

Neutron Scattering Studies of Non-NIPAM Based Microgels

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**JCNS Workshop 2019, October 7th – October 10th, 2019
Tutzing**

Bielefeld Conspiracy



https://en.wikipedia.org/wiki/Bielefeld_Conspiracy

Bielefeld Conspiracy

6 ways to divide Germany



- beautiful nature and cities
- ugly wastelands
- Hannover



- ALDI Nord
- ALDI Süd



- absurd gobbledegook
- funny dialect
- dreadful dialect
- passive-aggressive dialect
- almost normal German



- never shut up
- talk sufficiently
- don't talk at all



- hardcore conservatives
- pseudo-ecofriendly conservatives
- libtards
- precariat
- nazis
- all of the above



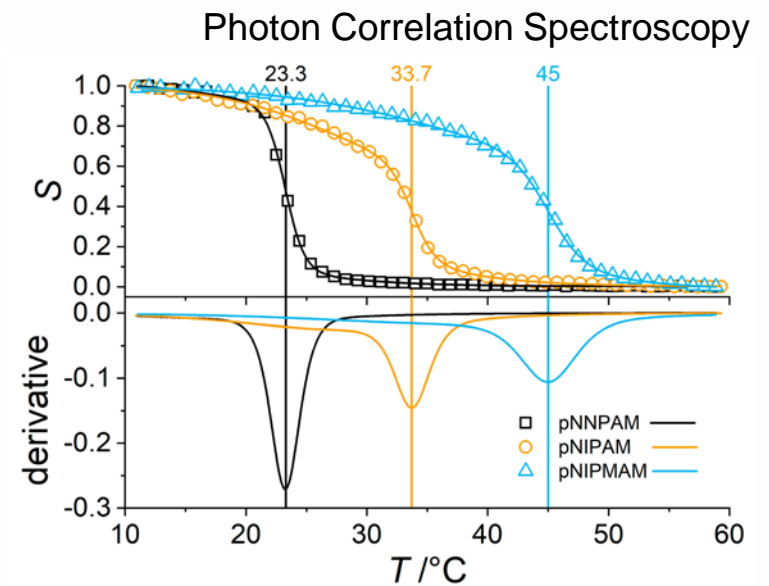
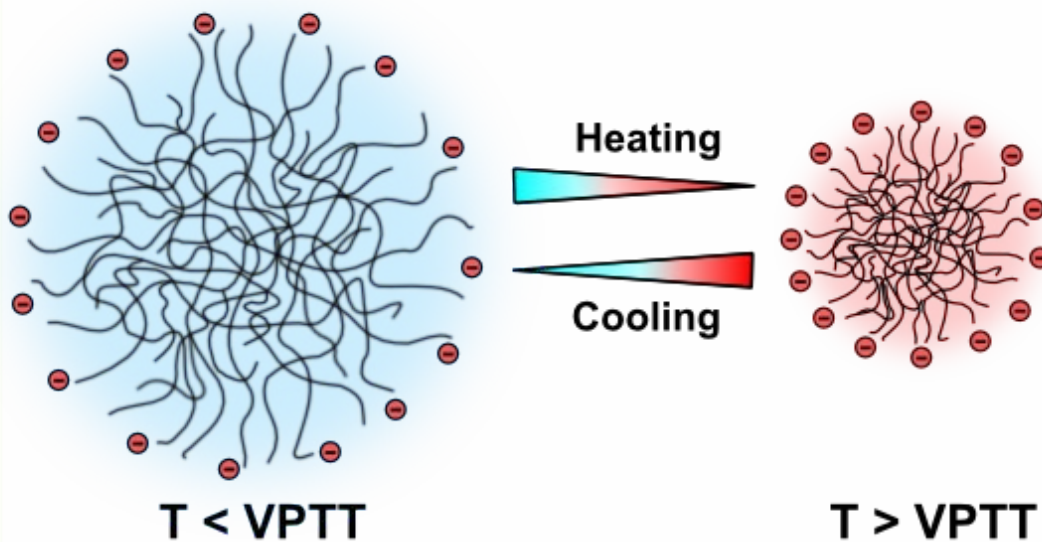
- make jokes about Bielefeld being non-existent
- hate jokes about Bielefeld being non-existent

Outline

1. Smart microgels – preparation, properties, and applications
2. Microgel response kinetics
3. Non-NIPAM based core-shell microgels
4. Conclusion/Outlook

Thermoresponsive Microgels

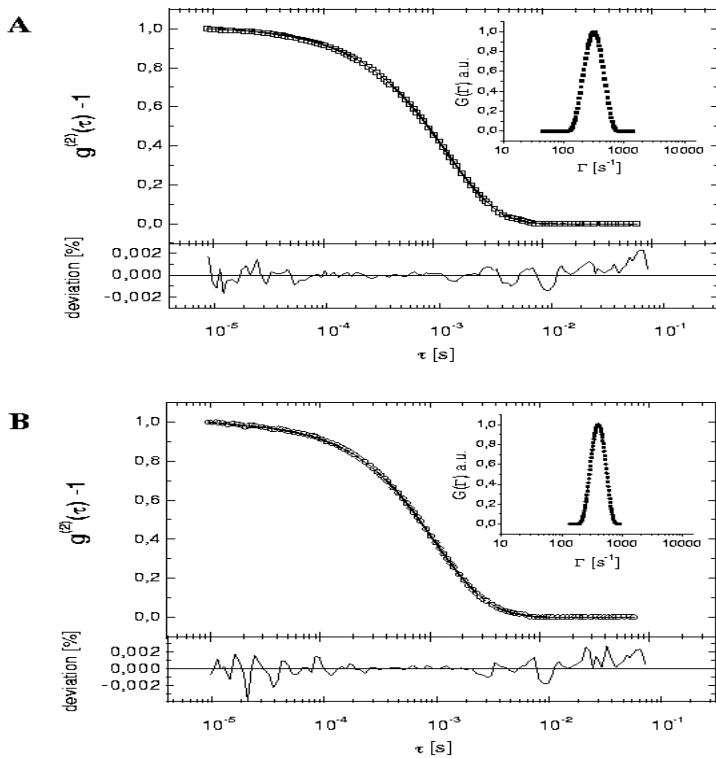
- Colloidal polymer-gel particles
- Reversible volume phase transition (VPT) at a specific temperature



R. H. Pelton, P. Chibante *Colloids and Surfaces* **1986**, 20, 247-256

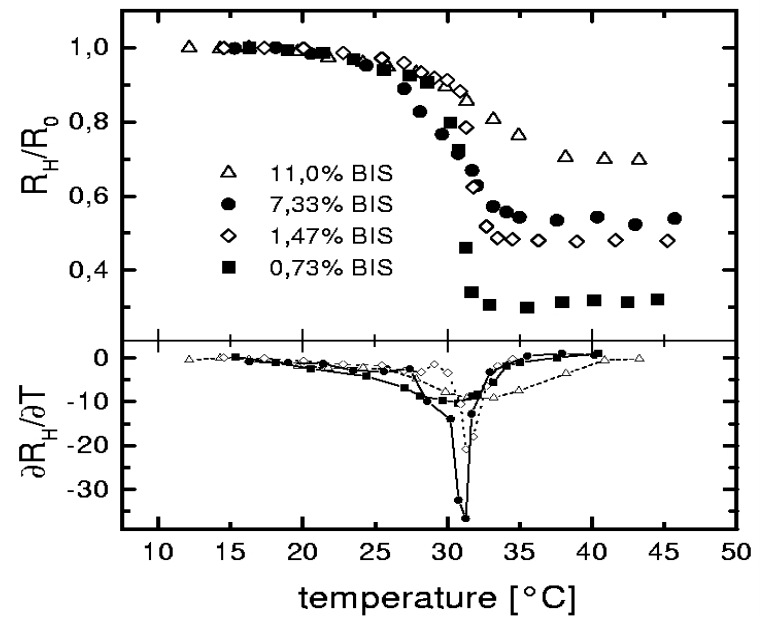
DLS experiments to study the swelling behavior

Typical DLS correlation functions for BIS crosslinked microgels (2 and 10 mol% BIS)



The inset shows the narrow relaxation rate distribution

DLS can be used to follow the particle swelling as function of temperature



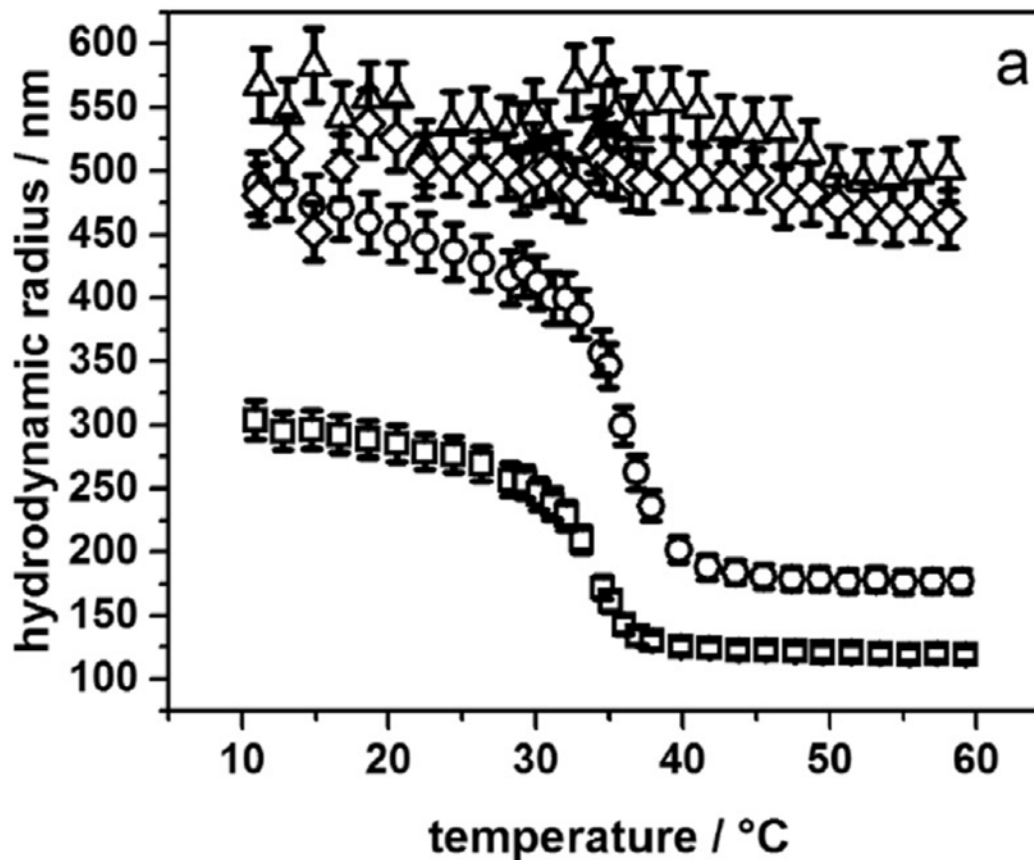
Swelling capacity decreases

K. Kratz, TH, W. Eimer; Polymer, **42** (2001) 6631.



Lars Wiehemeier

PNIPAM copolymer microgels with acrylic acid: DLS experiments to study the swelling behavior



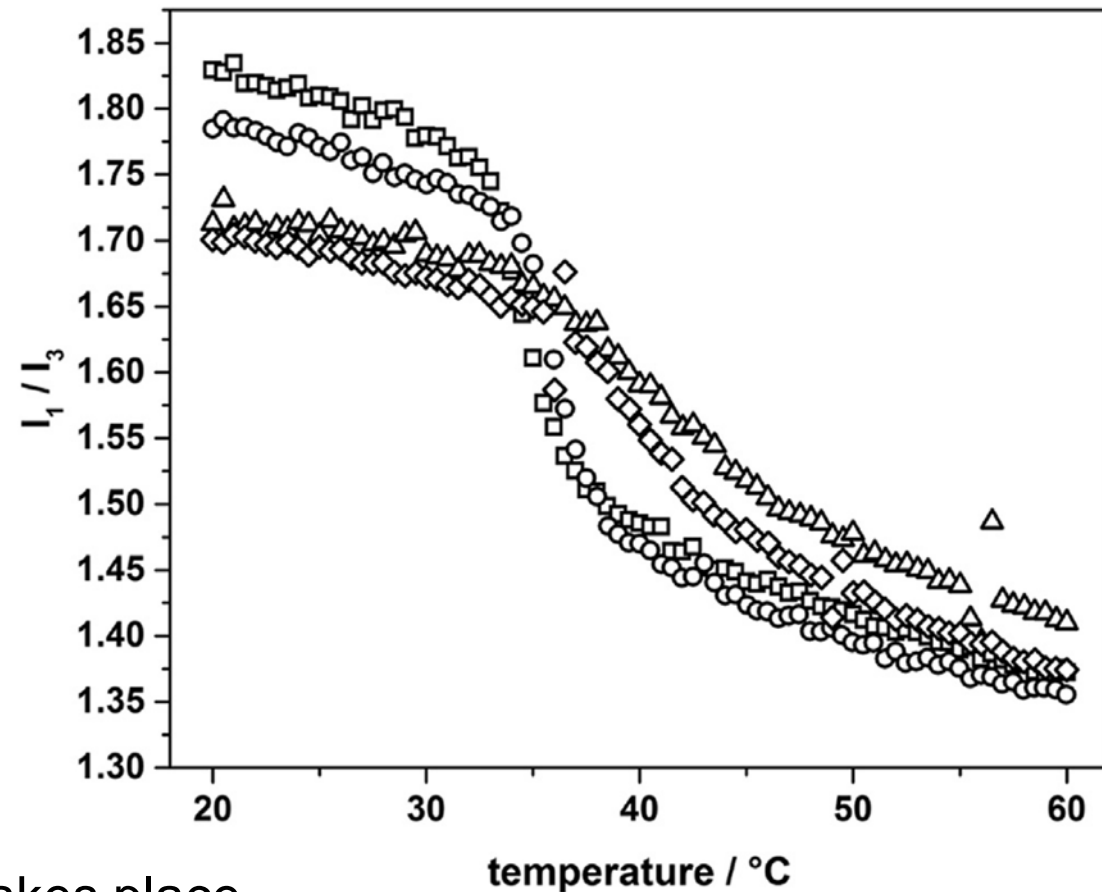
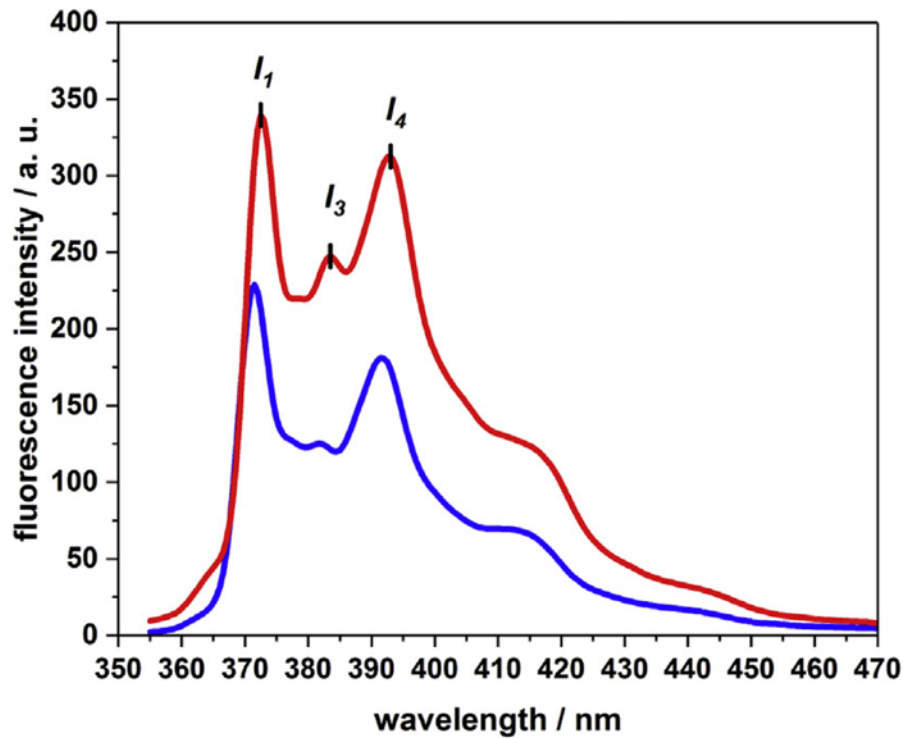
PNIPAM(squares) and PNIPAM-co-AAc microgels. The changes in the hydrodynamic radius (a) and in the swelling ratio (b) are given. The nominal AAc concentration during the synthesis was 5 mol% (circles), 10 mol% (triangles) and 15 mol% (diamonds).



Timo Brändel

T. Brändel, L. Wiehemeier, T. Kottke, T. H.,
Polymer 125 (2017) 110-116

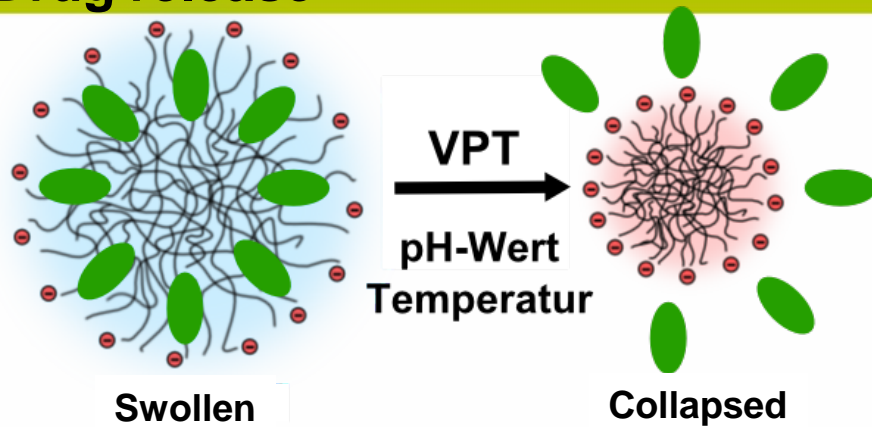
Pyren Fluorescence to study the swelling behavior: Copolymers with acrylic acid



Locally the PNIPAM collapse still takes place

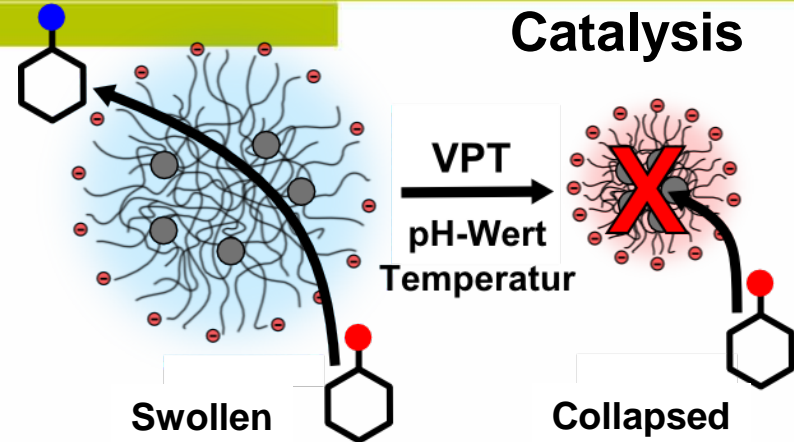
Thermoresponsive Microgels: Applications

Drug release



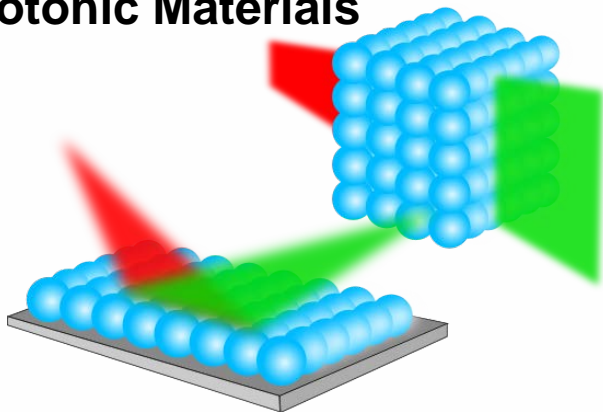
Dirk Schmaljohann, *Adv. Drug Deli. Rev.*, **2006**, 58, 15, 30, 1655–1670

Catalysis



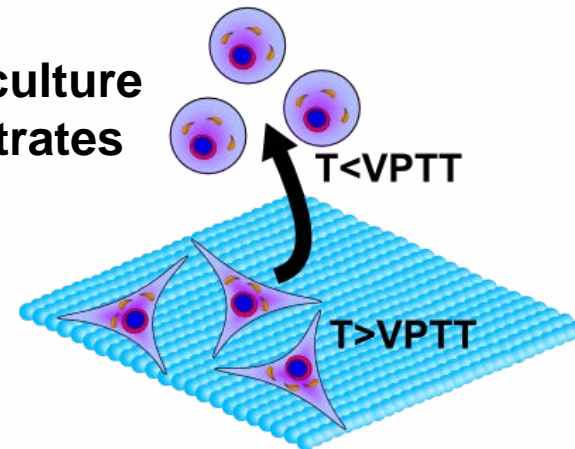
Y. Lu, S. Proch, M. Schrinner, M. Drechsler, R. Kempe, M. Ballauff, *J. Mater. Chem.* **2009**, *19*, 3955-3961

Photonic Materials



L. A. Lyon, J. D. Debord, et al., *J. Phys. Chem. B*, **2004**, 108 (50), 19099–19108; Hellweg, T., Dewhurst, C. D., Bruckner, E., Kratz, K., & Eimer, W., *Coll. Polym. Sci.*, **2000**, 278, 972-978

Cell culture substrates



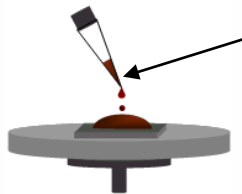
K. Uhlig, T. Wegener, J. He, M. Zeiser, J. Bookhold, I. Dewald, N. Godino, M. Jaeger, T. Hellweg, A. Fery, C. Duschel, *Biomacromolecules*, **2016**, 17(3), 1110-1116.

Possible applications

L929 mouse fibroblast cells

Spin coating

Deposition



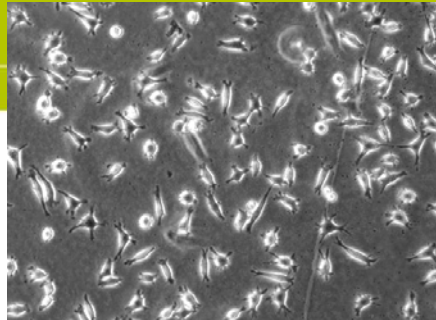
Rotation



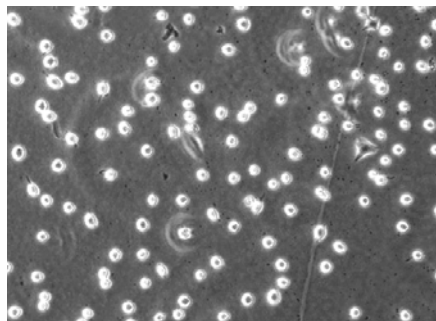
Evaporation



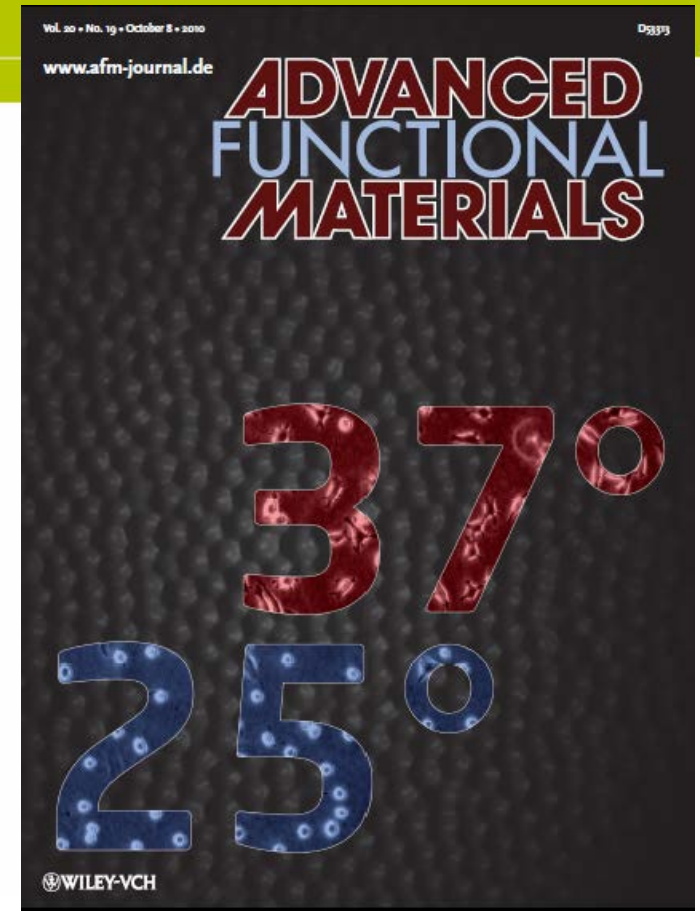
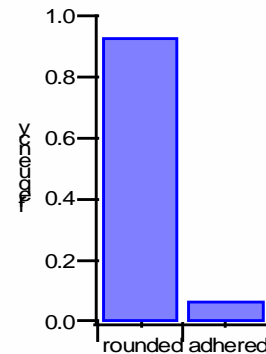
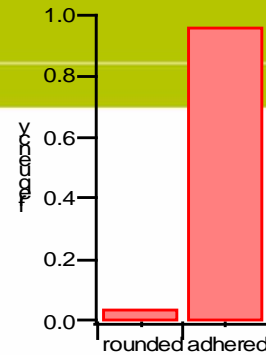
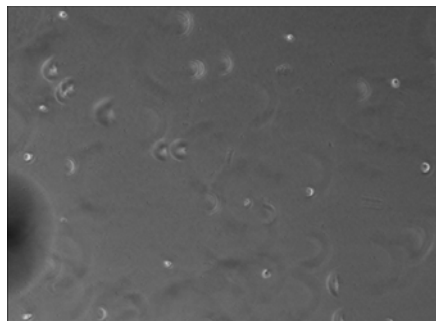
37 °C



25 °C

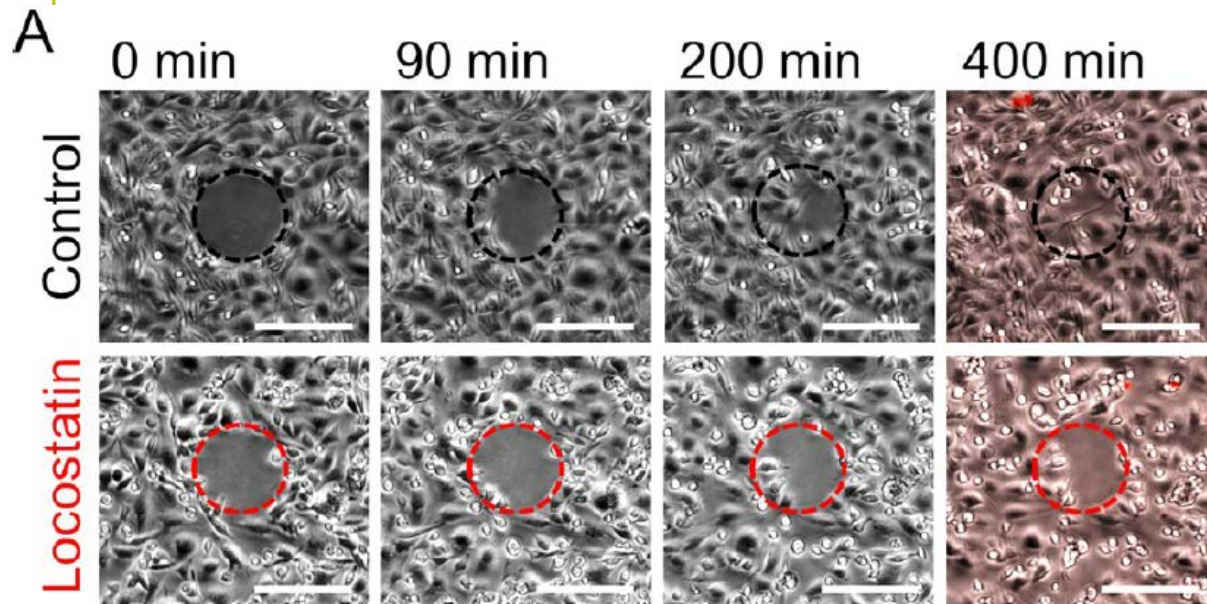


25 °C, after rinsing

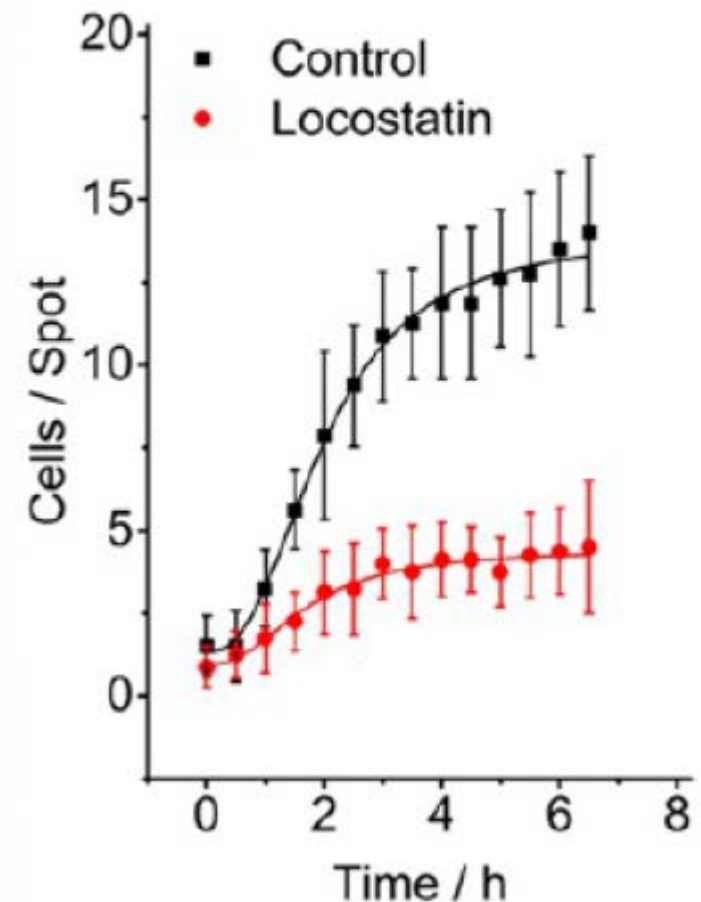


Schmidt, Zeiser, TH, Duschl, Fery, Möhwald, Adv. Func. Mater. (2010) **20**, 3235

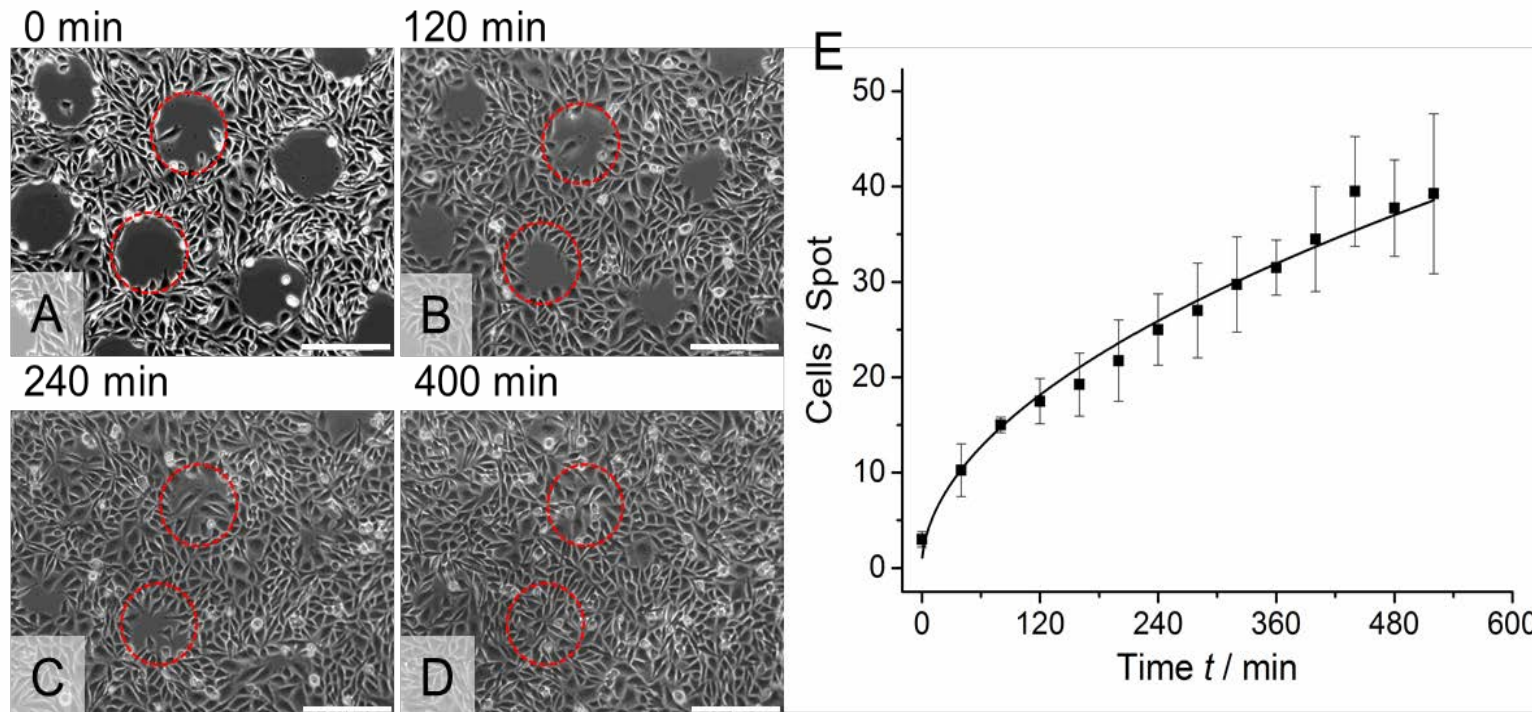
Assay with cell-migration inhibitor Locostatin



Uhlig, K., Wegener, T., He, J., Zeiser, M., Bookhold, J.,
Dewald, I., Godino, N., Jaeger, M., TH, Fery, A.,
& Duschl, C.; *Biomacromolecules*, **17** (3), (2016) 1110-1116.

B

CHO-K1 cells from hamster ovaries



Also in this case the cell attachment is nicely controlled

K. Uhlig, T. Wegener, Y. Hertle, J. Bookhold, M. Jaeger, TH, A. Fery, C. Duschl,
Polymers, 10, (2018) 656, DOI:10.3390/polym10060656

Recent Review on Microgels (Open Access)

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LANGMUIR

Cite This: *Langmuir* 2019, 35, 6231–6255

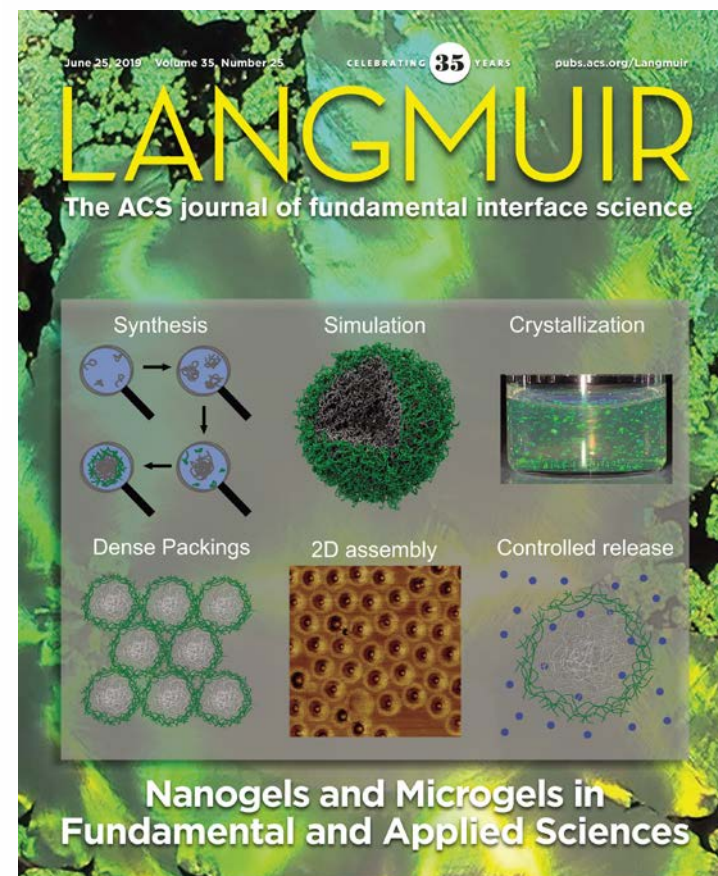
Invited Feature Article

pubs.acs.org/Langmuir

Nanogels and Microgels: From Model Colloids to Applications, Recent Developments, and Future Trends

Matthias Karg,^{*,†} Andrij Pich,^{‡,§} Thomas Hellweg,^{||} Todd Hoare,[⊥] L. Andrew Lyon,[#]
J. J. Crassous,[∇] Daisuke Suzuki,^{○,◆} Rustam A. Gumerov,^{‡,||} Stefanie Schneider,[∇]
Igor I. Potemkin,^{‡,||,△} and Walter Richtering^{*,∇}

DOI:10.1021/acs.langmuir.8b04304



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Outline

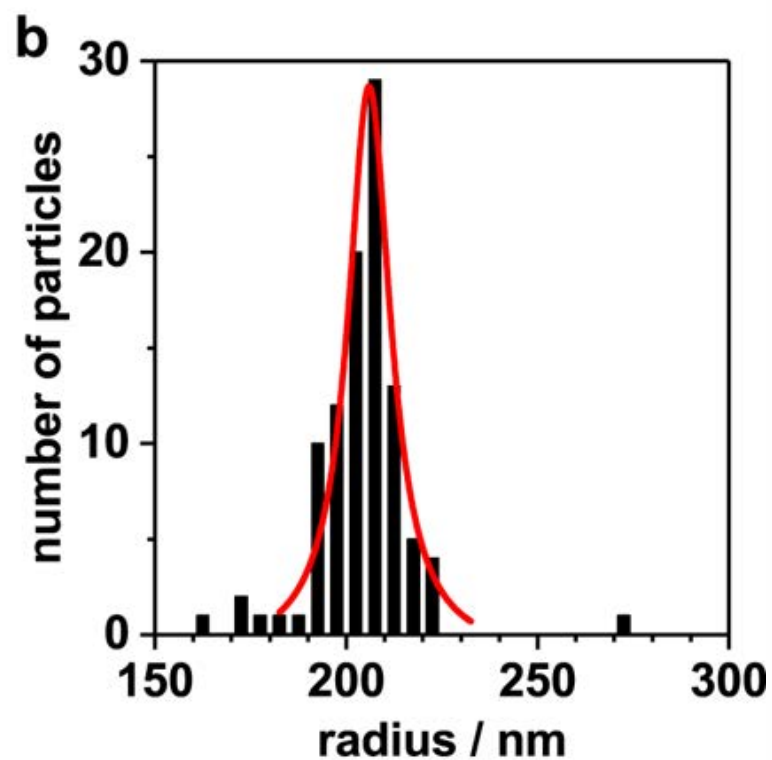
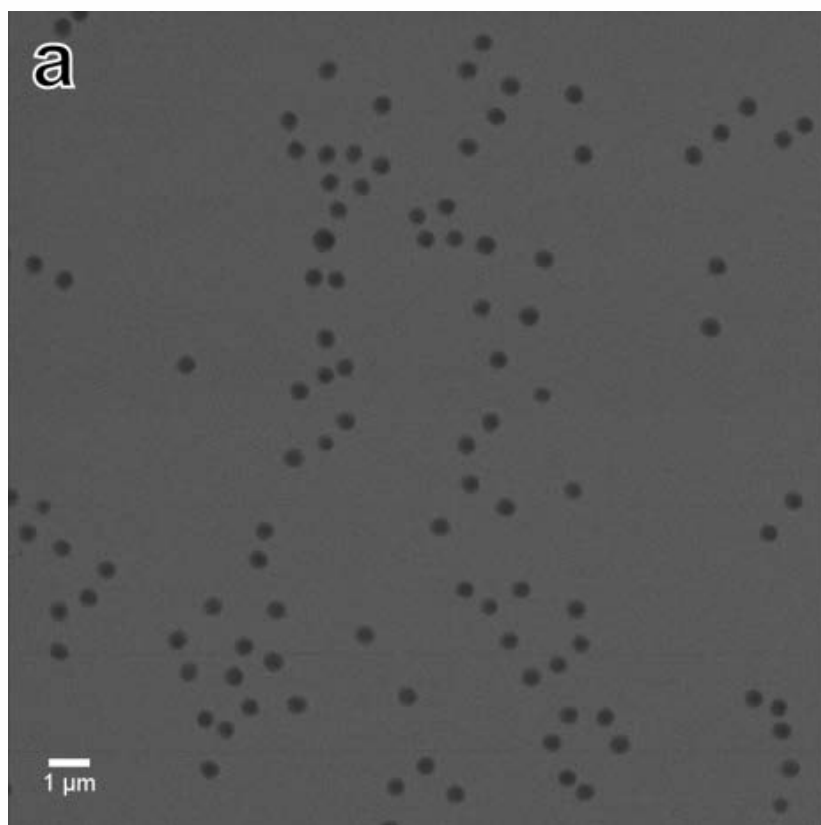
1. Smart microgels – preparation, properties, and applications
2. Microgel response kinetics
3. Non-NIPAM based core-shell microgels
4. Conclusion/Outlook



Oliver Wrede

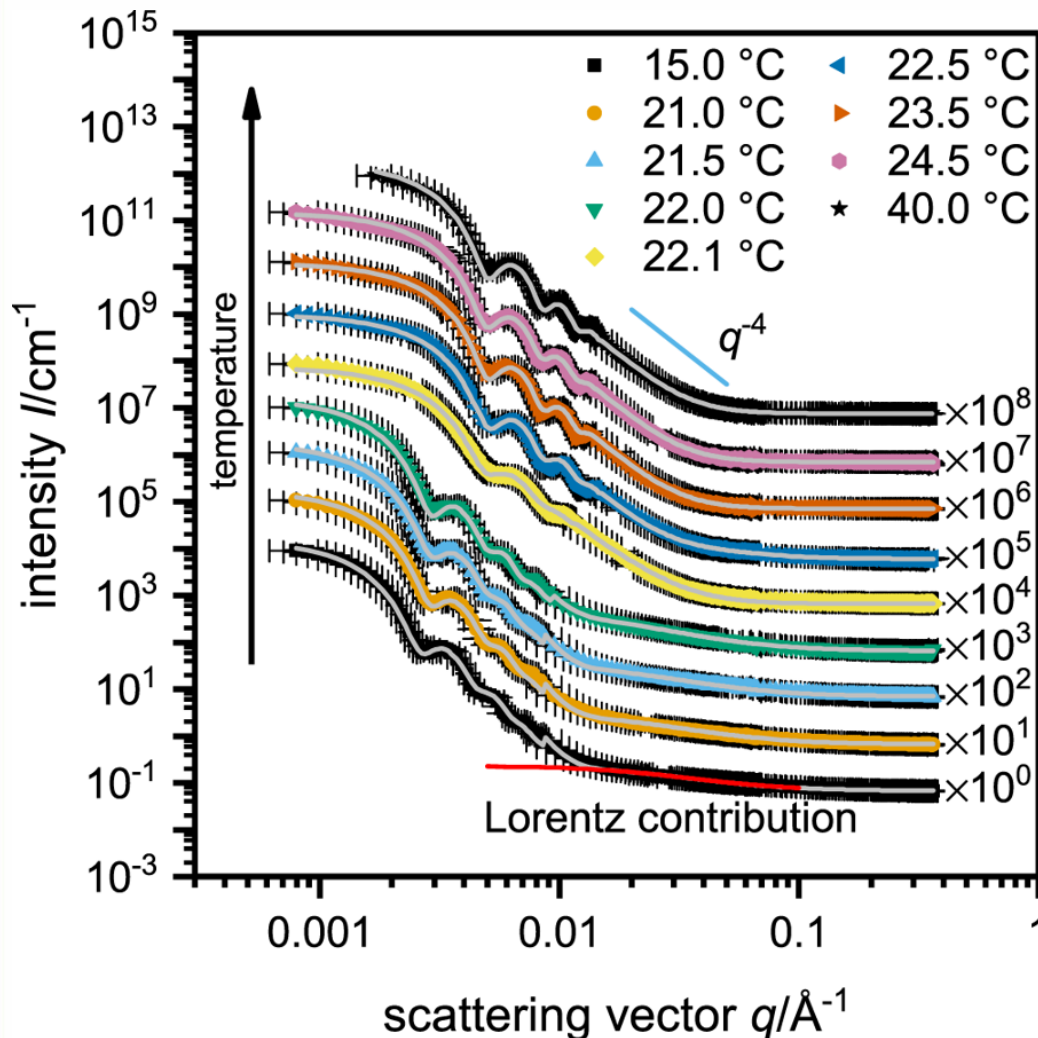
Non-NIPAM based microgels: PNNPAM

HIM-Image of PNNPAM microgels



O. Wrede et al., Scientific Reports (2018) 8:13781

Microgel response kinetics: Stroboscopic p-jump Small Angle Neutron Scattering



PNNPAM microgels:
Temperature dependence of the
particle size as seen by SANS



Extremely sharp volume
transition

O. Wrede et al., Scientific Reports (2018) 8:13781

Microgel response kinetics: Stroboscopic p-jump Small Angle Neutron Scattering

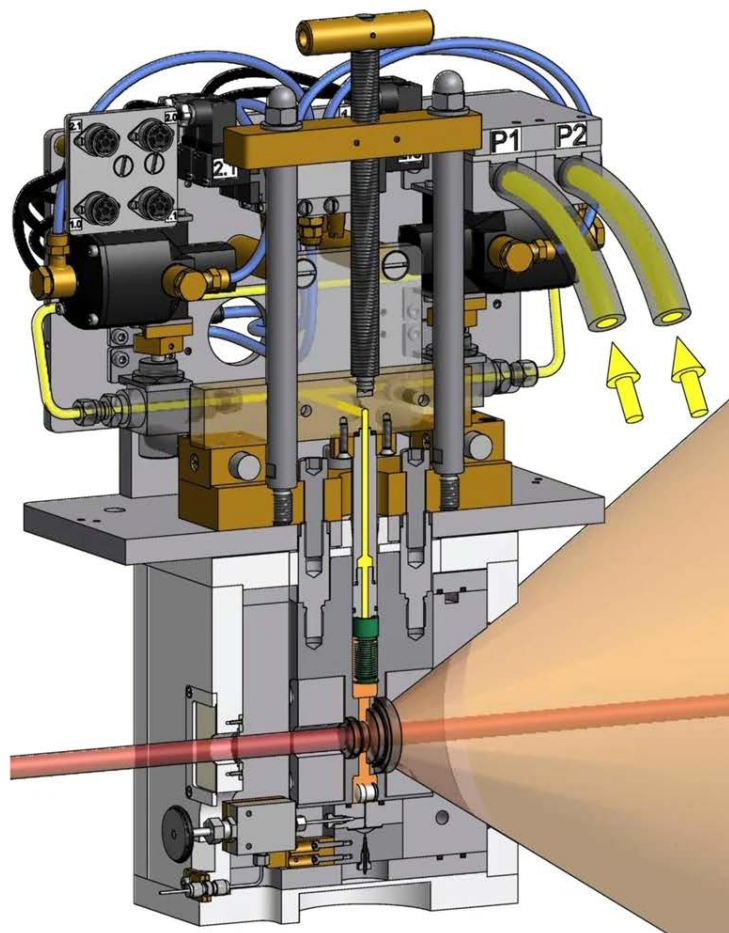
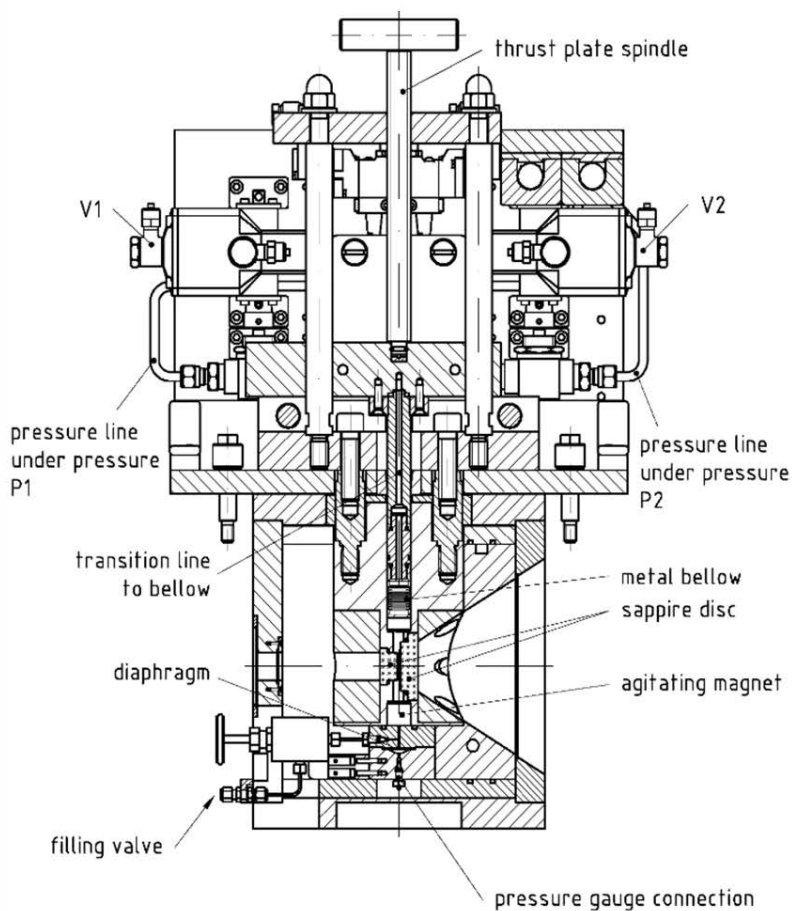


D11@ILL



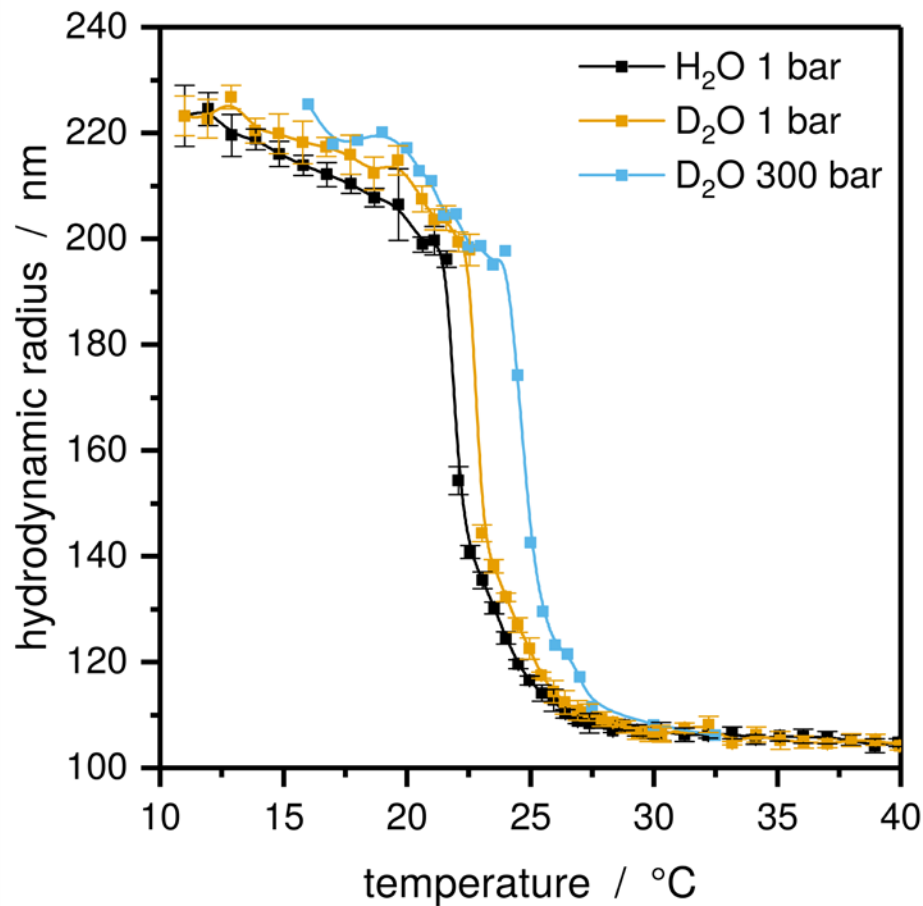
Pressure jump device:
1 to 300 bar
Deadtime 2 ms

Microgel response kinetics: Stroboscopic p-jump Small Angle Neutron Scattering



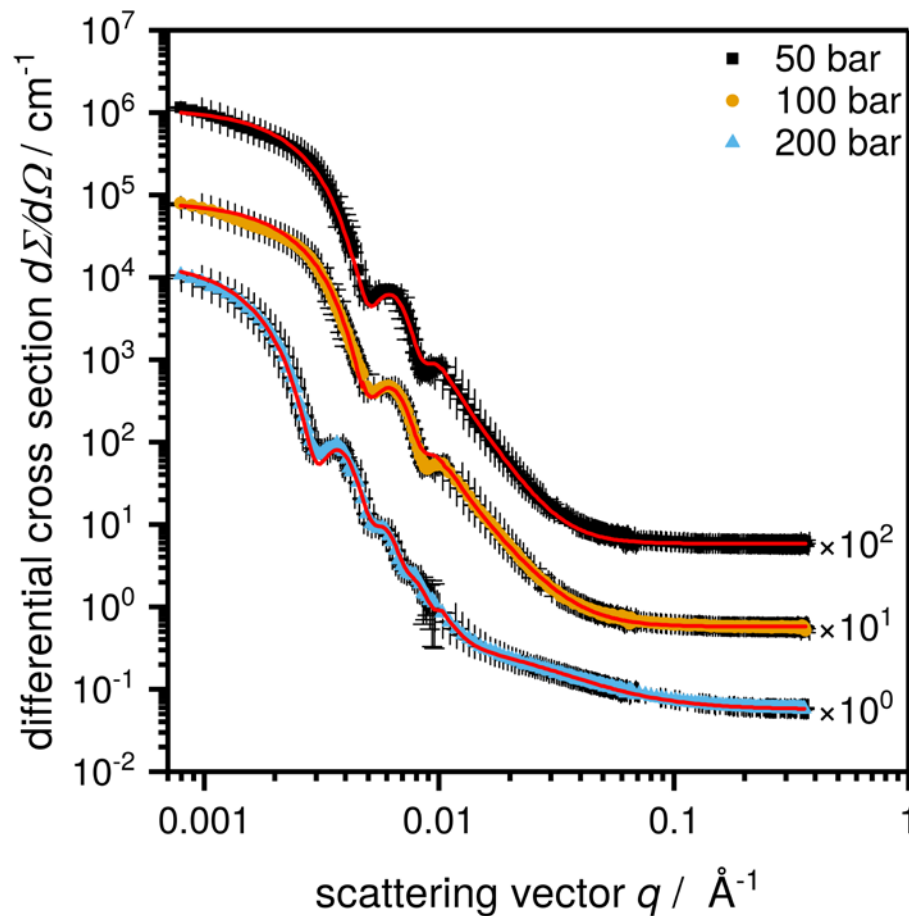
Pressure jump device:
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Microgel response kinetics: Stroboscopic p-jump Small Angle Neutron Scattering



PNNPAM microgels:
Pressure dependence of the
particle size as seen by DLS

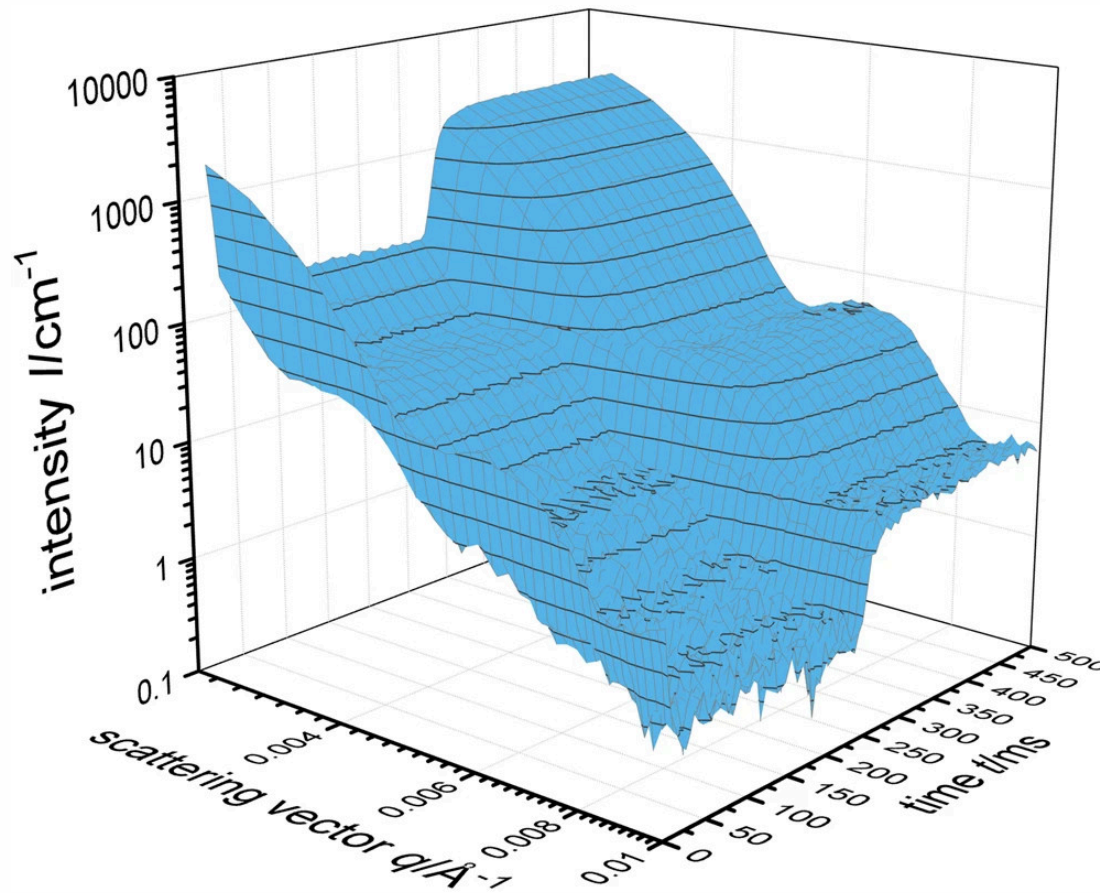
Microgel response kinetics: Stroboscopic p-jump Small Angle Neutron Scattering



PNNPAM microgels:
SANS data at different pressures

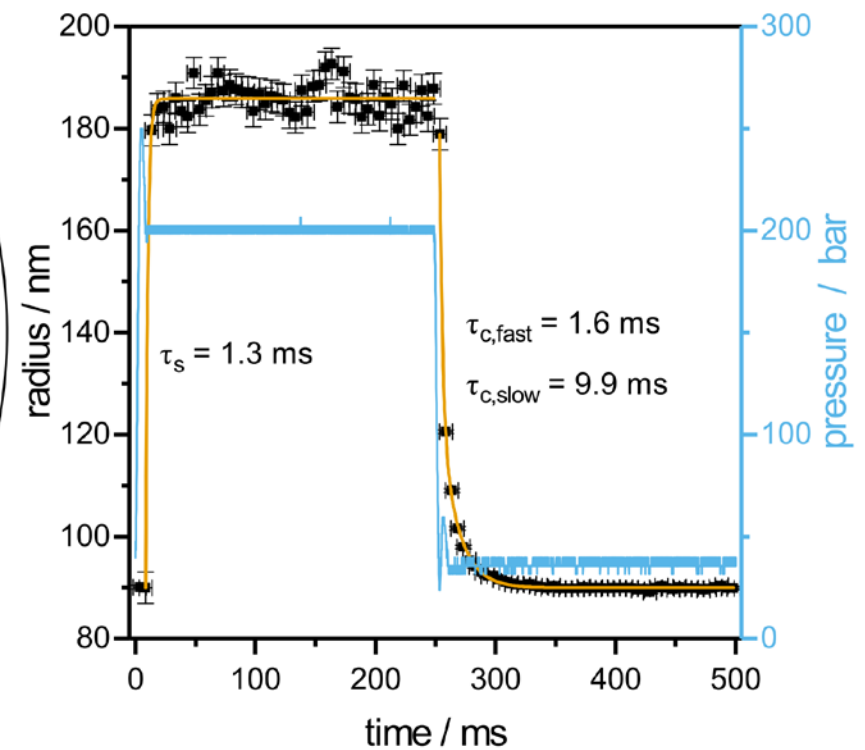
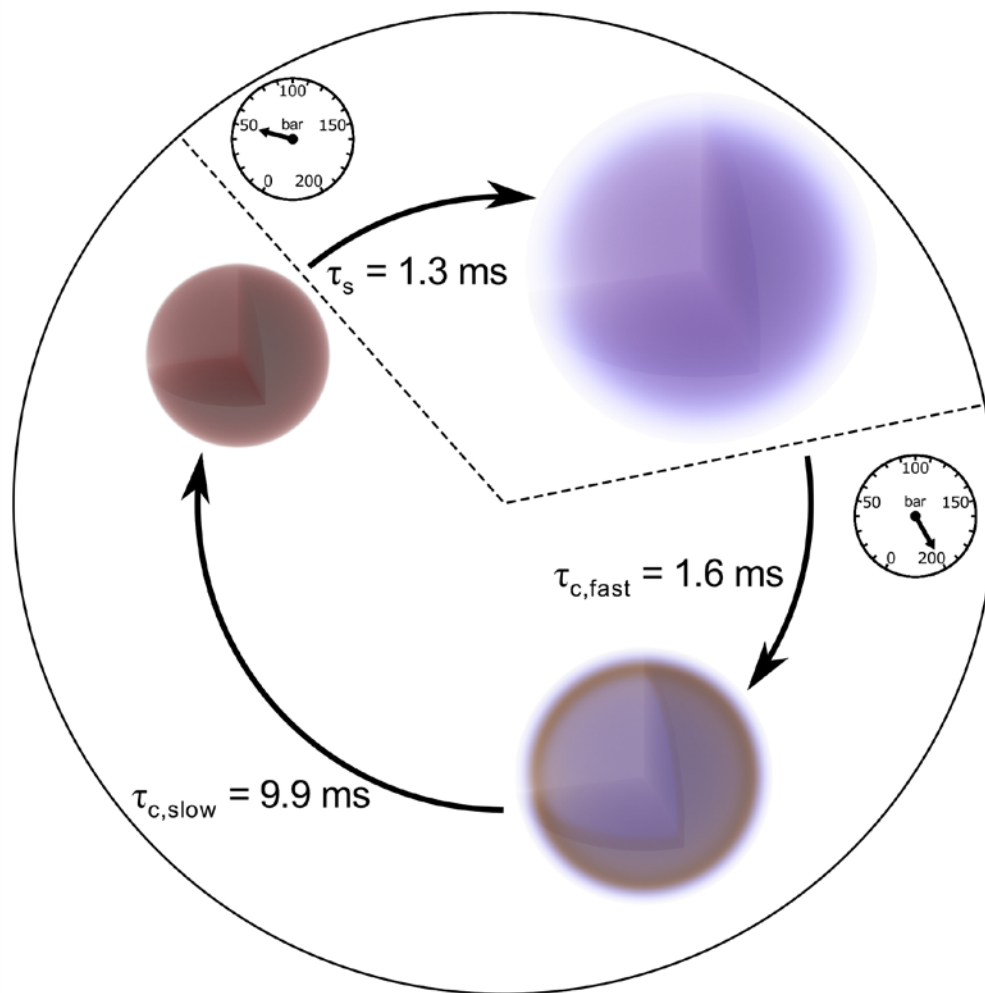
O. Wrede et al., Scientific Reports (2018) 8:13781

Microgel response kinetics: Stroboscopic p-jump Small Angle Neutron Scattering



Radius is calculated
for each of the curves

Microgel response kinetics: Stroboscopic p-jump Small Angle Neutron Scattering



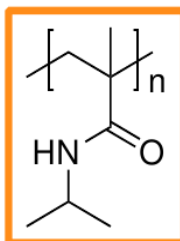
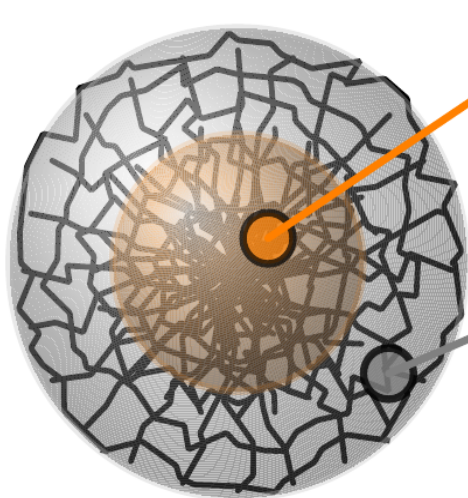
O. Wrede et al., Scientific Reports (2018) 8:13781

Outline

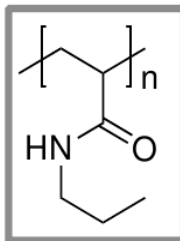
1. PNIPAM microgels – preparation, properties, and applications
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Synthesis of core-shell microgels with organic cores made of NIPMAM and NNPAM

Core-shell microgels (inspired by Richtering et al.)



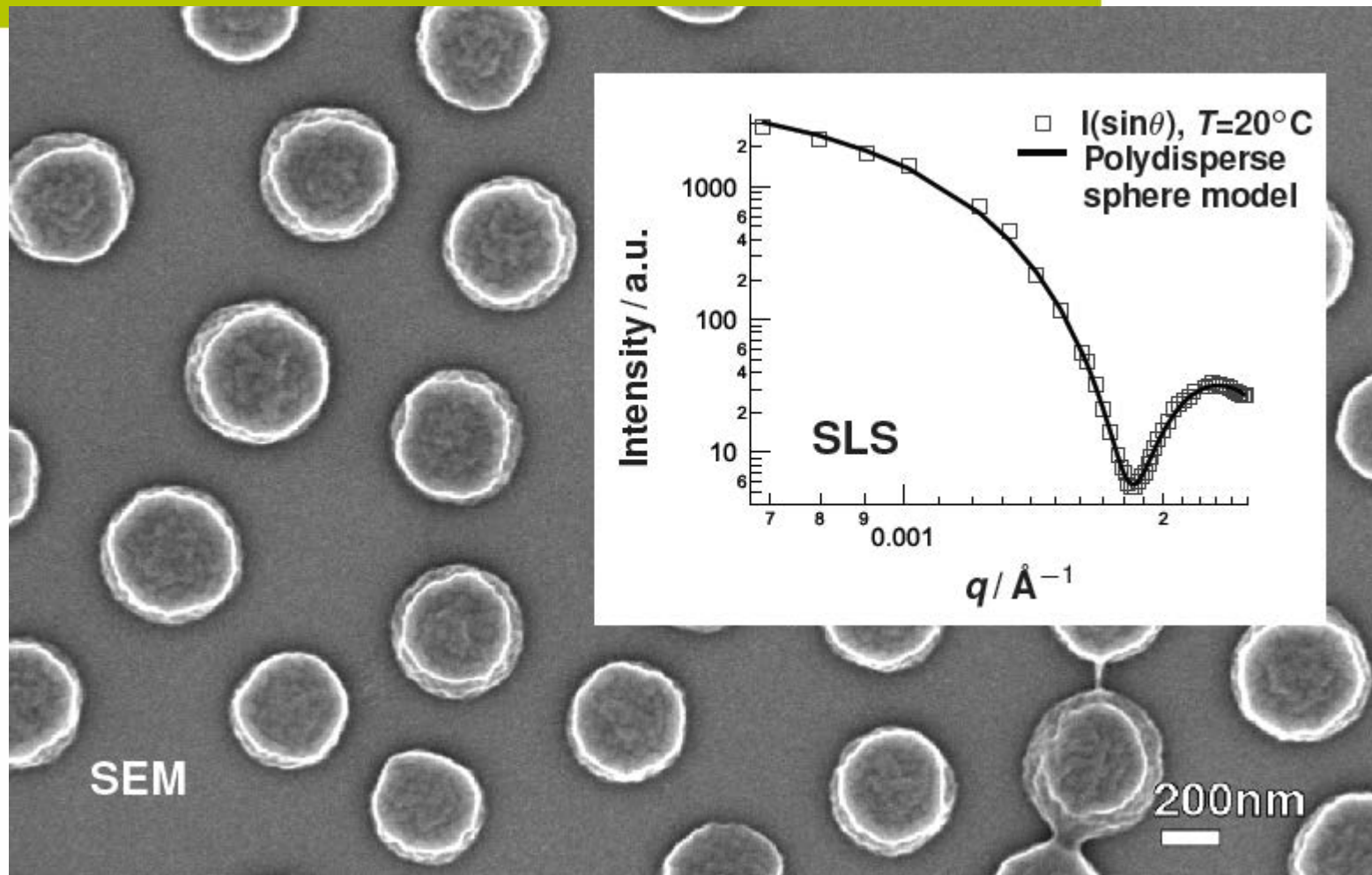
core: NIPMAM LCST: $\approx 44^{\circ}\text{C}$
var. BIS 2 - 20 mol%

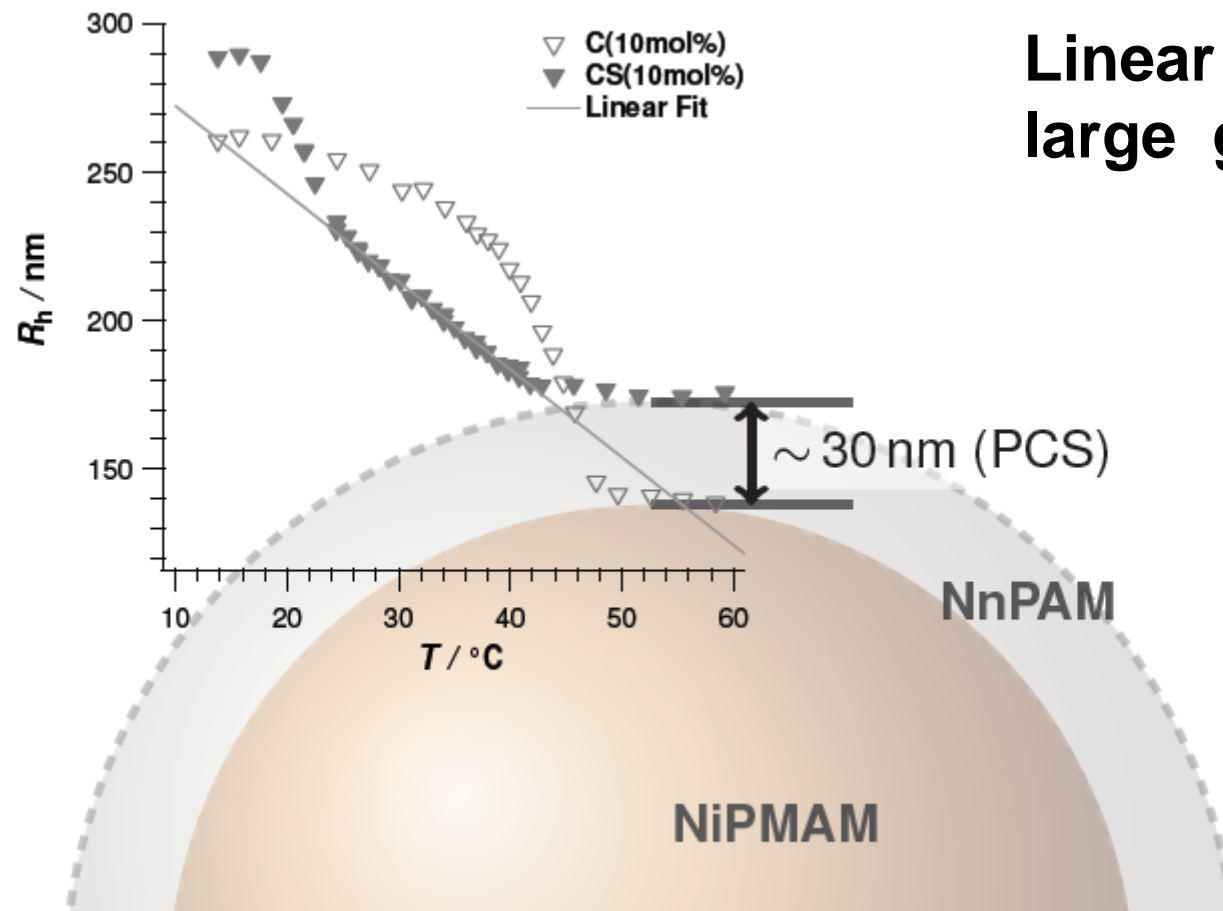


shell: NNPAM LCST: $\approx 23^{\circ}\text{C}$
const. BIS 2mol%

M. Zeiser, I. Freudensprung, TH, Polymer, 53: 6096-6101, 2012

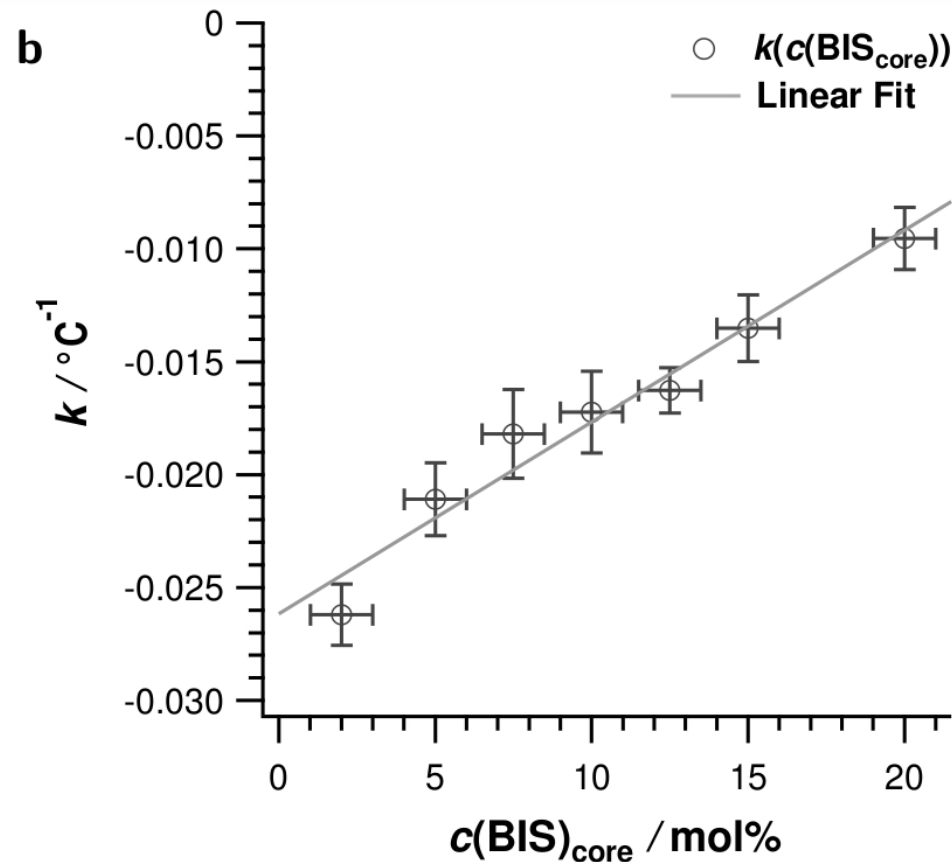
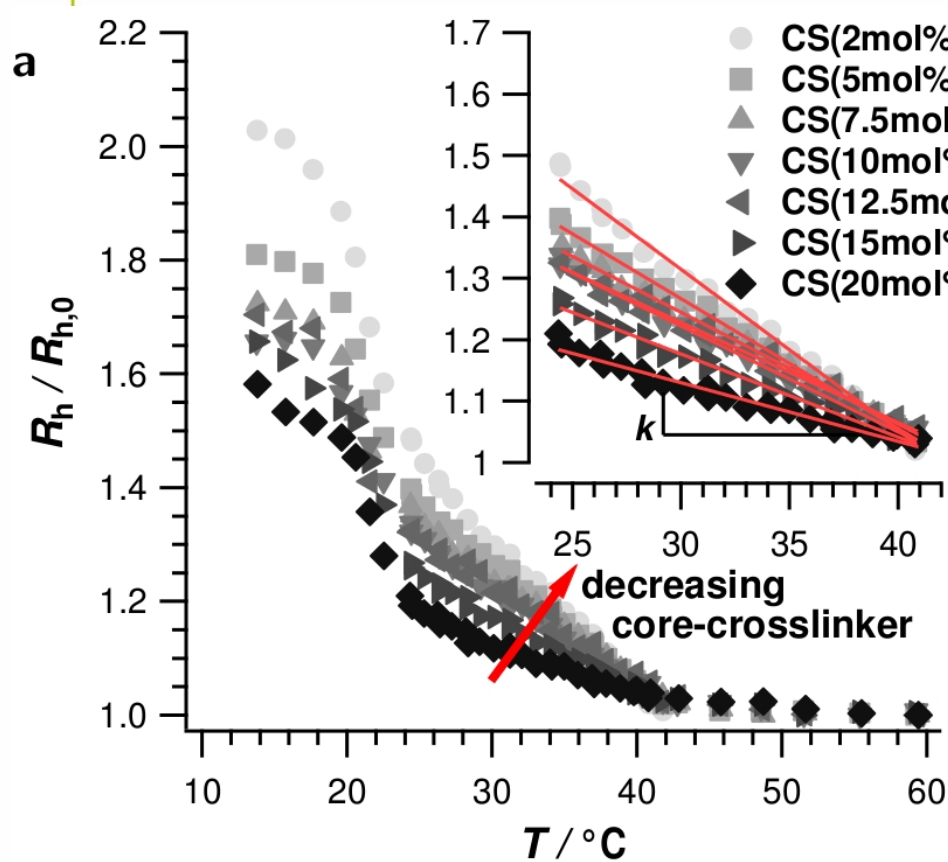
Spherical particles are made



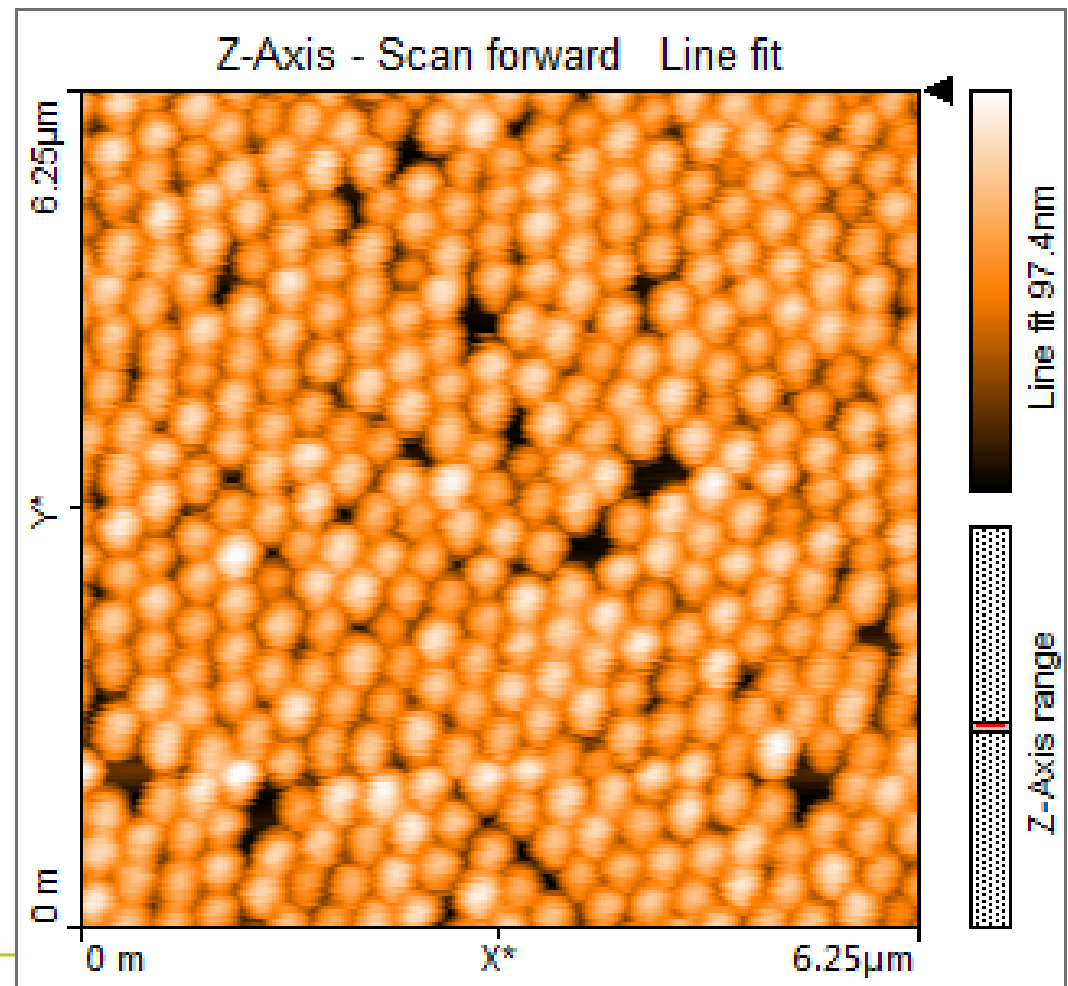
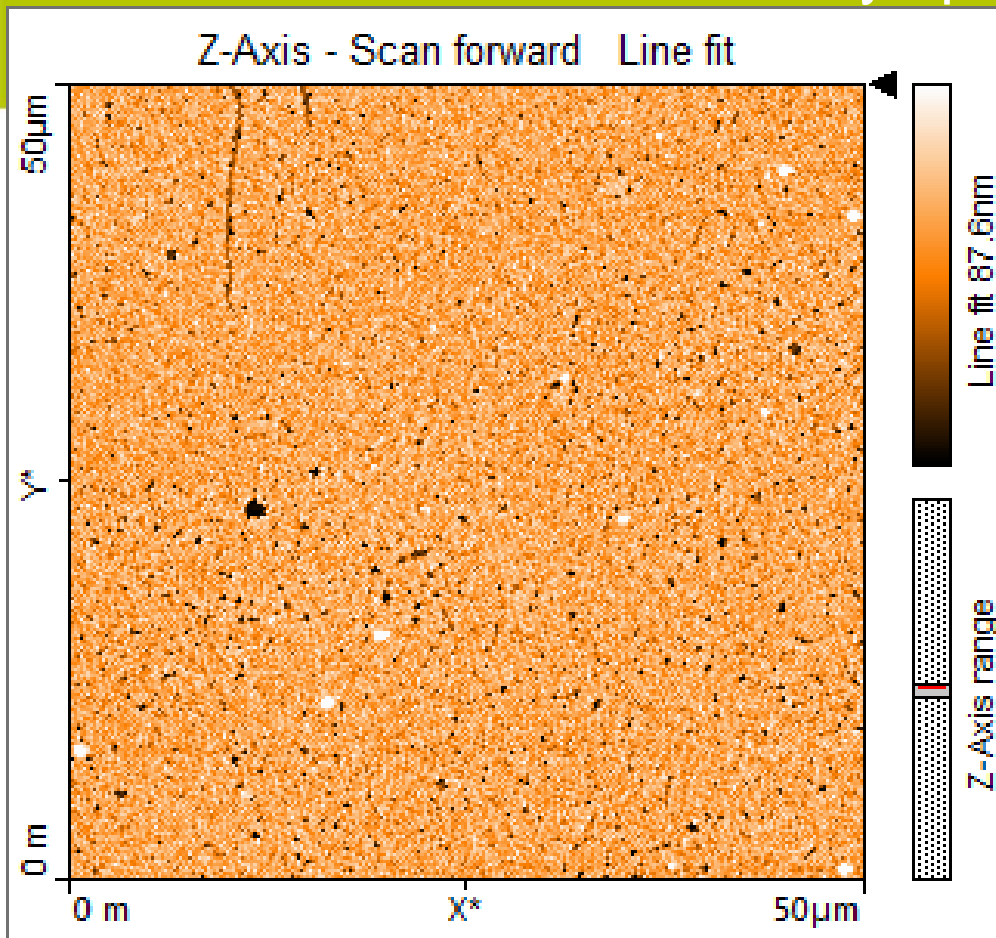


Linear Response due to large gap between LCSTs

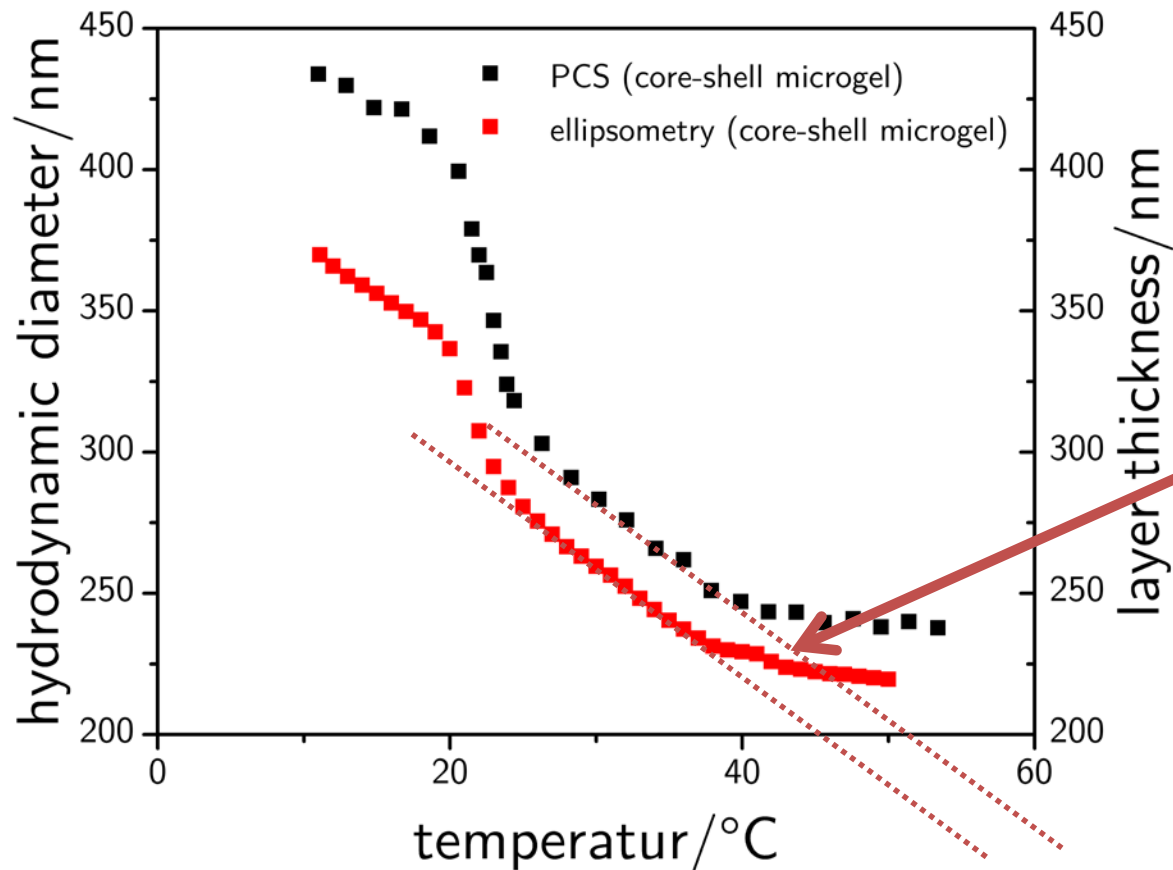
Linear control of the linear domain by the core cross-linker content



Deposition of the core-shell particles on silicon wafers by spin-coating



Linear swelling/de-swelling of adsorbed non-NIPAM based core-shell microgels



PNIPAM
Transition

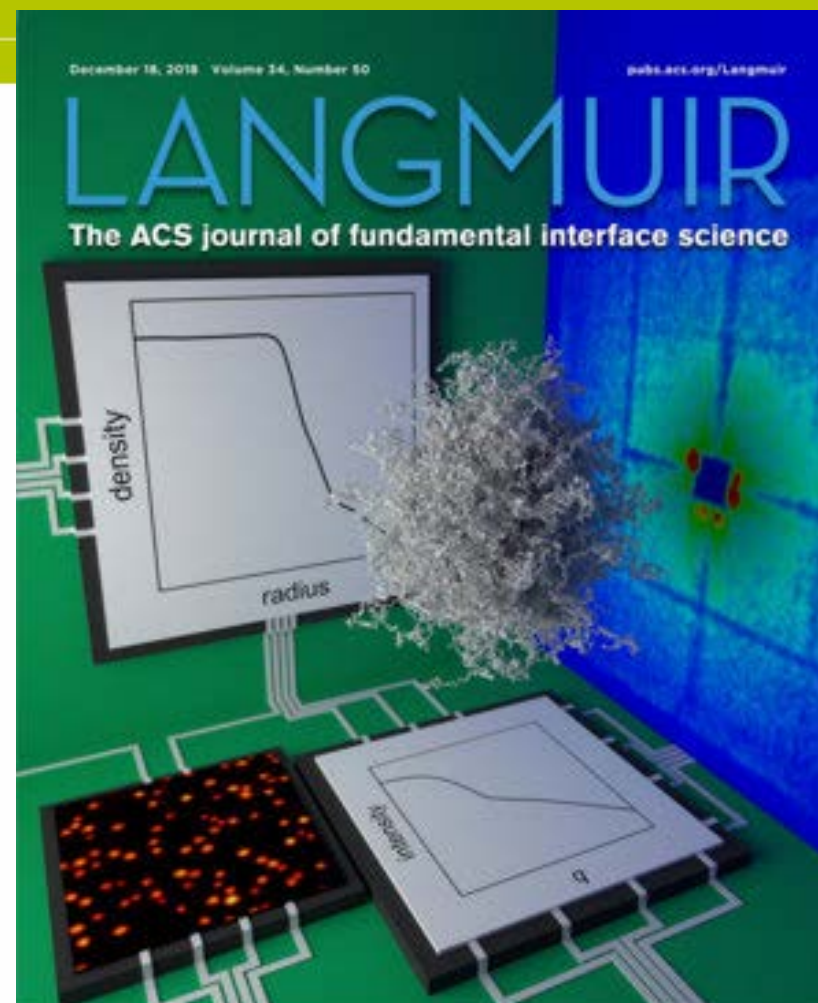
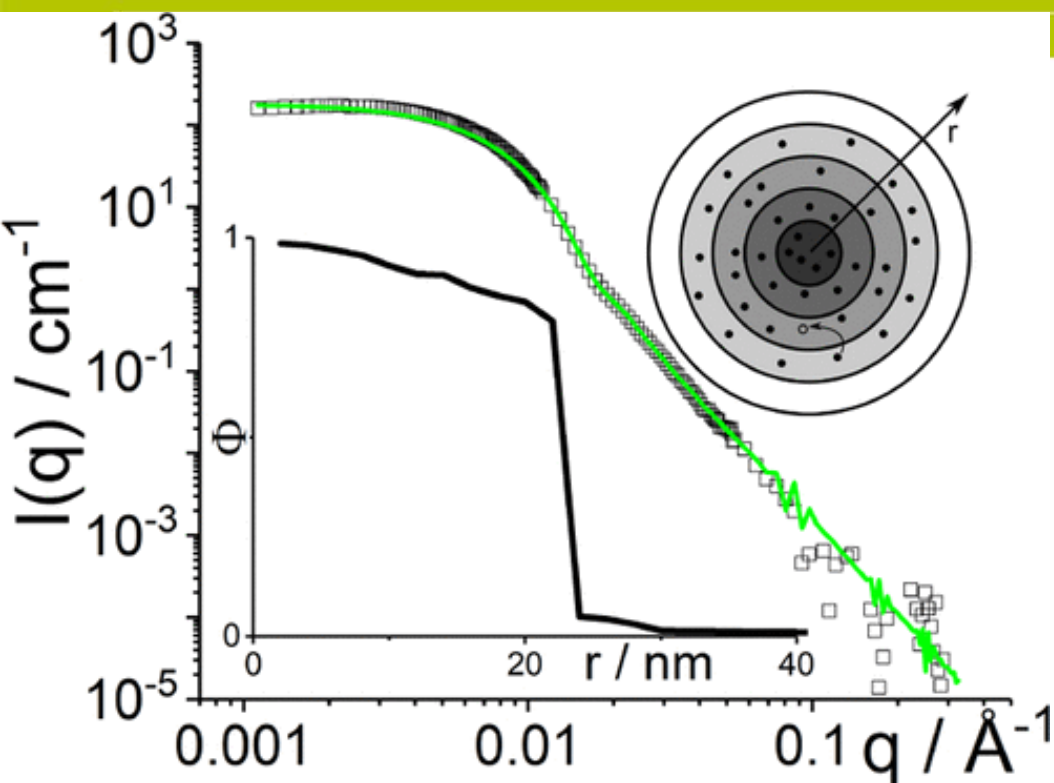
What is the reason for the linear swelling?

M. Cors, O. Wrede, A.-C. Genix, D. Anselmetti,
J. Oberdissse, TH, Langmuir **33** (2017) 6804



Marian Cors

Microgel structure: small angle neutron scattering on PNIPMAM



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→ www.uni-bielefeld.de

Cors, M., Wiehemeier, L., Hertle, Y., Feoktystov, A., Cousin, F., TH, & Oberdisse, J.

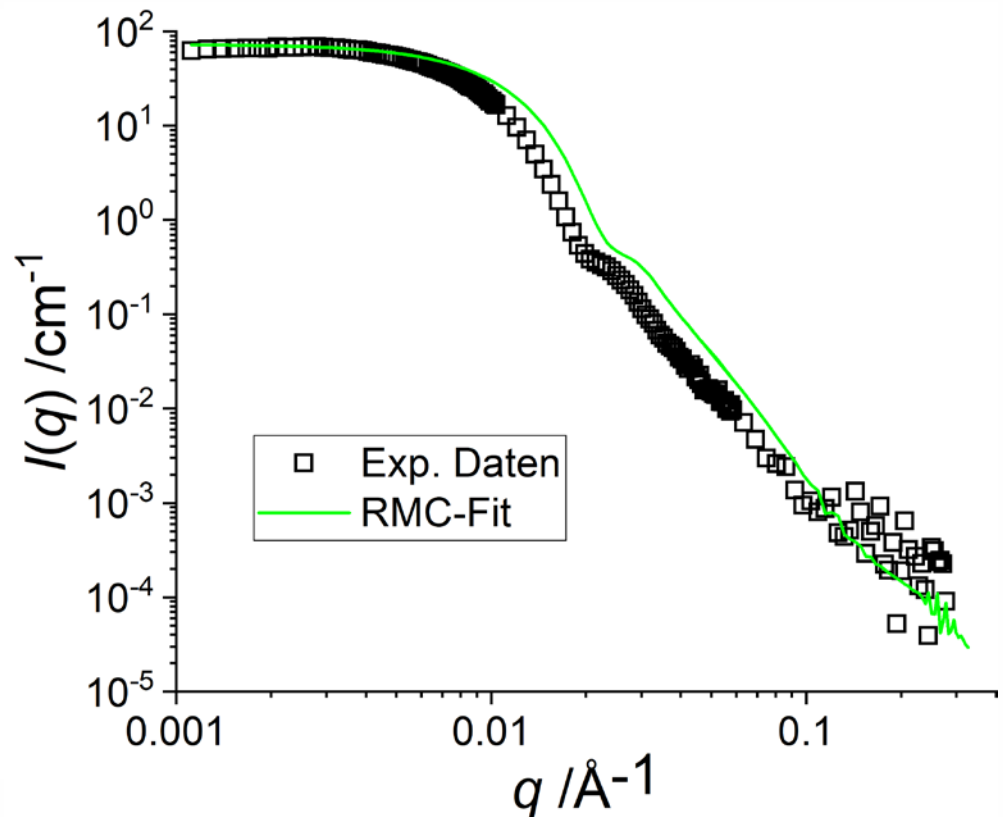
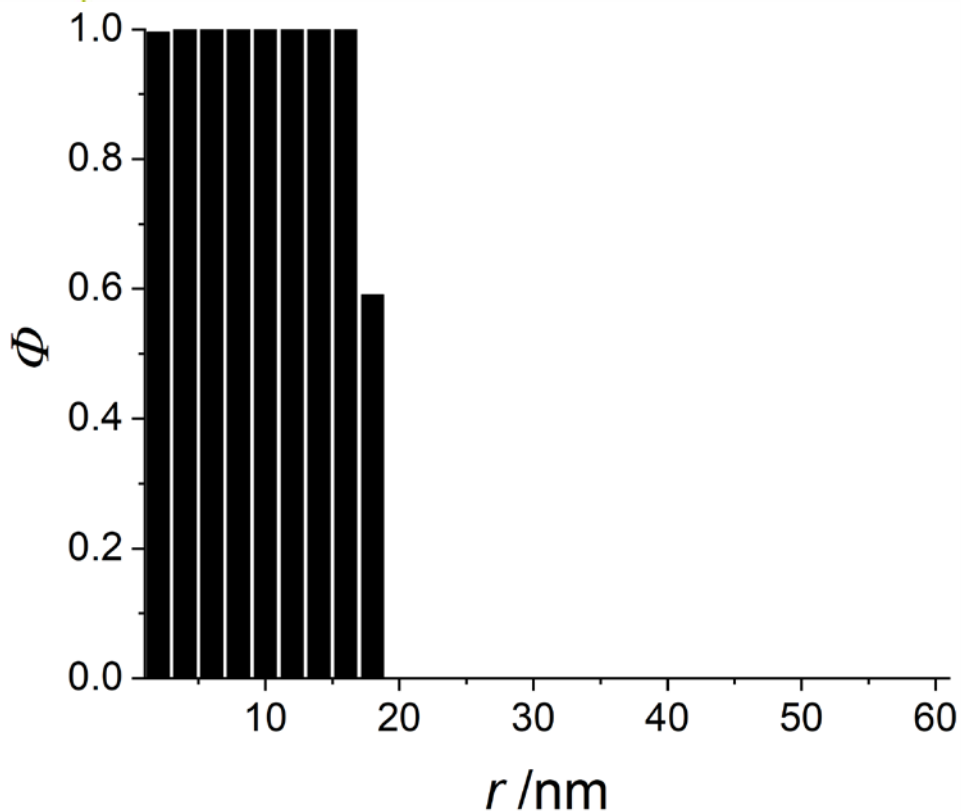
'Determination of internal density profiles of smart acrylamide-based microgels by SANS: A multi-shell reverse Monte-Carlo approach' *Langmuir*, (2019) 34 (50), 15403-15415



Marian Cors

Microgel structure: small angle neutron scattering on PNIPMAM

P(NIPMAM) Microgel at 55 °C



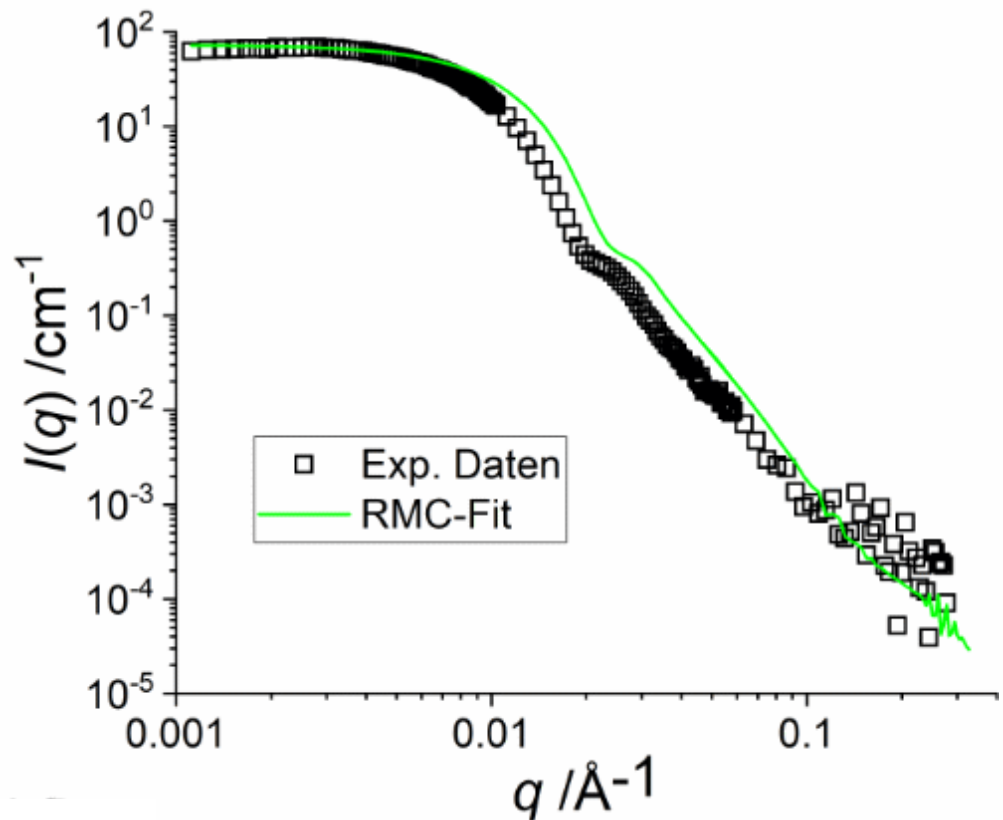
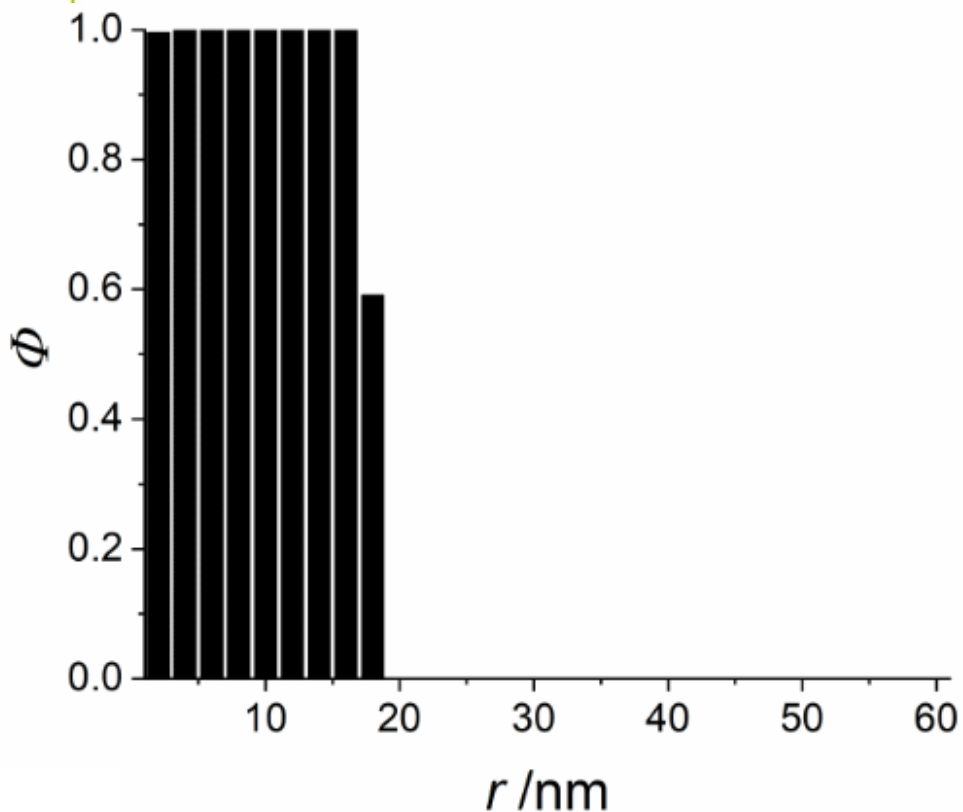


Marian Cors

Microgel structure: small angle neutron scattering on PNIPMAM

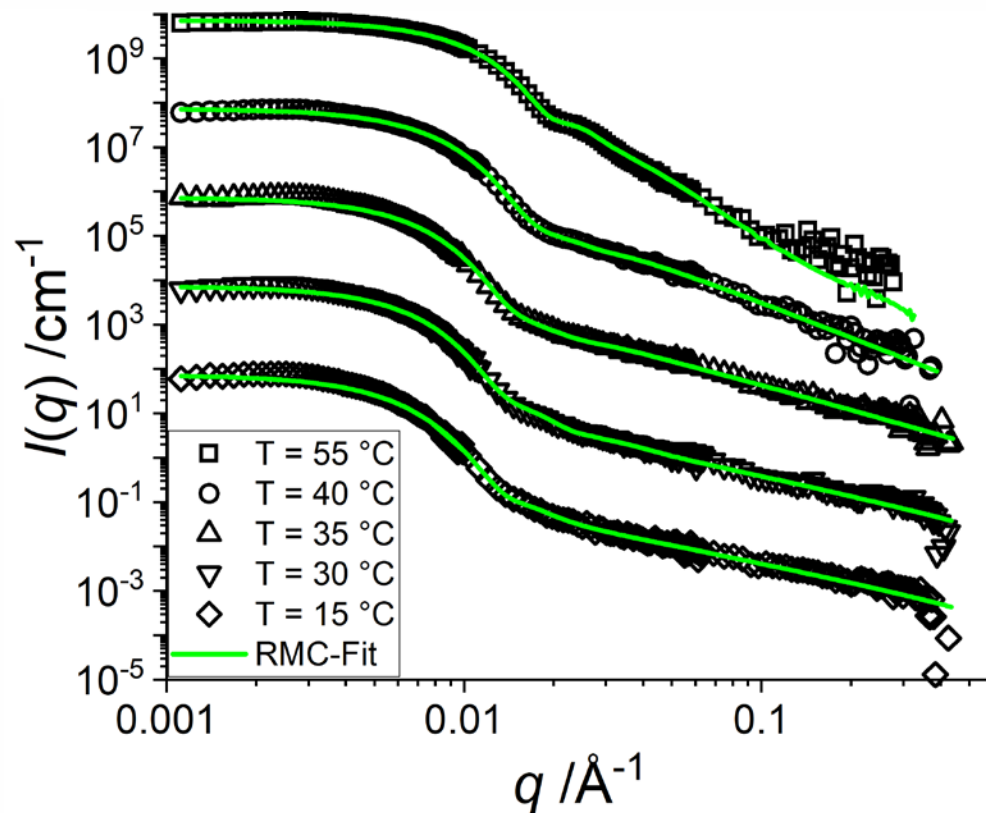
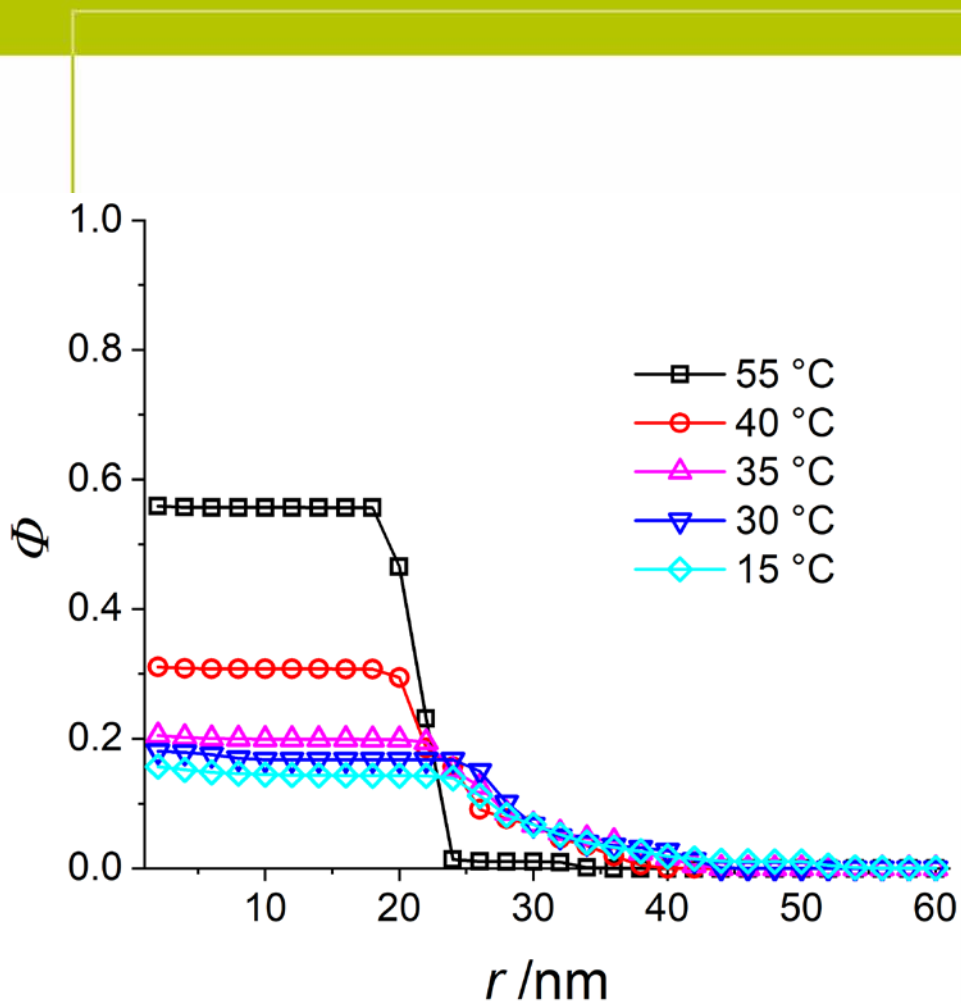
RMC-Fit of Exp. Data

PNIPMAM Microgel at 55 °C



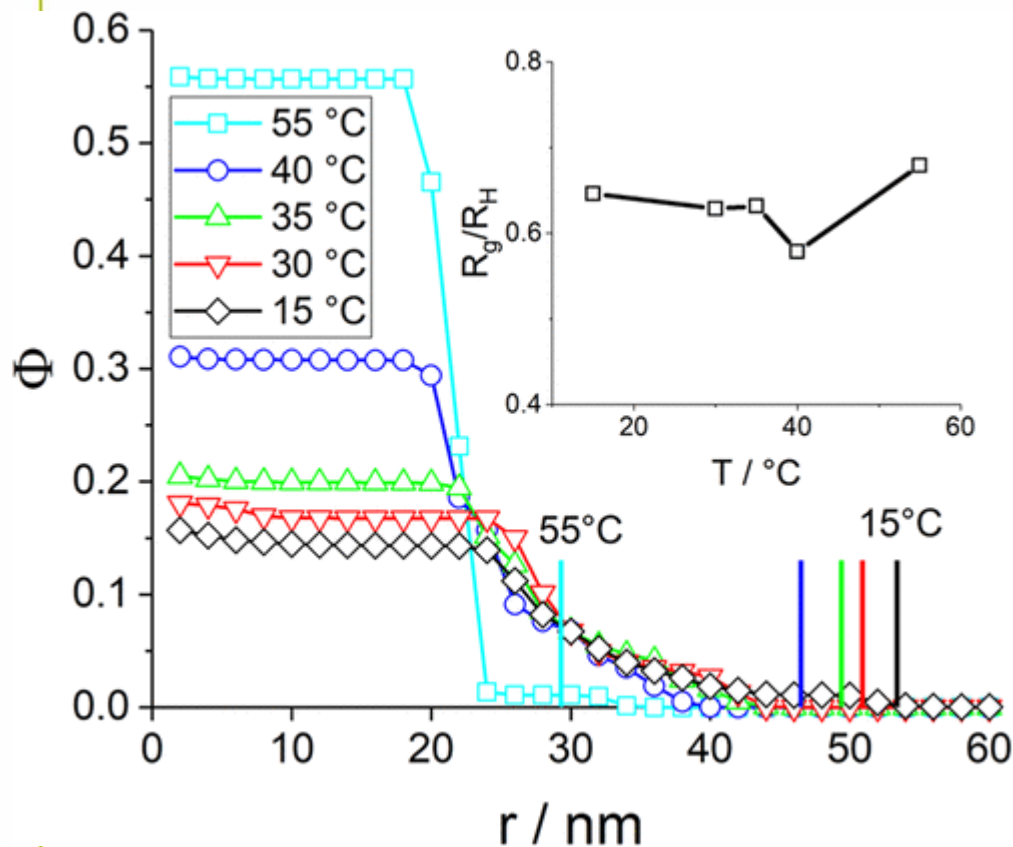
RMC-fit of exp. data

PNIPMAM Microgel



Cors et al., *Langmuir*, 2018.

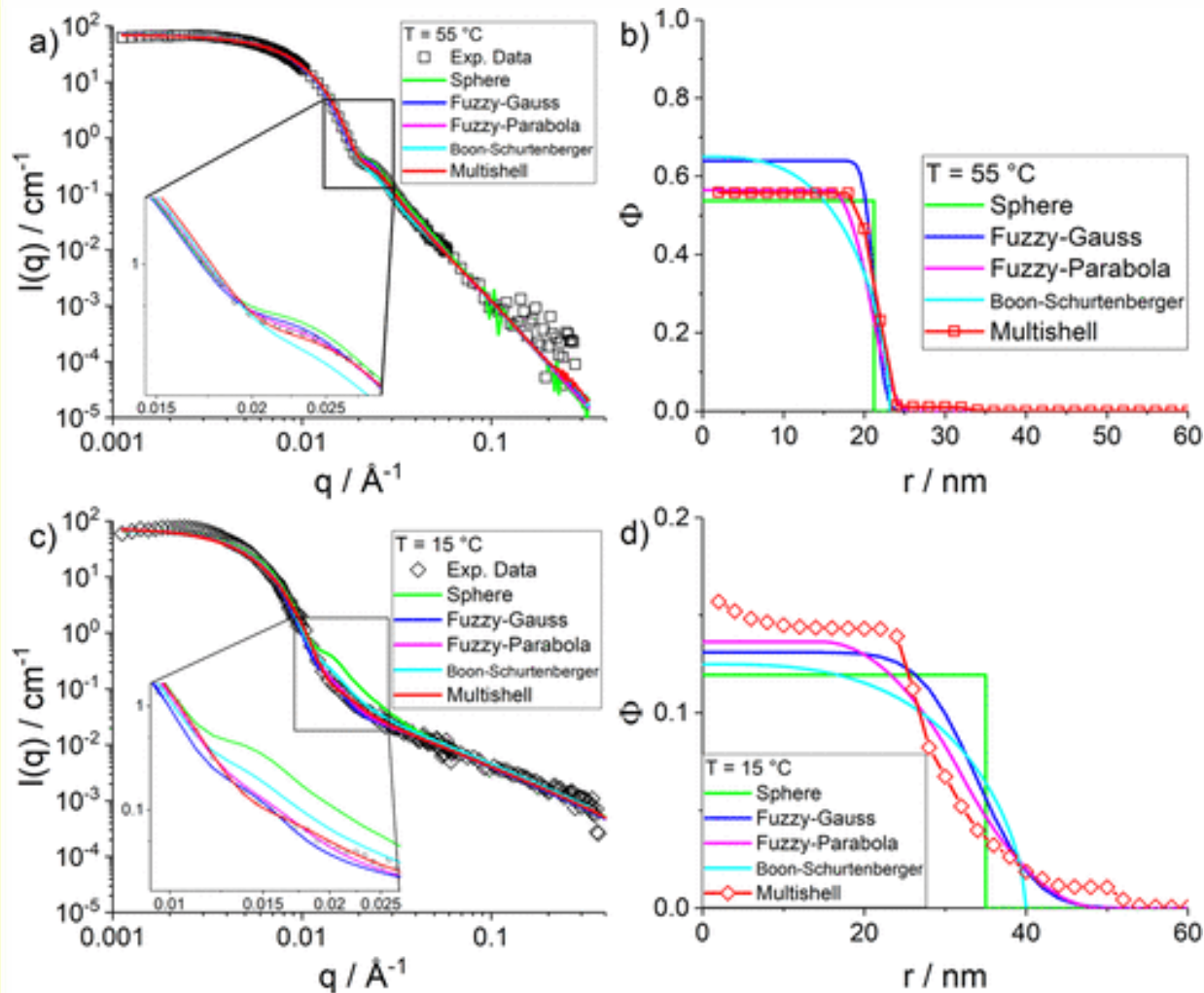
Microgel structure: small angle neutron scattering on PNIPMAM



Density profile of the microgel (CC = 10 mol %) at different temperatures as indicated in the legend. The vertical colored bars indicate the hydrodynamic radii of the same samples.

Cors, M., Wiehemeier, L., Hertle, Y., Feoktystov, A., Cousin, F., TH, & Oberdisse, J. 'Determination of internal density profiles of smart acrylamide-based microgels by SANS: A multi-shell reverse Monte-Carlo approach' *Langmuir*, (2018) 34 (50), 15403-15415

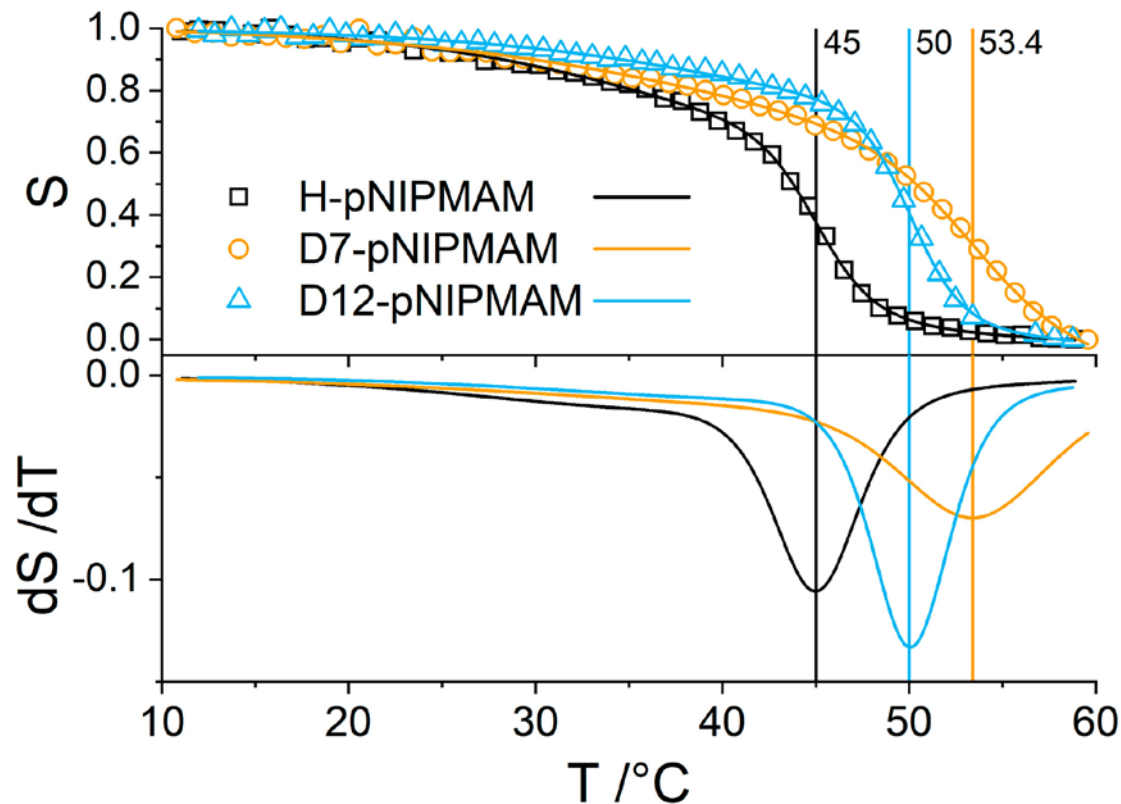
Microgel structure: small angle neutron scattering on PNIPMAM



Comparison of experimental intensities (10 mol % CC) with other models as indicated in the legend

Cors, M., Wiehemeier, L., Hertle, Y., Feoktystov, A., Cousin, F., T. Hellweg, & Oberdissse, J., *Langmuir*, (2018) 34 (50), 15403-15415

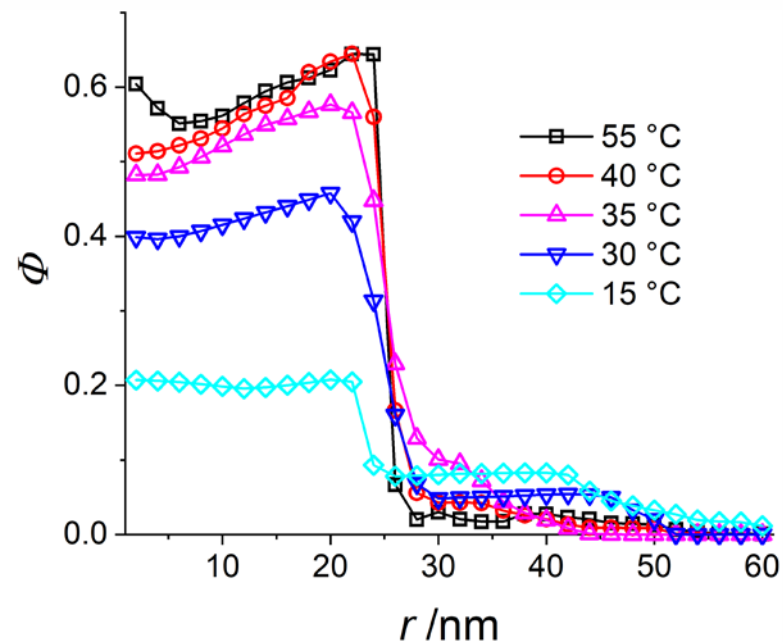
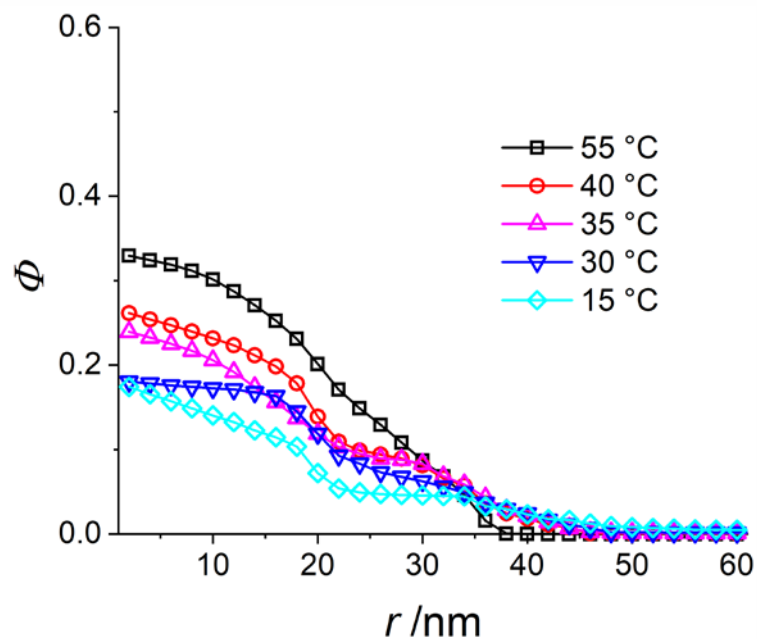
Core-shell particles: contrast variation



Deuteration can have an important influence on the particle behavior

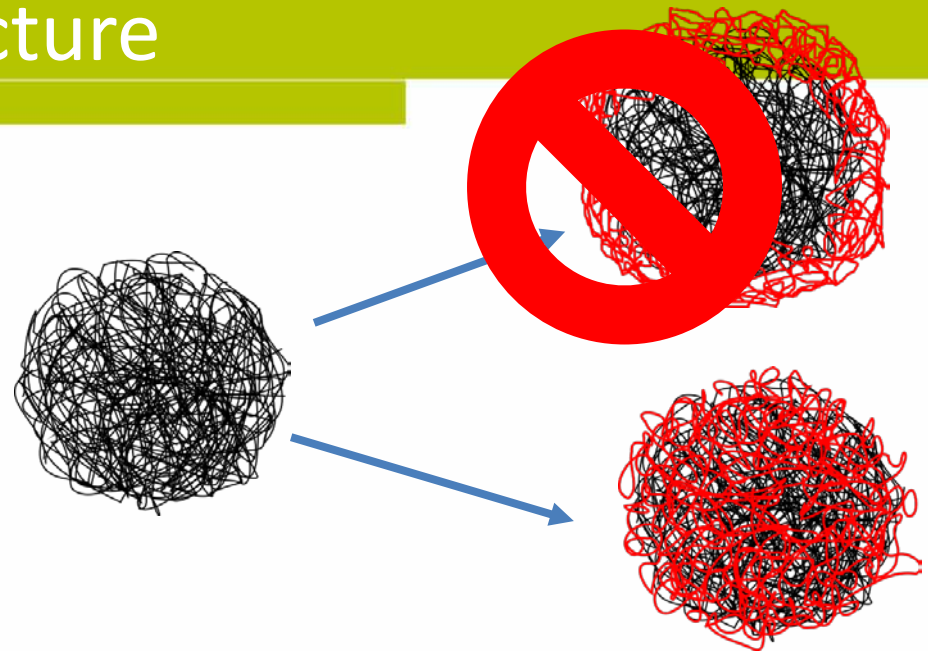
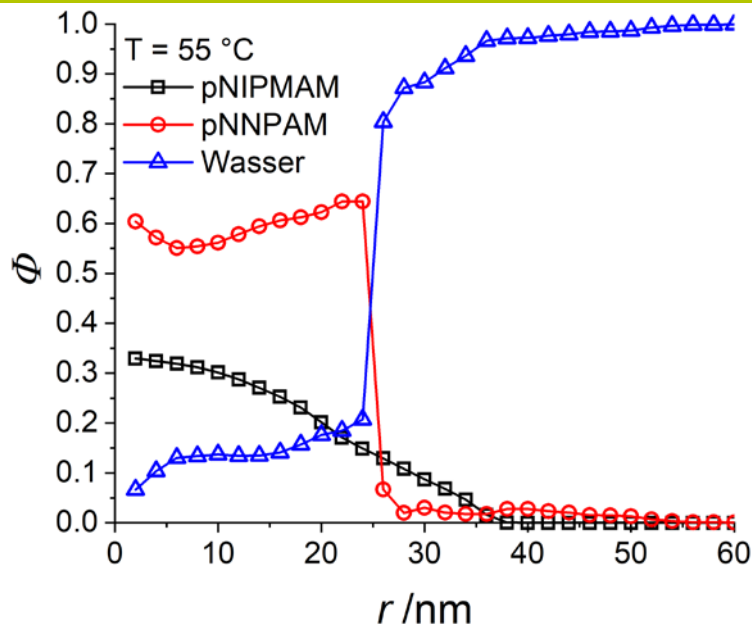
Cors, M., Wiehemeier, L., Oberdisse, J. and T. H.
'Deuteration induced VPTT shift of PNIPMAM microgels'
Polymers, (2019), 11 (4), 320.

Core-shell particles: contrast variation



Cors, M., Wrede, O., Wiehemeier, L., Feoktystov, A., Cousin, F., T. Hellweg, Oberdisse, J., Sci. Rep. (2019), 9, 13812. DOI:10.1038/s41598-019-41865-z

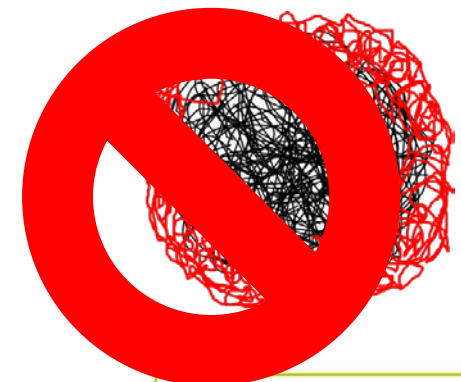
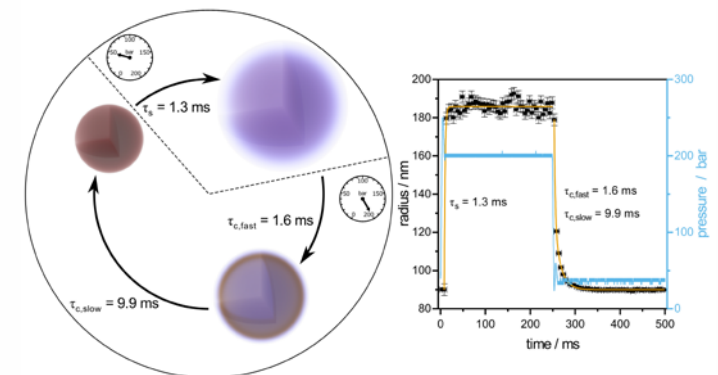
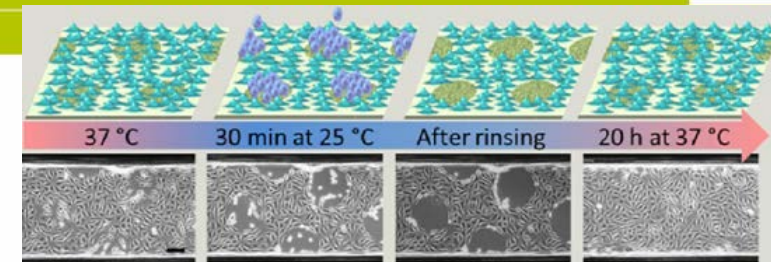
PNIPMAM@PNNPAM microgels structure



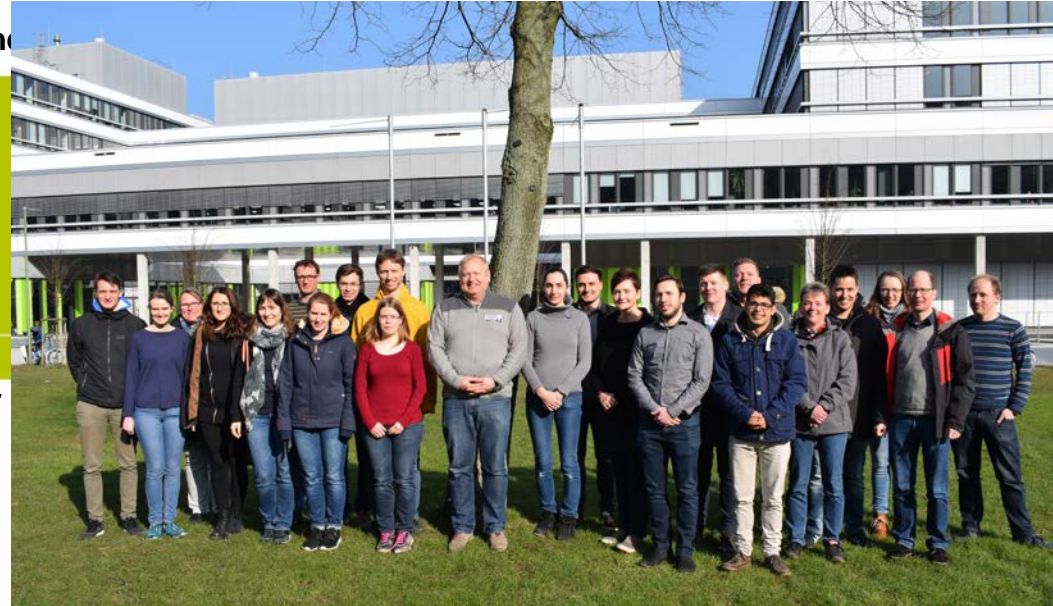
1. No real core-shell structure but interpenetrating network
2. No corset effect
3. Linear swelling most-likely due to a kind of copolymer gradient

Conclusion

- Microgels have high potential for new applications
- Response times are in the millisecond range
- The PNIPMAM@PNNPAM core-shell microgels are in fact interpenetrating networks with a very thin and fuzzy PNNPAM shell



Acknowledgement



Physical and Biophysical Chemistry

Dr. Johannes Bookhold (now Clariant)

Maxime Dirksen

Dr. Yvonne Hannappel

Marian Cors

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