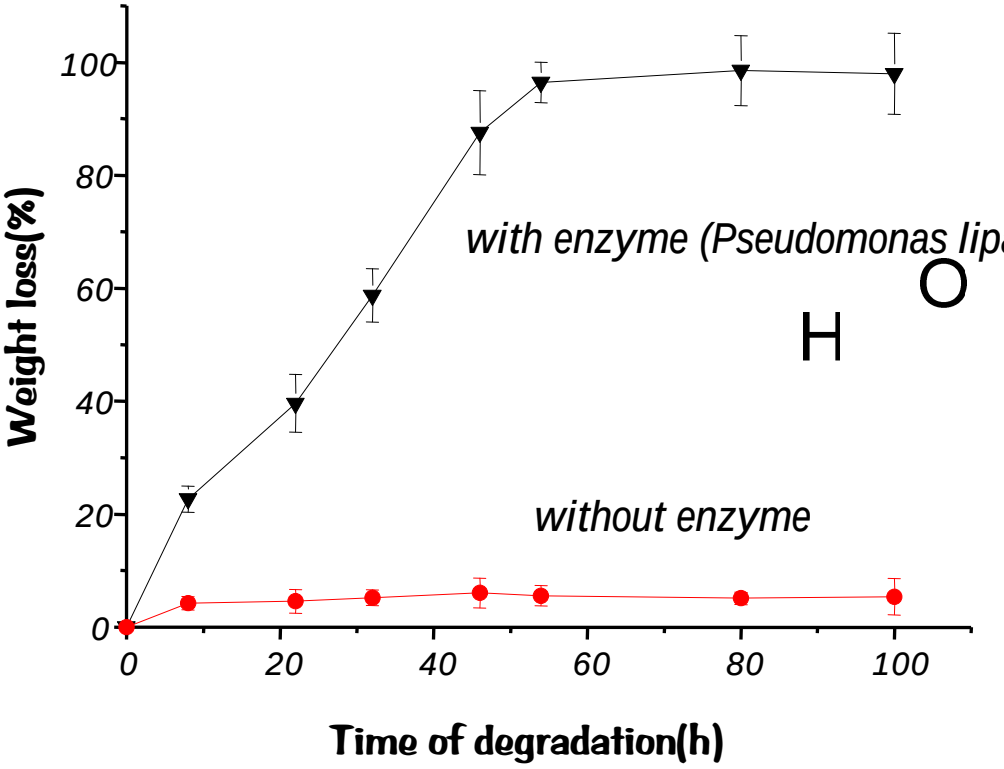
After water treatment for 2 days



Slight reduction of fiber diameter
No Brij78 and PEO left

How about the biodegradability

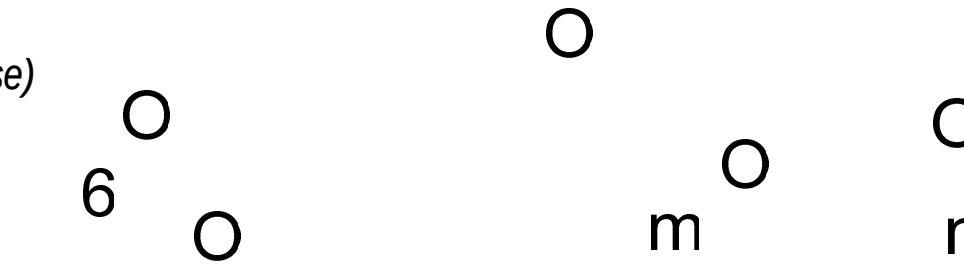




Fast enzymatic degradation

Slow hydrolytic degradation

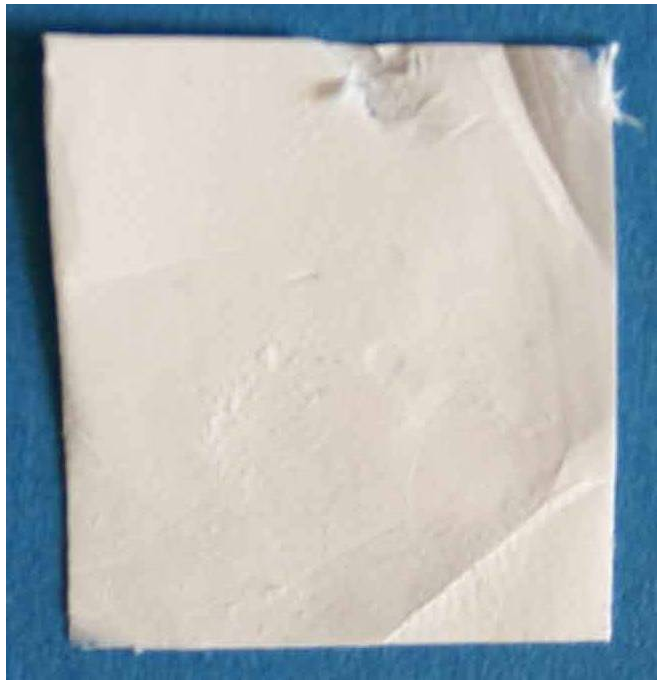
Low cytoxicity (without tenside)

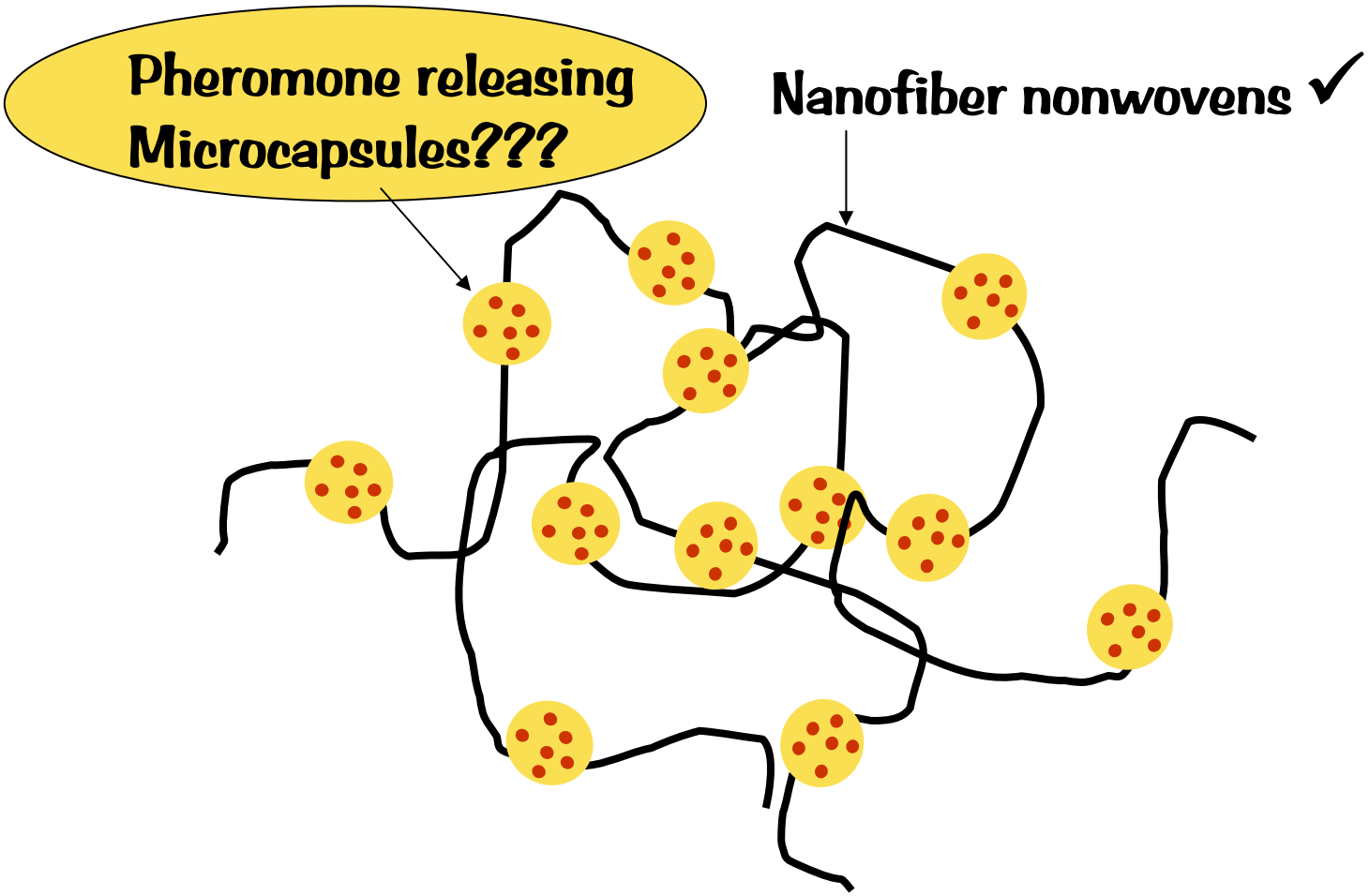


F. Chen
Y. Zhang

Take home message

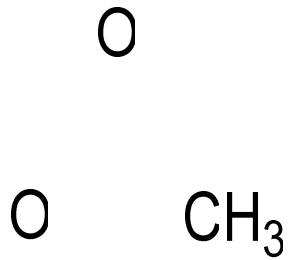
Electrospinning of secondary dispersions of alipahatic poly-esters results in water stable biodegradable nanofiber nonwovens




Pheromone releasing Microcapsules???
Nanofiber nonwovens ✓

Water dispersed phermone filled microcapsules

The pheromone



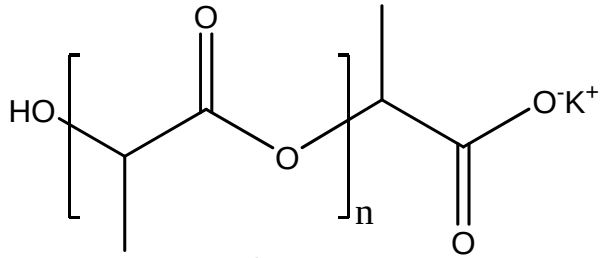
Requirements for microcapsules

- Uptake of large amount of hydrophobic pheromone
- Microcapsules should be biodegradable
- Microcapsules should allow release of pheromone
- Microcapsules of should be well dispersable in water

Water dispersed phermone filled microcapsules

The hypothesis

Oligolactides with hydroxy/carboxylate end groups will fullfill all requirements for water dispersion and biodegradability



OLA

The answer: It is wrong

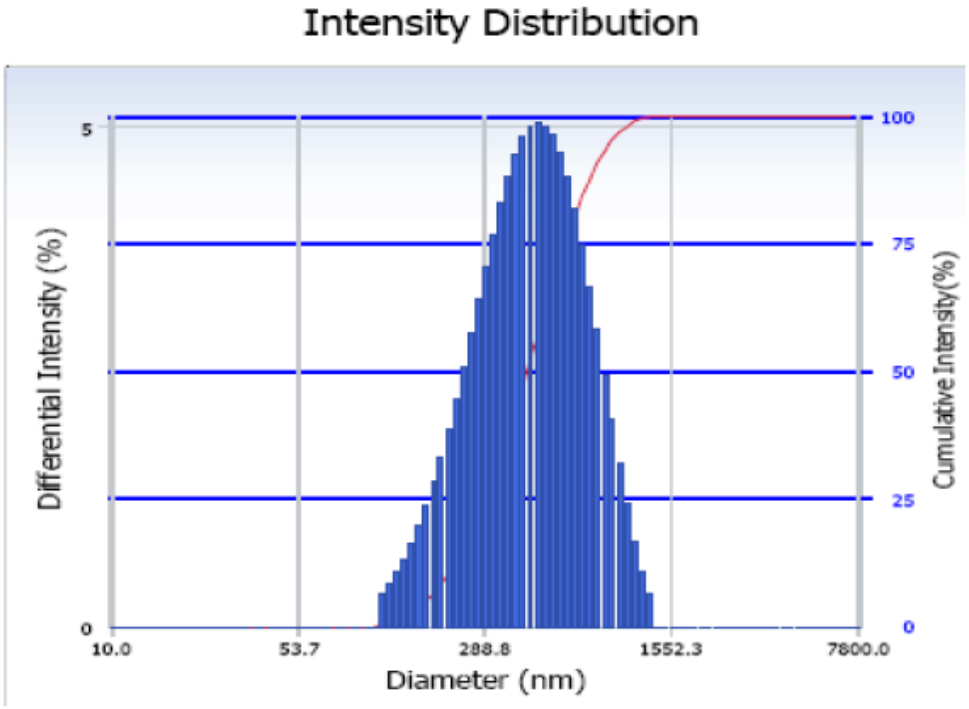
New hypothesis

Pheromone will act as hydrohob and thereby stabilize dispersions

The answer: It is right

The observation

Stable dispersions OLA with pheromone
No stable dispersions of OLA alone



OLA/pheromone/BrijS20
10 / 10 / 1 %

P. Bansal

With pheromone 👍

Without pheromone 👎

Take home message

Dispersions of OLA are only Stable up to 10 % with pheromone as stabilizer!!!

How to measure dispenser efficiency on field?

Our serendipty will continue

Pheromone release is not yet retarted enough

Take home message

- Biodegradable polyester nanoparticle dispersions up tp 20 %
- Biodegradable water stable polyester nanofibers from water
- High solid content OLA microcapsules dispersion with pheromones

The teams: Agarwal and Greiner group

Partners – Profs: S. Agarwal, J. H. Wendorff, G. Leithold

Support: University of Marburg, DFG, BMBF, BLE, BASF

**Poster D-PO4-27: Thermo- and photoresponsive Nanomats by Electrospinning…..
(Agarwal / Brandl) – today afternoon only!!!**

We do not risk because it is difficult – It is difficult because we do not risk

Seneca