Applications of Broadband Dielectric Spectroscopy in nanoscience

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Coauthors: F. Kremer, T.P. Russell
IDS financial support

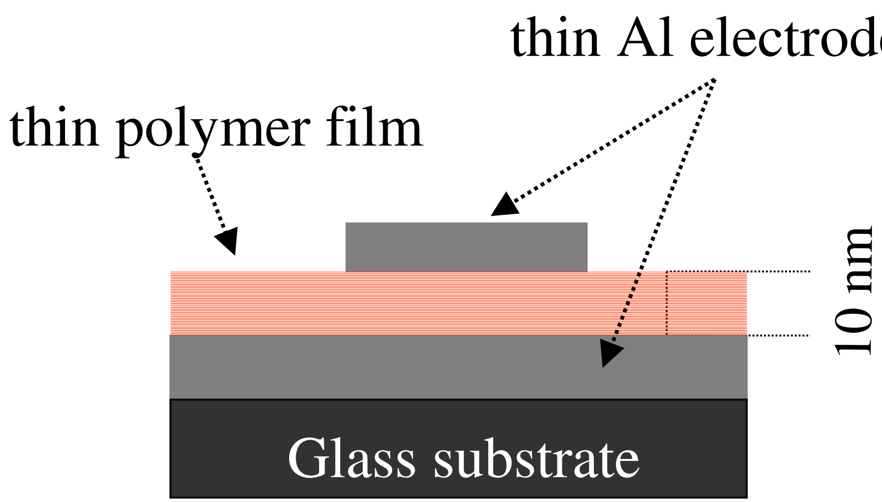
Applications of Broadband Dielectric Spectroscopy in nanoscience

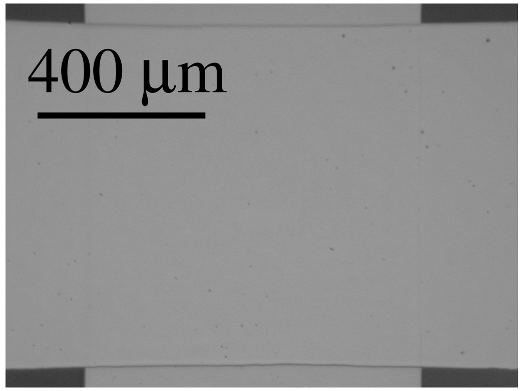
Outline:

1. Glassy dynamics of nanometric thin polymer films
2. Polymer nanofluidics
3. Phase transitions of ferroelectric polymer nanowires
4. Glass transition of polymer nanotubes
5. Phase transitions of grafted polymer monolayers

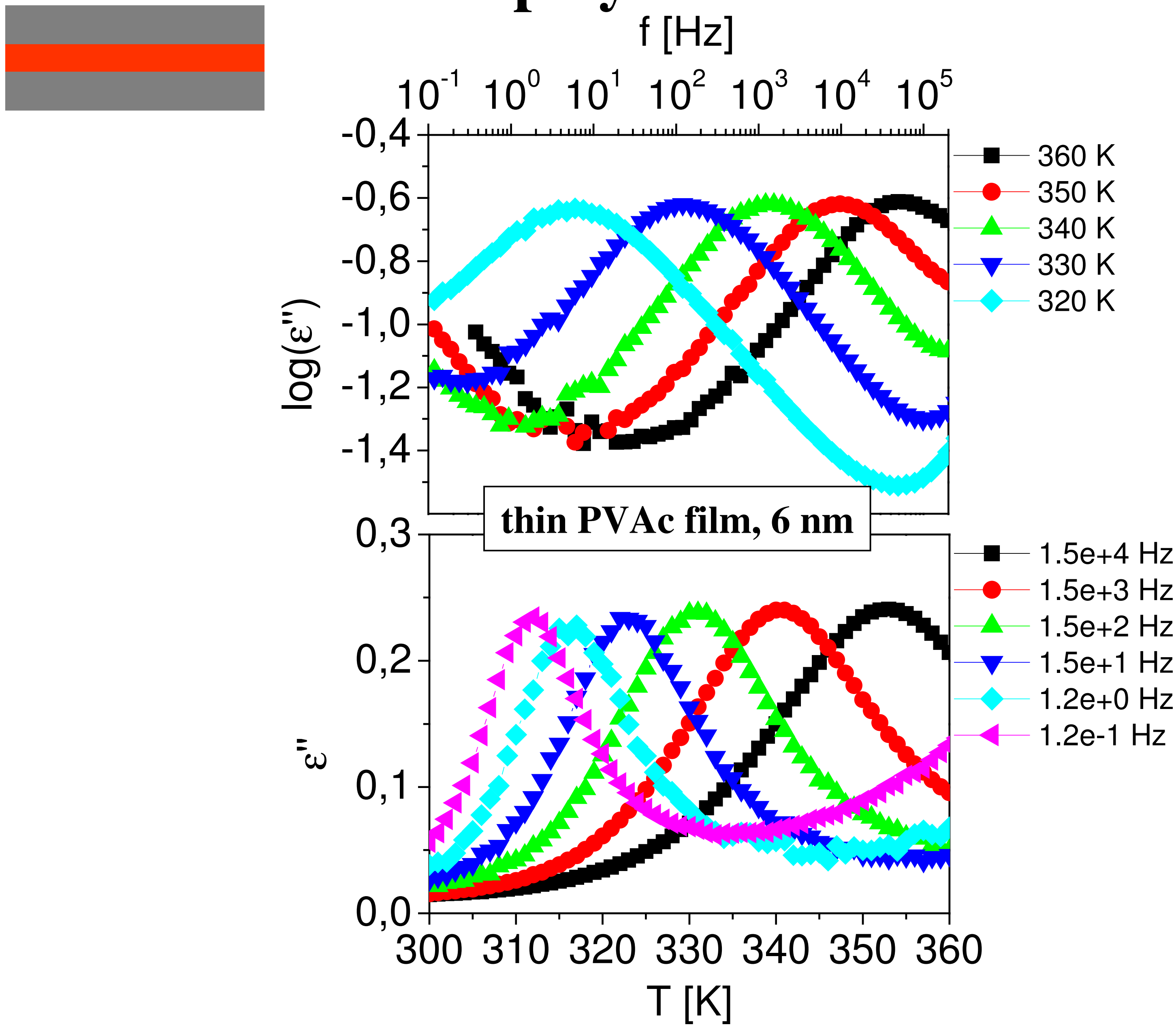
Molecular dynamics in ultra-thin polymer films

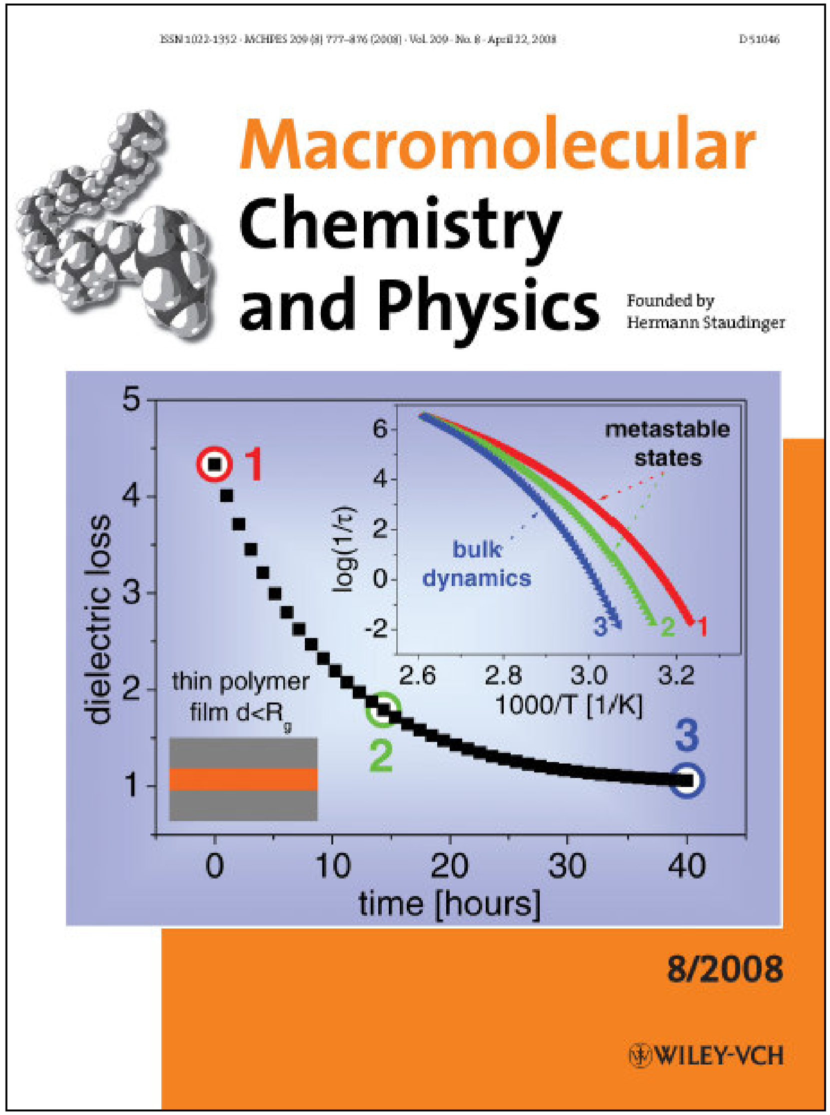
Standard preparation of capped polymer films





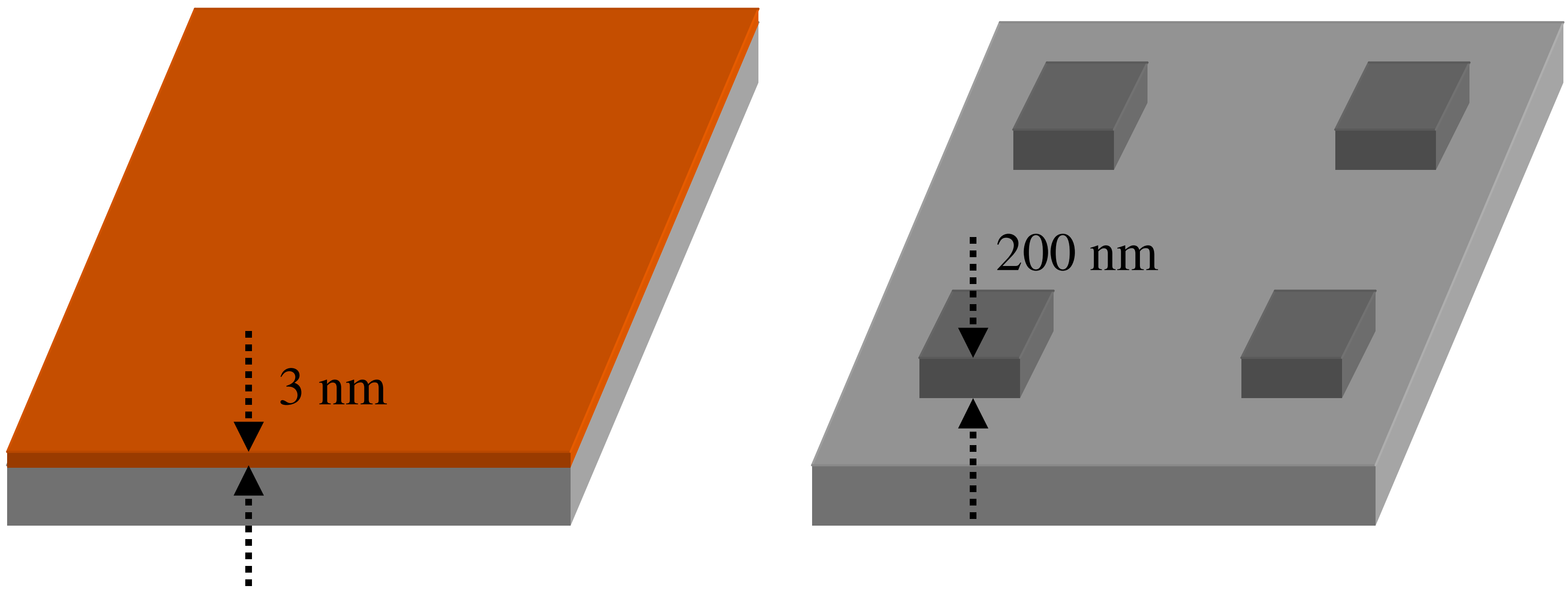
Molecular dynamics in ultra-thin (capped) polymer films



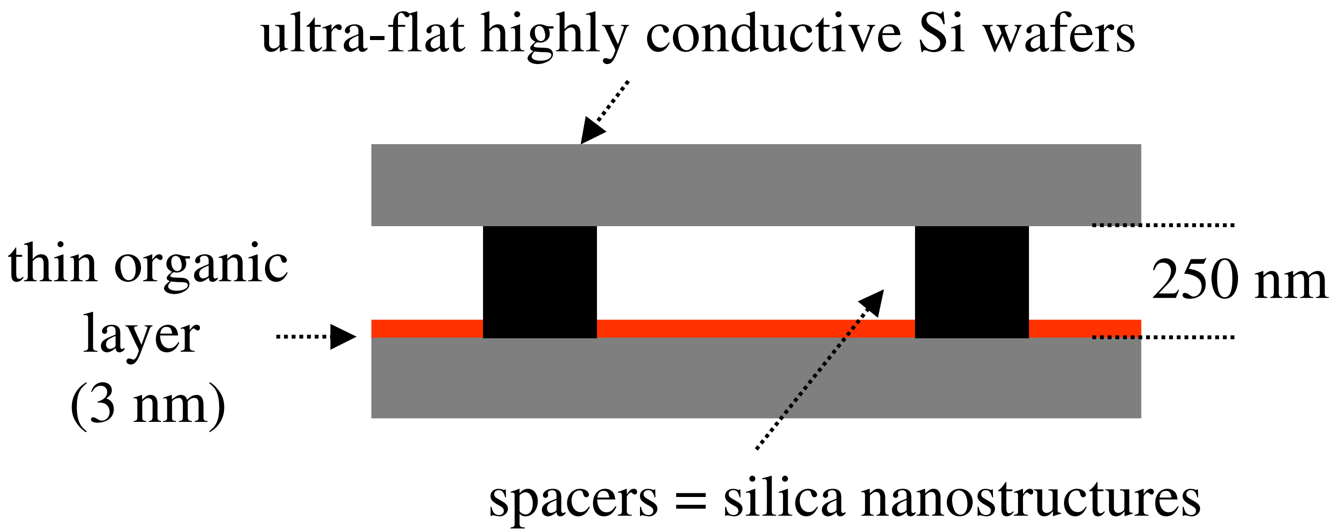


A. Serghei, and F. Kremer
"Metastable states of glassy dynamics, possibly mimicking confinement effects in thin polymer films"
Macromol. Chem. Phys. **209**, 810 (2008).

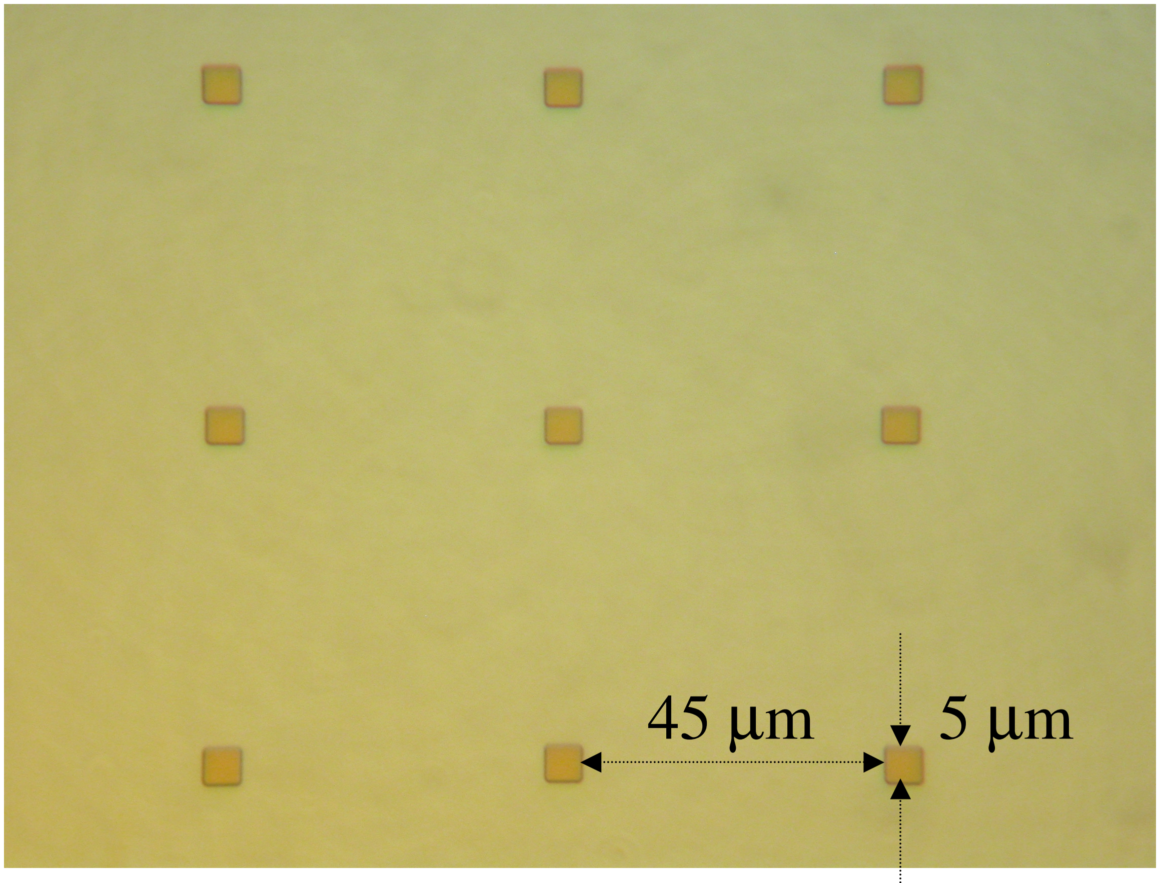
Measurements on thin films in an air gap geometry
- nanostructures as nanospacers -



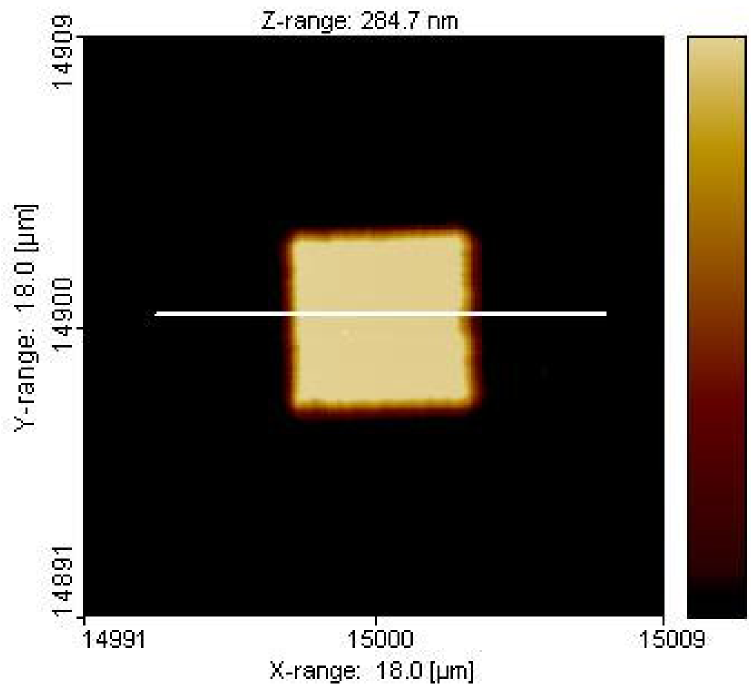
Measurements on thin films in an air gap geometry - nanostructures as nanospacers -

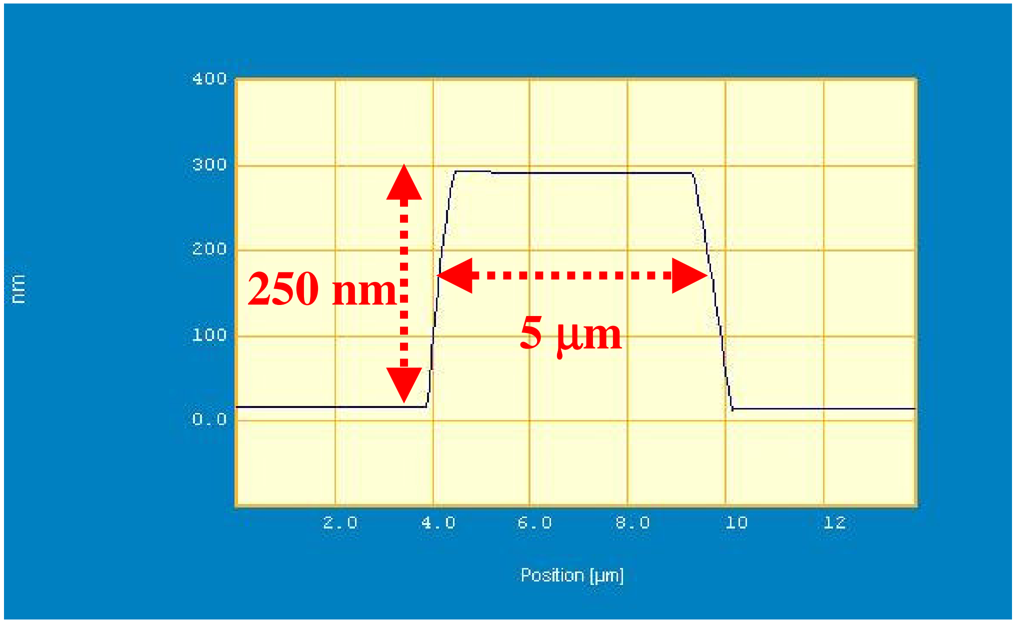


Nanostructures as nanospacers

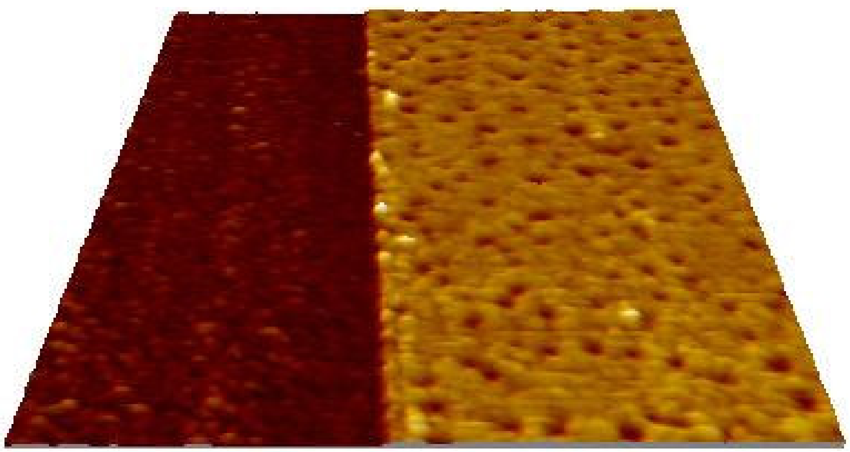


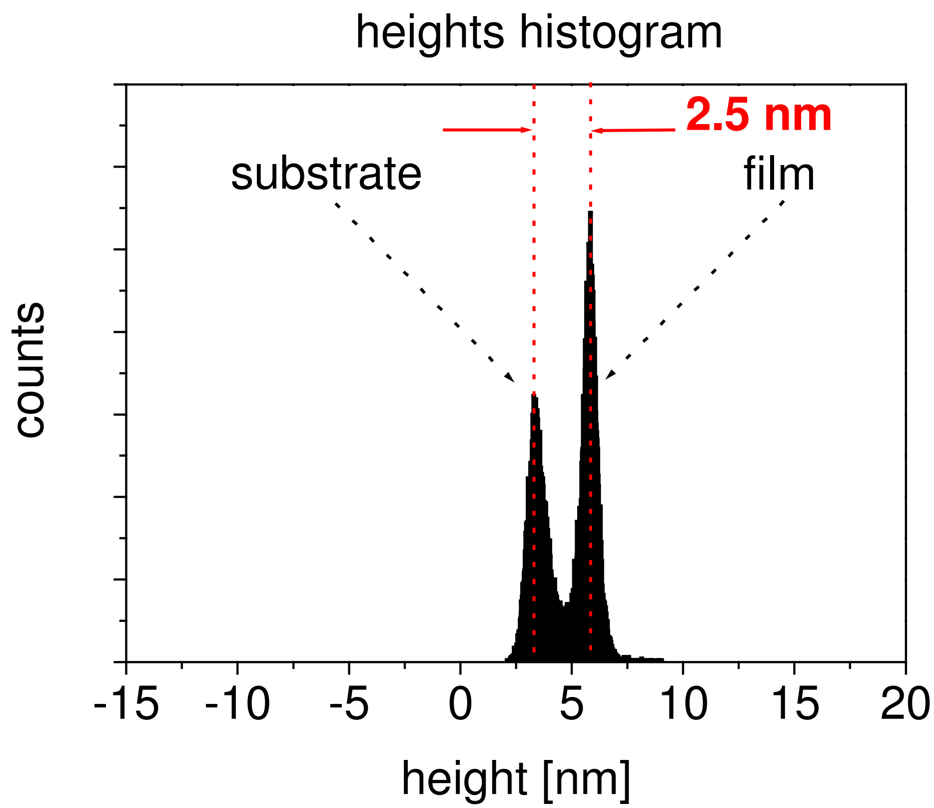
Nanostructures as nanospacers



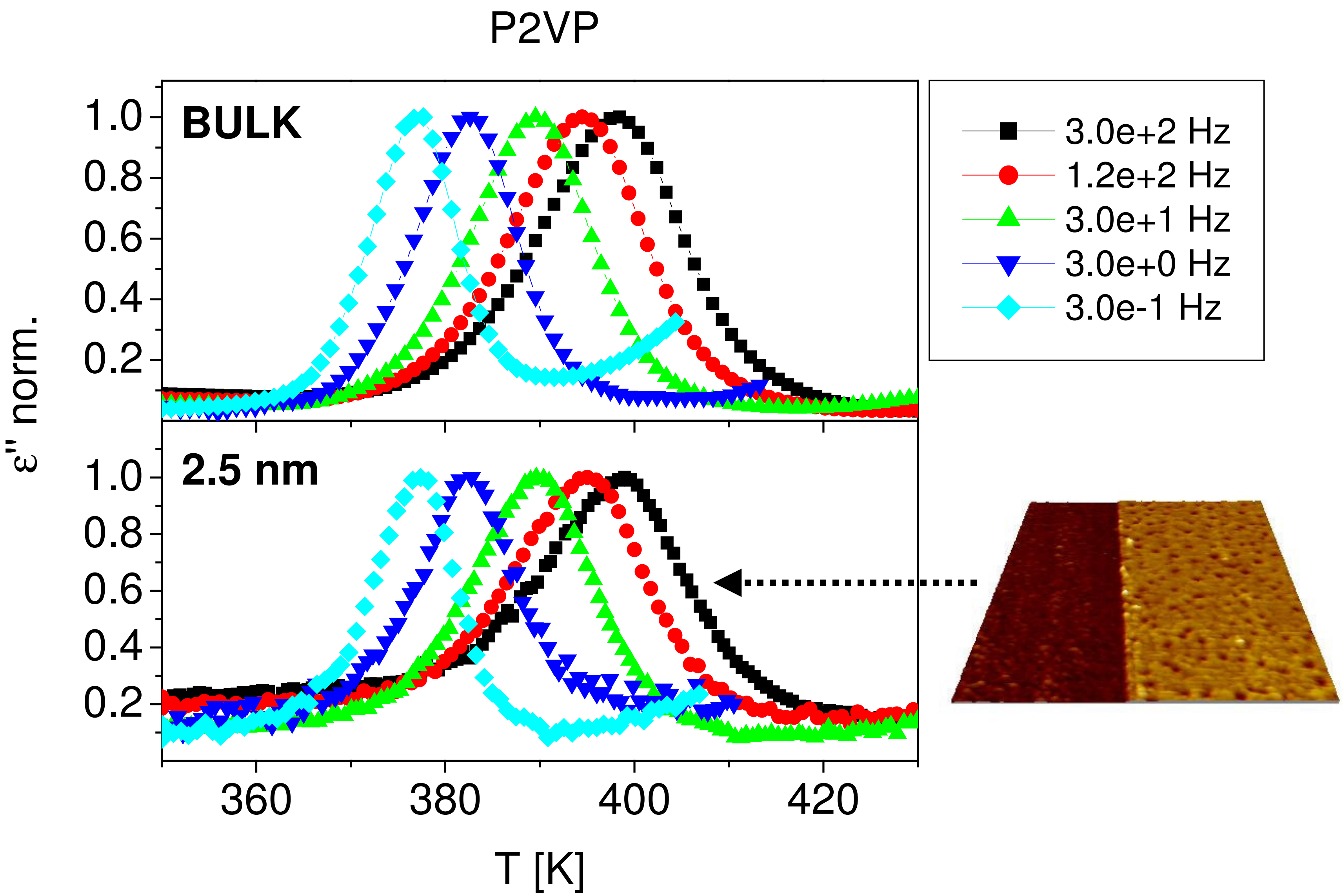


Ultra-thin films of P2VP (2.5 nm thickness)





Thin films of P2VP (2.5 nm thickness)



How to measure the glass transition of single polymer chains?

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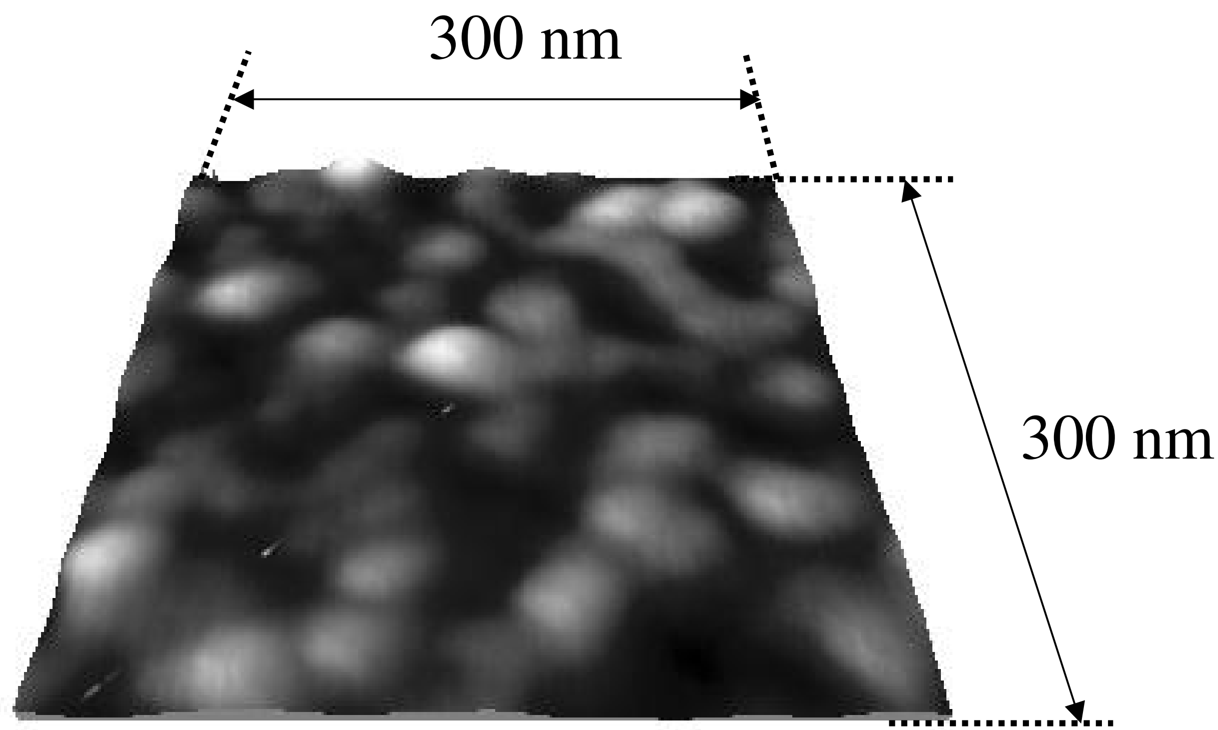
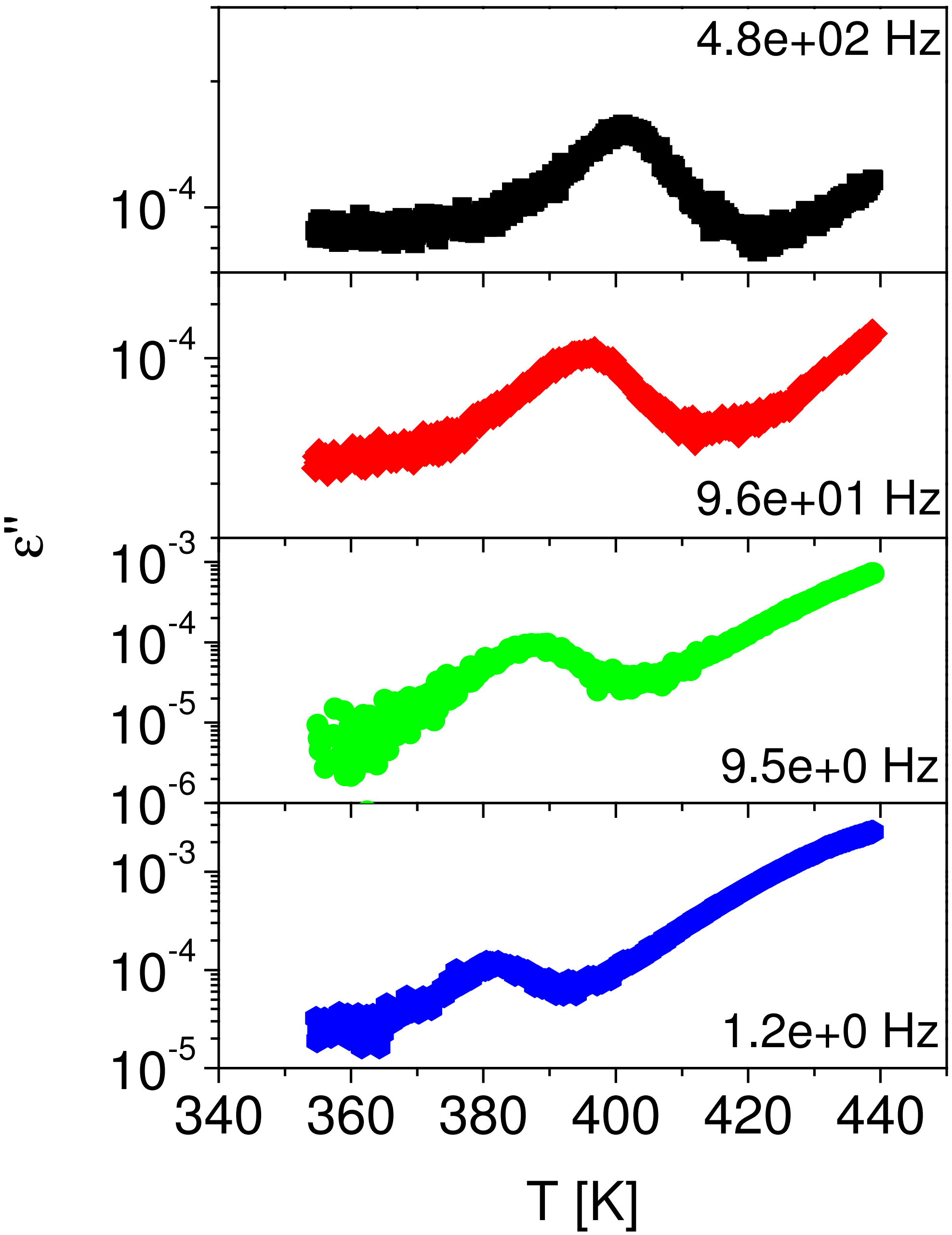
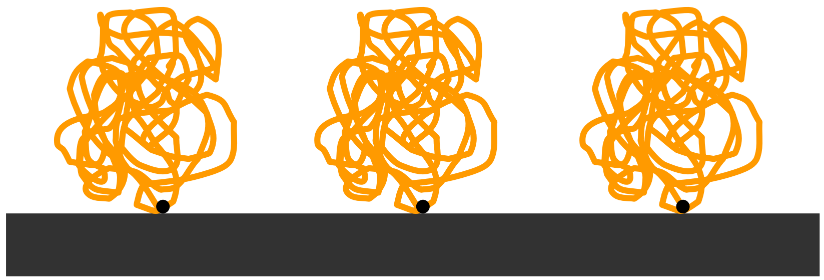
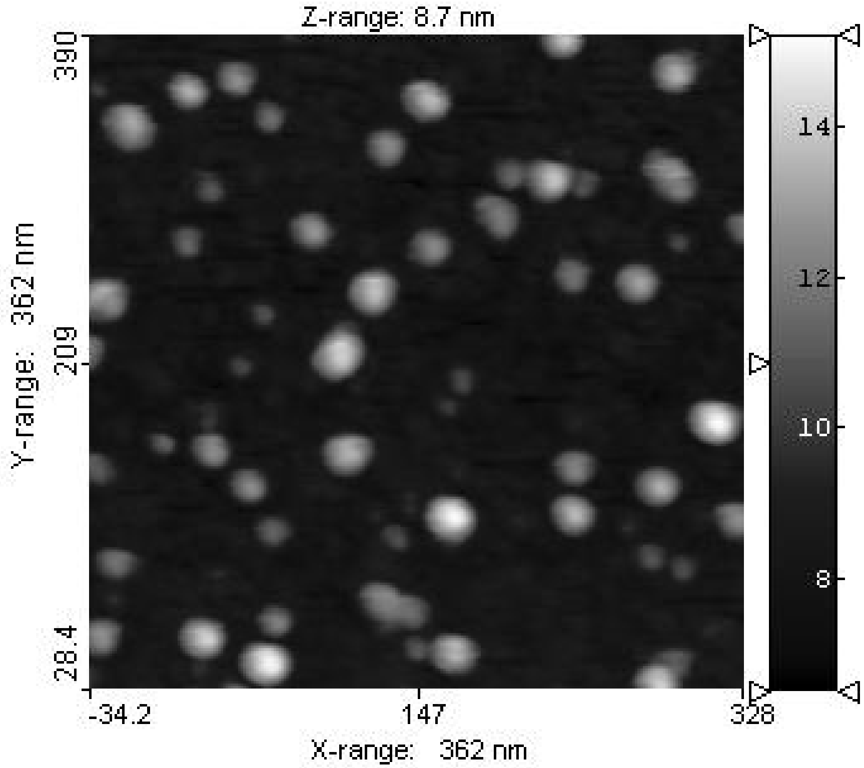


Individually recognizable polymer coils (P2VP)

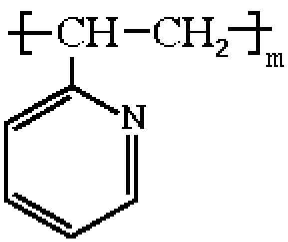


Grafted polymer chains (P2VP)





(Physically) grafted polymer chains
- strongly asymmetric diblock copolymers-

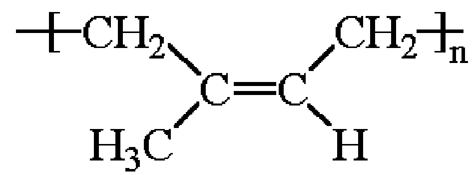


Poly(2-VinylPyridine)

M_W = 28500

m = 260

T_g ~ 377K



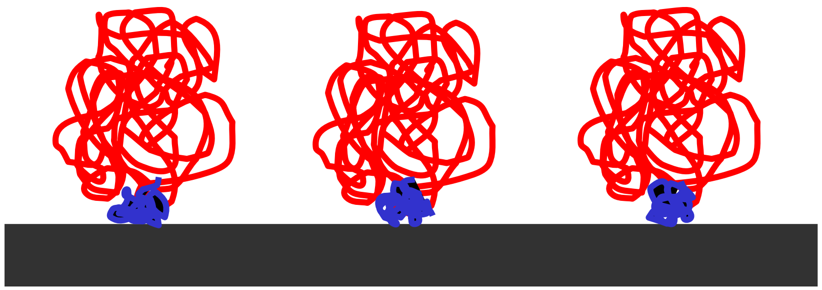
PolyIsoprene

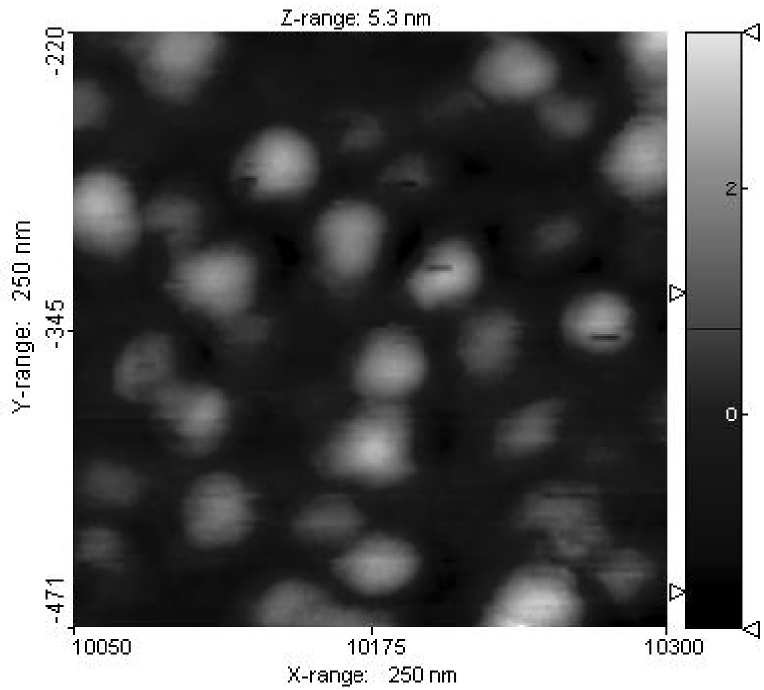
M_W = 285000

n = 4040

T_g ~ 206K

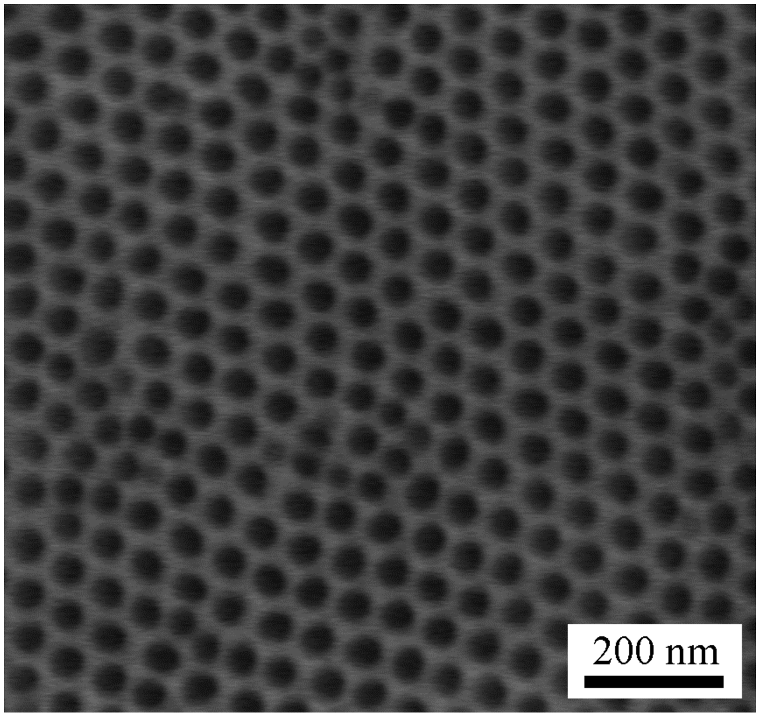
(Physically) grafted polymer chains (P2VP)
- strongly asymmetric diblock copolymers-

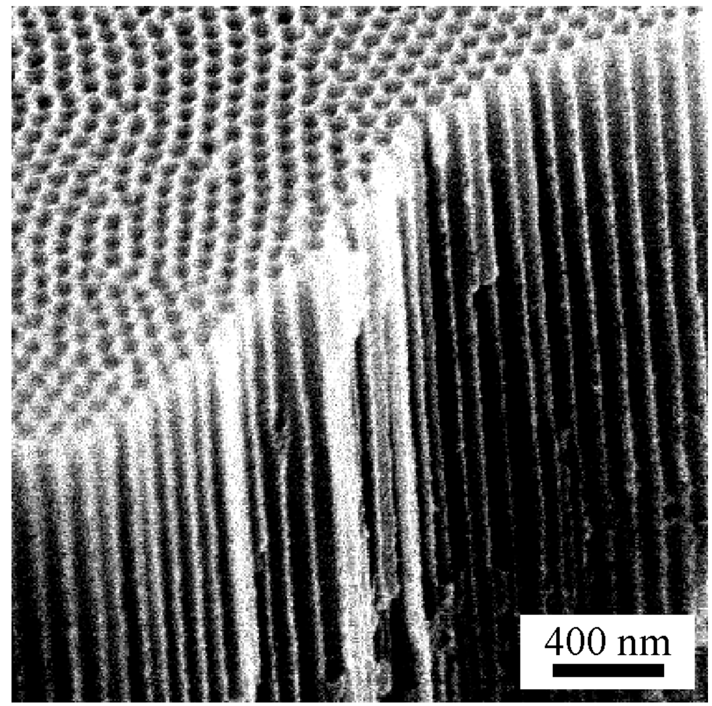




Molecular dynamics during capillary flow in geometrical nanoconfinement

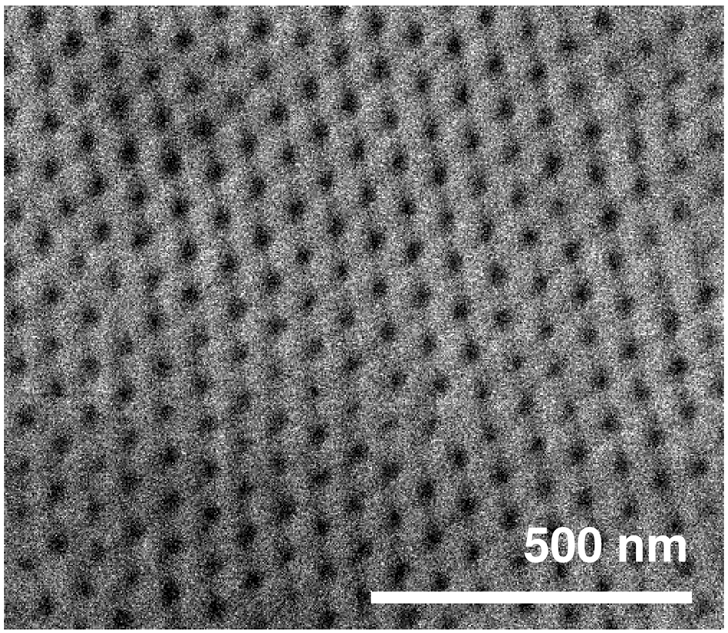
Measurement cells: nano-porous alumina membranes

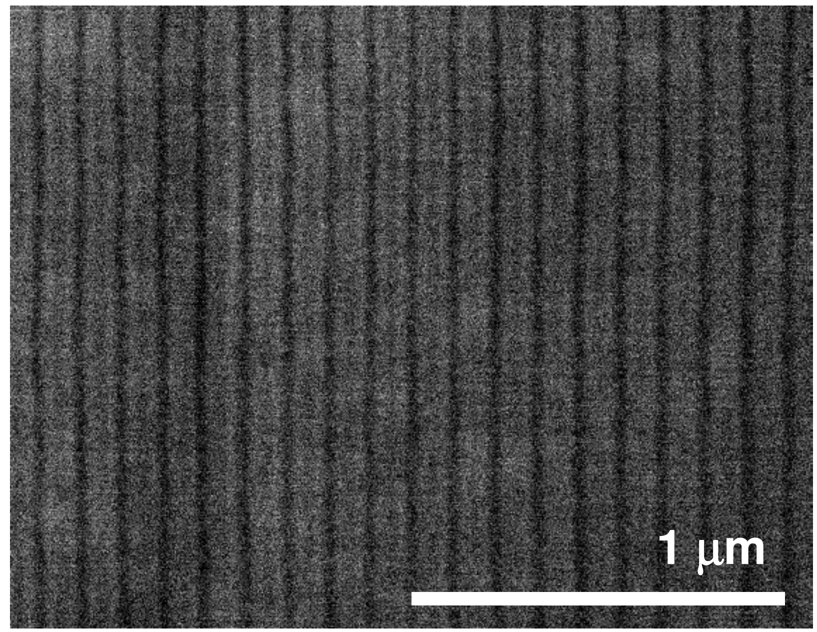




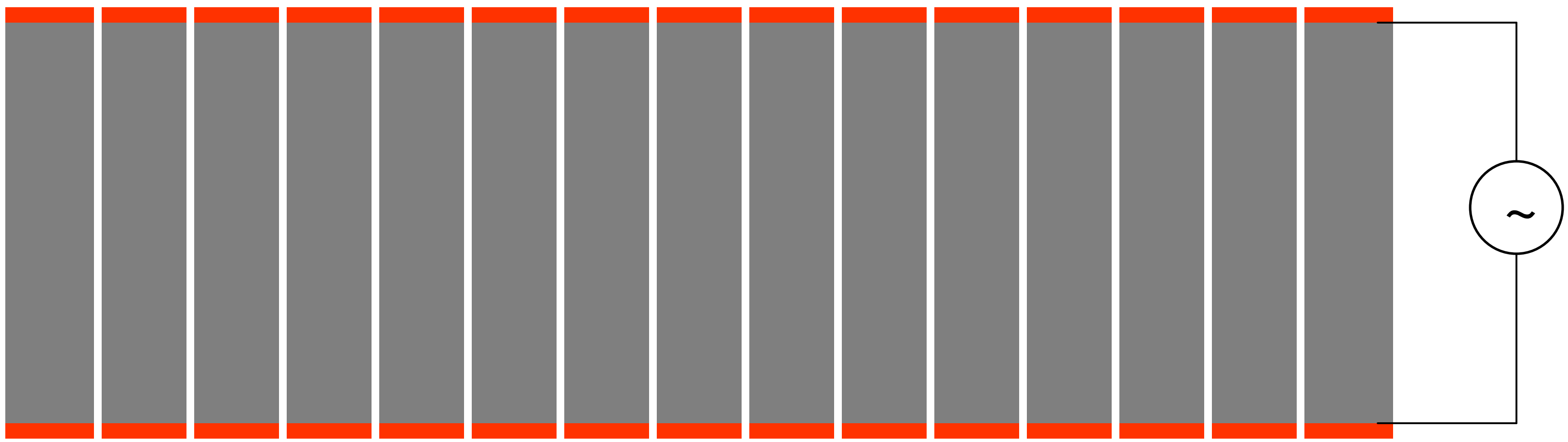
Prepared by electrochemical etching in a two step anodization process.
Pore diameters between 10 nm ... 400 nm, narrow distribution.

Measurement cells: nano-porous alumina membranes





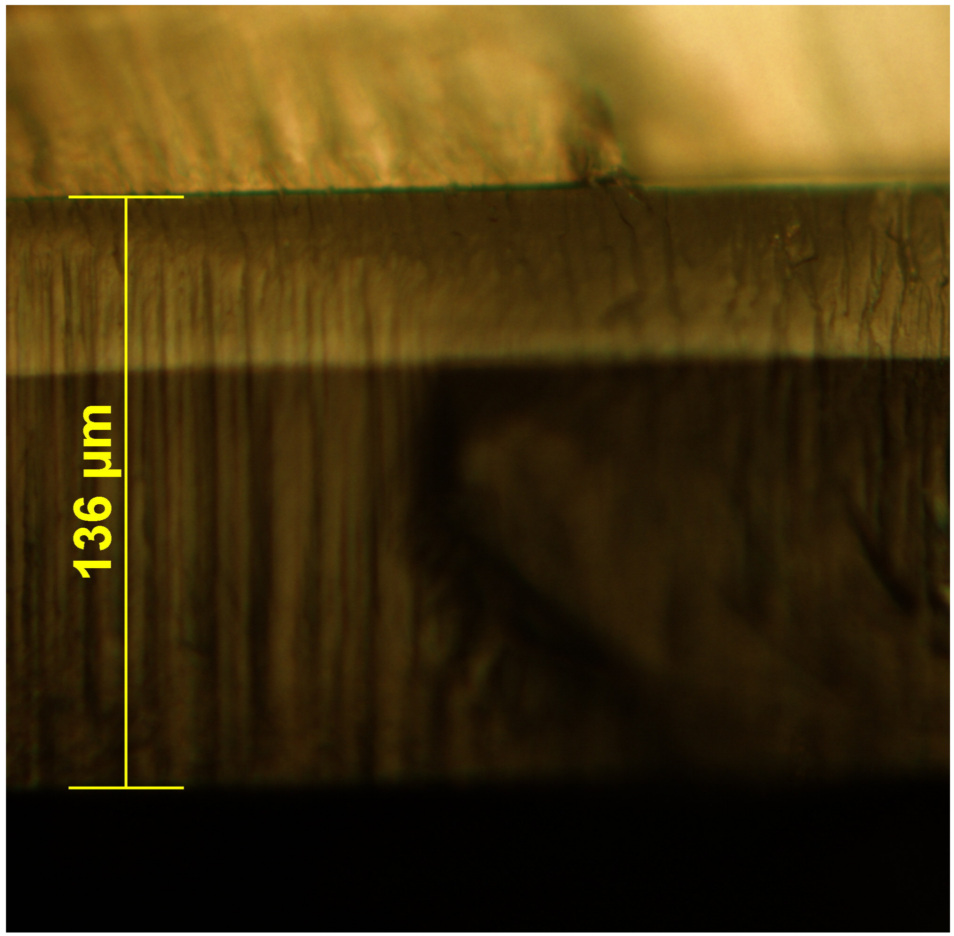
Using nanoporous membranes as dielectric cells



Using nanoporous membranes as dielectric cells

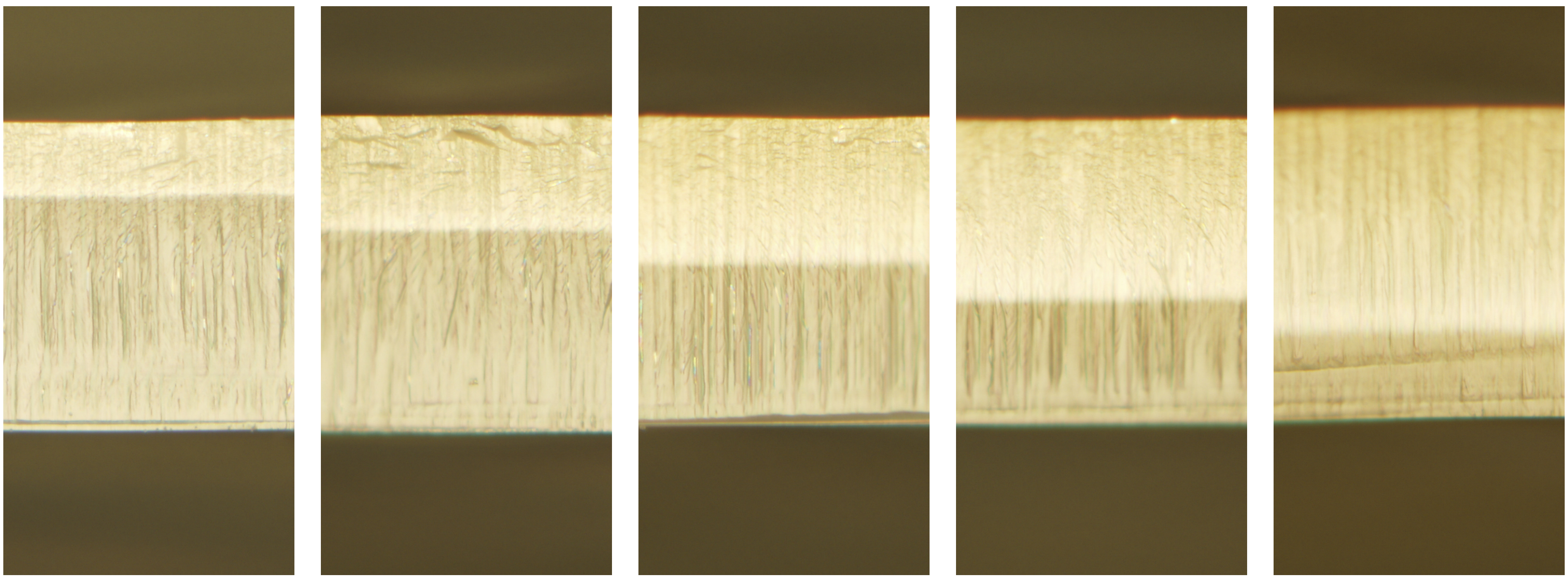
Using nanoporous membranes as dielectric cells

Capillary flow of polystyrene (Mw=105k) into nanoporous alumina membranes (15 nm pore diameter) after 48 h of annealing at 190 C

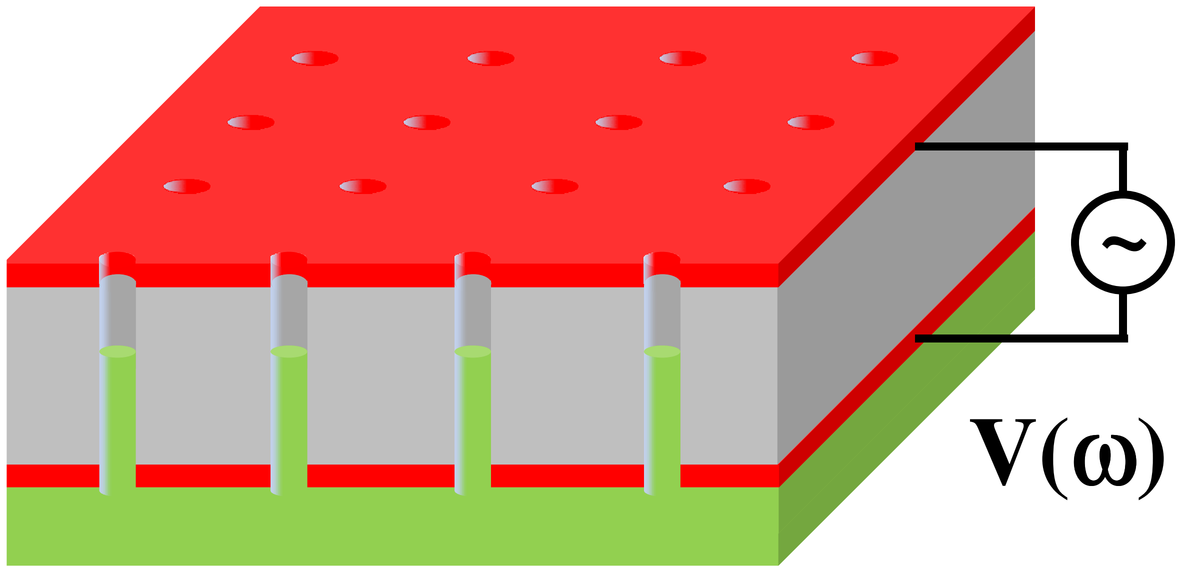


Capillary flow of PS-32k into nanoporous membranes (112 μm thickness, 15 nm pores, 156 C)

6h15min 12h15min 20h15min 30h55min 43h09min

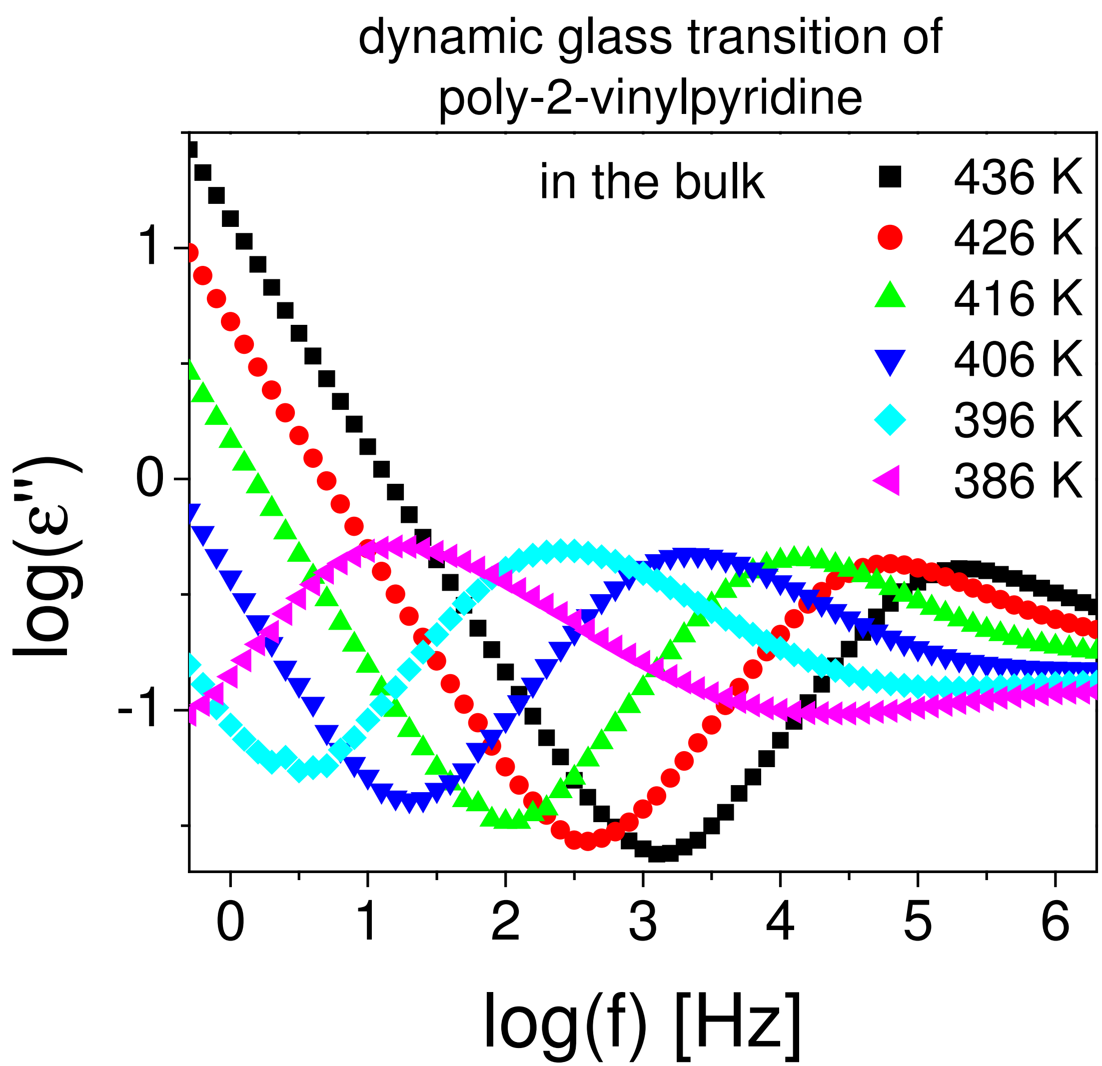


Polymer nanofluidics: measurement cell



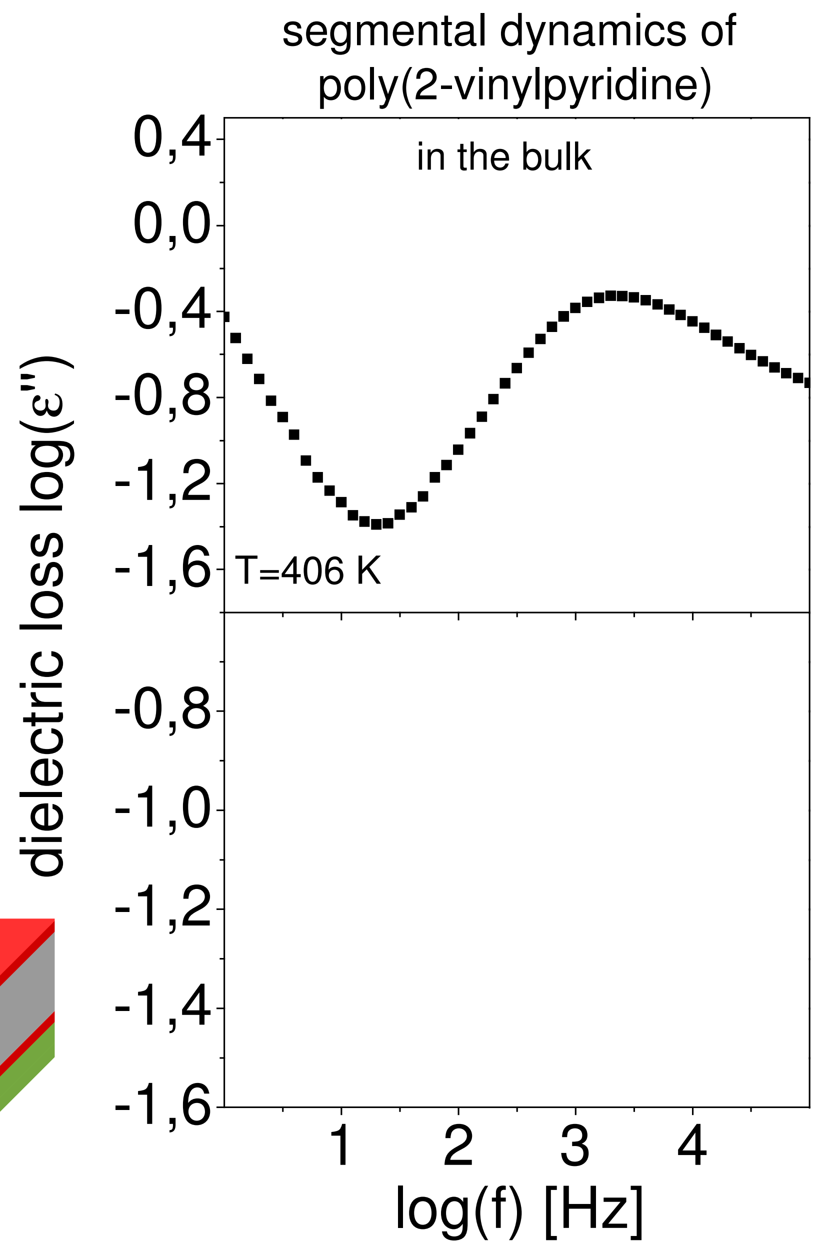
Thin electrodes of gold are sputtered on both sides of the nanoporous membranes.

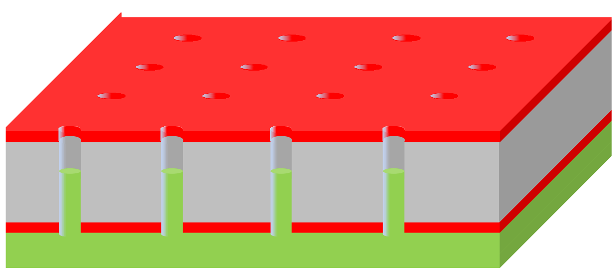
Glassy dynamics of poly-2-vinylpyridine in the bulk
Mw=35,000 g/mol



Segmental dynamics during capillary flow

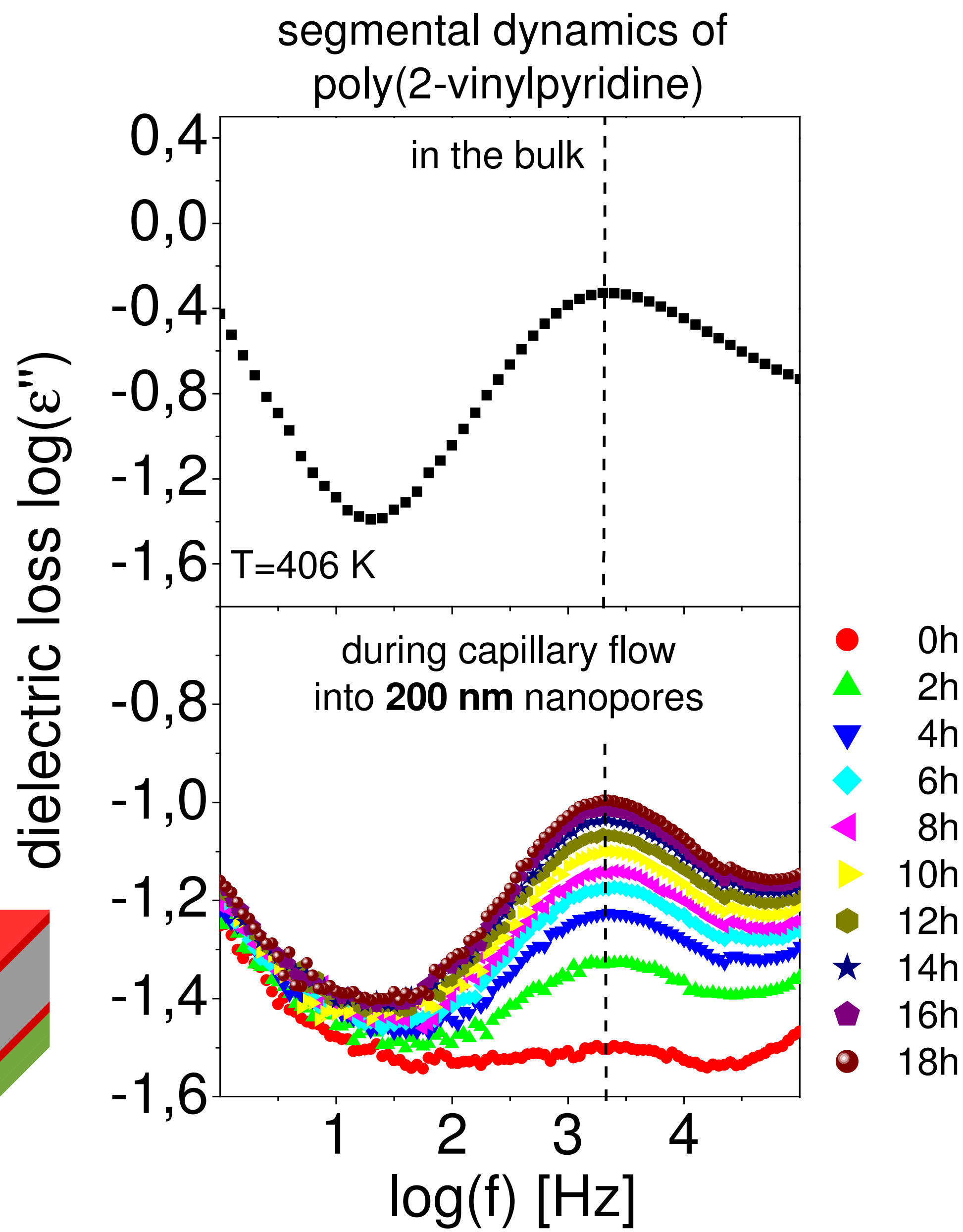
- 200 nm nanopores -

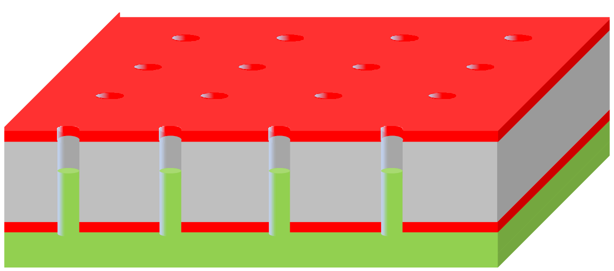




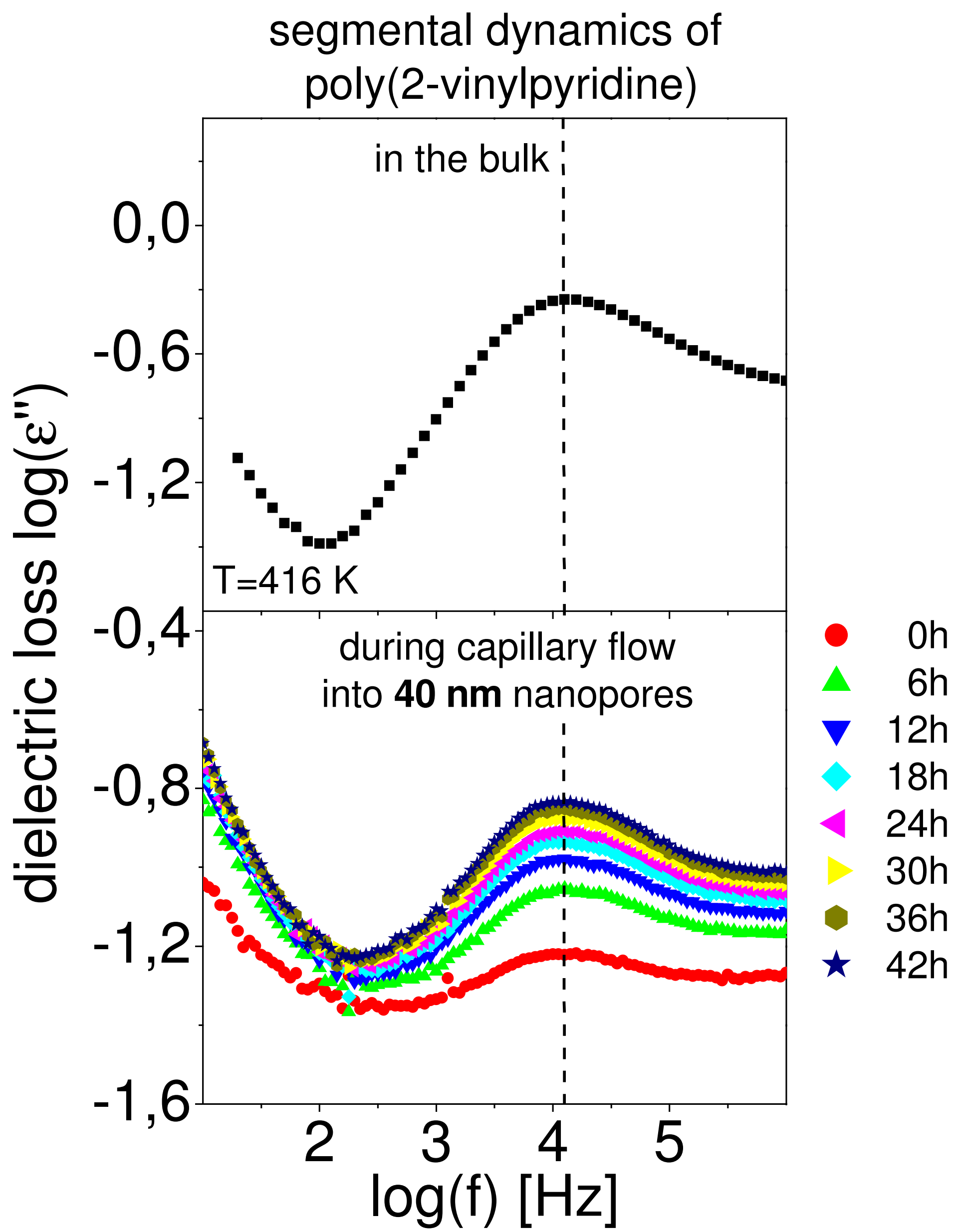
Segmental dynamics during capillary flow

- 200 nm nanopores -



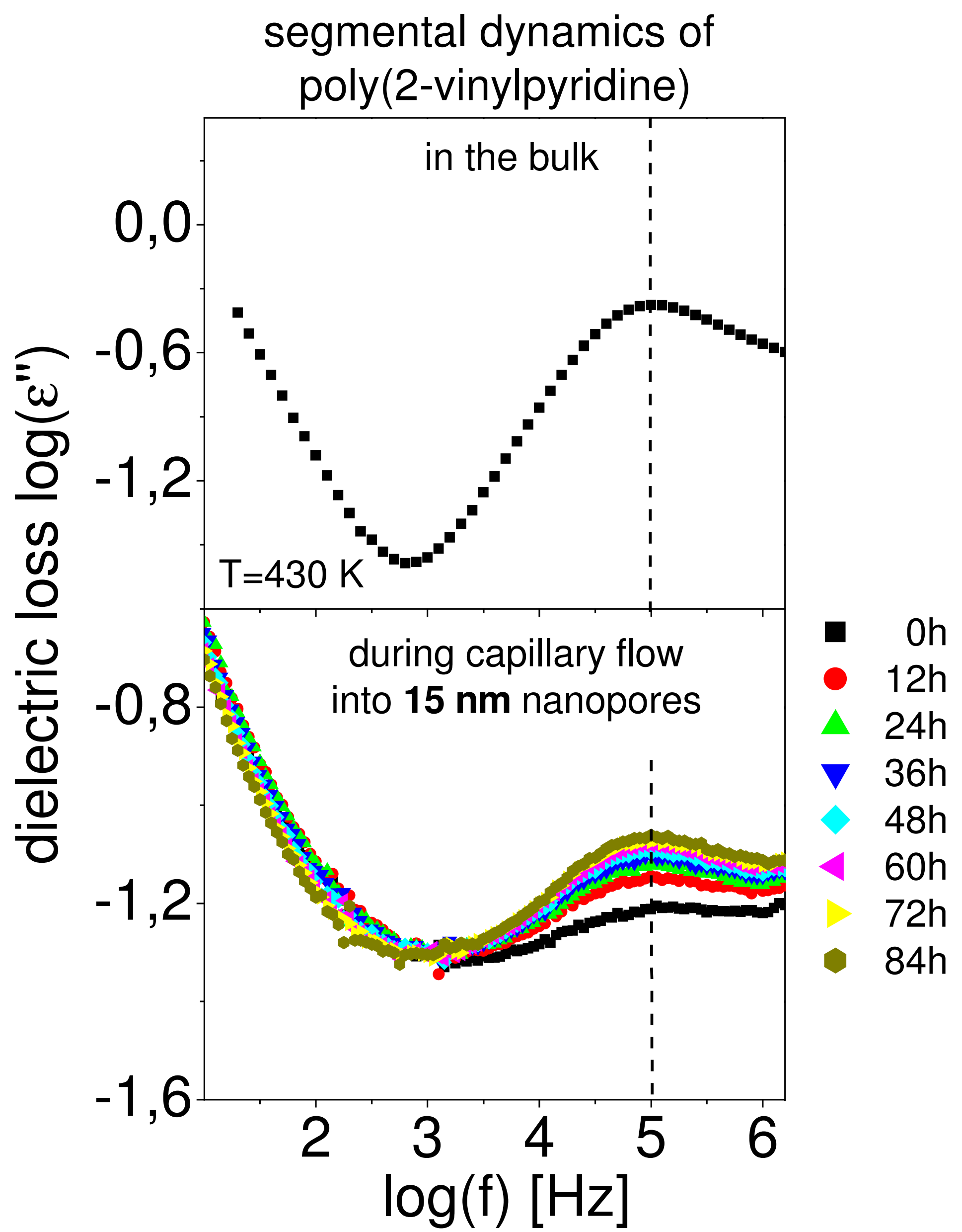


Segmental dynamics during capillary flow
- 40 nm nanopores -



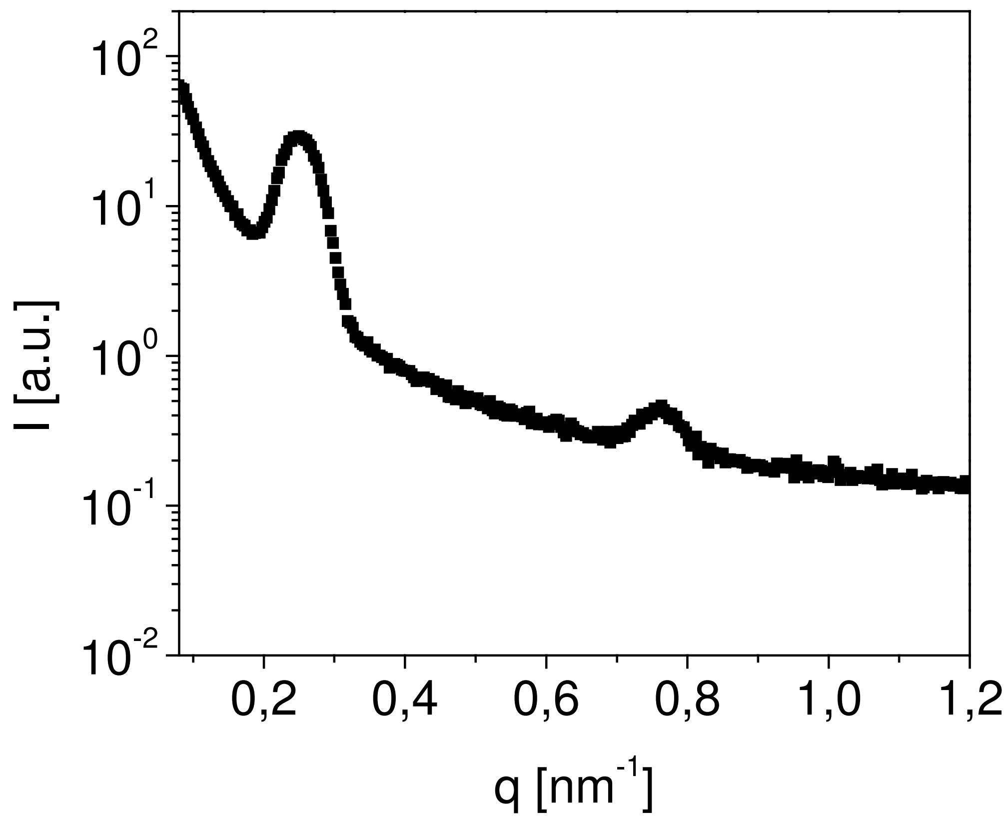
Segmental dynamics during capillary flow

- 15 nm nanopores -



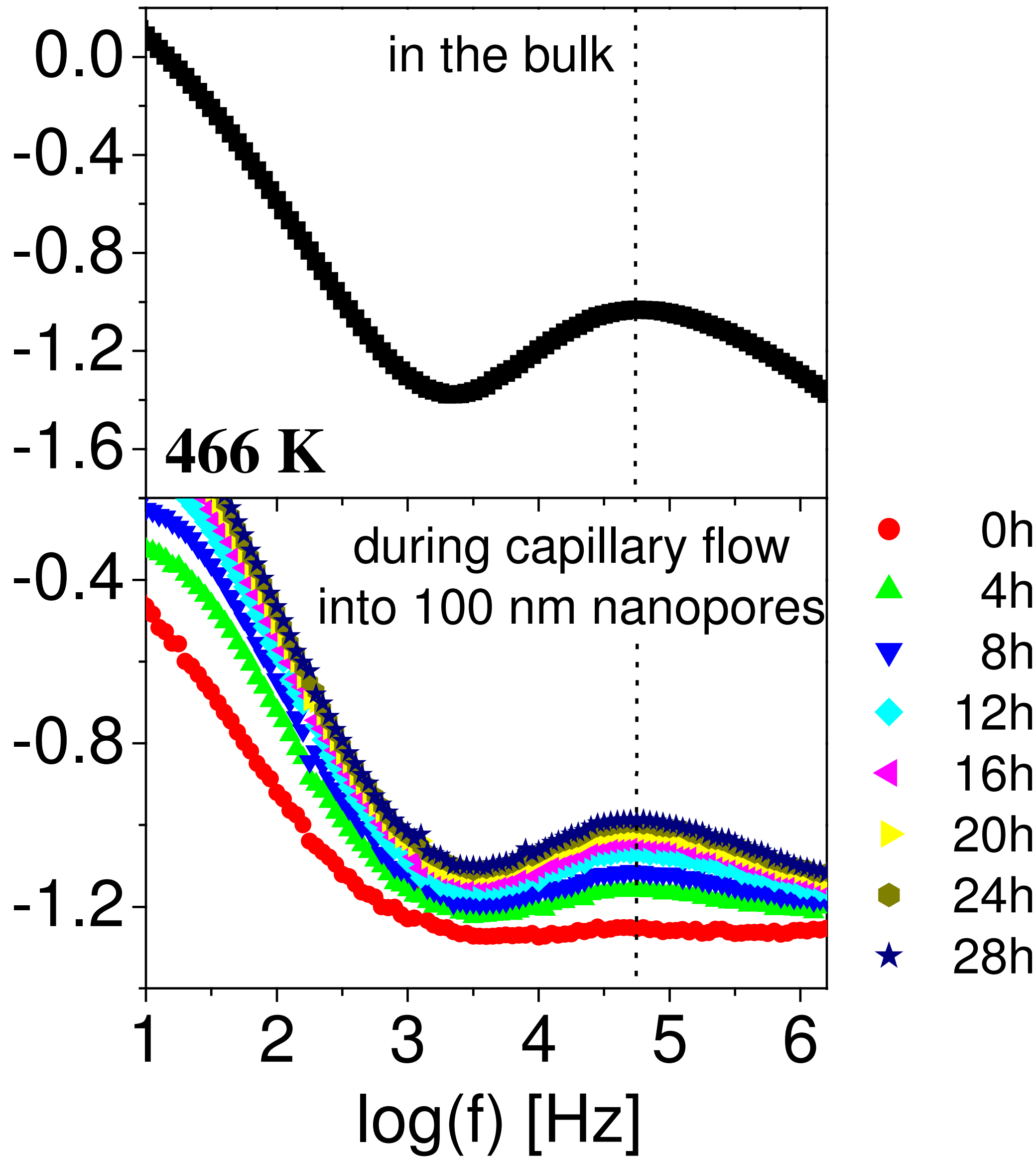
Capillary flow of phase separated diblock copolymers.

PS-b-P4VP (10k-b-10k)
- measurements by SAXS -

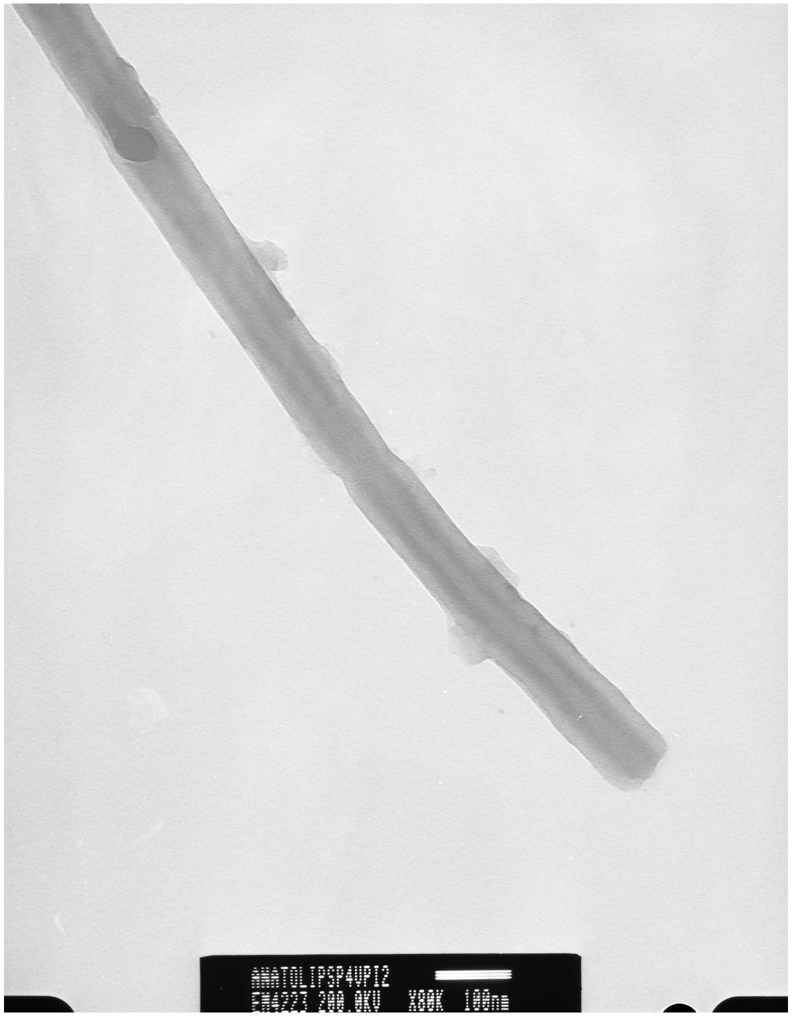


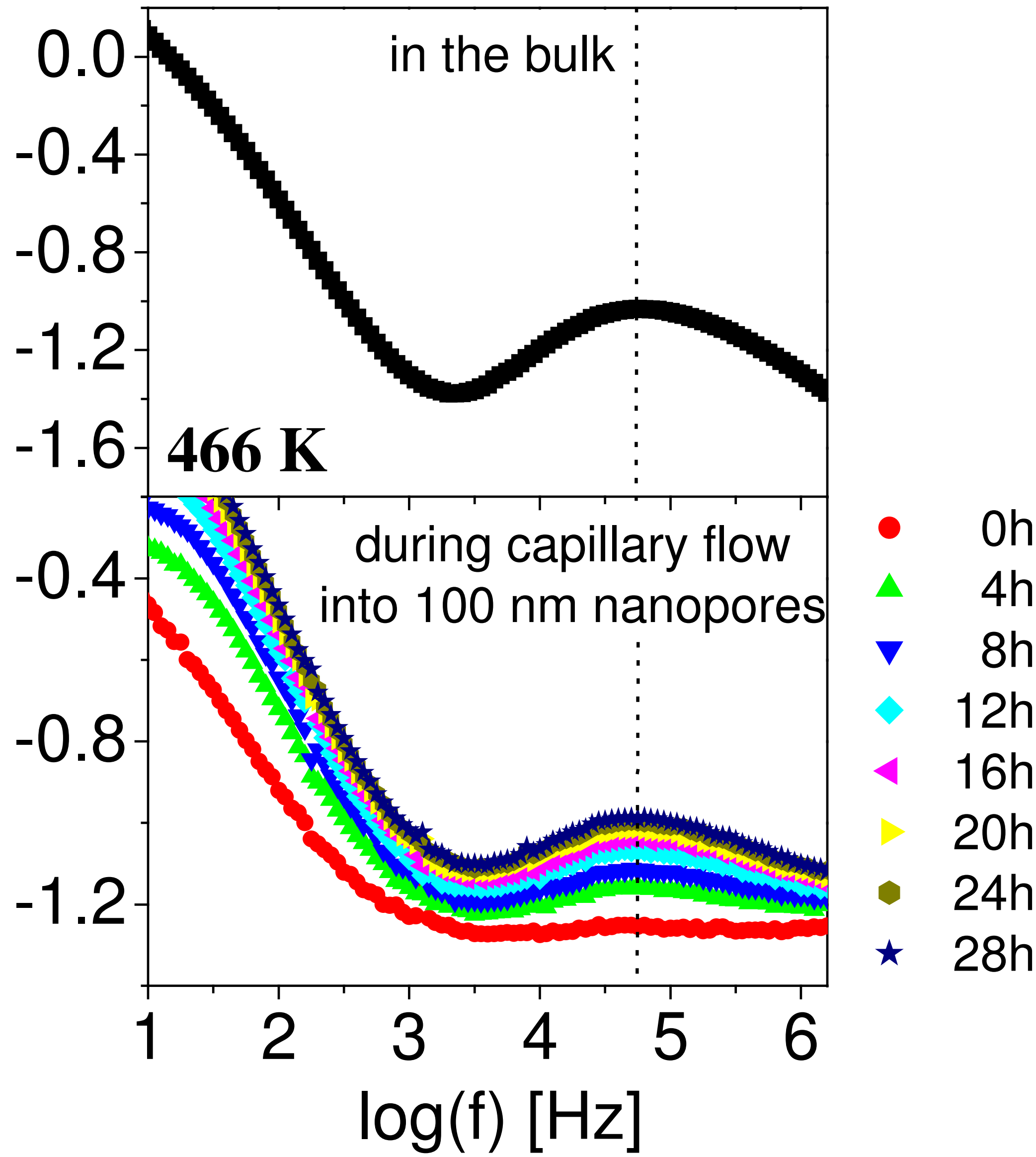
Lamella structure, domain spacing ~ 25 nm.

Segmental dynamics of phase separated PS-b-P4VP during capillary flow

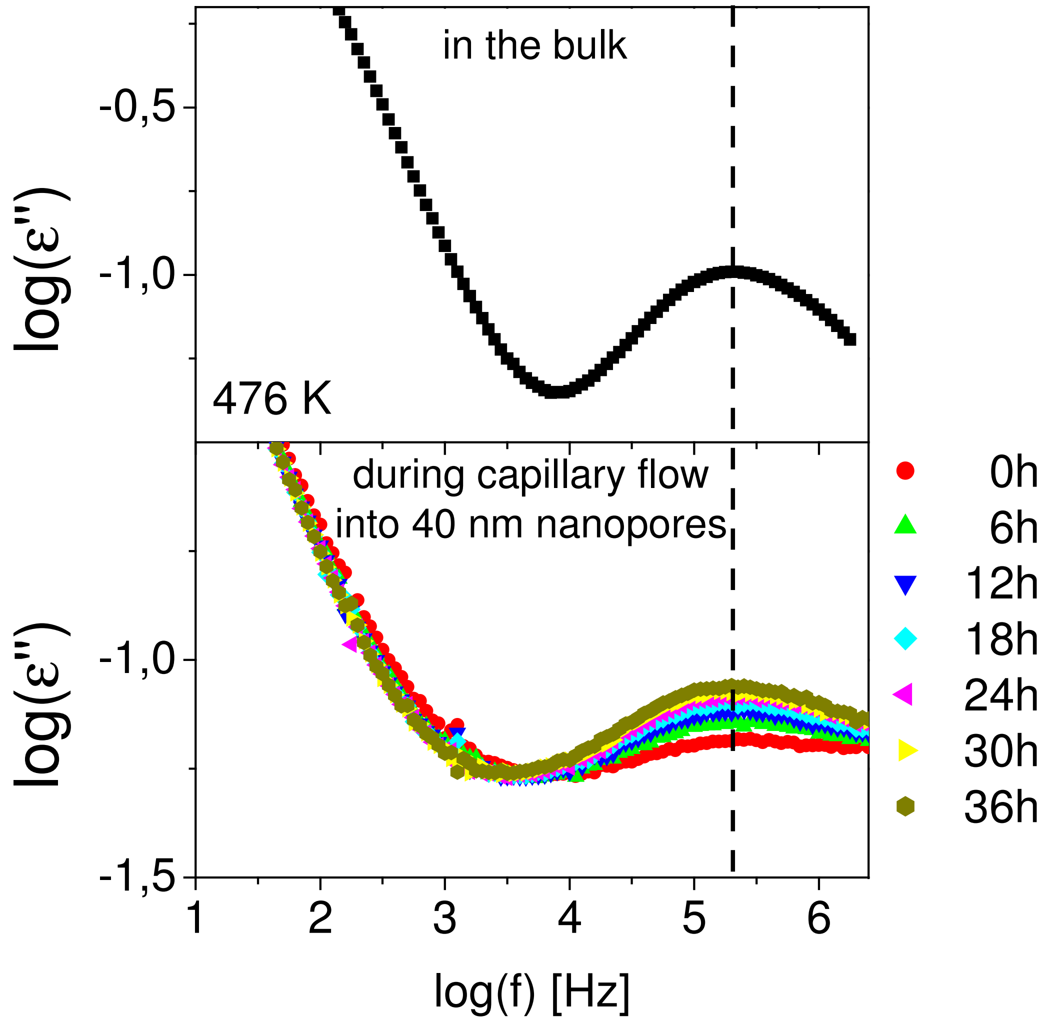


Segmental dynamics of phase separated PS-b-P4VP during capillary flow



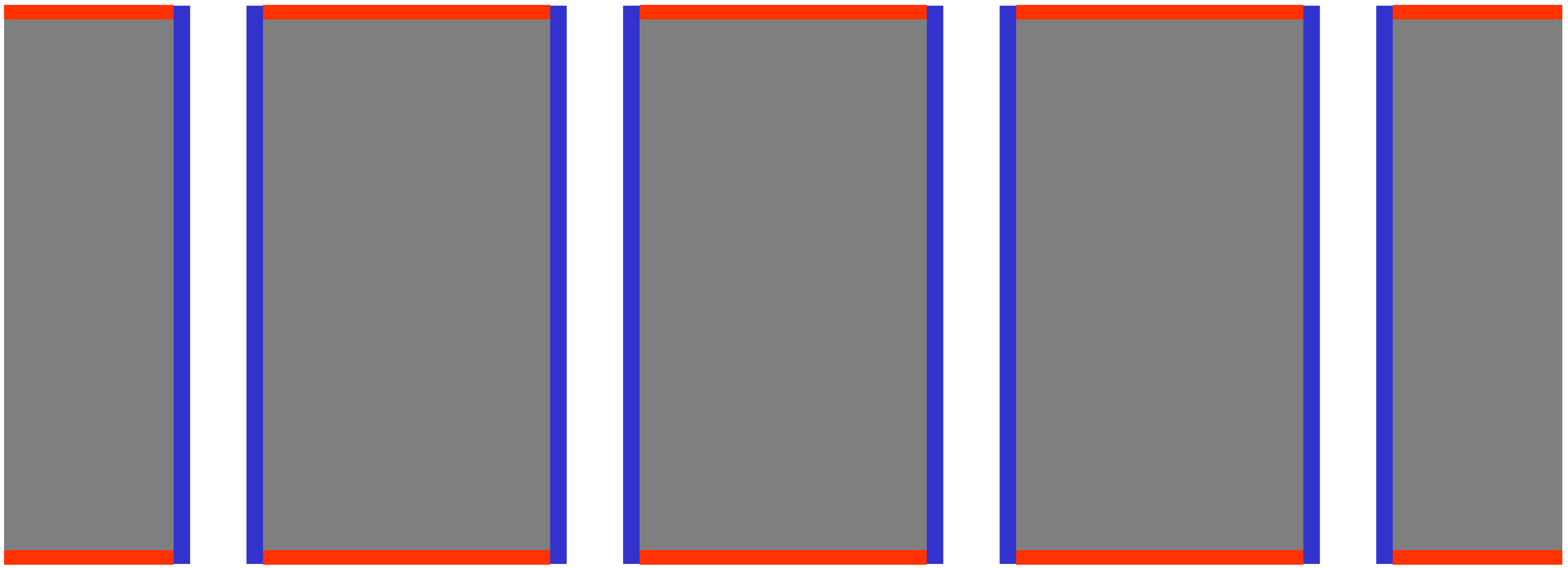


Segmental dynamics of phase separated PS-b-P4VP during capillary flow

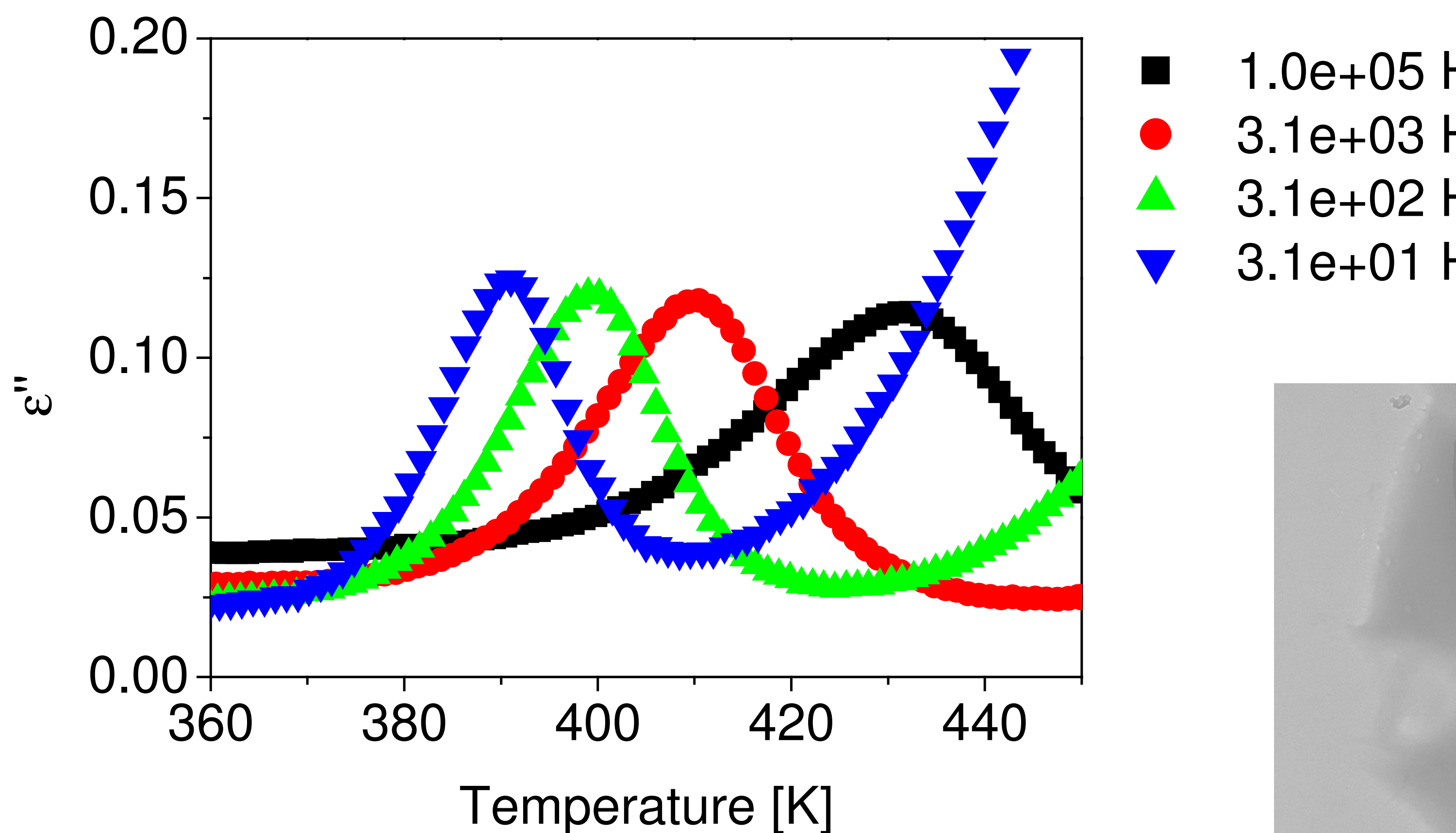


Glass transition of polymer nanotubes

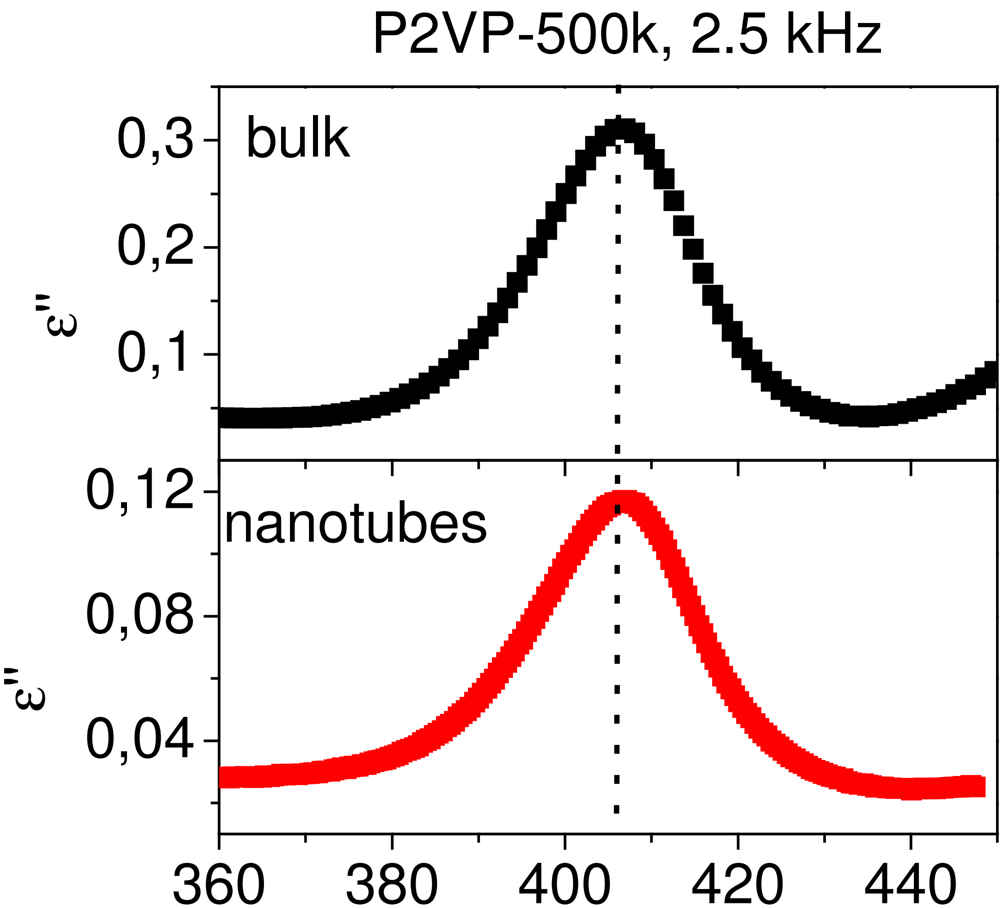
Polymer nanotubes by solvent casting from diluted solutions



P2VP-500k nanotubes in 200 nm pores (solvent casting, 5w%, chloroform solution)



P2VP-500k in the bulk and confined in nanotubes



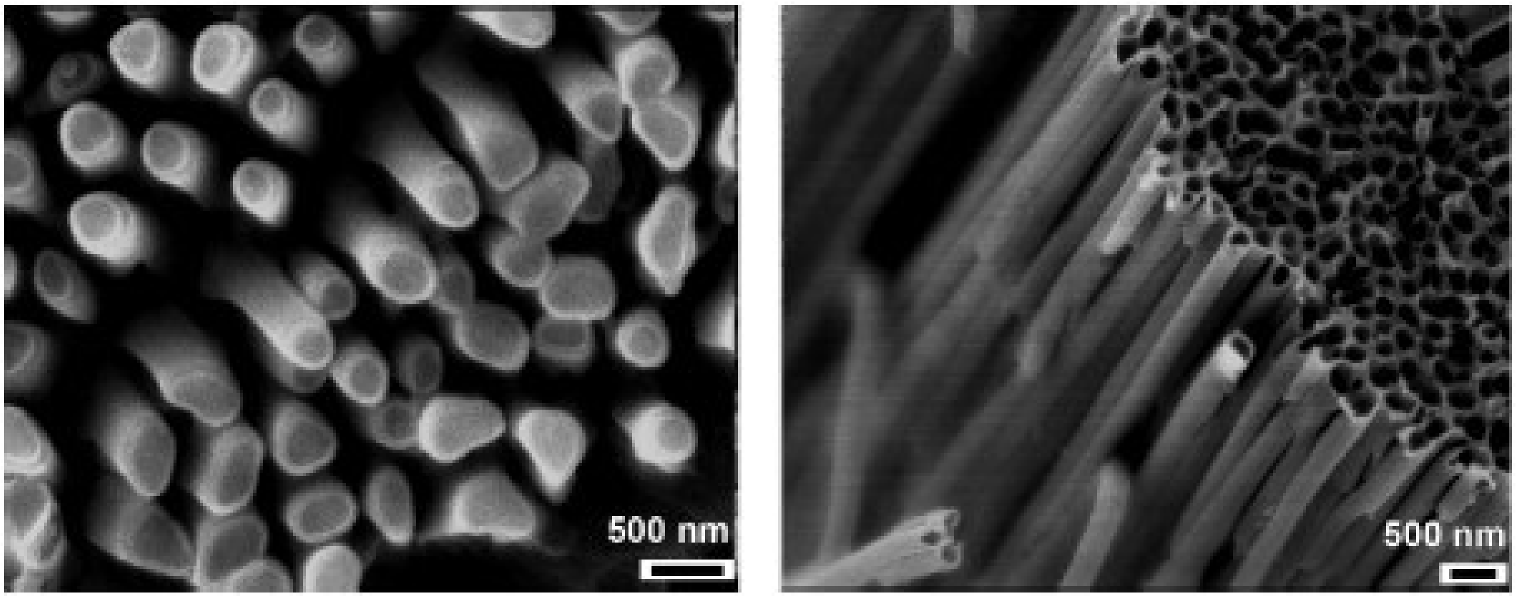
NANO LETTERS

Letter

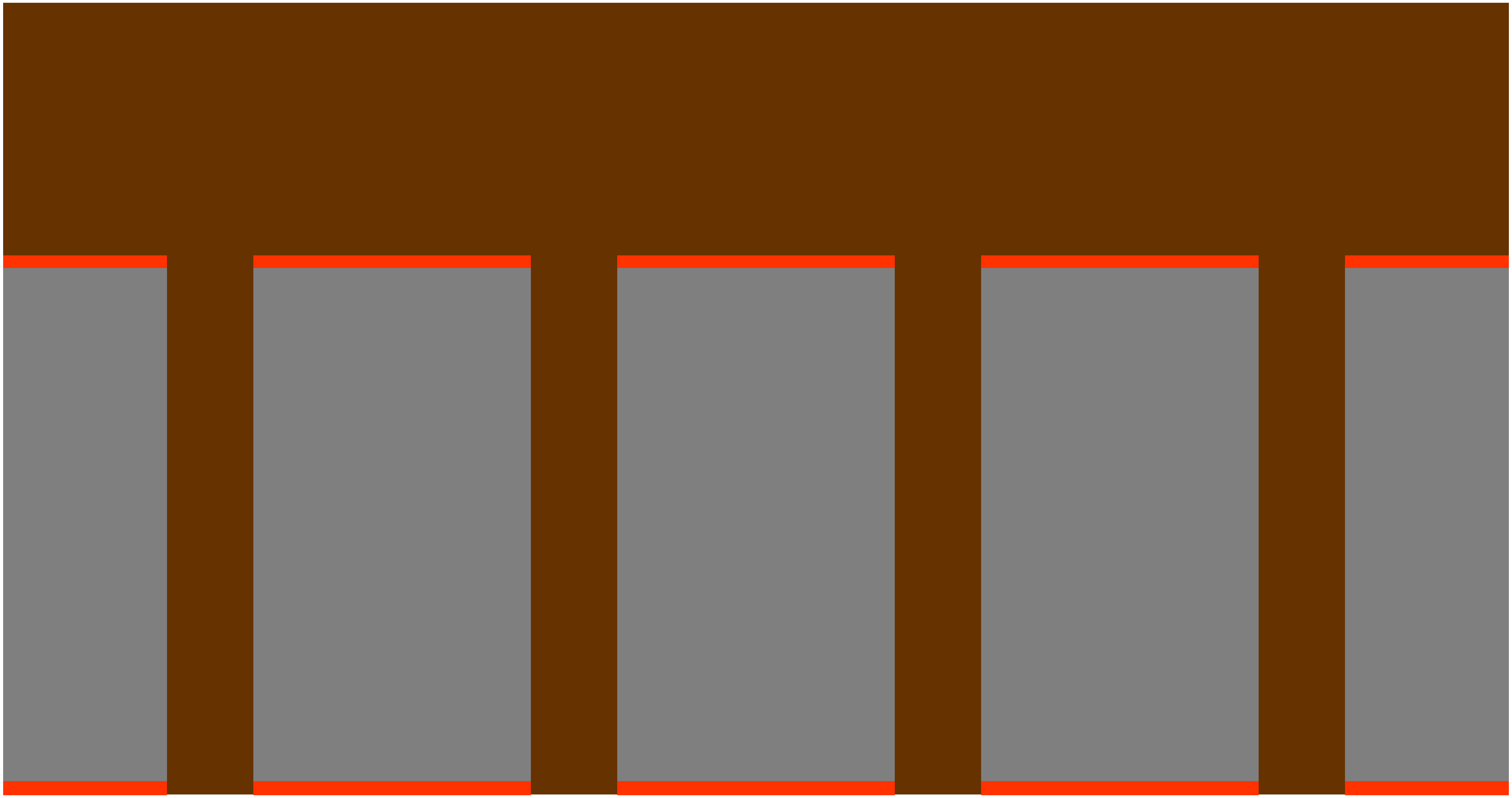
Wetting Transition in Cylindrical Alumina Nanopores with Polymer Melts

Mingfu Zhang, Priyanka Dobriyal, Jiun-Tai Chen, and Thomas P. RussellJessica OlmoAurora Merry

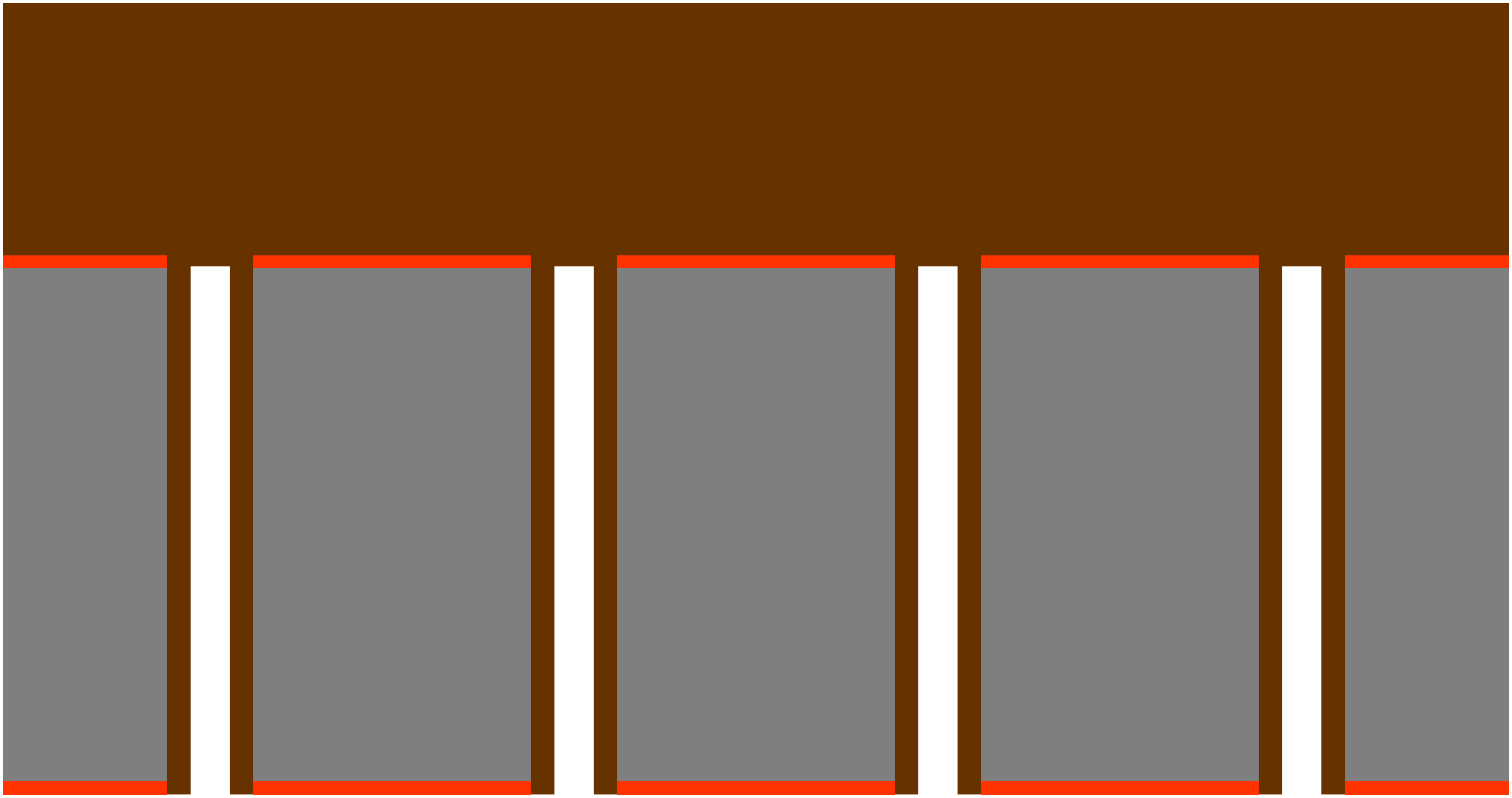
Nano Lett., **2006**, 6 (5), 1075-1079 • DOI: 10.1021/nl060407n



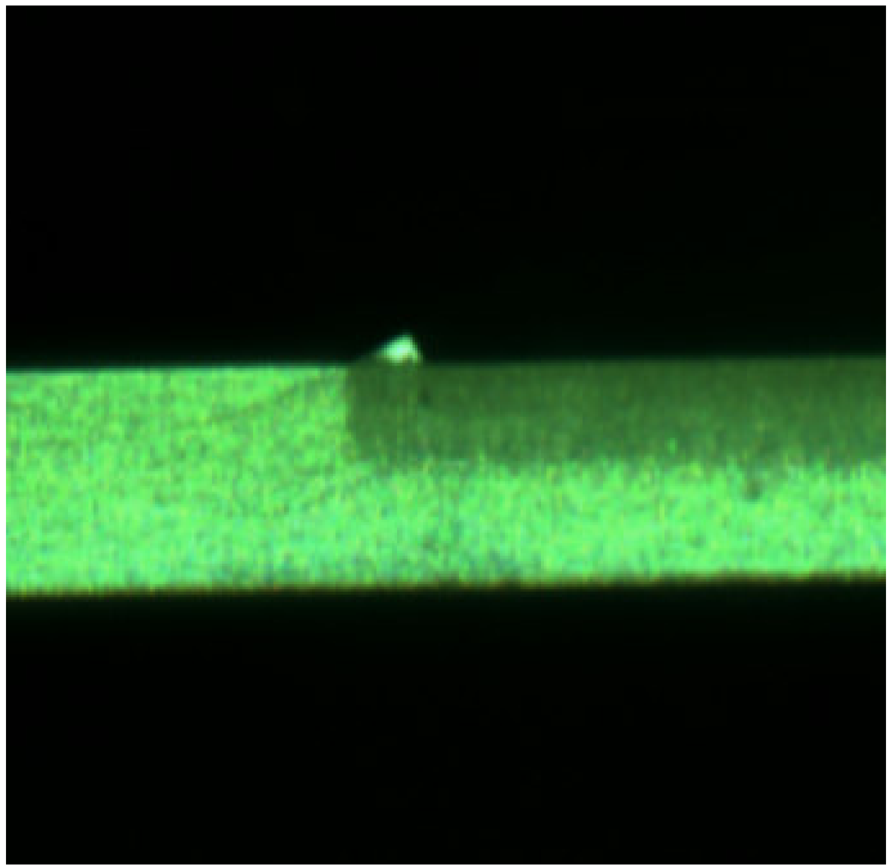
Polymer nanotubes by wetting



Polymer nanotubes by wetting



Nanotubes of PS-35k by capillary infiltration from the melt (10 sec, 205 ^{o}C, 200 nm pores, thickness 64 um)



Nanotubes of PS-35k
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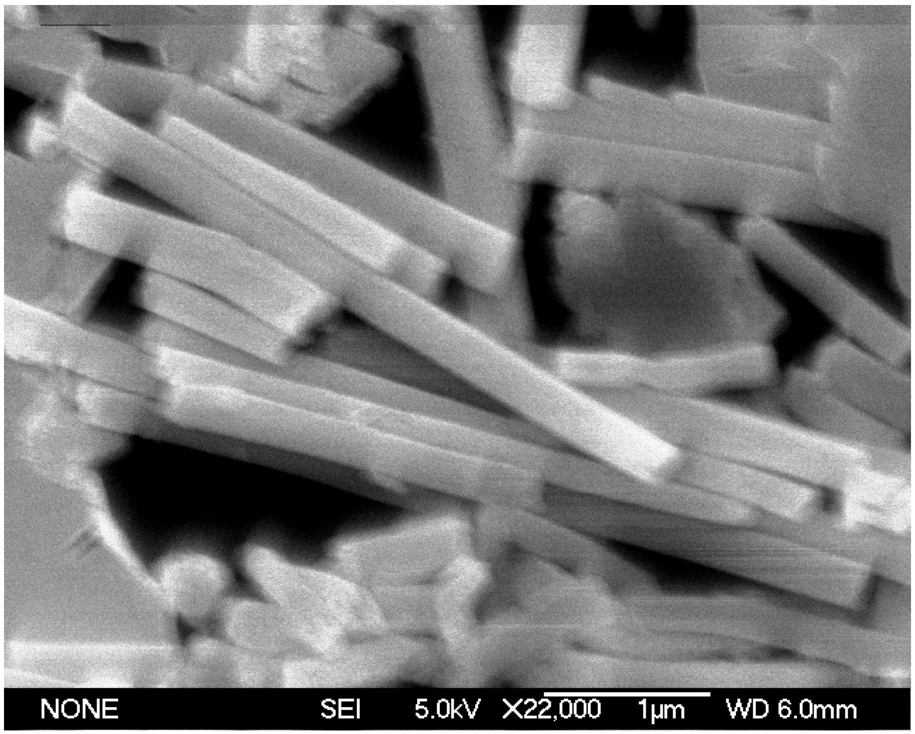

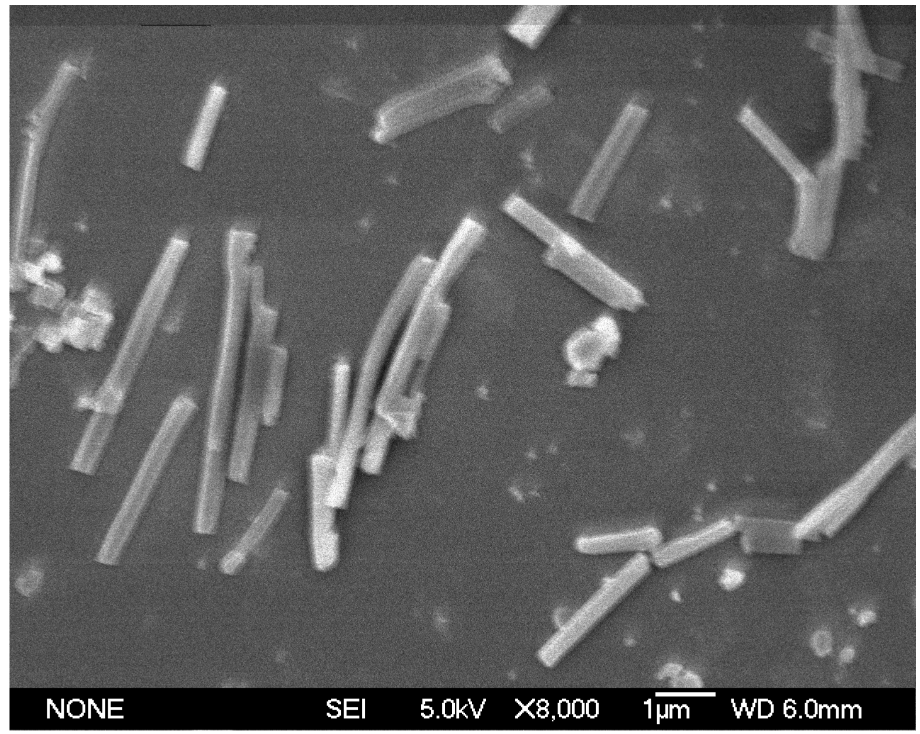

Nanotubes of PS-35k
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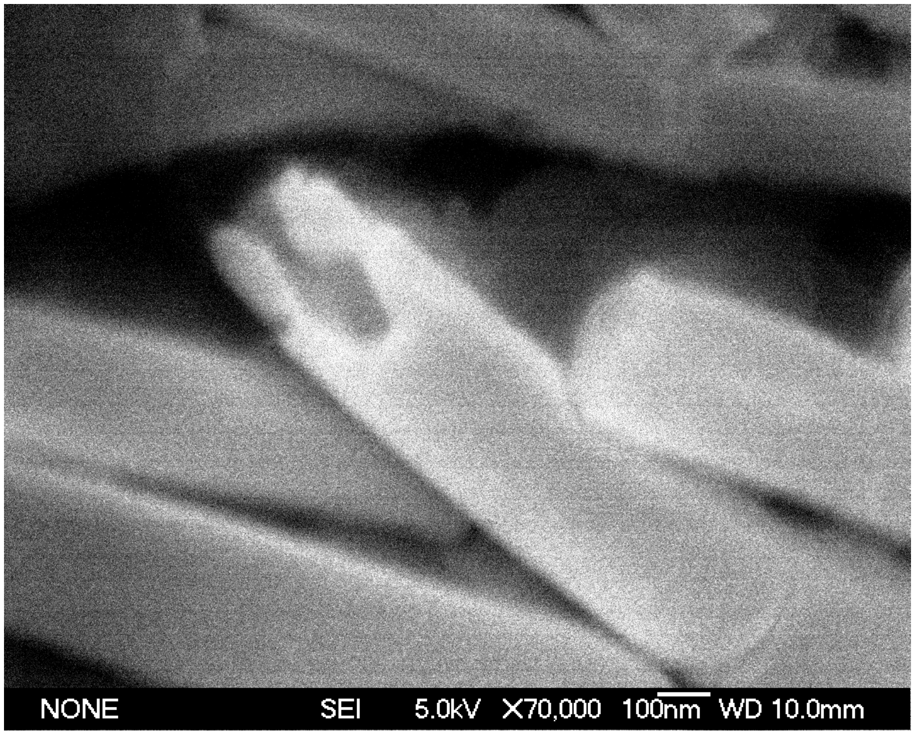
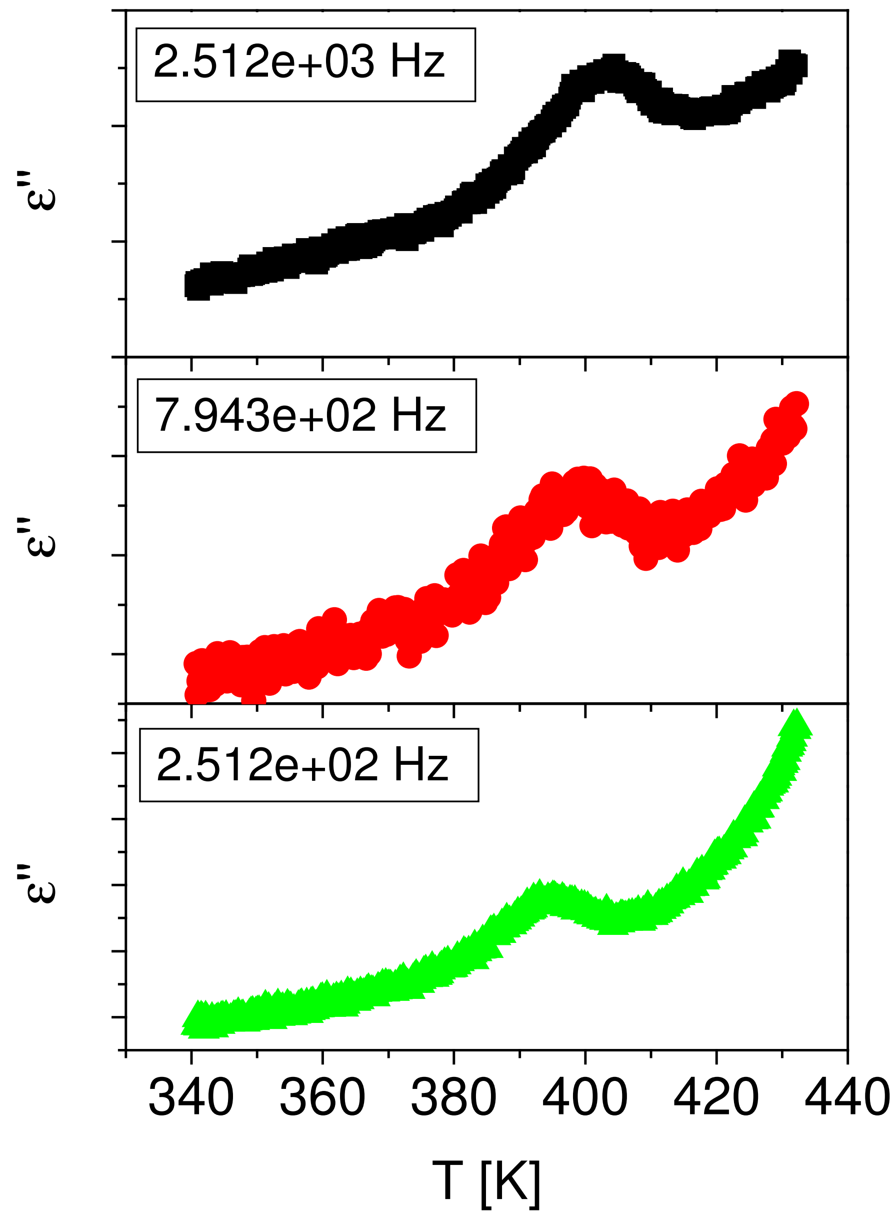
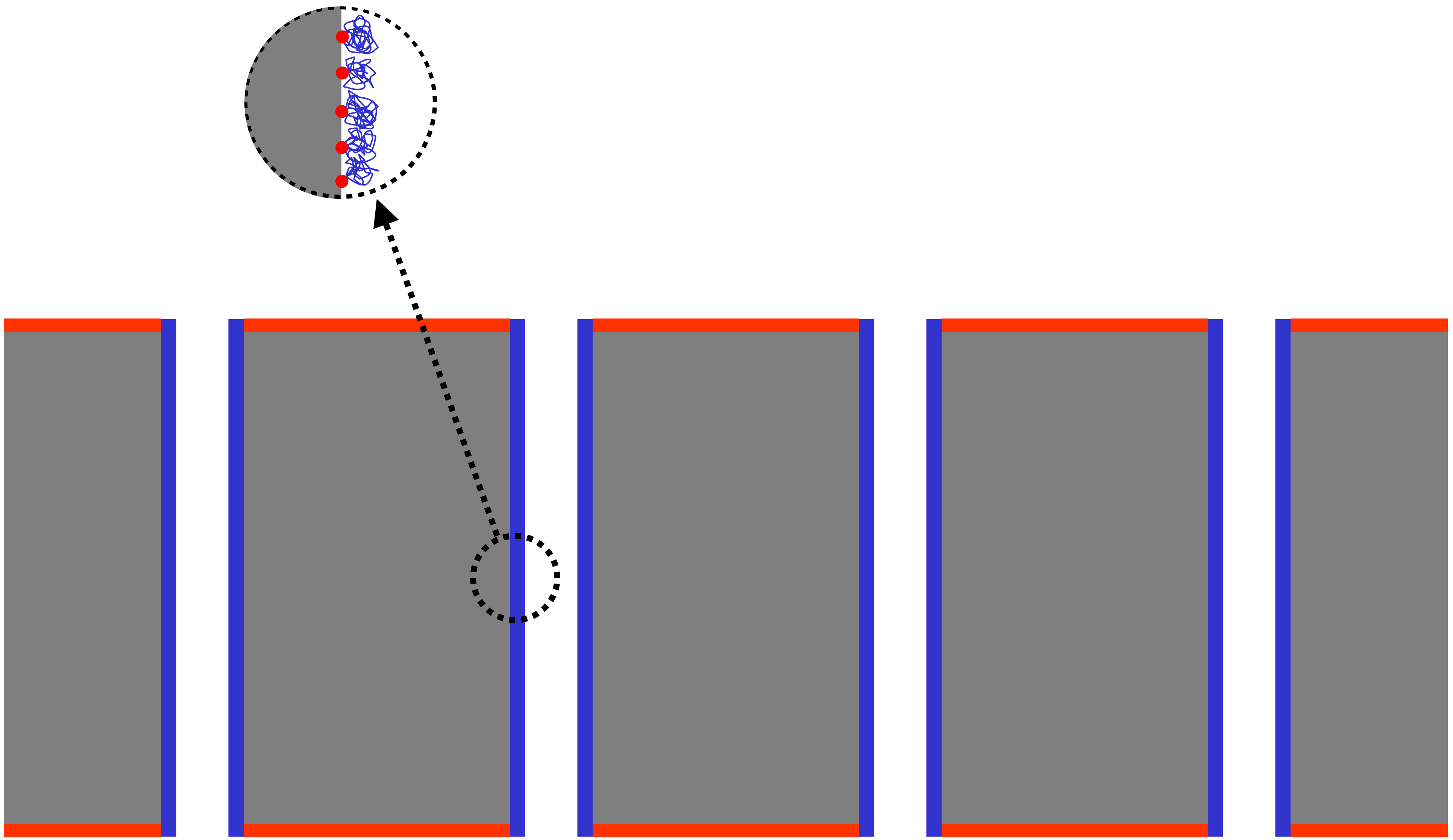


Glass transition of PS-nanotubes(35k)
(capillary infiltration from the melt at 205 ^{o}C)

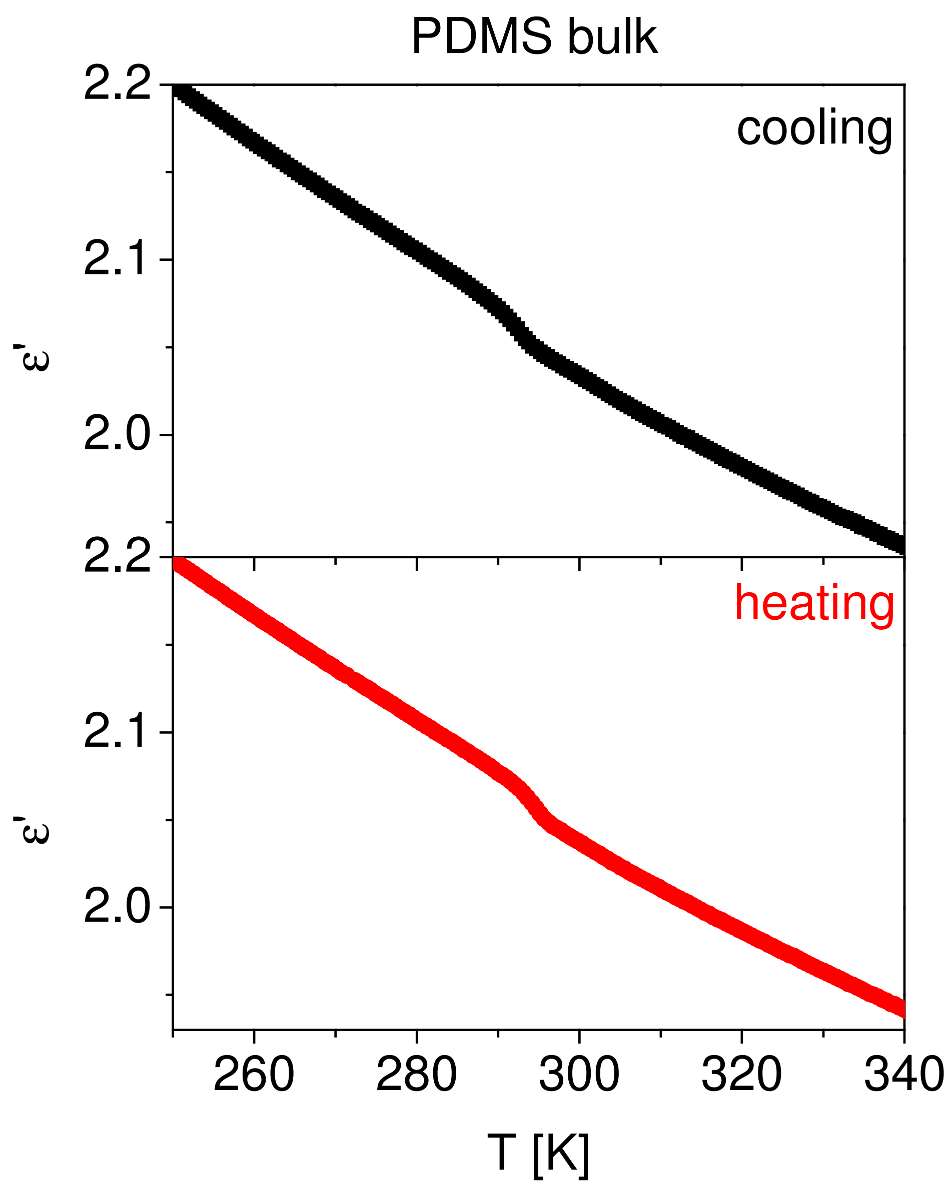


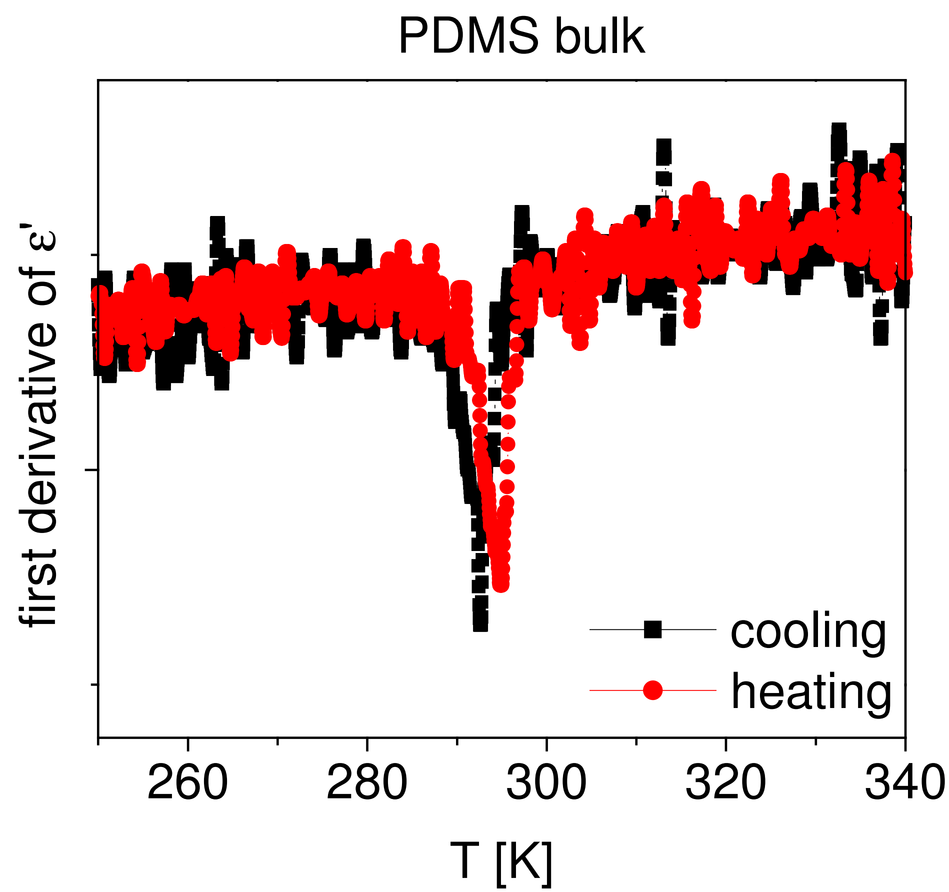
Phase transitions of grafted polymer monolayers

Monolayers of grafted polymers

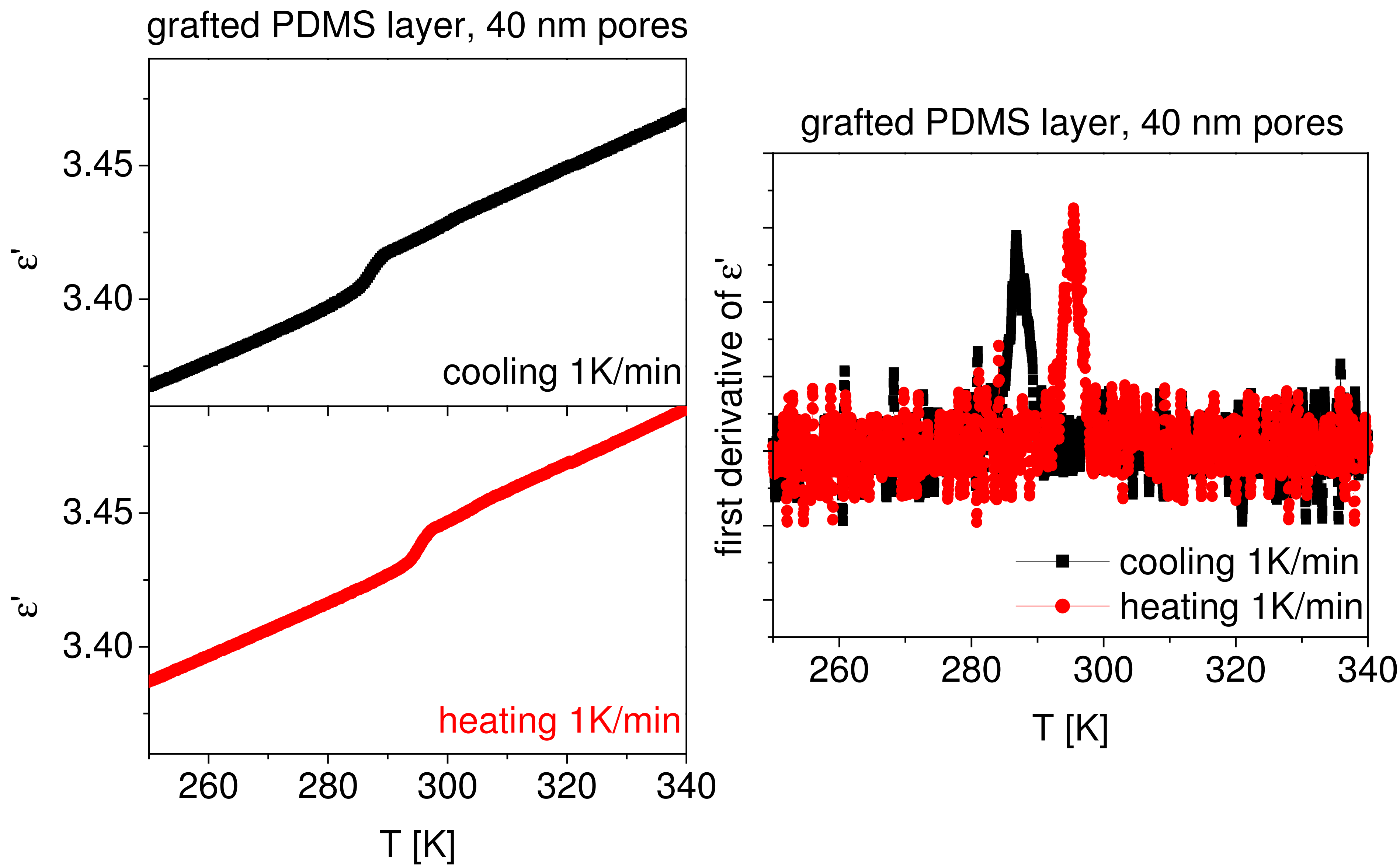


Phase transitions of PDMS-5k in the bulk



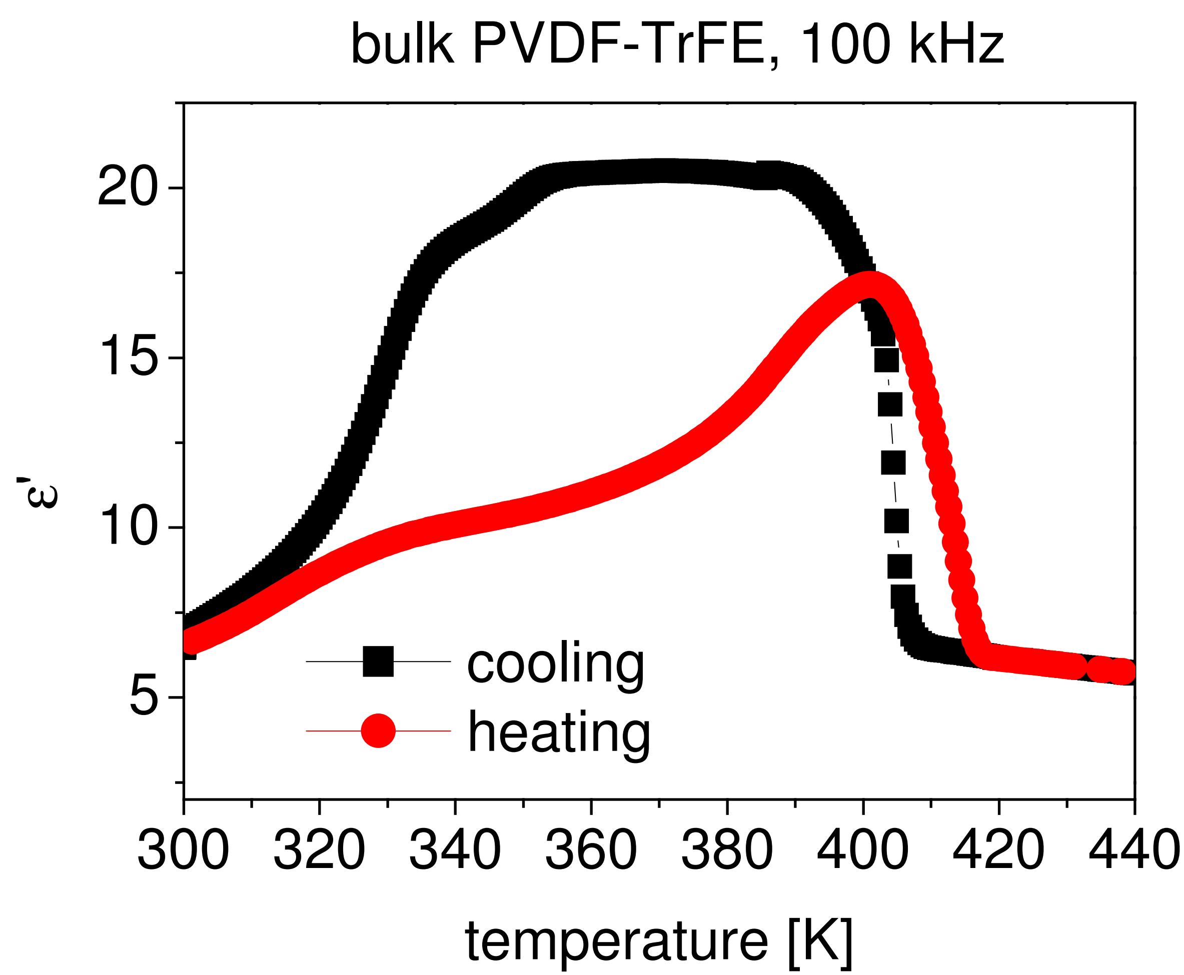


Phase transitions of grafted PDMS-5k



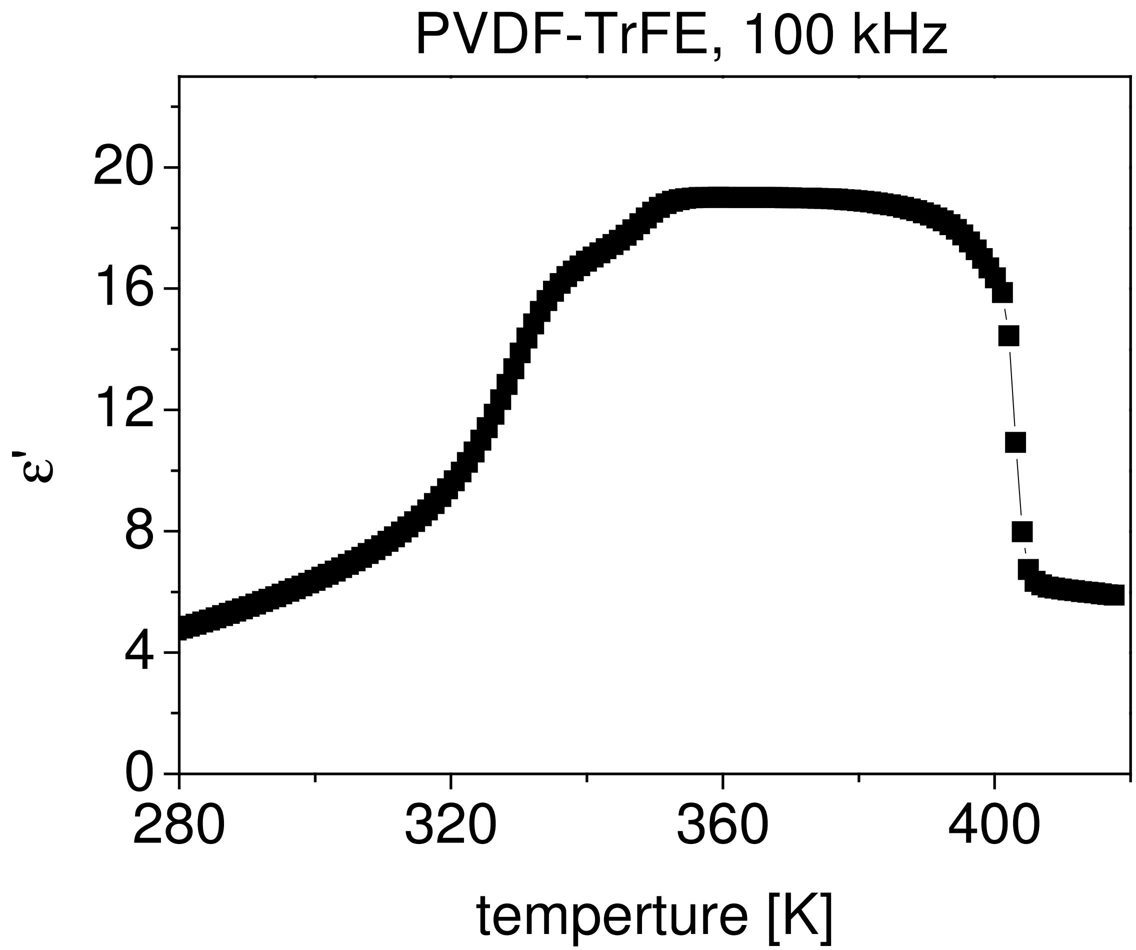
Phase transitions of ferroelectric polymer nanowires (PVDF-TrFE)

PVDF-TrFE in the bulk



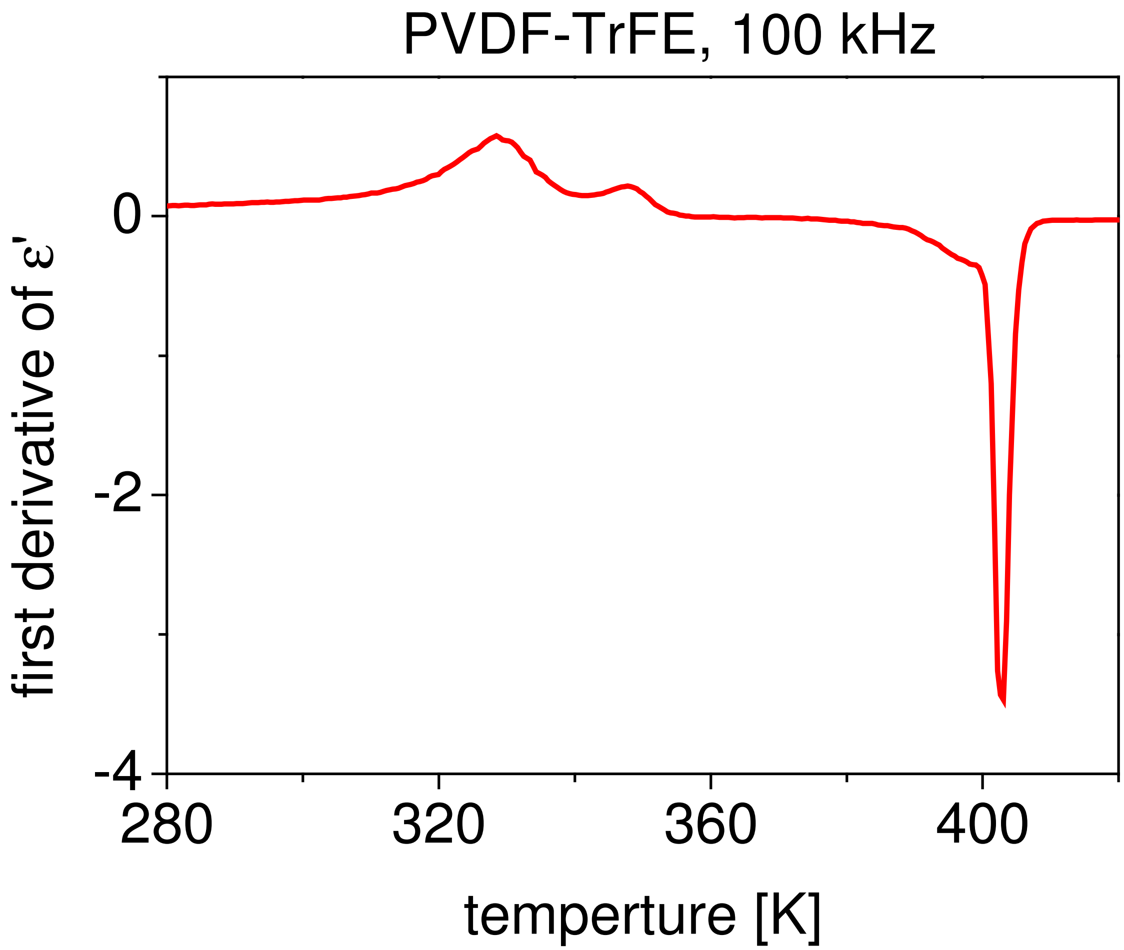
PVDF-TrFE in the bulk

- cooling run -

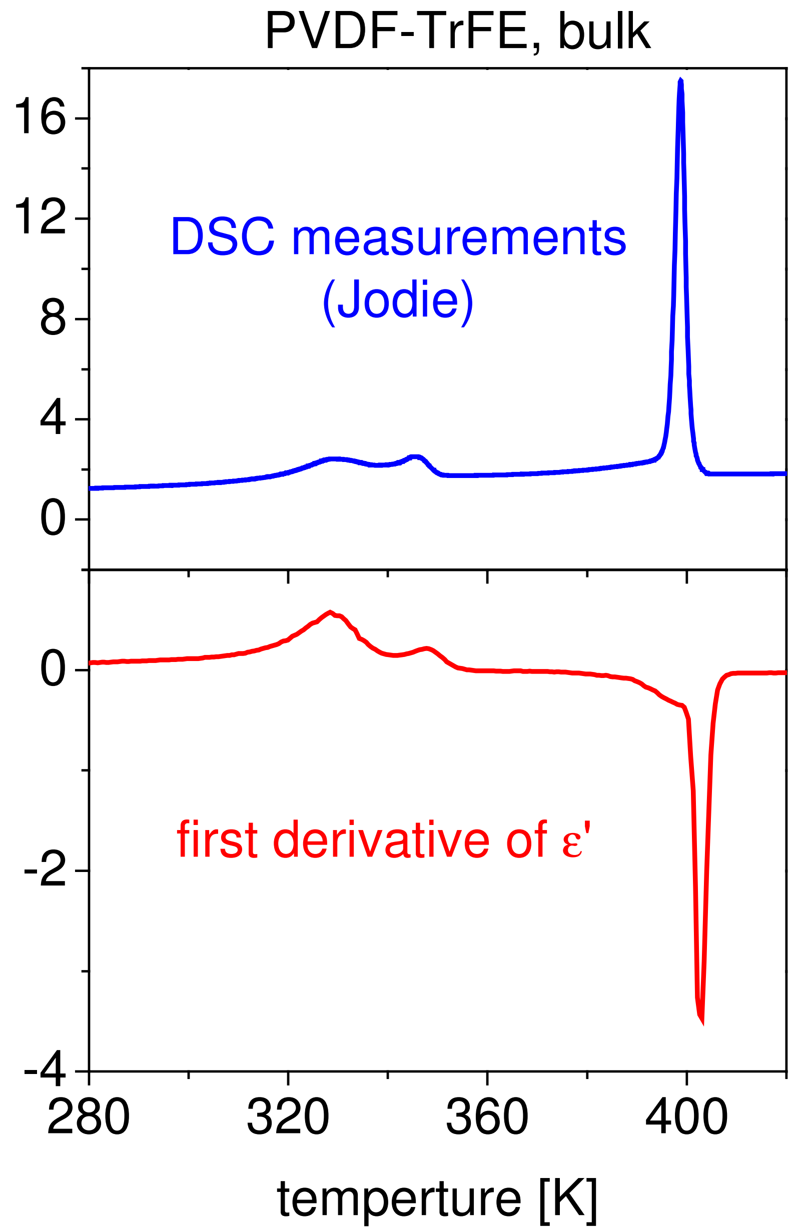


PVDF-TrFE in the bulk

- cooling run -



PVDF-TrFE in the bulk
- cooling run -



The Clausius-Mosotti relation

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{N_A \alpha_{mol}}{3\varepsilon_0 M} \rho$$

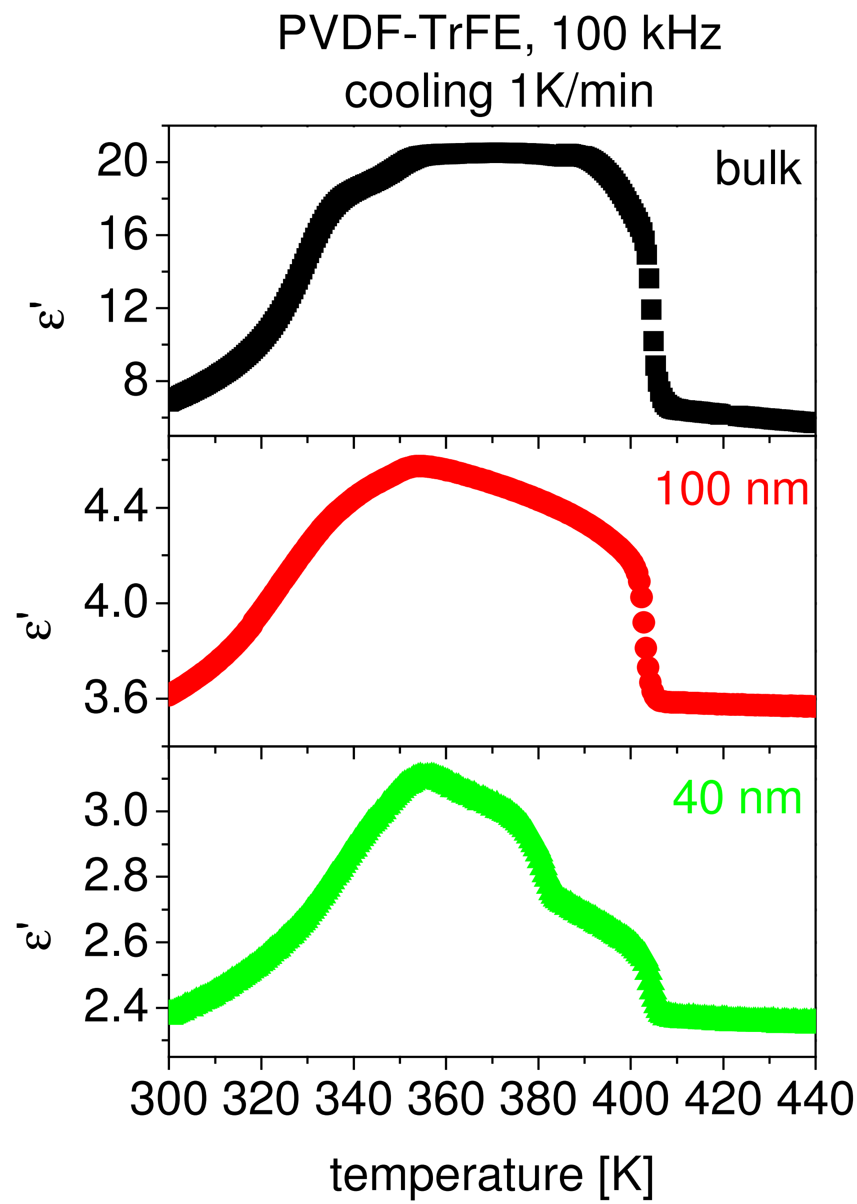
$$\frac{\partial \varepsilon}{\partial T}\left(\frac{3\varepsilon_0 M}{N_A \alpha_{mol}} - \rho\right) = \frac{\partial \rho}{\partial T}(\varepsilon + 2)$$

$$\frac{\partial \varepsilon}{\partial T} \sim \frac{\partial \rho}{\partial T}$$

Using AAO membranes as dielectric cells

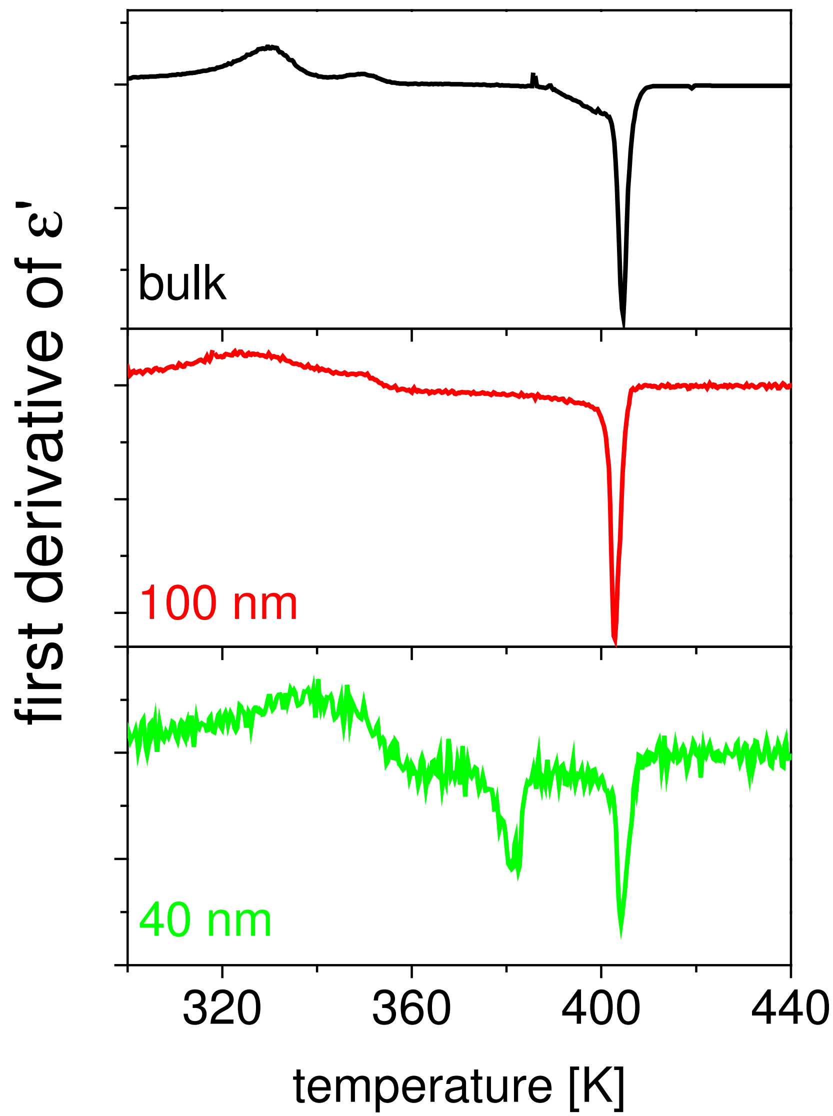
PVDF-TrFE: bulk vs. confinement

- cooling run -



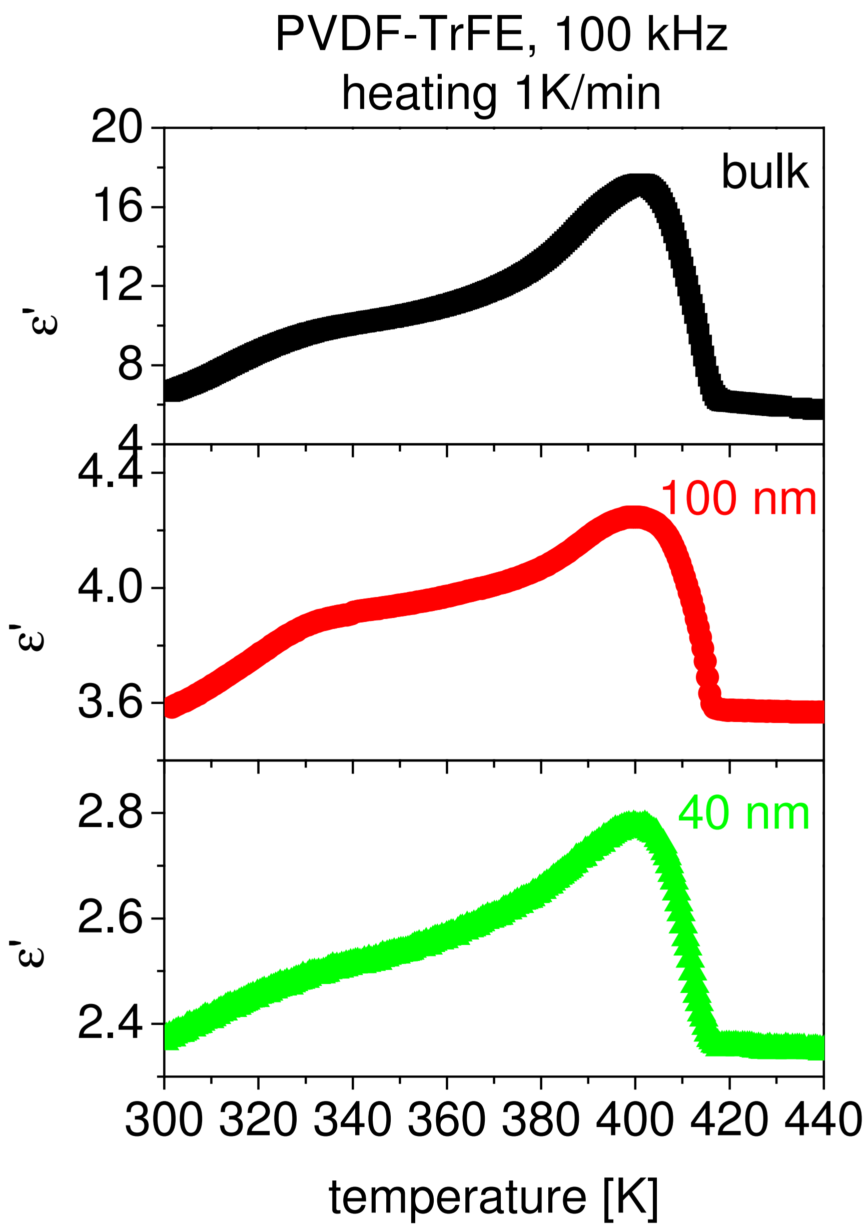
PVDF-TrFE: bulk vs. confinement

- cooling run -



PVDF-TrFE: bulk vs. confinement

- heating run -



Conclusions:

Broadband Dielectric Spectroscopy is a powerfull and versatile experimental tool in nanoscience.

It enables one studies on ultra-thin films, interfacial dynamics, single polymer chain, nano-pores, nano-tubes, nano-fludics, phase transition in nanometric confinement and at interfaces.