Combinatorial Surfaces of Grafted Polymers

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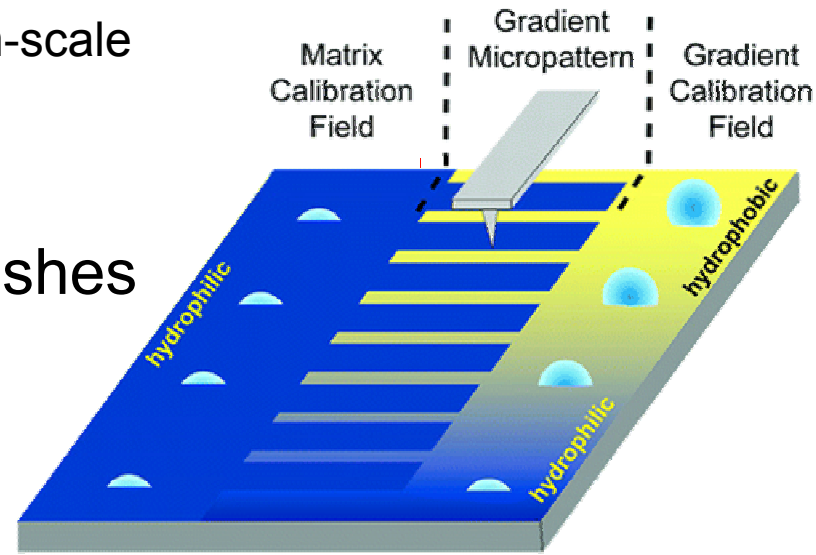
Combinatorial Surfaces of Grafted Polymer

- Combinatorial Surfaces
  - Gradient Surface
    - Composition, surface energy, thickness etc.
  - Pattern
    - Self-assembled monolayers (SAMs)
  - Patterned Gradient Surface
    - Combinatorial libraries with nm/μm-scale contrast and internal standards

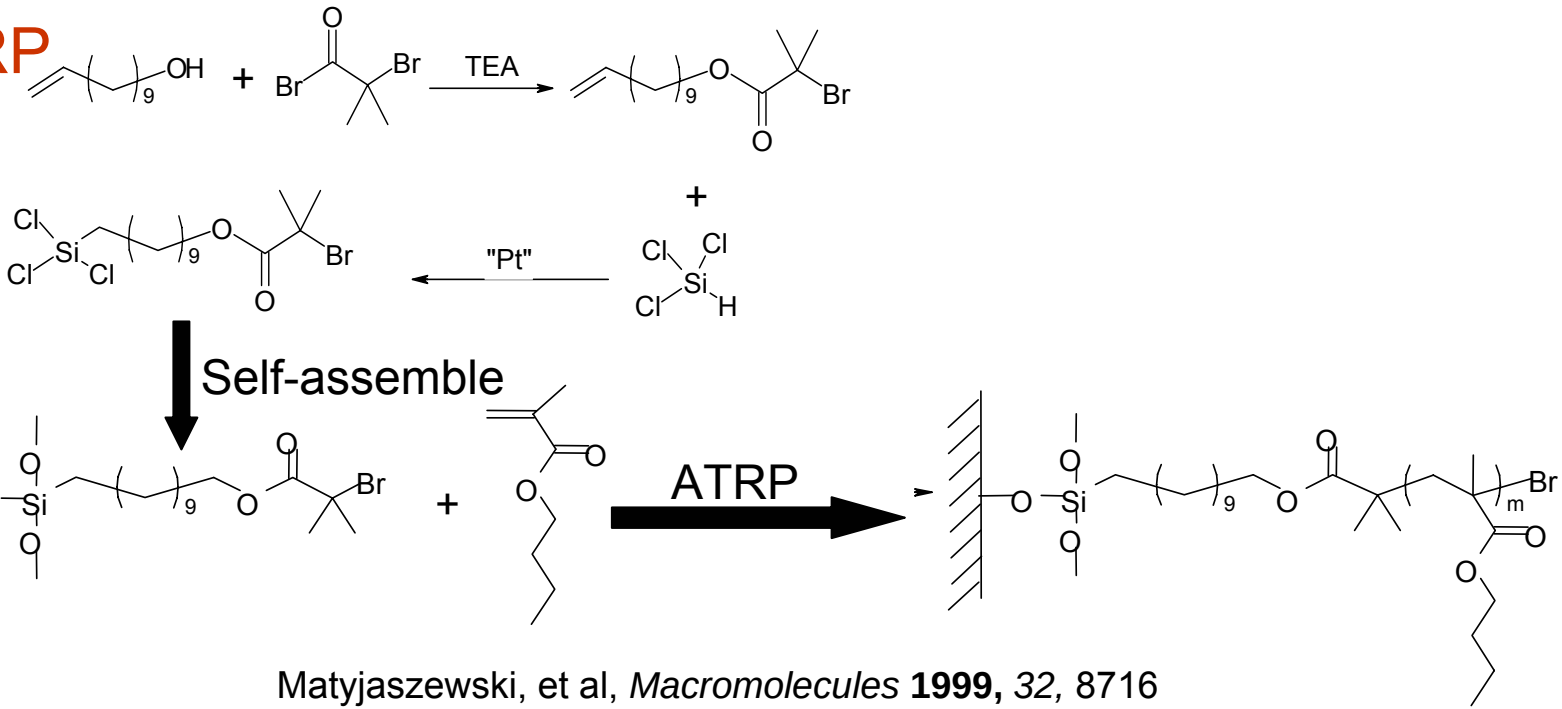


- Grafted Polymers / Polymer Brushes
  - Stability
  - Chemical versatility

Julthongpiput, D. et al. *Nano Lett.* **2005;** 1535-1540

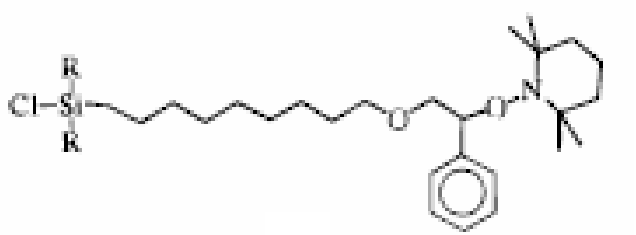
Surface-Initiated Polymerization

ATRP



Matyjaszewski, et al, *Macromolecules* **1999,** *32,* 8716

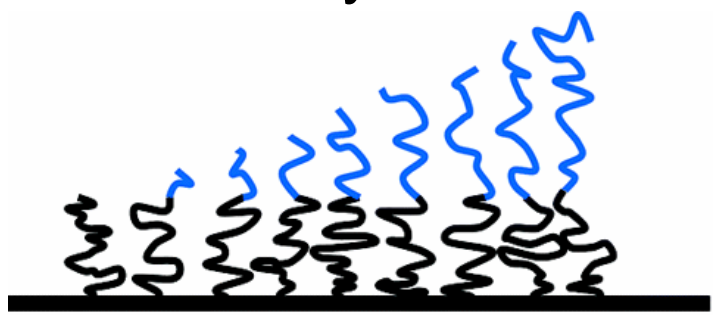
NMRP



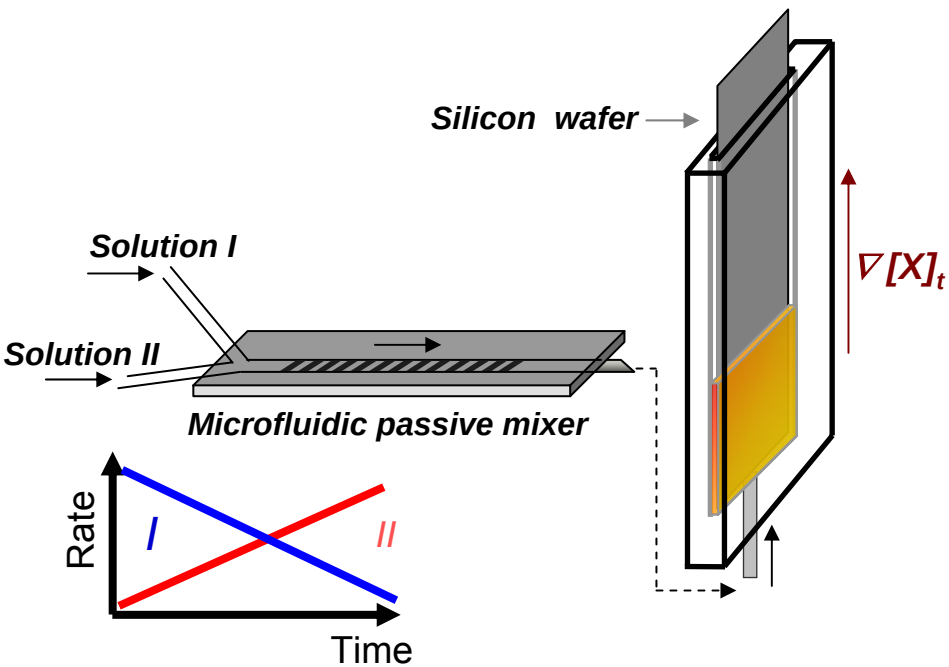
Husemann, et al, *J. Am. Chem. Soc.* **2000,** *122,* 1844

Methods to Generate Gradient/Patterned Grafted Polymers

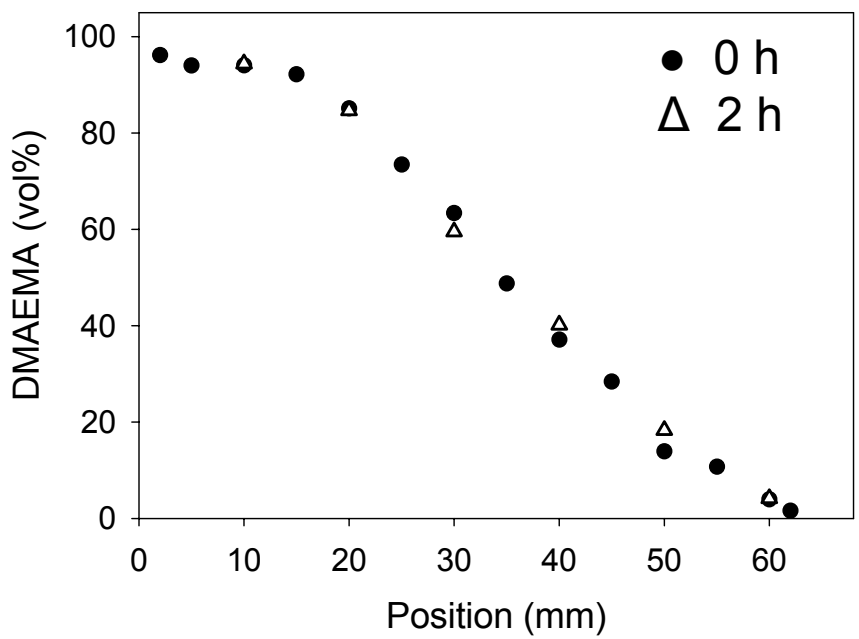
- Molecular Weight Gradients
  - Control reaction time in different regions of surface ***(J. Genzer et al.)***
- Grafting Density Gradients
  - Polymerization from initiator density gradient produced from diffusion of SAMs ***(J. Genzer et al.)***
  - "Grafting to" onto surface with thermal gradient ***(S. Minko et al.)***
- Patterns
  - Photo, e-beam, AFM, etc. ***(R. Jordan et al., S. Zauscher et al.)***
  - Soft lithography ***(C. Hawker et al.)***
- Microchannel Confined Surface-Initiated Polymerization (μSIP)
  - Composition gradient
  - Patterns



Microchannel Confined Surface-Initiated Polymerization 1. Solution Gradient Generation



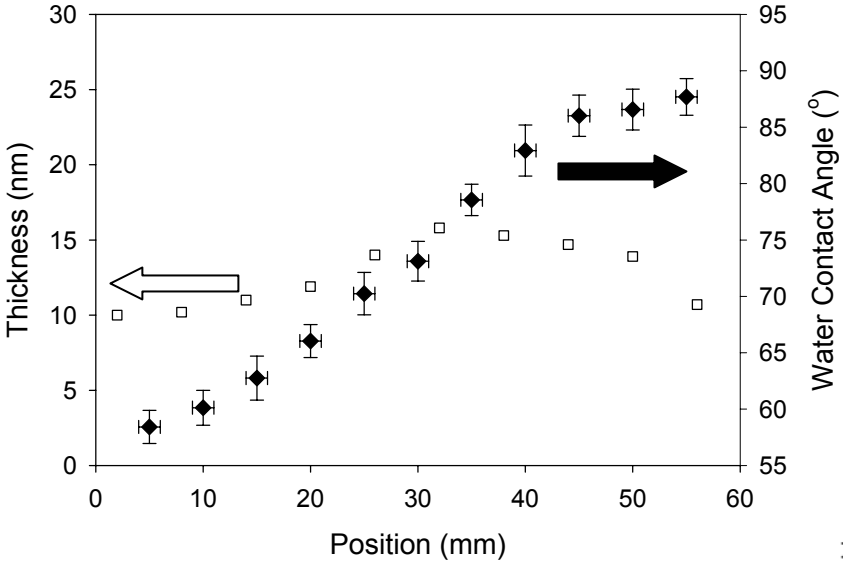
- Establishing a solution gradient through adjusting relative infusion rates of the two solution
- Solution gradient can be well-maintained inside the channel



A solution gradient of 2-(dimethylamino)ethyl methacrylate (DMAEMA) and isobutyric acid n-butyl ester (IABE) was established and maintained, as confirmed by Raman spectroscopy

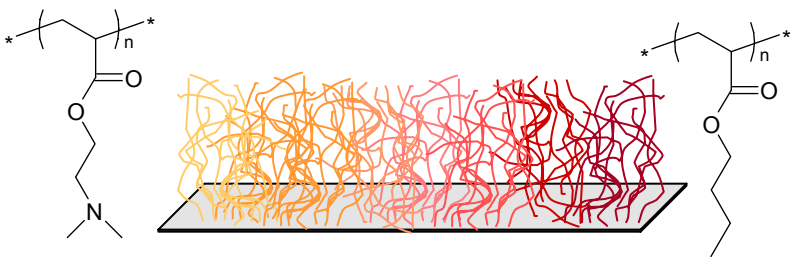
Xu et al. *Adv. Mater.* In Press

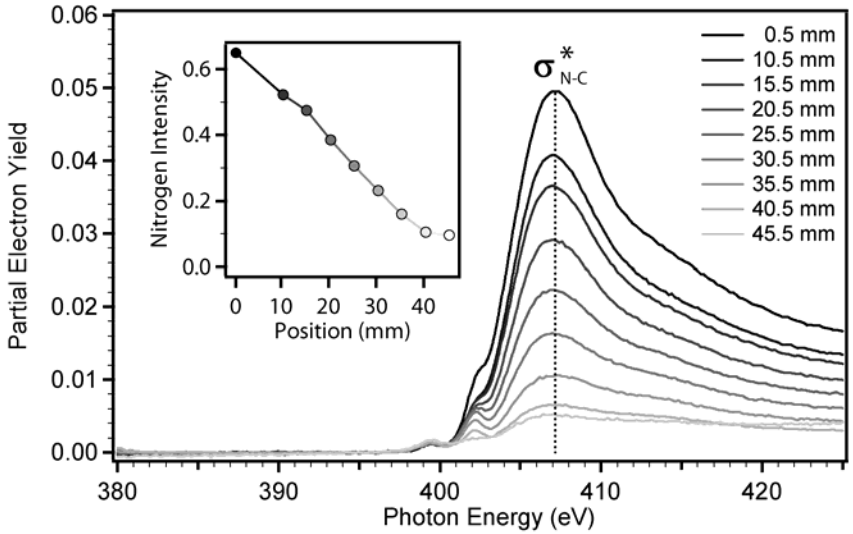
Microchannel Confined Surface-Initiated Polymerization 2. Surface Gradient Generation



- Establishing monomer concentration gradient
  - n-butyl methylacrylate
  - N,N-dimethylaminoethyl methacrylate
- Surface-Initiated ATRP transfer solution gradient onto the surfaces

NEXAFS and water contact angle confirm the formation of statistical copolymer brush gradient



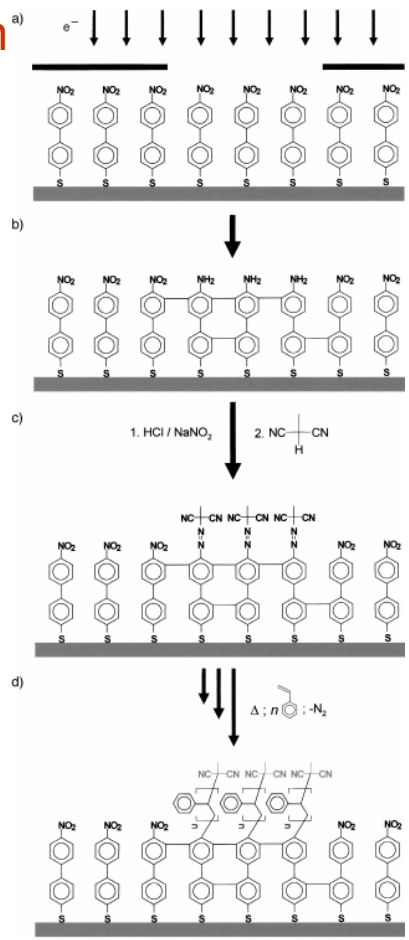


Xu et al. *Adv. Mater.* In Press

Patterned Polymer Brushes

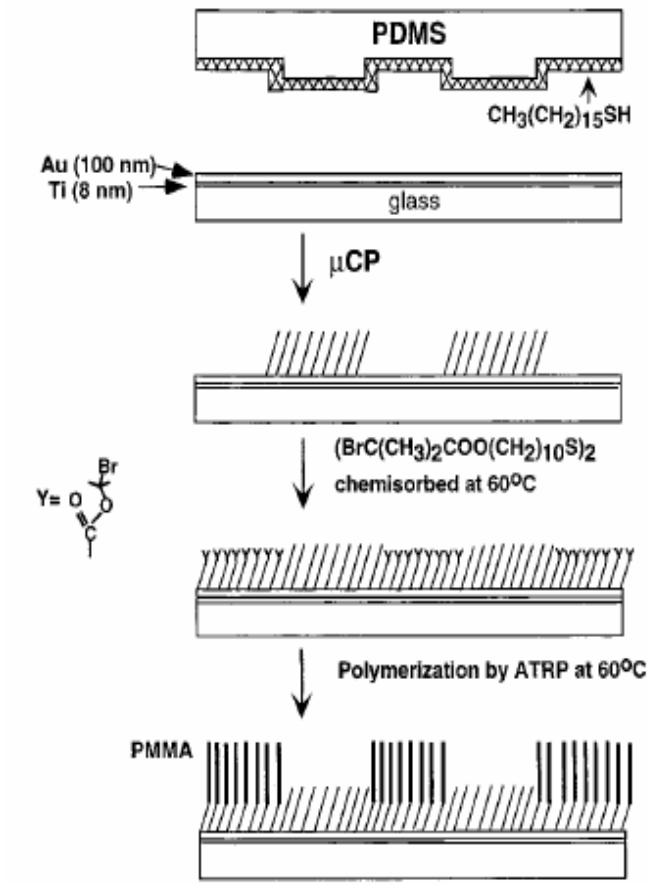
1. Generation of initiator patterns via lithography techniques
2. Surface-initiated polymerization

e-beam



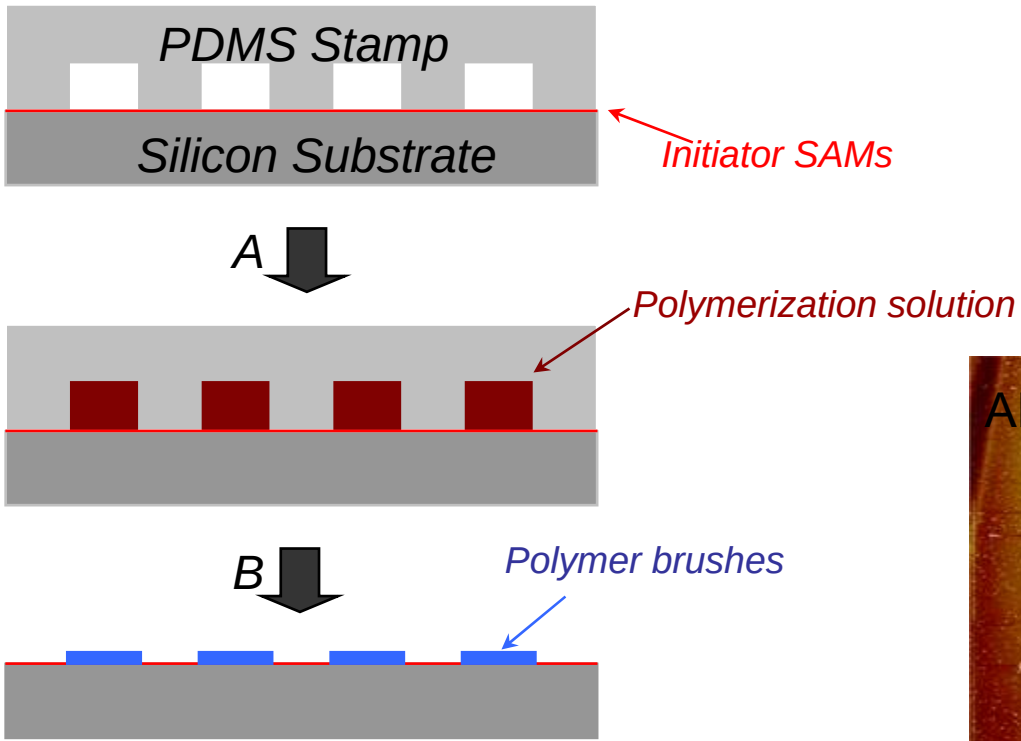
Jordan et al. *Angew. Chem. Int. Ed.* **2003,** *42,* 559

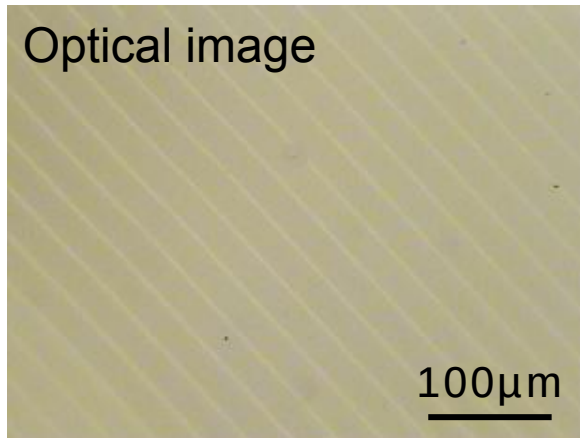
Soft lithography

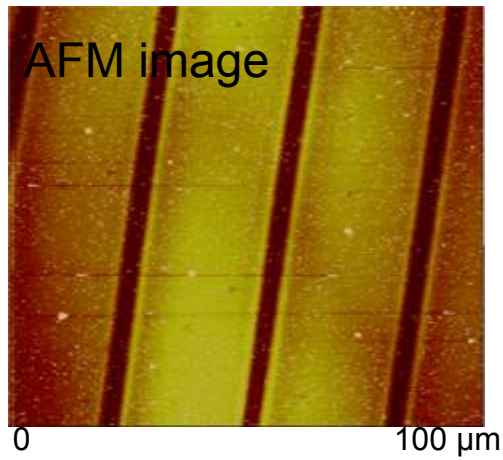


Abbott et al. *Macromolecules* **2000,** *33,* 597

Surface Patterning from Microchannel Confined Surface-Initiated Polymerization

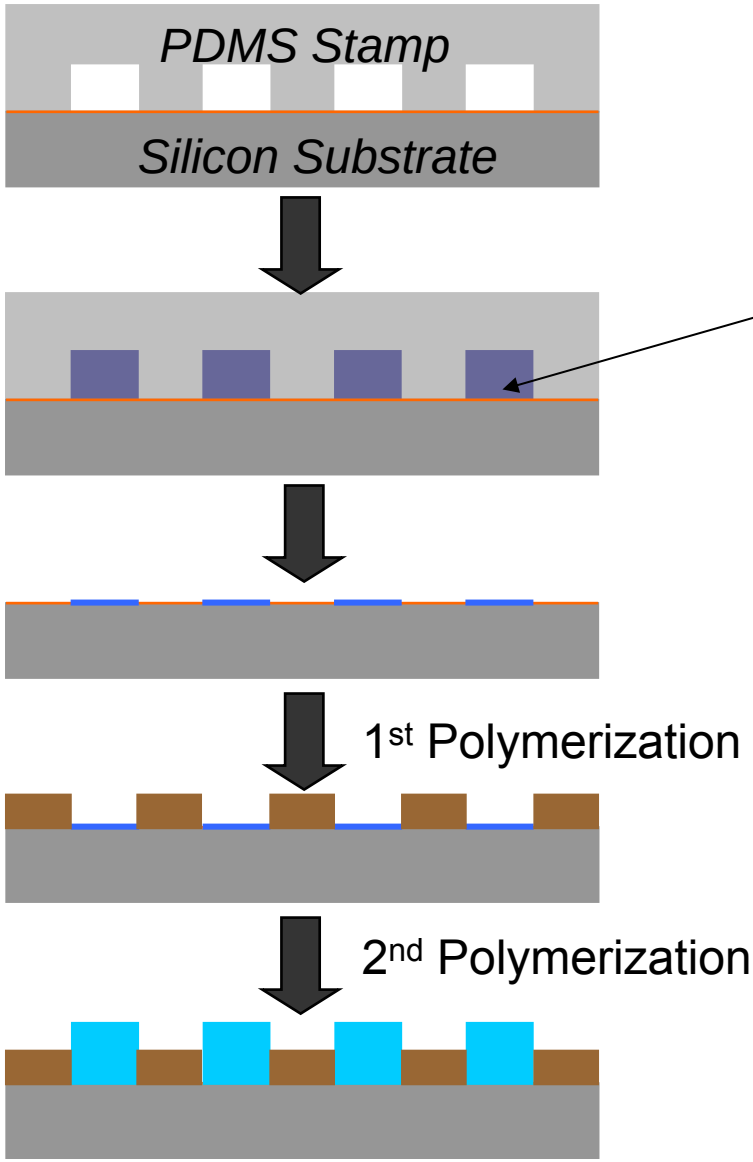


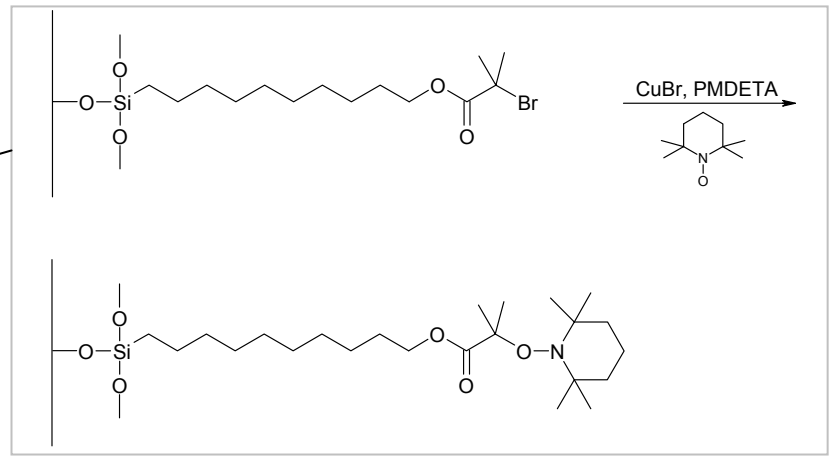




- Polymer brushes of HEMA and NIPAM were patterned on surfaces
- Disadvantages: solvent compatibility of PDMS and single reaction mechanism (ATRP)

Patterned Polymer Brushes via Microchannel Confined Surface Transformation

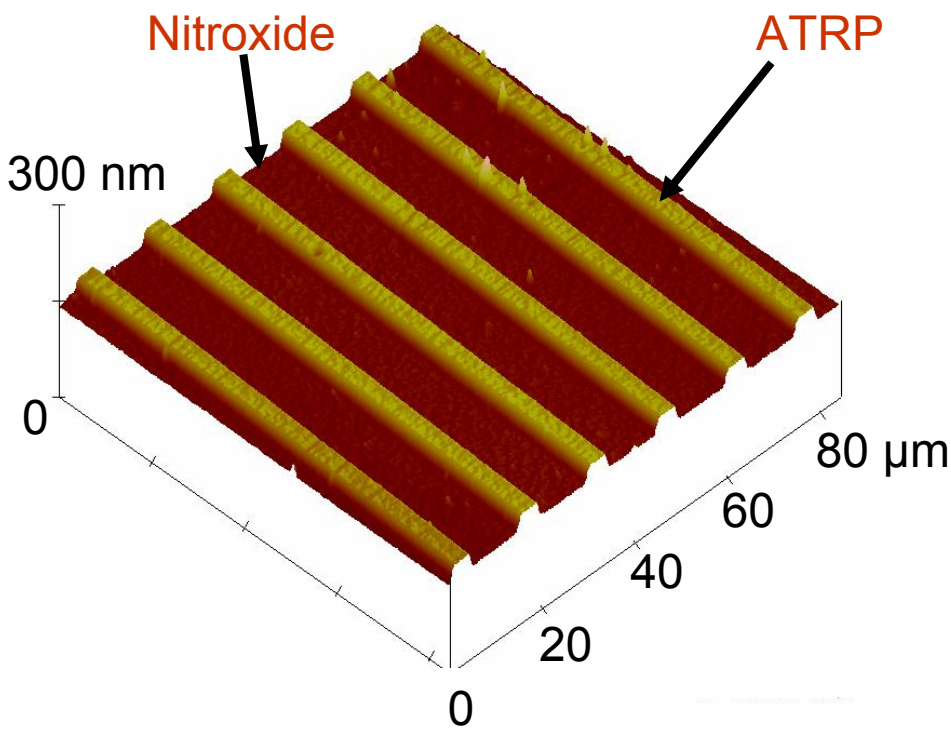




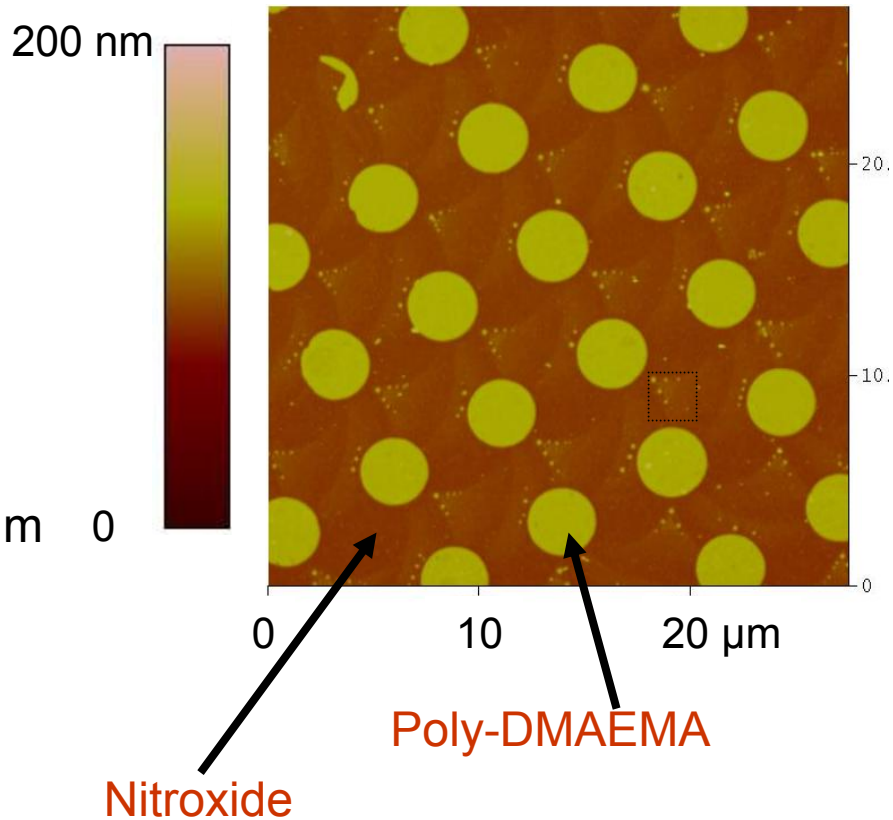
- Solution was pulled into the channel by capillary forces
- No limitation on the polymerization solution
- 2 different polymerizations render patterned binary polymer brushes

Patterned Polymer Brush from ATRP I

- Surface-initiated room temp. ATRP of HEMA and DMAEMA have been applied to pattern the surface with polymer brushes.
- Polymers only grow on areas previously protected by stamps.

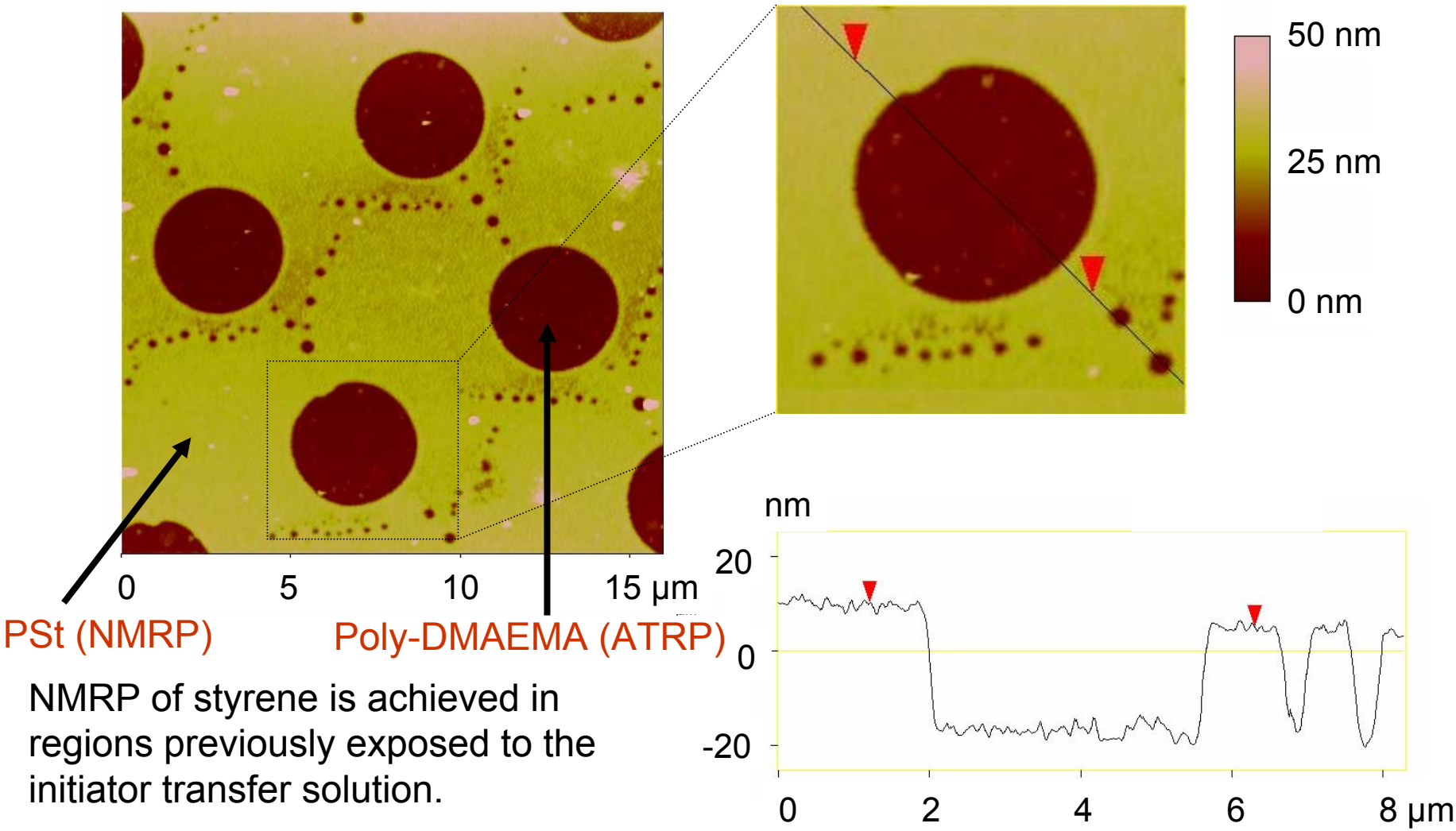


Patterned poly-HEMA



Patterned poly-DMAEMA

Patterned Binary Polymer Brushes



NMRP of styrene is achieved in regions previously exposed to the initiator transfer solution.

Conclusions

- A gradient surface of statistical copolymer brushes has been synthesized from a microchannel confined monomer gradient.
- Patterned polymer brushes have been synthesized by microchannel confined surface-initiated polymerization.
- Microchannel confined surface transformation provides patterned (binary) polymer brushes with resolution down to the nanometer regime.

Acknowledgement

- Kathryn L. Beers
- Michael J. Fasolka
- Susan E. Barnes
- Dean M. DeLongchamp
- Daniel Fischer
- Duangrut Julthongpiput
- NIST Combinatorial Methods Center