Phase transition kinetics in a doubly thermo-responsive poly(sulfobetaine)-based block copolymer thin film

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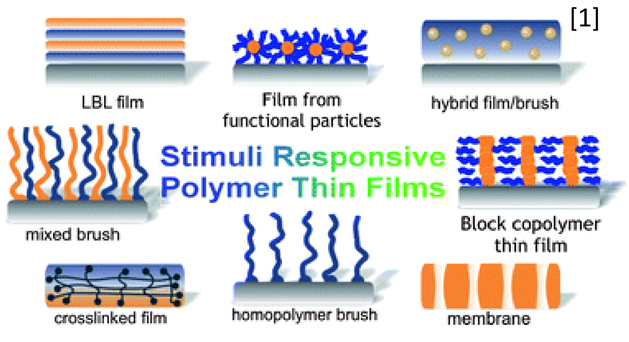
the high versatility of responsive thin films



[1]

- ✓versatile
- ✓fast response times
- ✓reversible response of polymer
- ✓low amount of material required
- ✓processable with large scale deposition methods

new doubly thermo-responsible diblock copolymer –> aim for a fundamental understanding

experimental design

diblock copolymer $PSPP_{500}$-*b*-$PNIPMAM_{150}$

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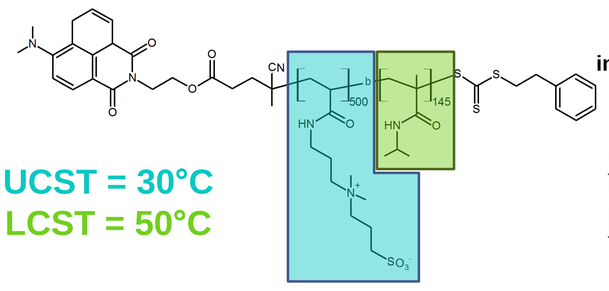
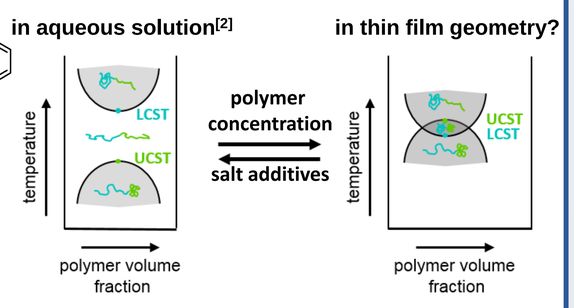
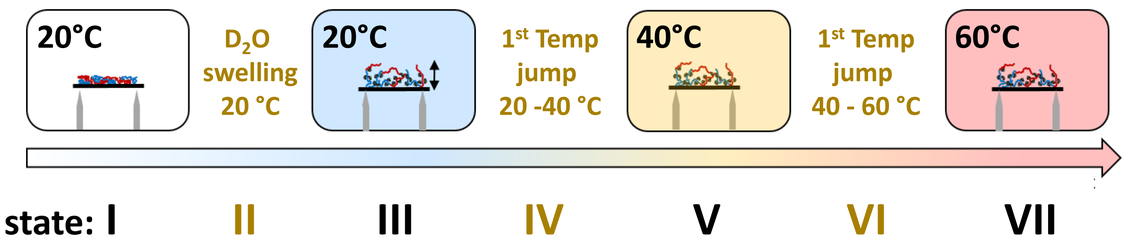


UCST = 30°C
LCST = 50°C

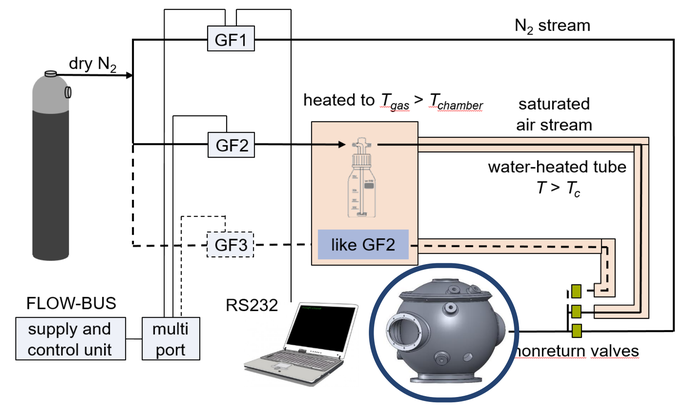


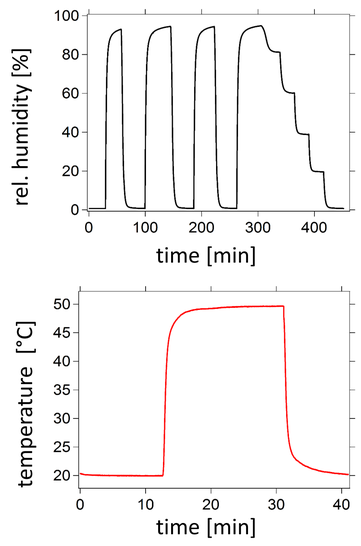
measurement protocol



flexiprobe @ REFSANS

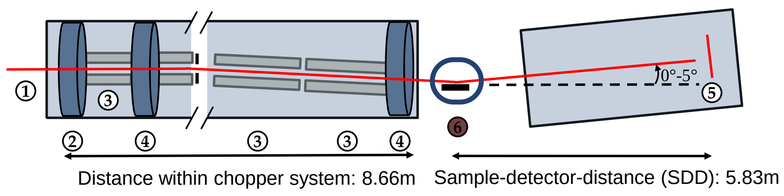
flexiProbe sample environment





custom-made gasflow setup allows, tunable, reliable, and fast changing atmosphere compositions

horizontal TOF reflectometer with GISANS option



$\alpha_i = 0.76°$
SDD = 5.828 m
time resolution = 30 s

① neutron guide NL2b
② master chopper
③ neutron guide elements
④ slave chopper 1&2
⑤ 2D detector: 500x500mm
⑥ polymer film inside vapor chamber

investigation of mesoscopic parameters such as film thickness and water content in-situ

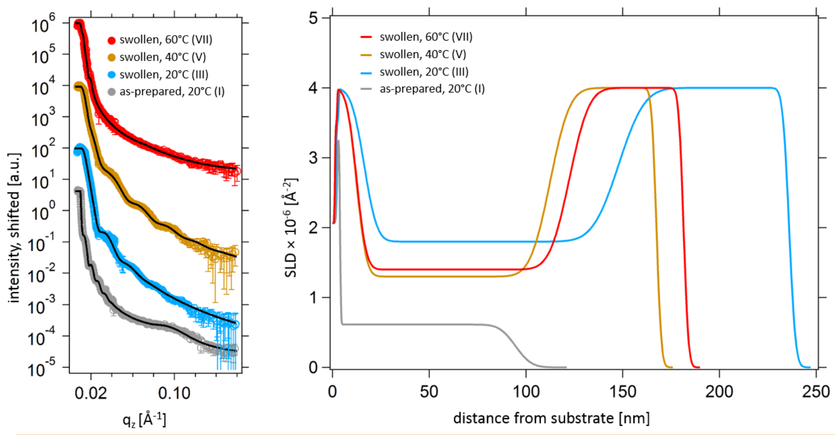
phase behavior of the thin film

In-situ ToF-NR

(time-of-flight neutron reflectometry)

How does the film look like in equilibrium?

(states I, III, V, and VII)



state	d [nm]	SLD [10^{-6}Å^{-2}]	Φ_{water} [%]
I	76	0.8	0
III	191	4.1	60
V	148	3.5	49
VII	76	2.7	37

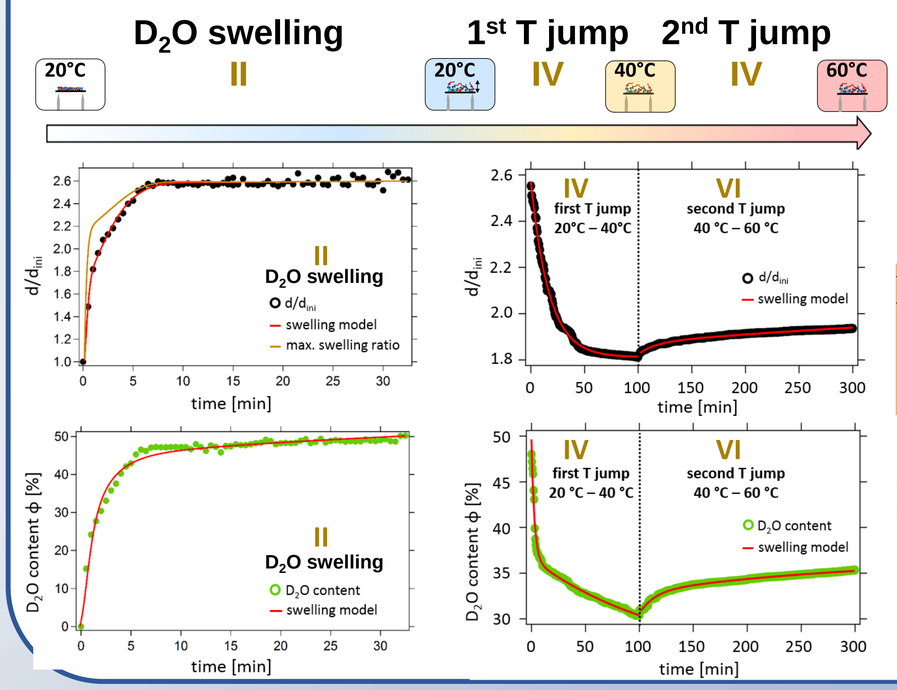
$$\Phi_{water}(t) = \frac{SLD_{meas}(t) - SLD_{dry}}{SLD_{water} - SLD_{dry}}$$

- ➢ D_2O enrichment layers near both interfaces (Si and air – polymer)
- ➢ collapse (1st) + re-swelling (2nd) upon temperature increase

What happens in between?

(states II, IV, and VI)

link to paper[3]

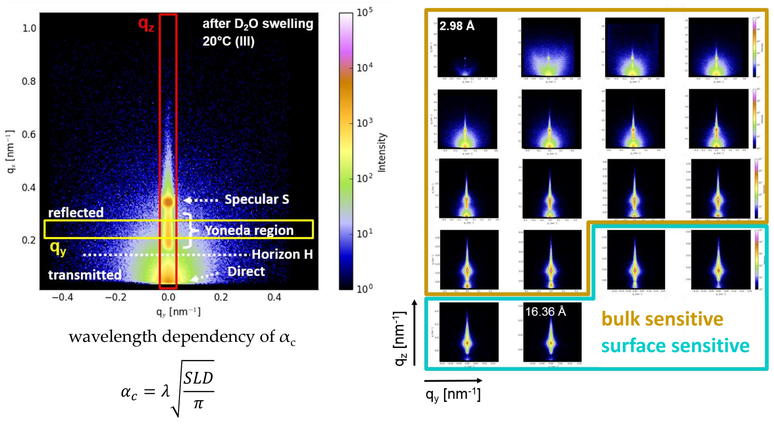


- ➢ very fast and strong D_2O swelling (diffusion limited)
- ➢ collapse and re-swelling need much more time

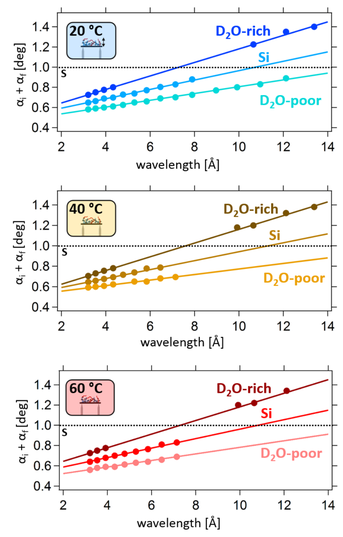
thin film morphology

ToF-GISANS

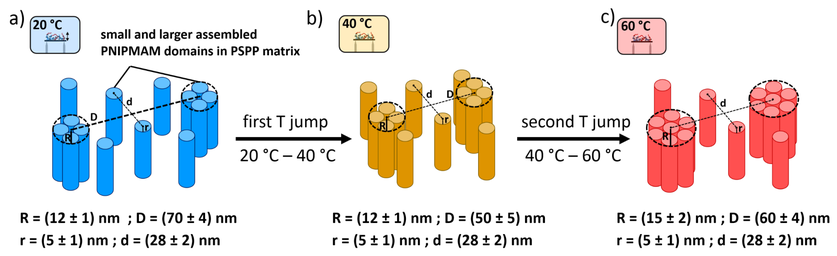
(time-of-flight grazing-incidence small angle neutron scattering)



$$\alpha_c = \lambda\sqrt{\frac{SLD}{\pi}}$$



bulk and surface sensitive measurement technique



vertical cuts yield D_2O enrichment layers

changing thin film morphology upon increasing temperature

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Chair for Functional Materials

[1] I. Tokarev et al., J. Mater. Chem., **2009**, 19, 6932

[2] N. Vishnevetskaya et al., *Macromolecules*, ***2017***, 50, 3985

[3] L. P. Kreuzer et al., *Macromolecules* **2020**, 53, 2841

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