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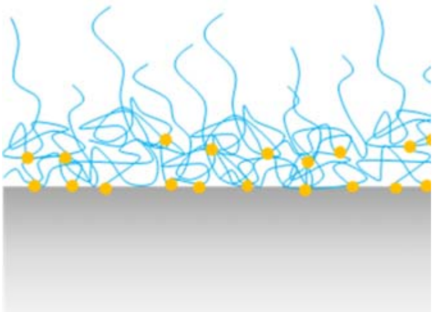
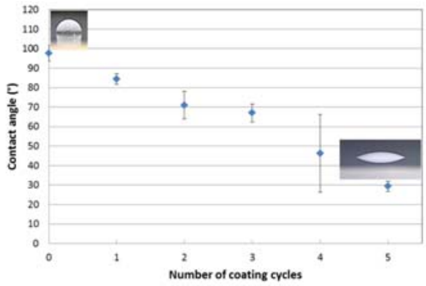
Electron beam grafting – a versatile strategy for the modification of polymer surfaces

Swiss MNT Event «Trends in Micro Nano», Brugg, 23.4.2015





Prof. Dr. Per Magnus Kristiansen, Institute of Polymer Nanotechnology (INKA)
University of Applied Sciences and Arts Northwestern Switzerland (FHNW)

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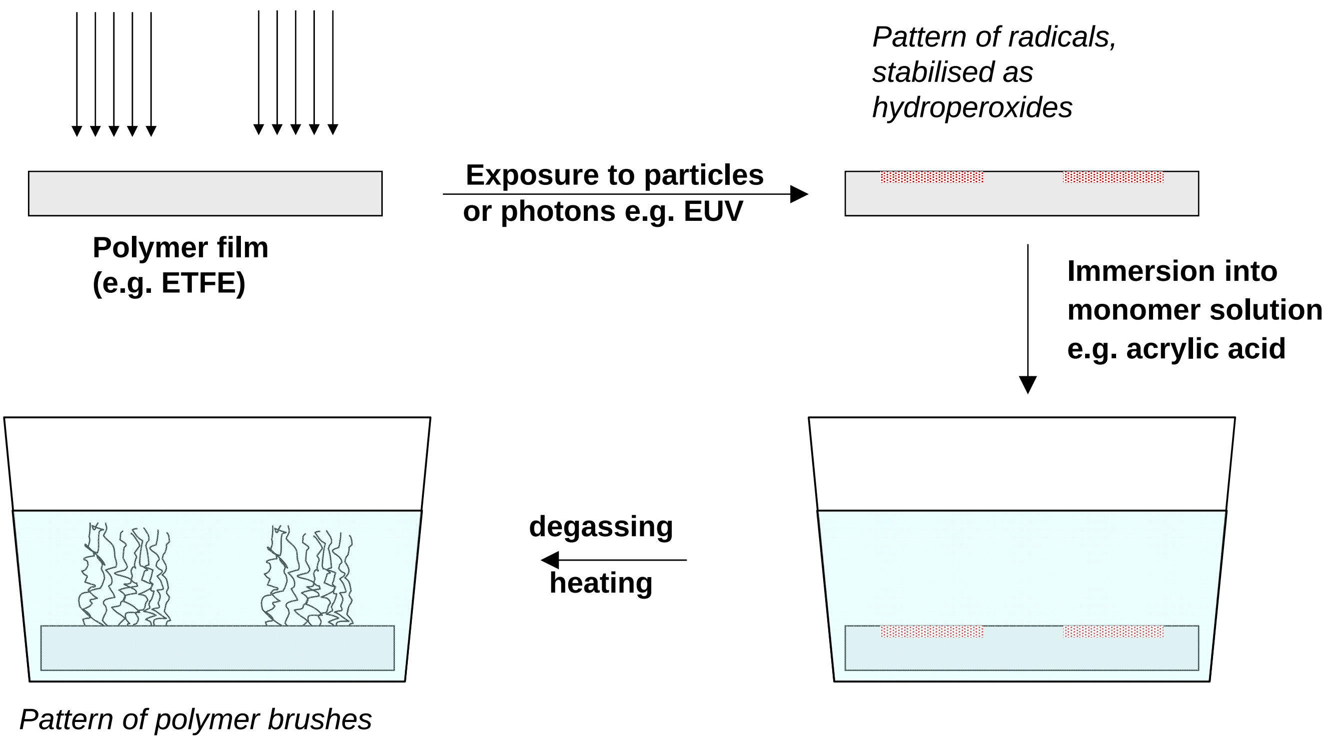
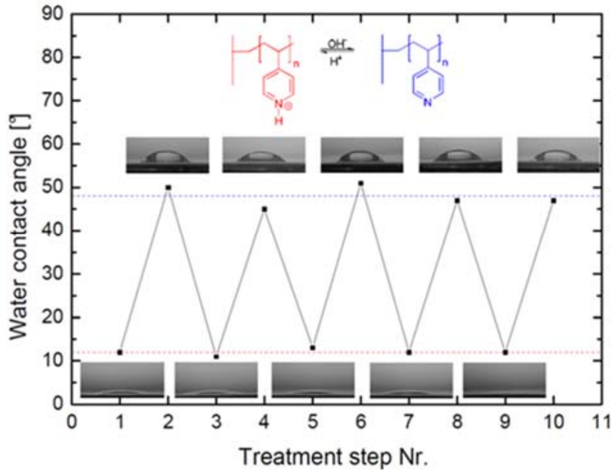
Grafting of polymer brushes on polymers



Grafting experience at INKA – some examples from academic research

pH-induced wettability switching of weak polyelectroly brushes

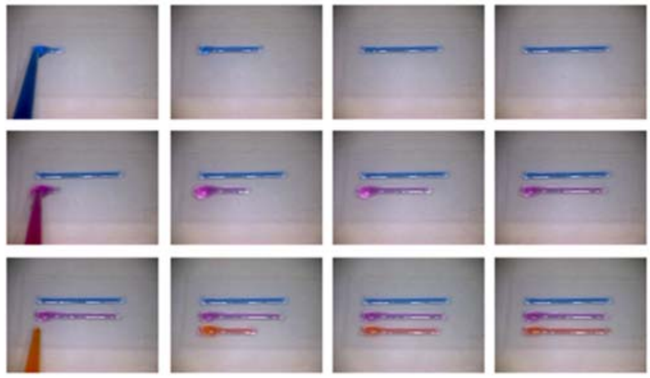


Reversible changes in contact angle with changes in pH

Ref: S. Neuhaus, "Functionalization of Polymer Surfaces with Polyelectrolyte Brushes", Dissertation at the ETH Zurich, 2011

Selective grafting of vinyl formamide from ETFE[1] surfaces.

[1] poly(ethylene-alt-tetrafluoroethylene)



Filling of the lines with colored liquids is based solely on the strong wettability contrast between the graft polymer and the ETFE surface

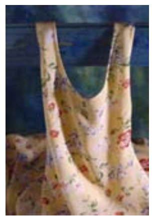
Electron beam processing in the polymer industry today

Typical applications for EB cross-linking




Materials: PE, PVC, PVDF, EPR, EVA
Dose: 50 – 200 kGy
Energy: several MeV

Typical applications for EB degradation

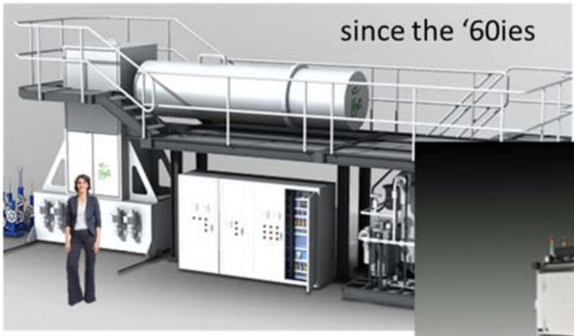



Degrading polymer materials

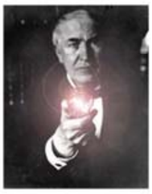
PTFE → for powders
PP → to improve formability
Cellulose → to produce viscose

Ref: «Industrial radiation processing with electron beams and X-rays», IAEA - International Atomic Energy Agency, Revision 6, May 2011

Historical development of e-beam Systems – COMET’s revolutionary development



SWISS TECHNOLOGY AWARD



the ebeam «light bulb»

- small
- affordable
- hermetically sealed
- integrated vs. designed around
- high life (~8000h)
- «consumable» vs. high O&M

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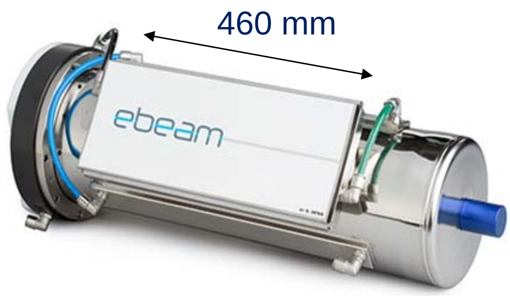
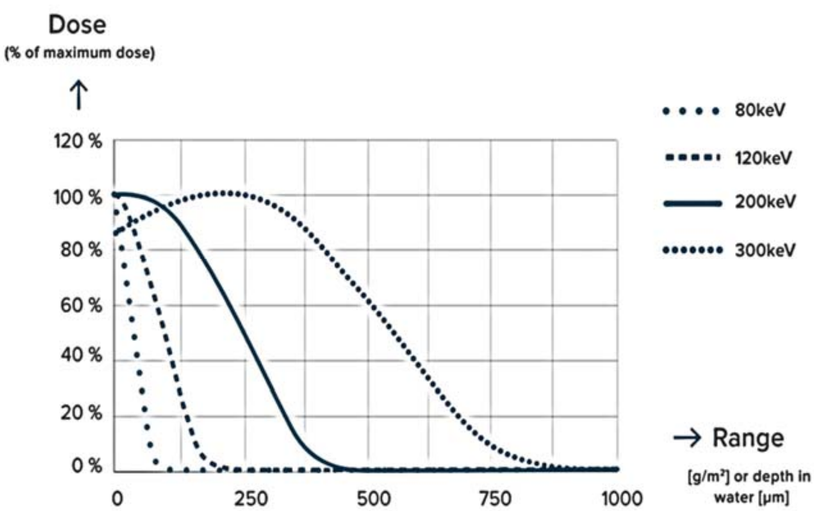
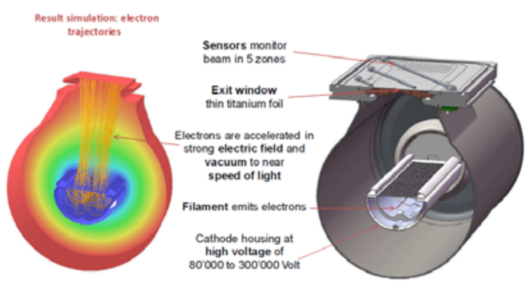
COMET’s unique sealed beam emitter technology

- **“beam shower”; no beam deflection**
- **low voltage: 200-300 kV, 4 kW**







EBLab 200 - COMET'sLaboratory e-beam Emitter system

- radiation-proof protected
- weight: 1'300 kg
- footprint: ~1 m^2
- treatment of samples up to A4
- low voltage version: up to 200 kV
- transport speed up to 30 m/min
- nitrogen purging (standard)
- option: ozone filtration for beaming in air

EBLab 200 installed at INKA 10.07.2014 (placement contract with COMET)

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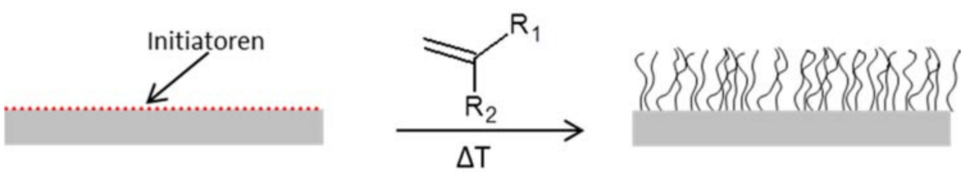
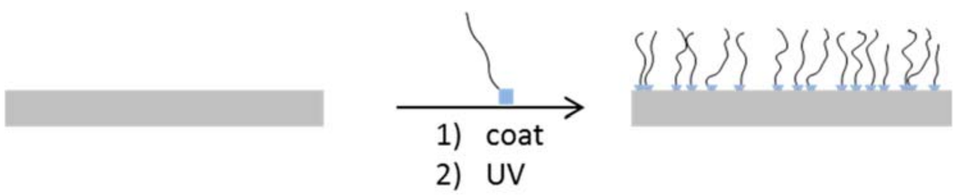
Grafting approaches for surface functionalization

- **«Grafting from» - established method**
  1. Activation of surface by irradiation (X-rays, e-beam, particles, plasma)
  2. Immersion into monomer solution, **degassing**
  3. Heating of solution → Polymerization (**exothermal**), **oxygen exclusion** required



- **«Grafting-to» - conventional**
  - requires **functional groups** on substrate & suitable **linkers** on graft molecules

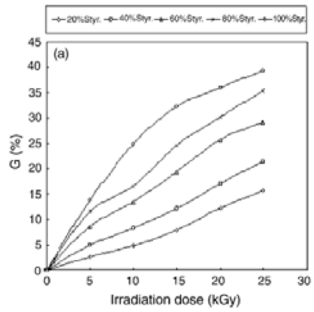


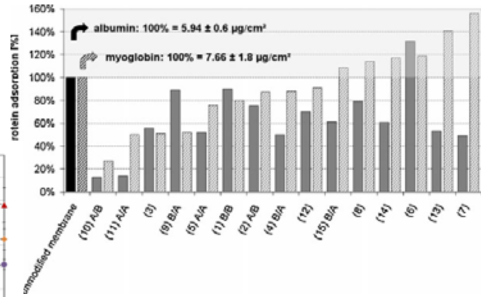
«Grafting-to» approaches using e-beam (novel tendency)

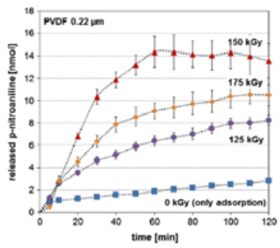
Direct coupling or polymerization of functional molecules, polymers, proteins by ebeam

Examples:

- **Hydrophilization of membranes [1]**
  - ➢ Direct polymerization of styrene into pores upon EB exposure
- **Functional PES membranes [2]**
  - ➢ in situ grafting of carboxylic acids, sulfonic acids and amines
- **Biofunctionalized membranes [3]**
  - ➢ covalent coupling of trypsin in membranes → protein functionality remains intact







References:
1) M.M. Nasef et al., J of Membrane Sci 2006, 268, 106
2) A. Schulze et al., Macromol Rapid Commun 2010, 31, 467
3) S. Starke et al., Reactive & Functional Polymers 2013, 73,698

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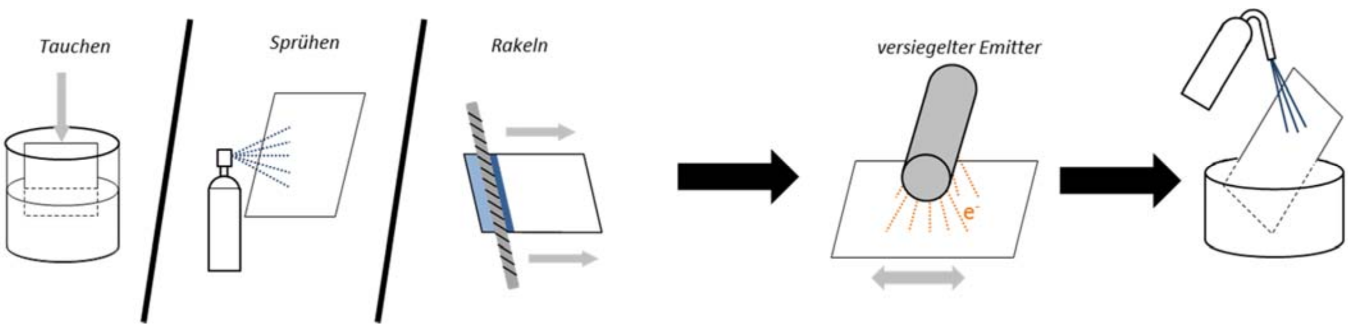
Schematic of the e-grafting process

Process steps

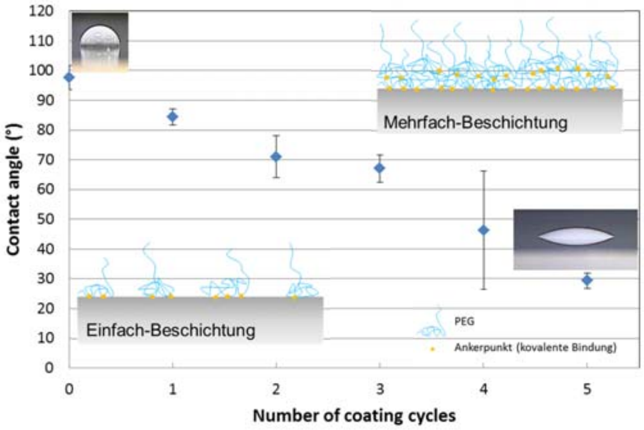
1. **Coating of substrate with functional polymer (from solution)**
2. **e-beam treatment (under variation of process parameters)**
3. **Rinsing of samples for removal of unreacted material**



e-grafting is simple and fast

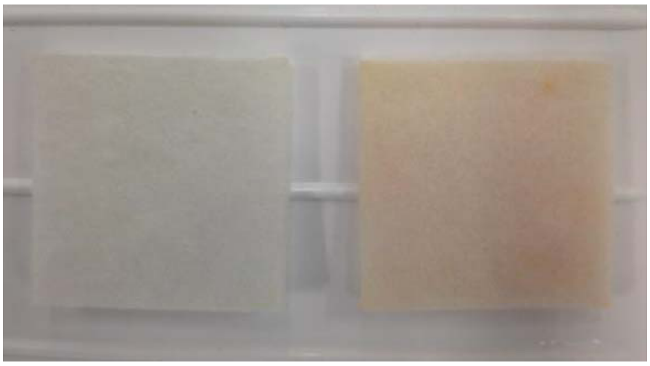
Proof of concept

Hydrophilization of hydrophobic polymers
(feasibility study, completed)



Demonstration of increasing hydrophilicity with multiple e-grafting modification steps

e-grafting modification of nonwovens
(running project)



untreated nonwoven modified nonwoven

Demonstration of successful grafting by selective staining of functional groups

Opportunities and challenges for e-grafting

- **Advantages**
  - 1-step coating procedure
  - Broad variety of functional polymers commercially available
  - High flexibility in substrate choice
  - Covalent attachment → high stability anticipated

+

- **Open questions**
  - Potential wetting issues depending on solution & substrate material
    → substrate pre-treatment may be required
  - Functionality retention after e-grafting (looks good so far)

?

- **Challenges**
  - Coupling mechanisms not completely understood
  - Only very few substrate/graft combinations investigated to date
  - Applicability to 3-dimensional objects (of interest for some applications)

-

Versatile functionlization strategy – many possible surface effects

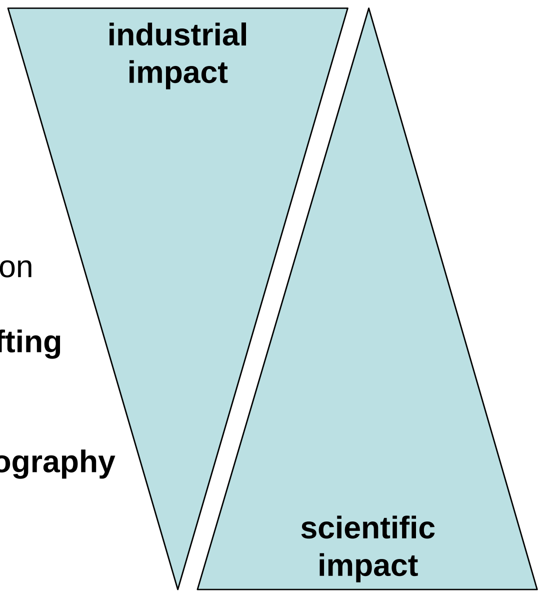
- **modified wettability:** hydrophilic, hydrophobic, oleophobic, omniphobic(?)
- **modified surface chemistry**: acidic, basic, specific functionalities
- **responsive/adaptive:** pH, temperature, light (photochromic), deformation, swelling
- **biofunctional/-active:** specific binding, enzyme imobilisation
- **tribological:** reduced friction, self-lubrication
- **protective:** non-fouling, antibacterial, antimicrobial, antistatic

- **Additional benefits of ebeam:** tunable penetration depth, sterilization for free
- **Substrate choice**: films, membranes, textiles and nonwovens (3D parts to come)

There is plenty of options at the top of and within the surface of polymers

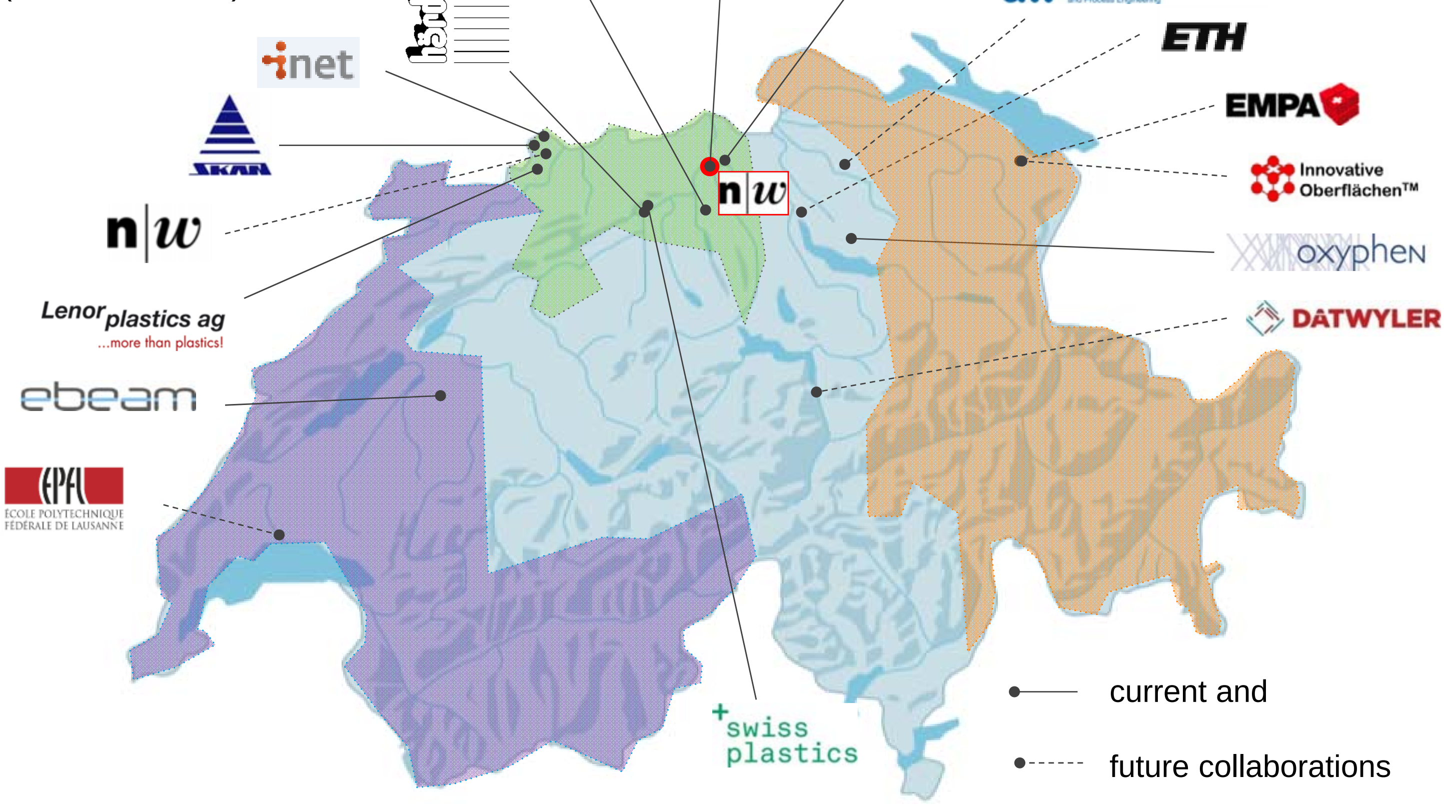
Our broadband vision

- **Elevation of Technology Readiness Level**
  - customized EBLab extensions (special sample holders)
  - Explore in-line e-grafting (and scalability)
- **Demonstration of effects** for different applications
- **Mask-assisted e-grafting** for selective surface modification
- **Combination of micro- and nanostructures with e-grafting**
  - Bio-inspired surface effects
- **Flood exposure in context with grayscale e-beam lithography**
- **Fundamental understanding of e-grafting process**
  - with selected academic partners



→ Exploiting the potential in an open, collaborative user network …!

INKA's e-grafting network
(Status 5.1.2015)



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