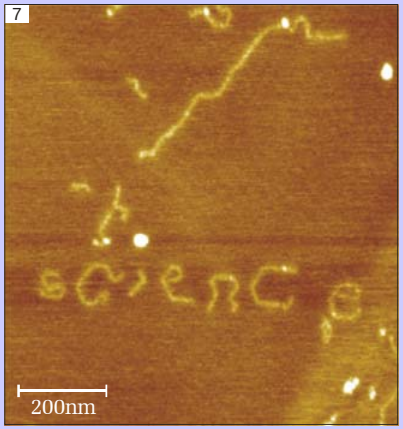
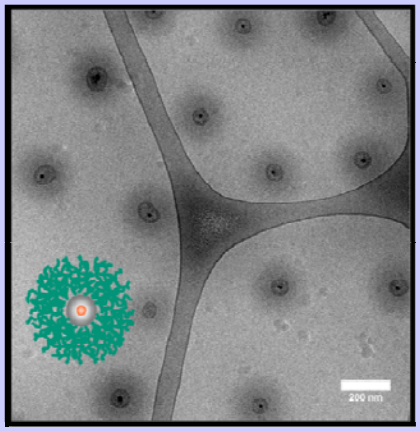
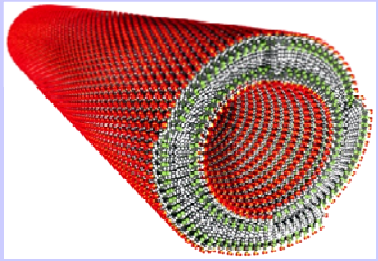
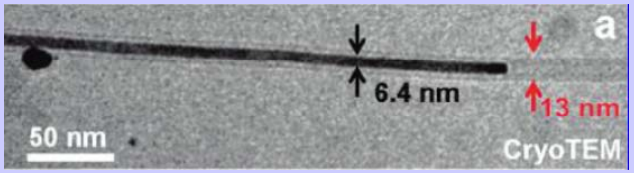
40572 Introduction to Physics of Macromolecules II

Lectures, Excercises and Seminars (P23.3.1)









Prof. Jürgen P. Rabe & Prof. Matthias Ballauff

www.physik.hu-berlin.de/pmm/lehre

Friday 09-11 NEW 15 2‘101

Tuesday 11-13 NEW 14 1‘10

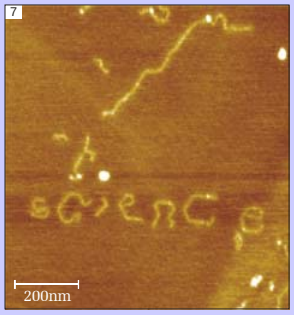
Credit Points (5 SP/ECTS): Seminar Presentation or Oral Exam

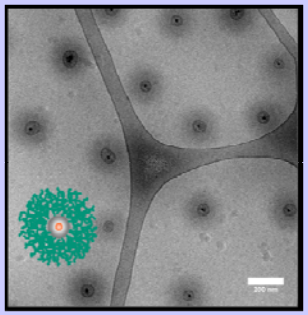
40572 Introduction to Physics of Macromolecules II

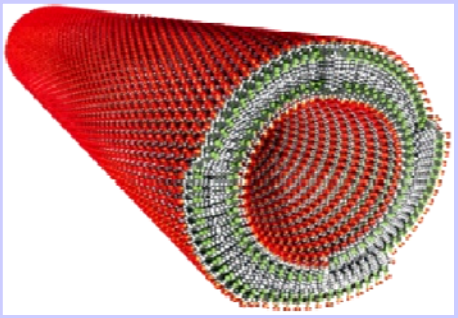
Lectures, Excercises and Seminars

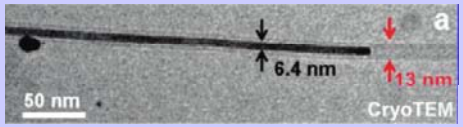
Program

- Introduction
- Polymerization Reactions & Molar Mass Distributions
- Single Macromolecules
- Macromolecular Nanostructures
- Rubber Elasticity
- Biomacromolecules
- Polyelectrolytes
- Molecular Machines









40572 Introduction to Physics of Macromolecules II

Lectures, Excercises and Seminars

Literatur:

M. Rubinstein & R. H. Colby: „Polymer Physics“

Oxford University Press, USA, 2003

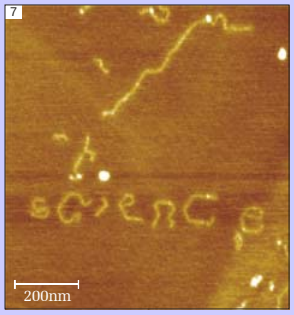
Seminar Topics (J.P. Rabe)

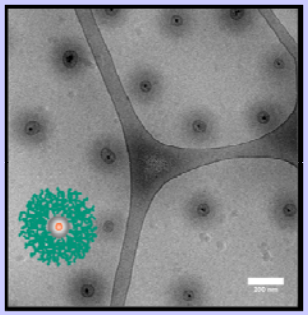
14.05. Single Macromolecules

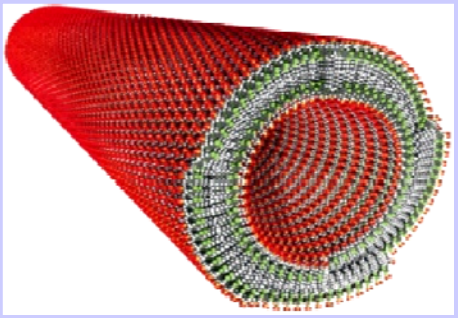
21.05. Single Macromolecules

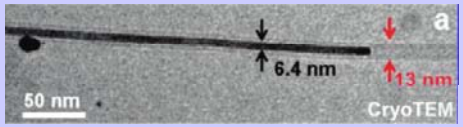
28.05. Macromolecular Nanostructures

02.07. Biomacromolecules

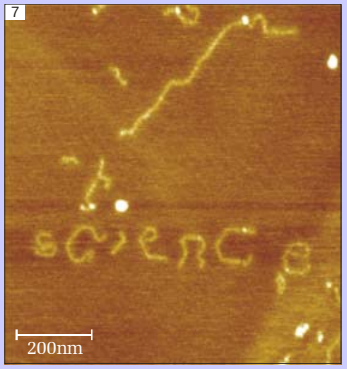








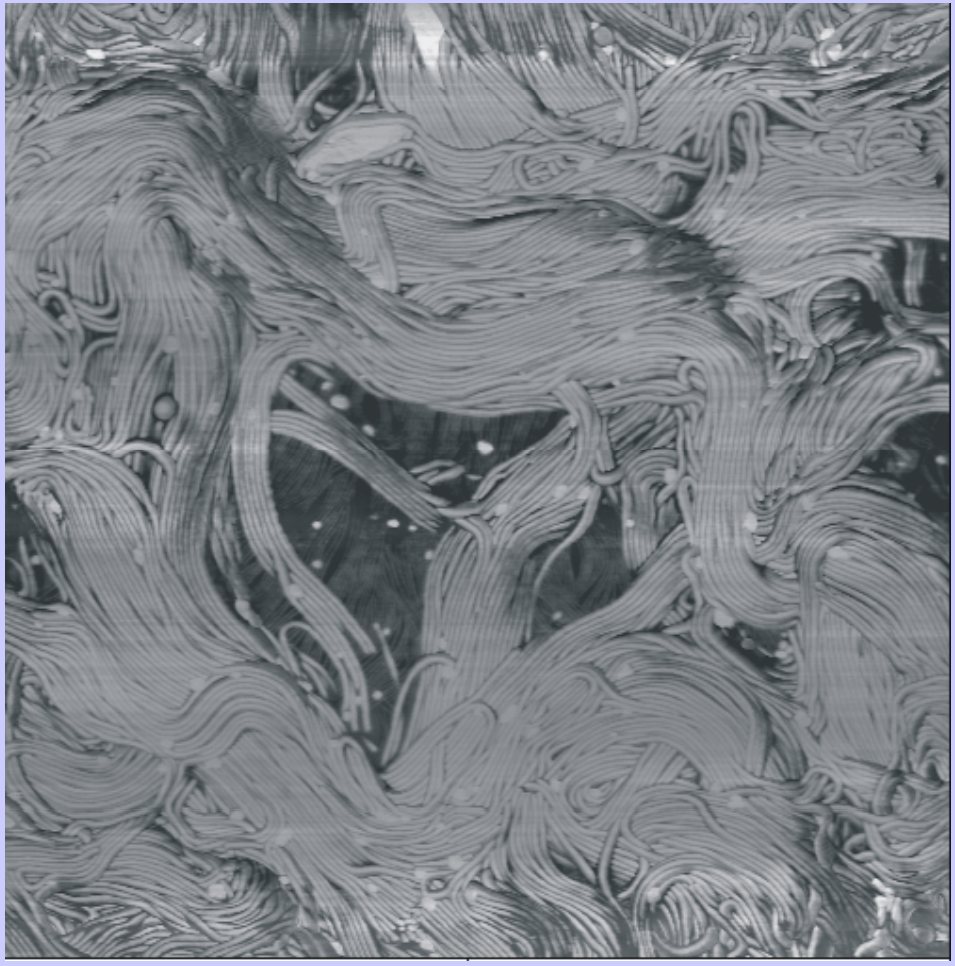
Introduction to Physics of Macromolecules II



- Structure and Mechanical Properties

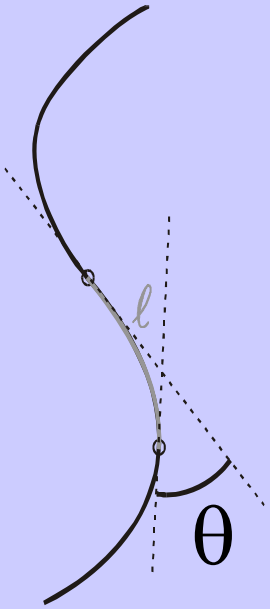
  - Synthetic polymers as worm-like chains
  - Biopolymers with specific interactions
  - Bio-synthetic hybrids
  - Single macromolecules at surfaces

Synthetic Polymers: Worm-Like Chains

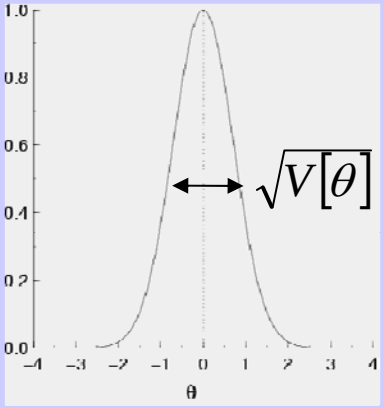


100 nm

Worm-Like Chain-Model



$$\mathbf{p}(\theta) = \sqrt{\frac{\ell_P}{2\pi \cdot \ell}} \cdot \exp\left\{-\frac{\ell_P \theta^2}{2\ell}\right\}$$



$$\langle\theta\rangle = 0$$
$$V[\theta] = \ell / \ell_P$$

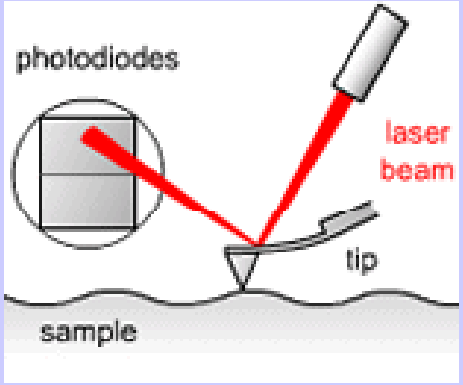
Force to stretch end-to-end distance to α * contour length:

$$F = 3k_B T \frac{\alpha}{l_p}$$

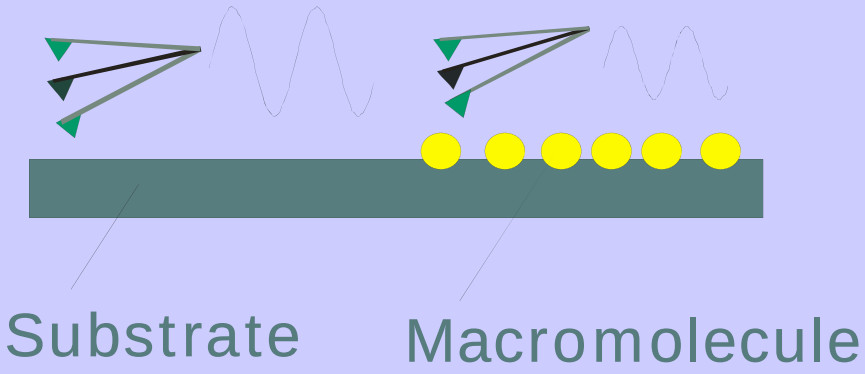
$$\alpha=1;\ \ l_p \approx 1nm\,;T \approx 300K: \quad \frac{3k_B T}{l_p} \approx 10 \frac{pN}{Molecule}$$

Conformation of Single Macromolecules from Scanning Probe Microscopies

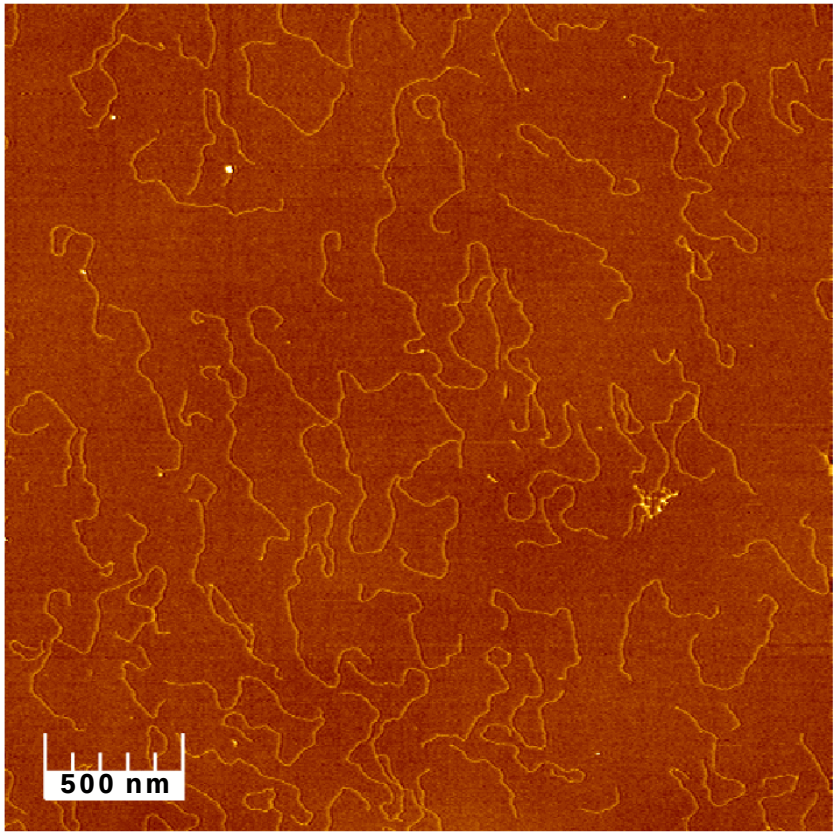
„Contact-Mode“

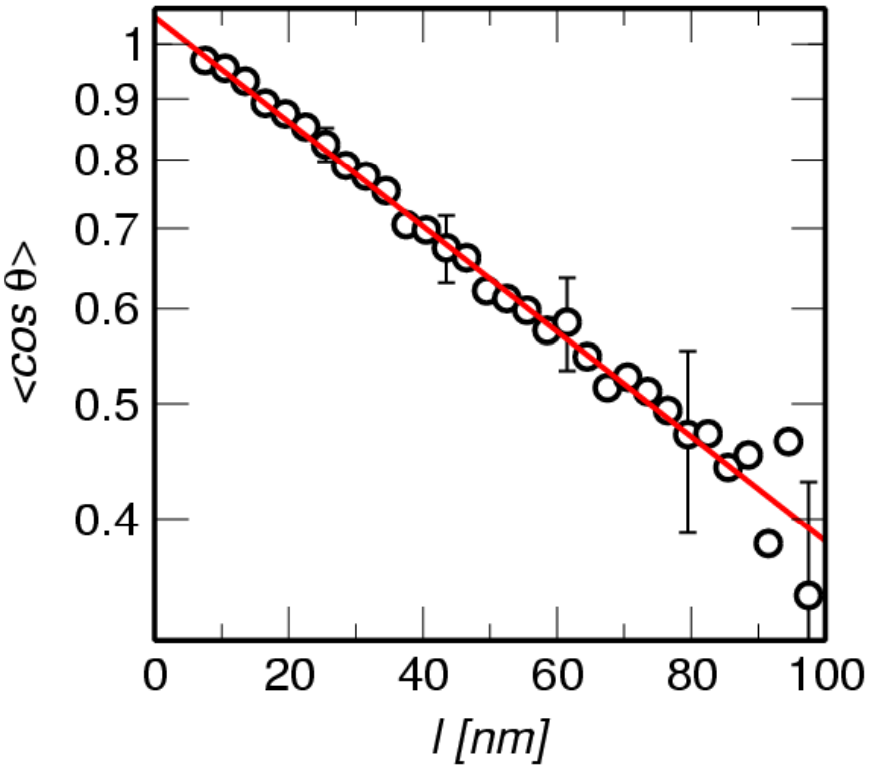


„Tapping-Mode“



Determination of the persistence length of DNA
- Equilibration in 2 D -

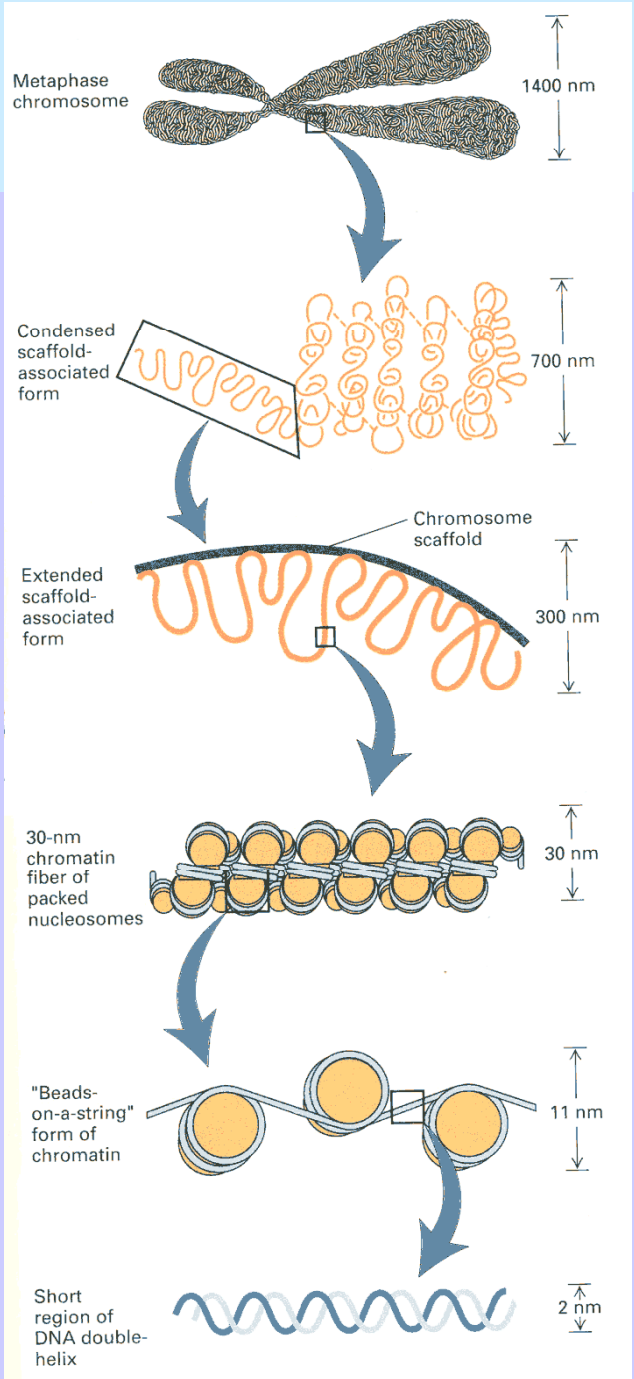


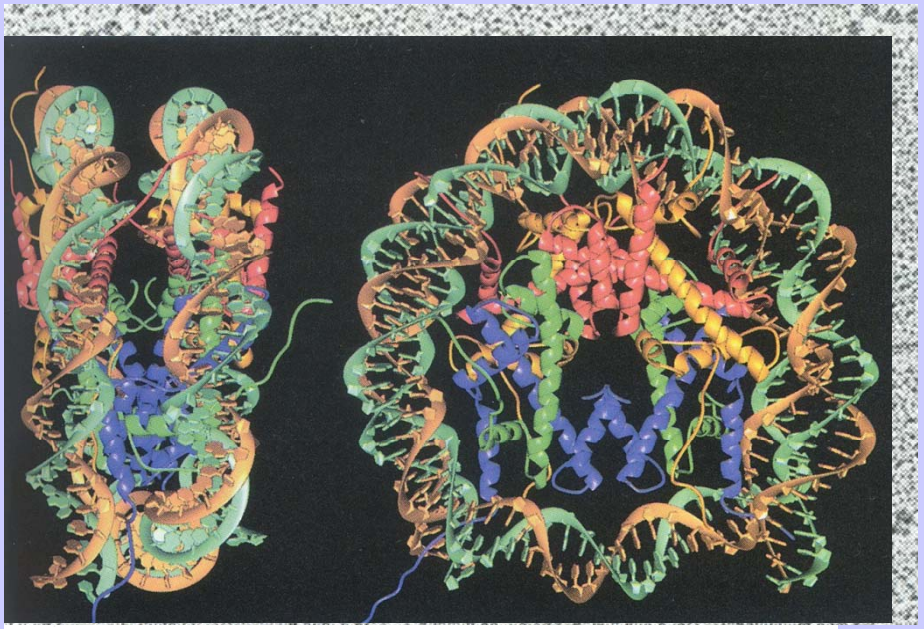


J.P.R. in *Topics in Current Chemistry*, P. Samorí (ed.), Springer, 285 (2008) 77

Biopolymers

DNA in Chromosomes





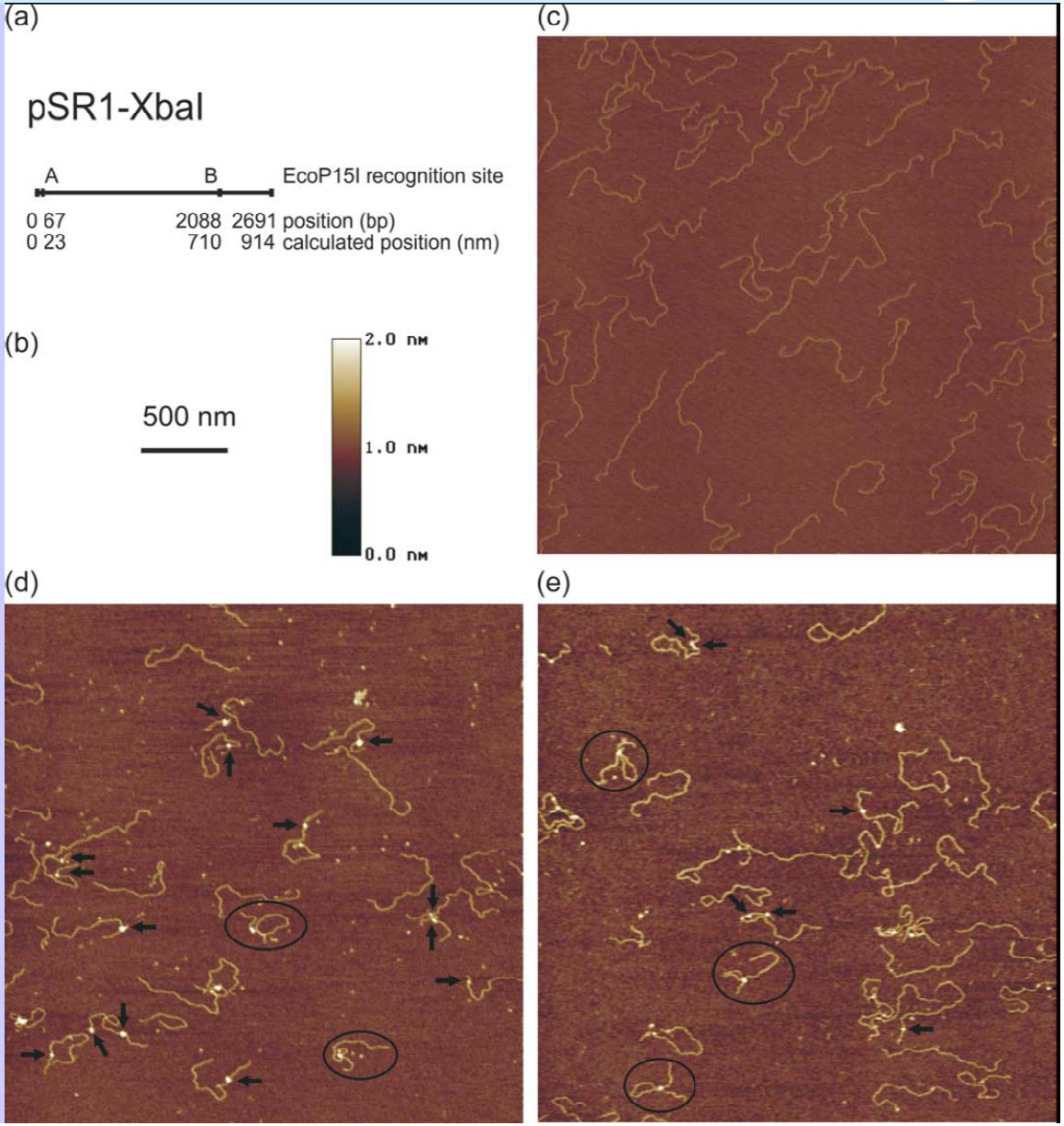
DNA-Split after Enzyme-Recognition

Biochemistry

- Restriction enzymes split DNA at certain positions

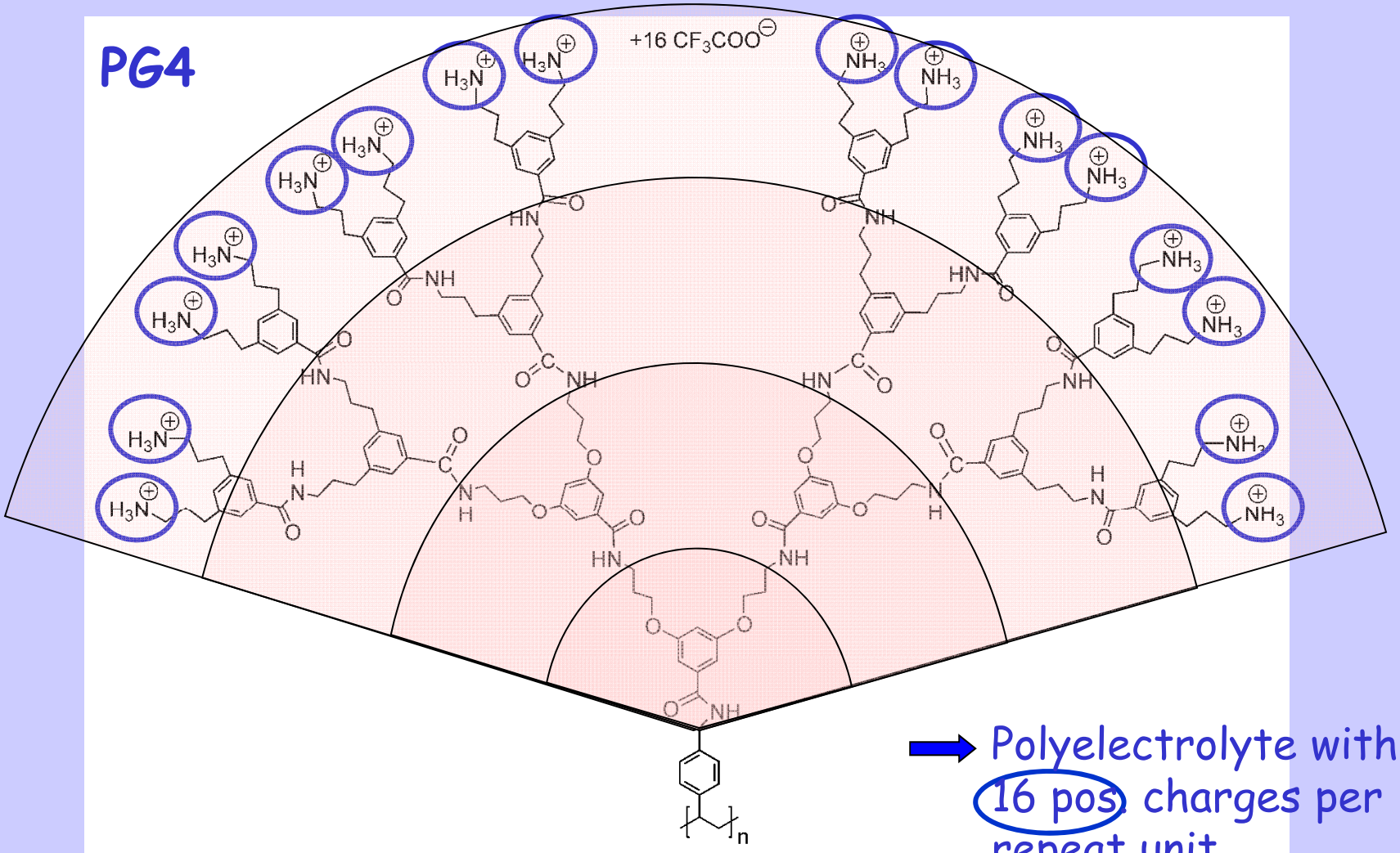
Microscopy

- DNA rings form if 2 enzyme-DNA complexes meet (precursor for split)



S. Reich, I. Gössl, M. Reuter, J.P.R., D.H. Krüger, *J. Molec. Biol.* (2004)

Dendronized Polymers as Model Systems

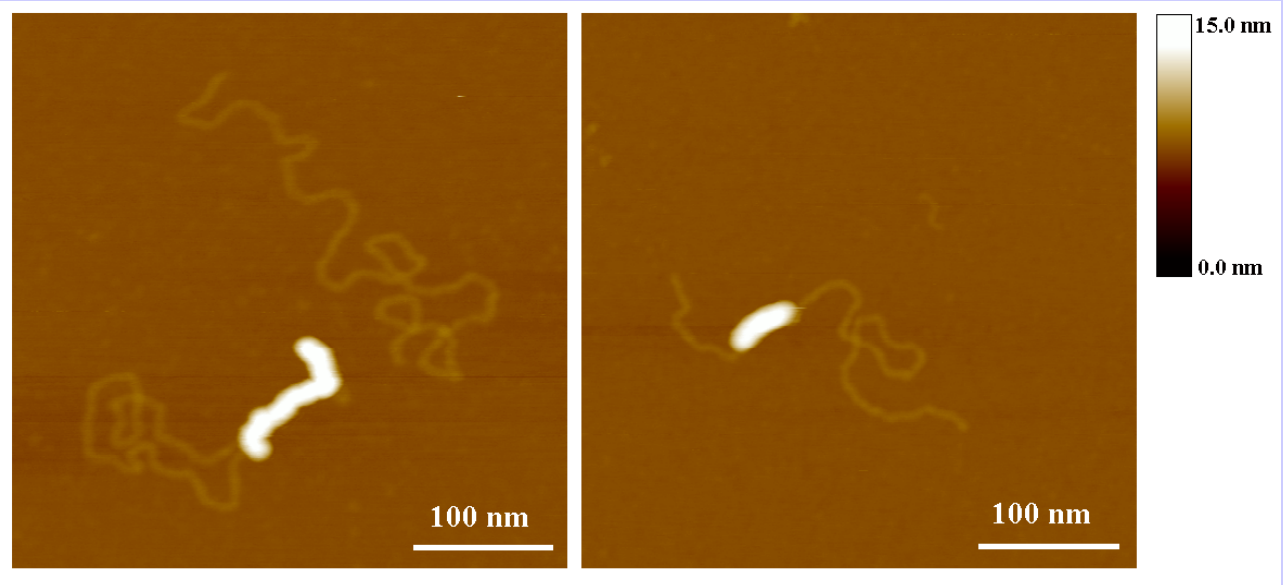


→ Polyelectrolyte with 16 pos. charges per repeat unit

A.D. Schlüter, J.P.R., *Angew. Chem. Int. Ed.* 39 (2000) 864

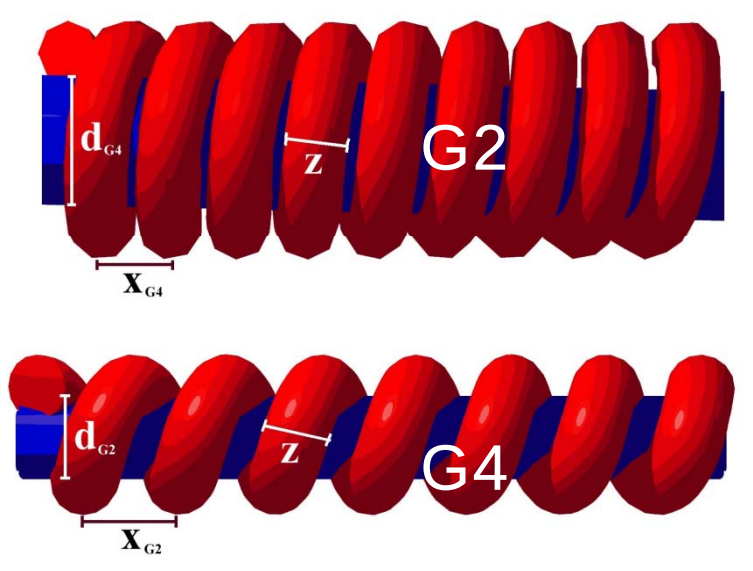
Complexation of DNA with Dendronized Polymers

Charge Ratio: 1:1 to 1:0.2



I. Gössl, L. Shu, A.D. Schlüter, J.P.R., *J. Am. Chem. Soc.* **124** (2002) 6860

Model



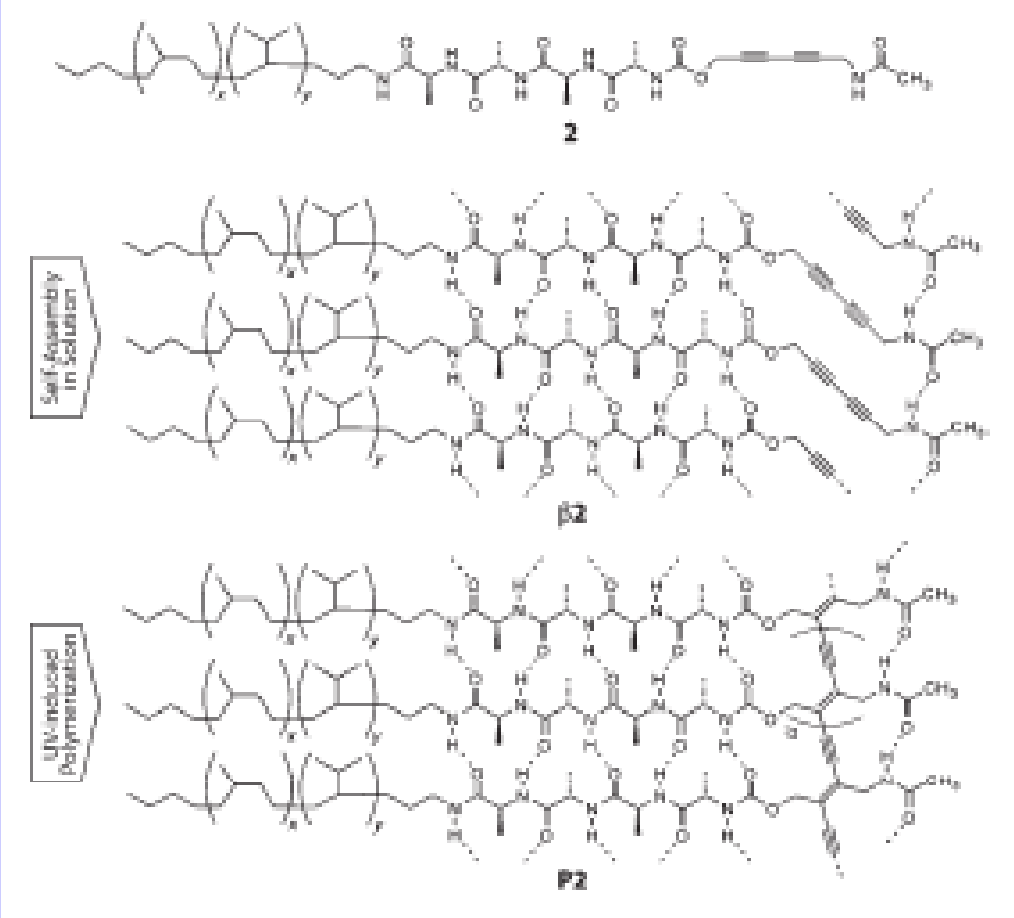
Negative Extra Charge of the Complex -

Determined by Dendron-Generation!

I. Gössl, L. Shu, A.D. Schlüter, J.P.R., *J. Am. Chem. Soc.* **124** (2002) 6860

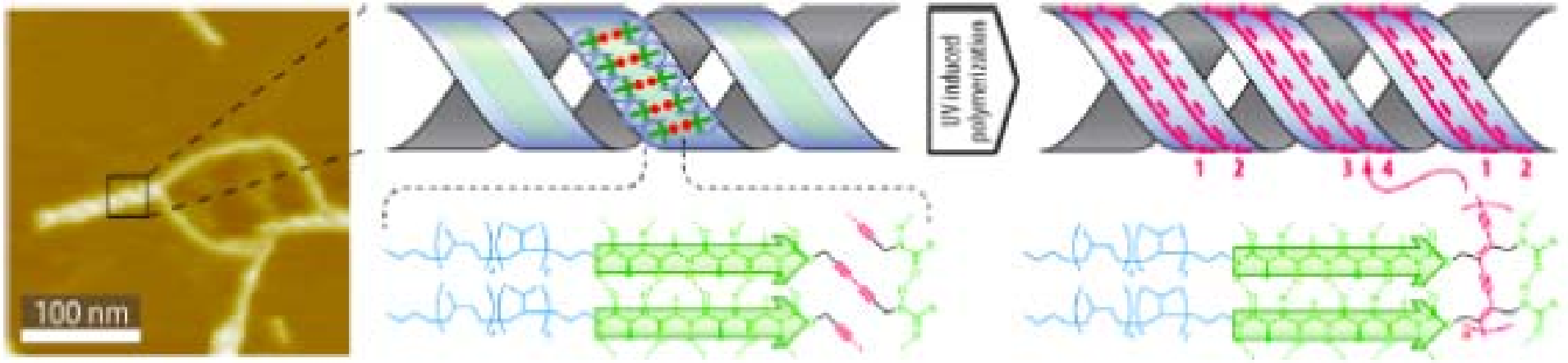
Bio-Synthetic Hybrids

Topochemical Polymerization of Self-Assembled Diacetylene-Oligopeptide-Derivatives



N. Severin, J.P.R.,
H. Frauenrath et al.,
Angew. Chem. Int. Ed.
45 (2006) 5383

Double Helices of Poly(diacetylene-oligopeptide)

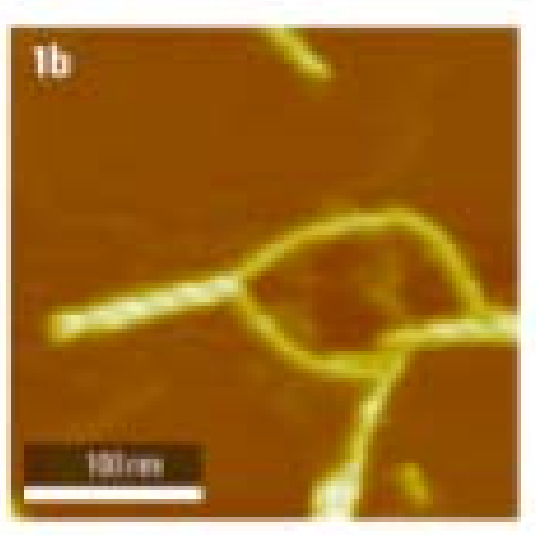


=> Biocompatible Conjugated Polymer

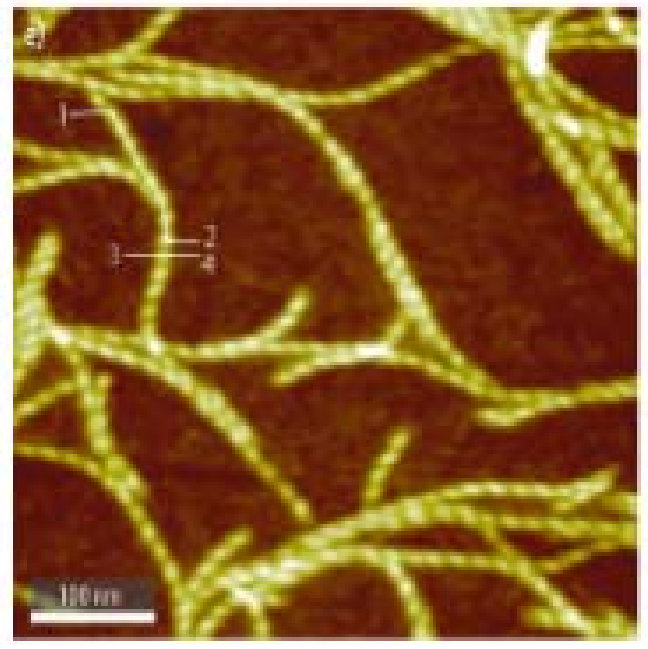
N. Severin, J.P.R., H. Frauenrath et al.

Angew. Chem. Int. Ed. 45 (2006) 5383 & *Macromol. Biosci.* 7 (2007) 136

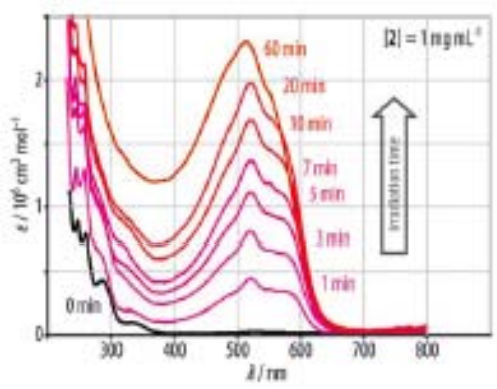
Self-Assembled Diacetylene-Oligopeptide



=> Double Helix



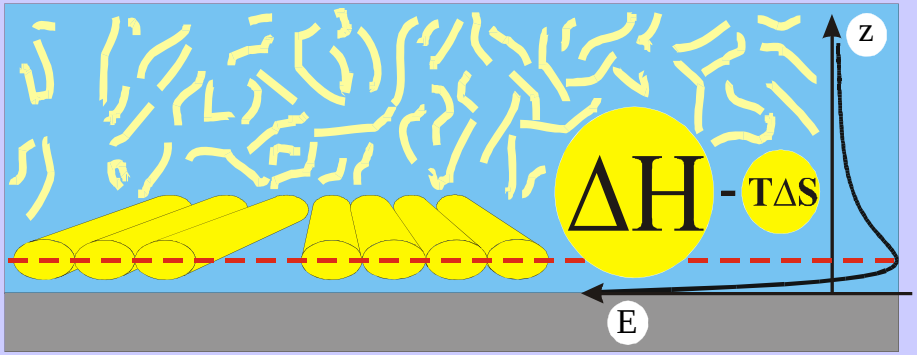
Stacking of Double Helices



UV-Polymerization

N. Severin, J.P.R.,
H. Frauenrath et al.,
Angew. Chem. Int. Ed.
45 (2006) 5383

Molecular Self-Assembly at Solid-Liquid Interfaces

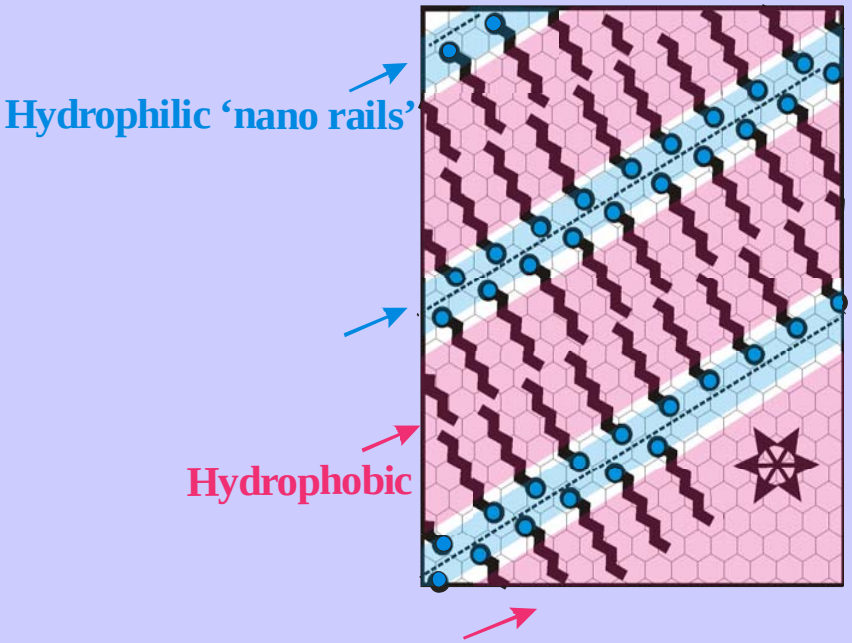


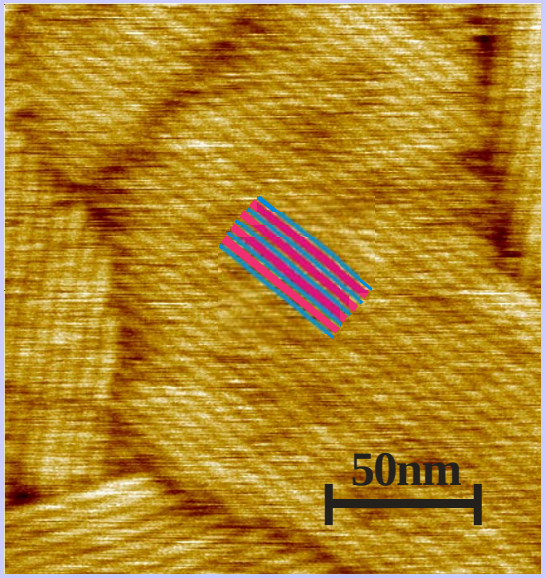
- Minimizing enthalpy (H)
  => Maximum adsorbate density at surfaces
- Maximizing entropy (S):
  => Adsorption of large and rigid molecules from solution
  (since less translational and conformational entropy is lost)

↳ Minimizing free energy (G): 2D cystals of large and rigid molecules

J.P.R., S. Buchholz, *Science* 253 (1991) 424; *Phys. Rev. Lett.* 66 (1991) 2096
P. Samori, N. Severin, K. Müllen, J.P.R. *Adv. Mater.* 12 (2000) 579

Amphiphiles on HOPG

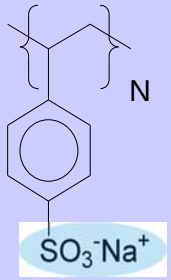




SFM image of octadecylamine

→ Nanostructured surface

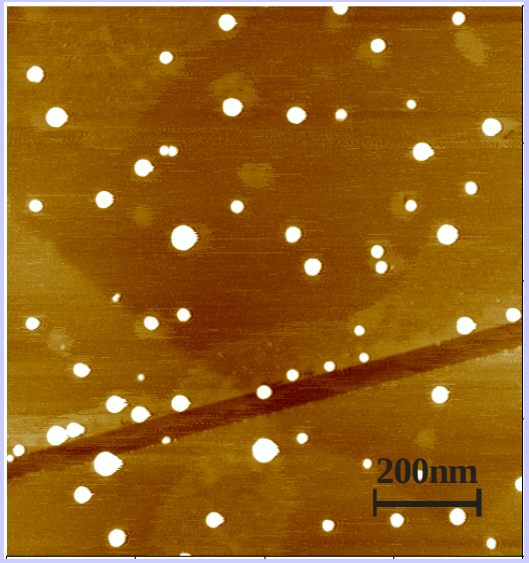
Immobilization of Poly(styrenesulfonate) (PSS)



Coil-globule transition of PSS in mixtures ethanol/water and deposition on octadecylamine

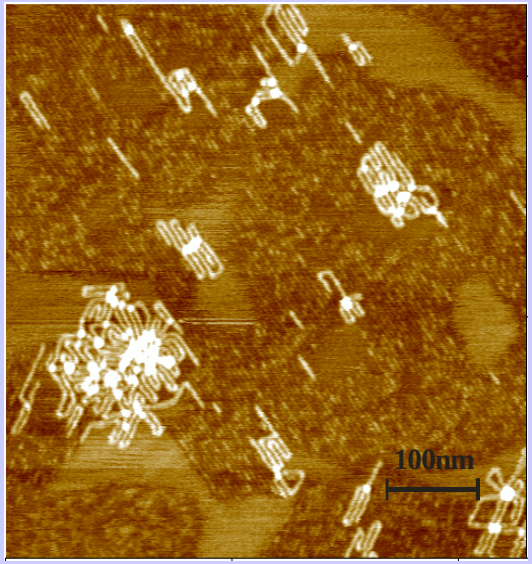
N. Severin, I.M. Okhapkin, A.R. Khokhlov, J.P.R., *Nano Letters* in press.

globule



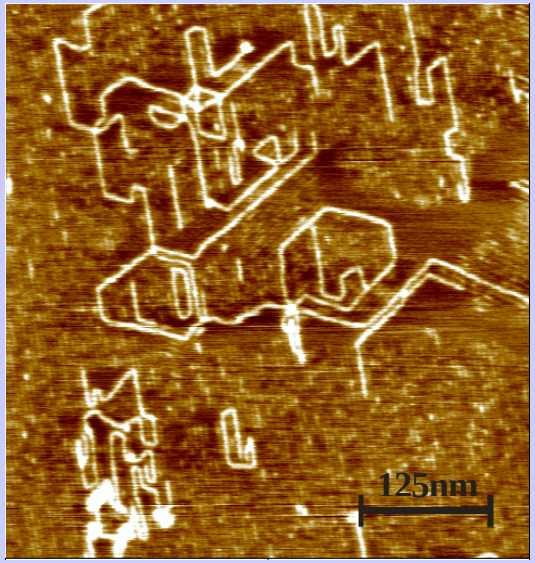
80-100%

transition



60-80%

coil



0-60%

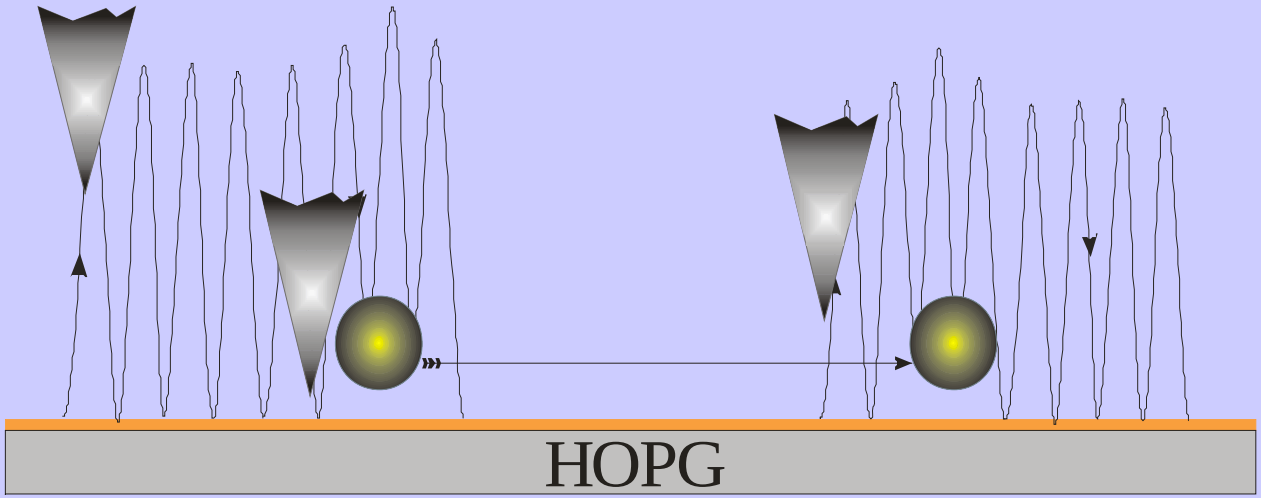
fraction of ethanol in water

'global' conformation on surface is projection of conformation in solution

'local' conformation determined by surface template

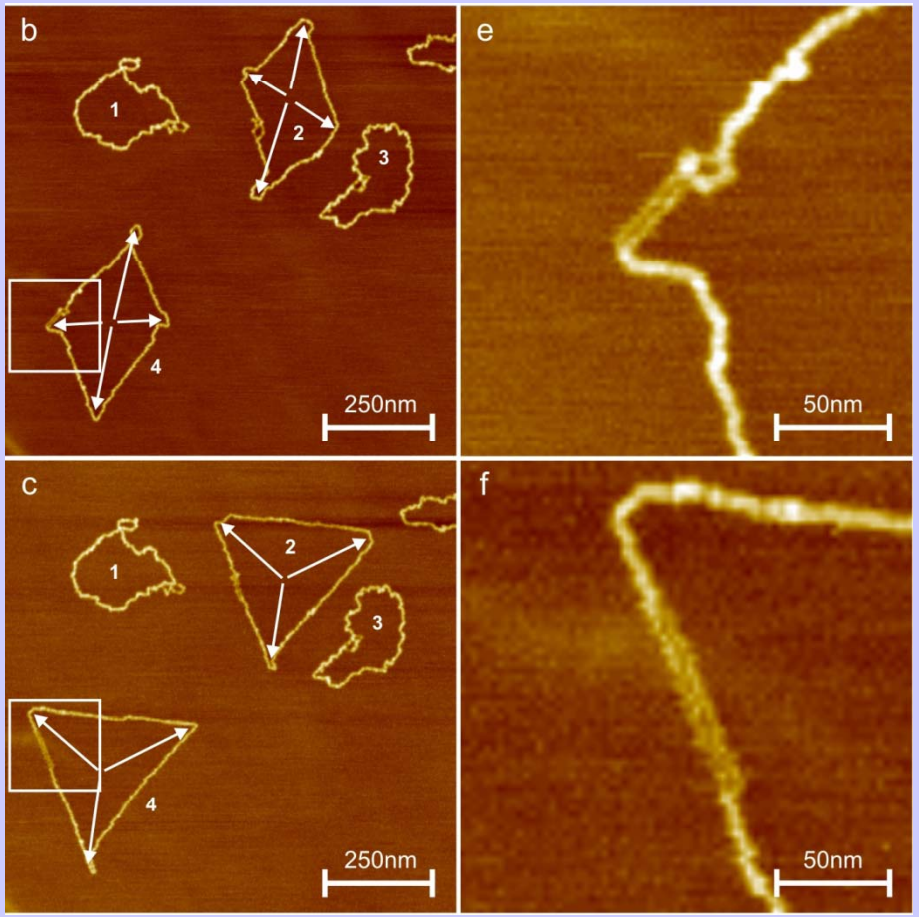
Free manipulation by SFM tip

Imaging in tapping mode → Manipulation in contact mode → Imaging in tapping mode



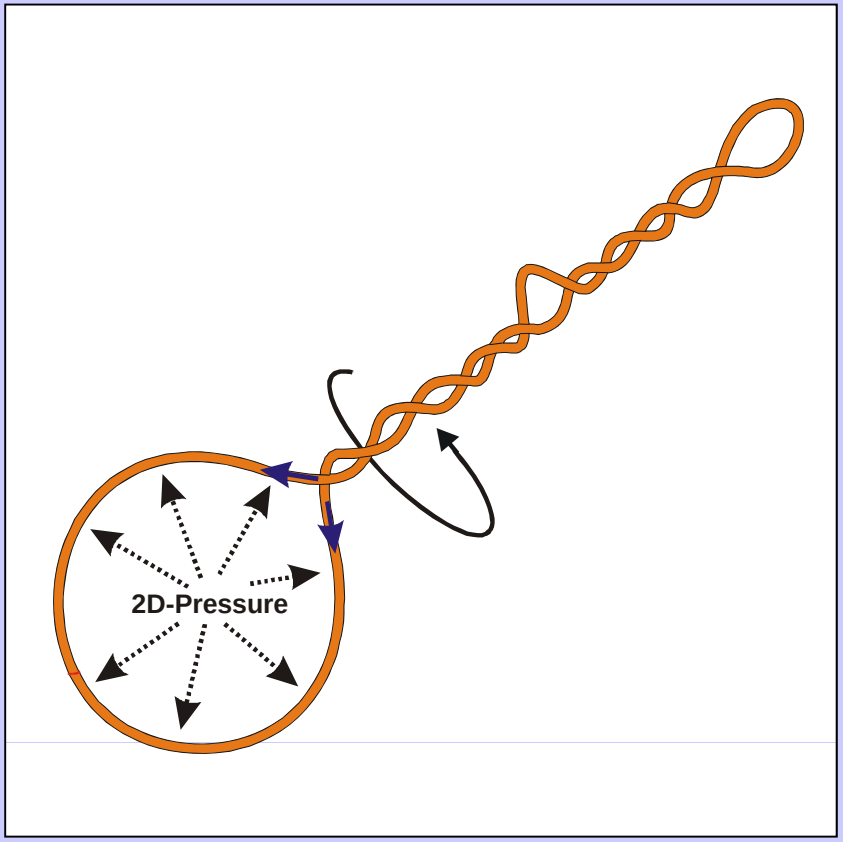
- Polymer molecules are imaged in tapping mode
- For manipulation scanning is stopped,
  tip is pushed to contact and moved in a chosen direction
- After manipulation tapping is continued

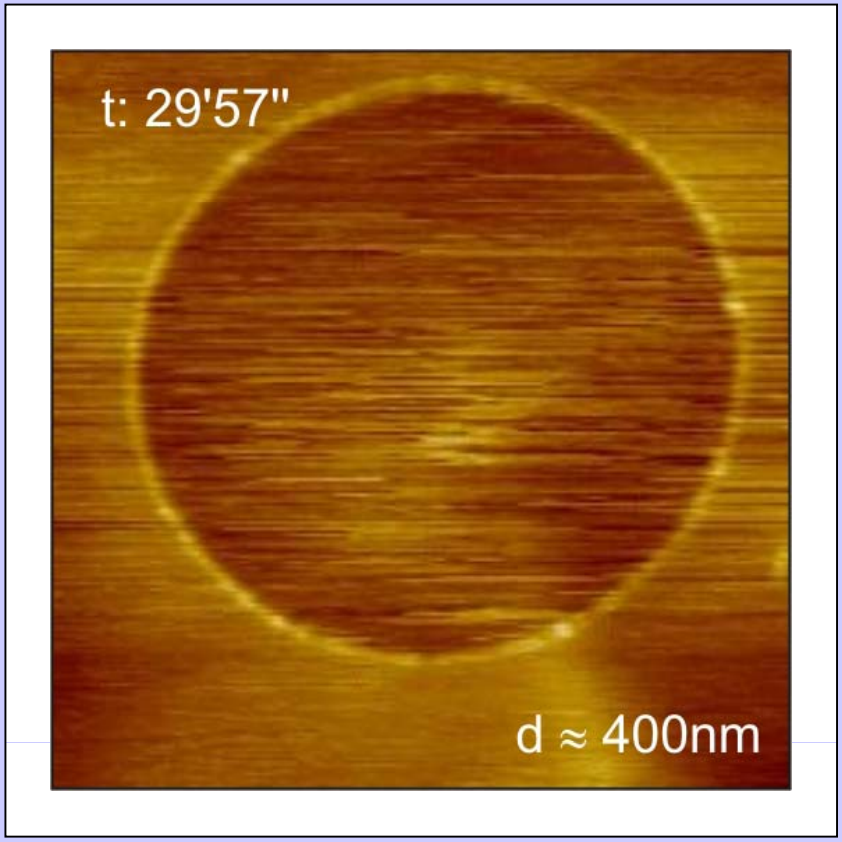
Manipulation of Single DNA-Molecules



N. Severin, J. Barner, A. Kalachev, J.P.R., *Nano Lett.* 4 (2004) 577

Unraveling supercoiled DNA





Supercoiled Plasmid-DNA ➡ 2-fold overstretched B-Form DNA