Institute of Mechanical Process Engineering
and Mineral Processing

*TU Clausthal
Clausthal University of Technology

Nanoparticles in Organic Solvents with Polymers

Stability and Consequences Upon Material Synthesis Through Spray Drying

Martin Rudolph, Urs A. Peuker

Deutsche Forschungsgemeinschaft

German Research Foundation
project: **PE1160/7-1**

June 29th 2011
NanoFormulation 2011

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Outline

1) Motivation
2) Solution Method
3) Preliminary Investigations
4) Theory of Nanoparticle Interactions
5) Experiments - Stability
   a) Destabilization with non-adsorbing PMMA, PC, PS
   b) Stabilization with adsorbing PVB
6) Summary and Conclusion

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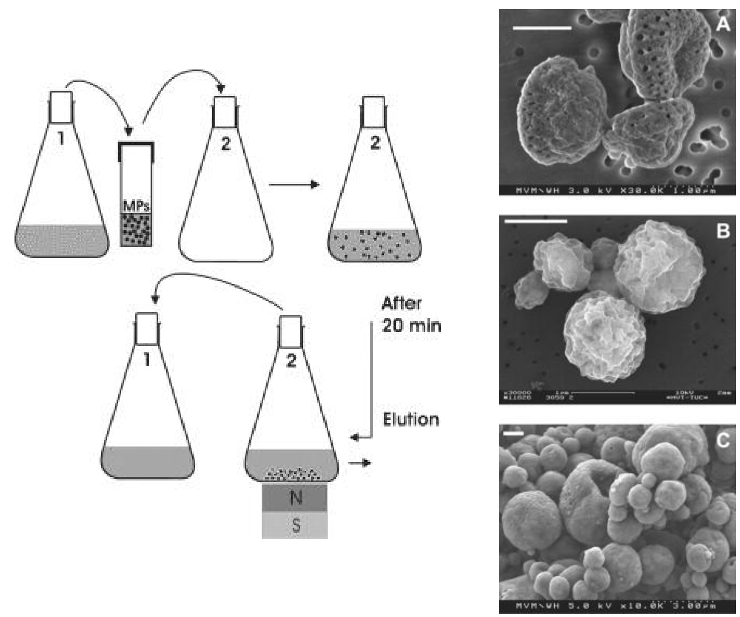
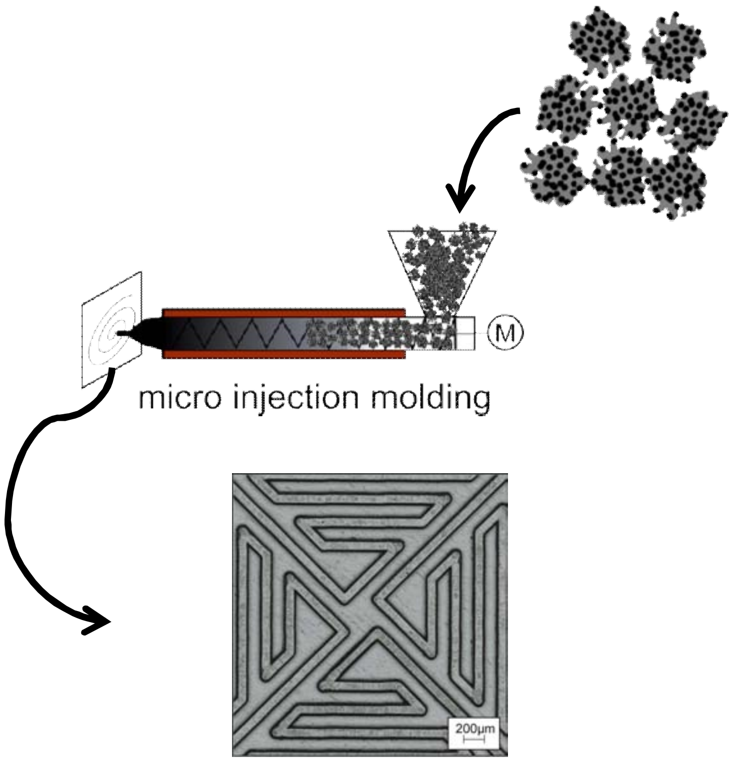
- Synthesis of highly filled polymer nanoparticle composites ($\varphi_{\mathrm{Nano}} > 10\ \%$)



Magnetic Beads for sorptive Bioseparation

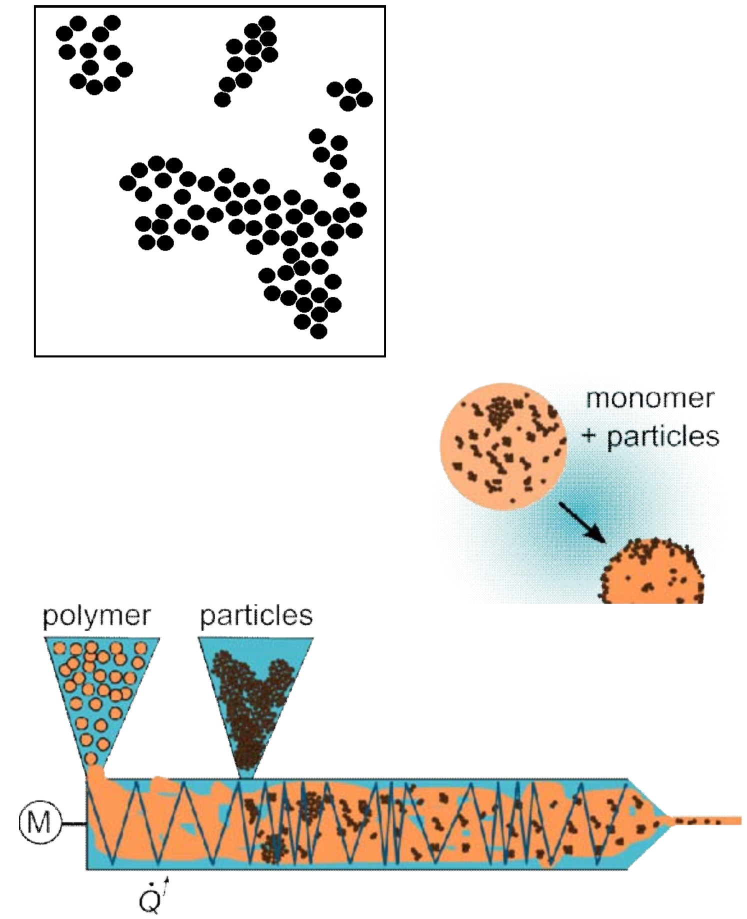
Hickstein, B., Peuker, U.A.
J Appl Poly Sci, 112, 2366

- Synthesis of highly filled polymer nanoparticle composites (φ_{Nano} > 10 %)



Composite Micropowder for Micro Injection Molding

- Synthesis of highly filled polymer nanoparticle composites (φ_{Nano} > 10 %)
- Overcoming problem of dispersing (deagglomeration + mixing)



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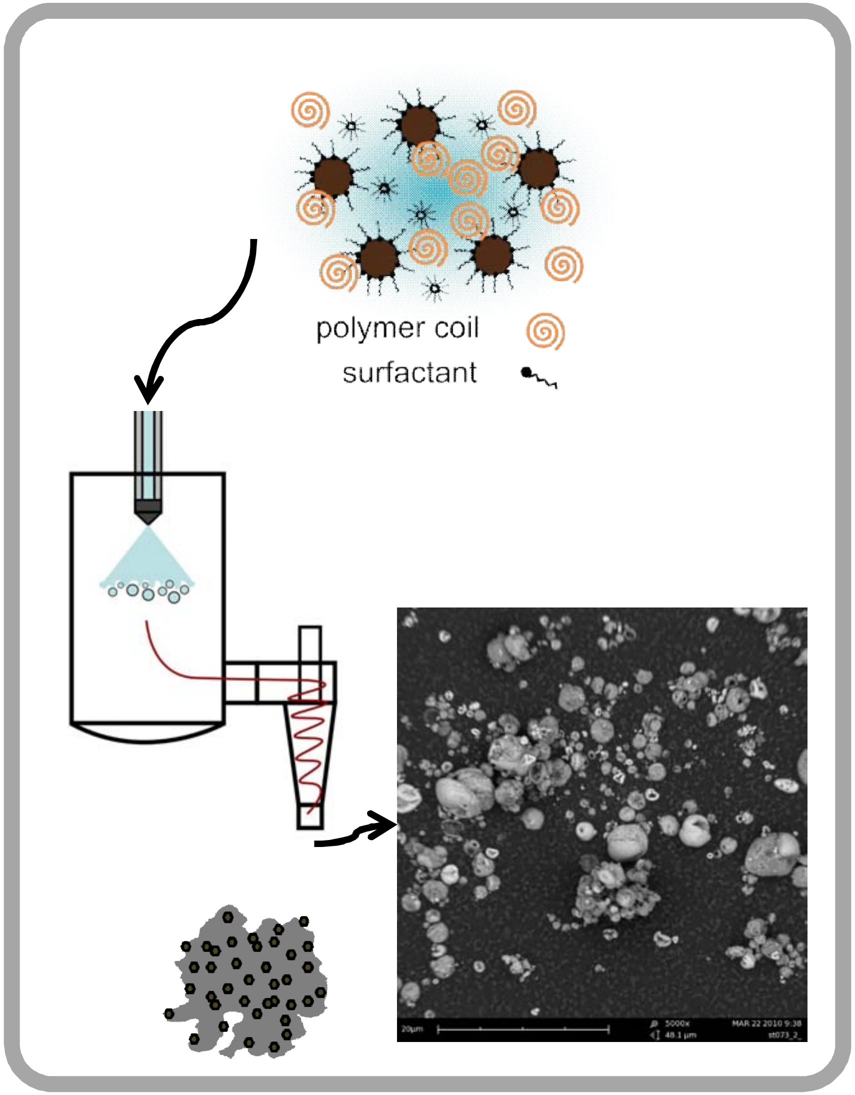
- Synthesis of highly filled polymer nanoparticle composites (φ_{Nano} > 10 %)
- Overcoming problem of dispersing (deagglomeration + mixing)
- We present an alternative modular process with the solution and spray drying method



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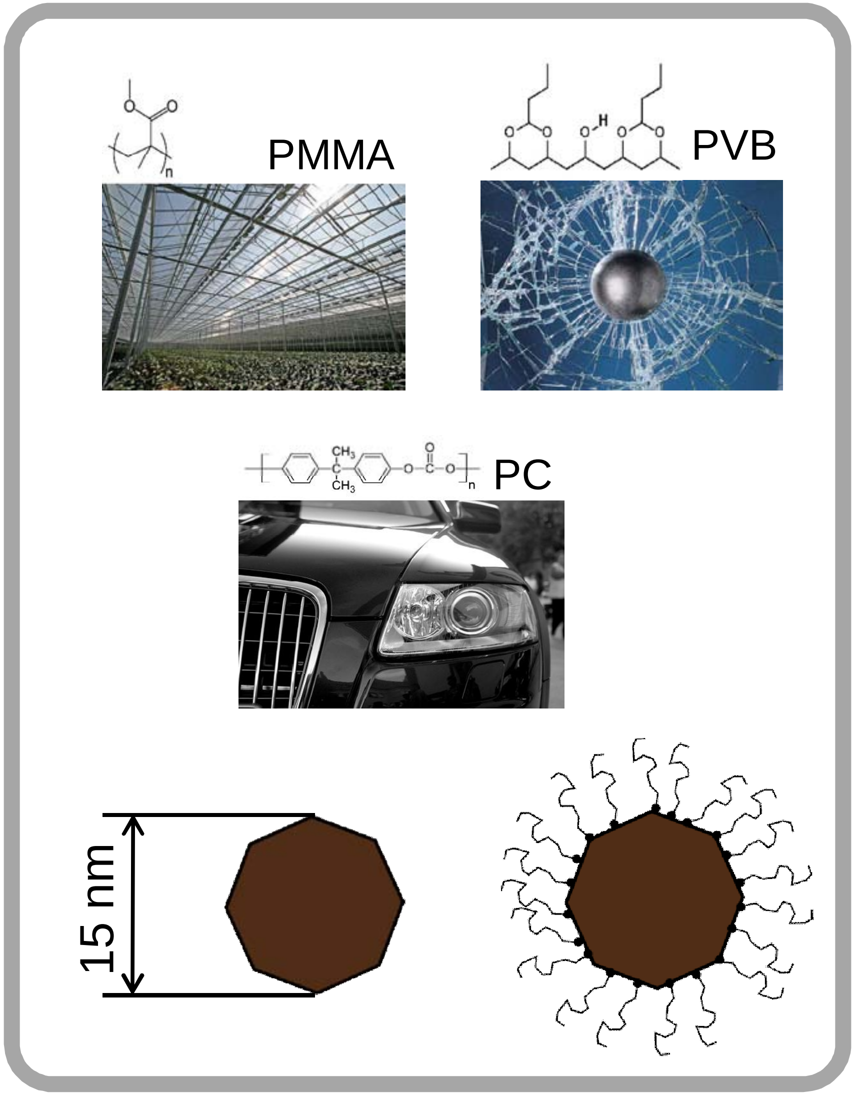
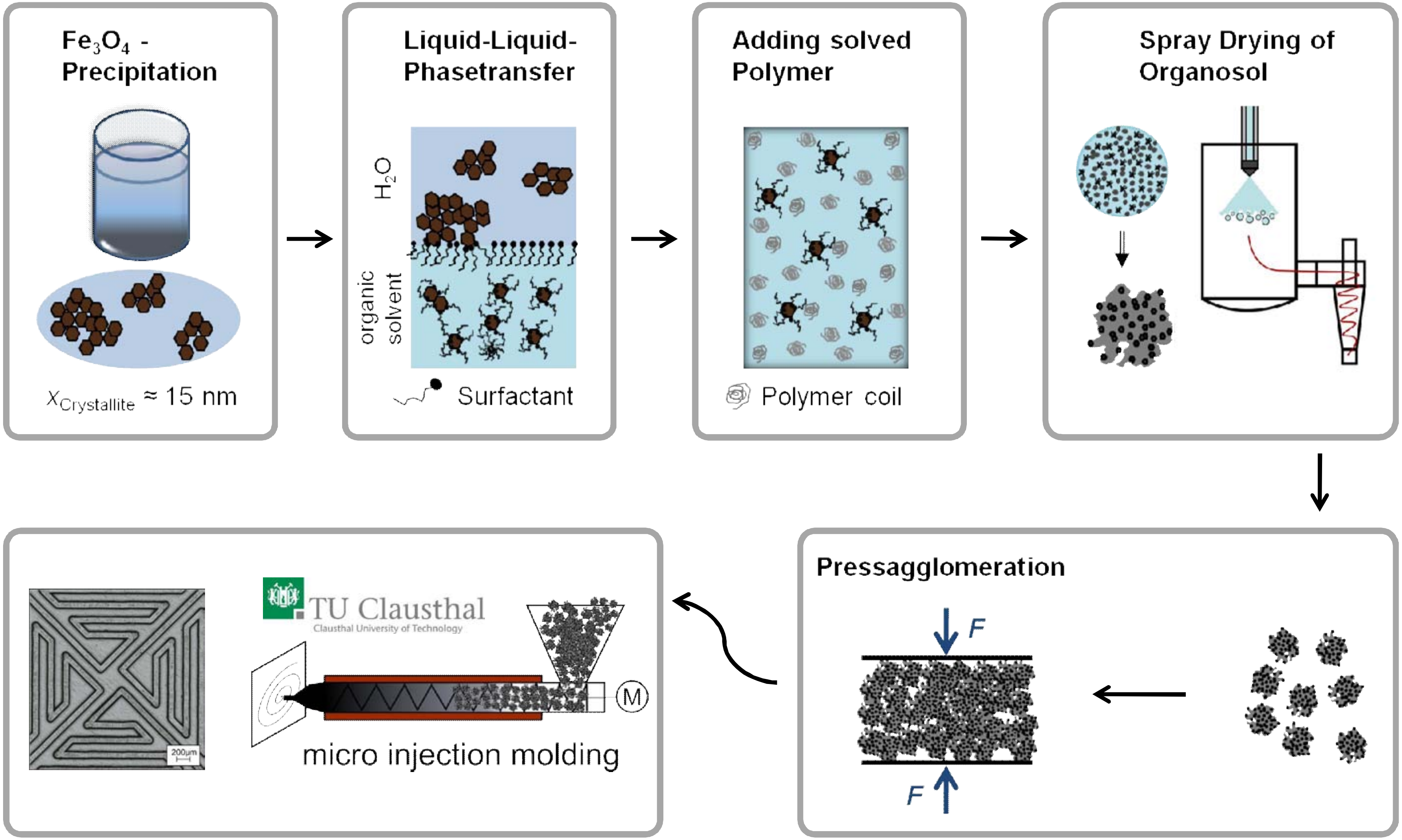
2 Solution Method

- **Polymers**
  - Poly(methyl methacrylate)
  - Poly(vinyl butyral)
  - Poly(bisphenol A carbonate)
- **Nanoparticles**
  - Fe_3O_4 magnetite, superparamagnetic
- **Solvent(s)**
  - Dichloromethane
  - Ethyl Acetate
- **Surfactants**
  - carboxylic acids (C14 - C18)





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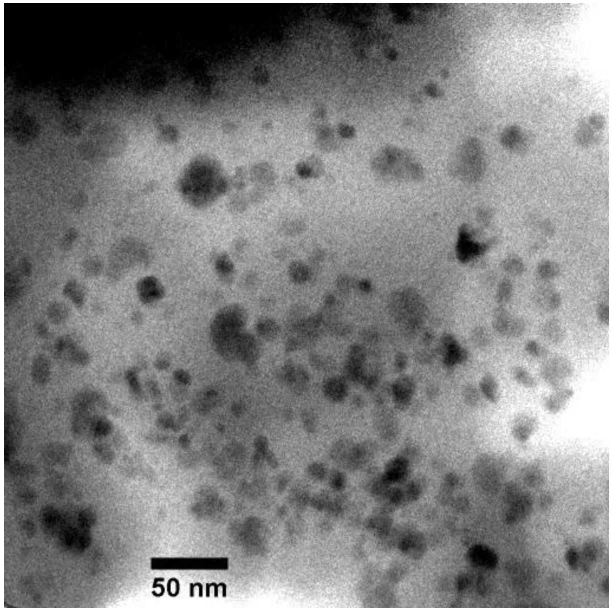
Investigations with TEM and pc-AFM

- TEM
  good distribution for spray dried microcomposite particle



TEM, spray dried particle

PMMA49 **RS**21 **MAG**30

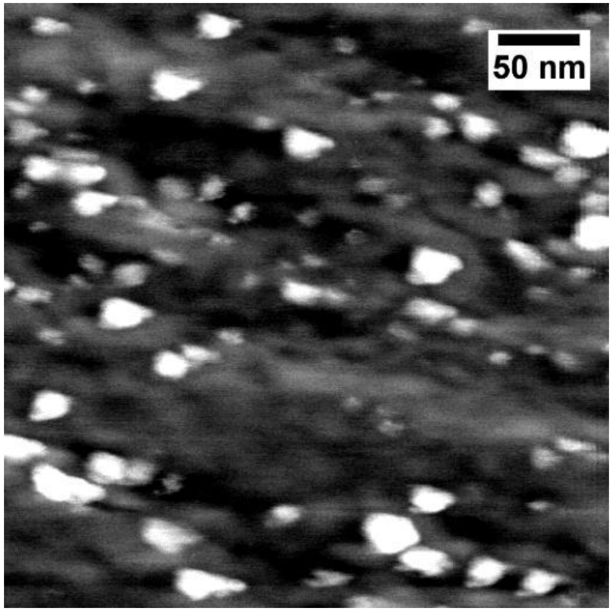
Investigations with TEM and pc-AFM

- TEM
  good distribution for spray dried microcomposite particle

- phase contrast AFM
  shows good distribution in an injection moulded sample

  Rudolph,M. *Chem Ing Tech,* 82, 2189 (2010)

- **BUT**: both investigations only have a very narrow field of view

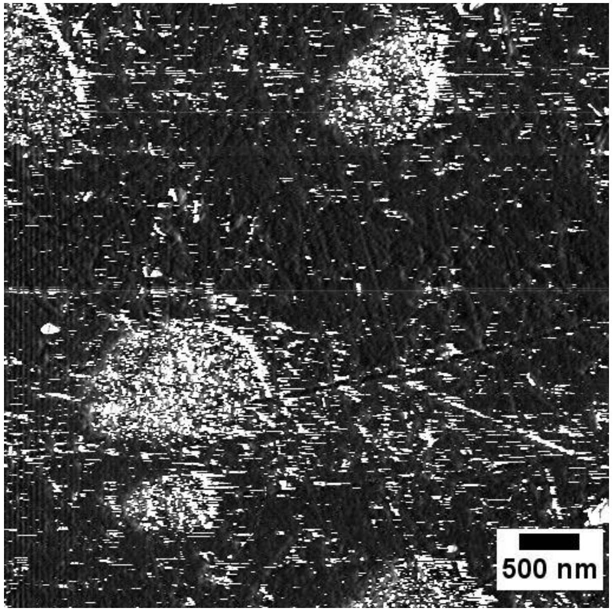


phase contrast AFM, injection moulded sample

PMMA64 **RS**06 **MAG**30

Investigations with TEM and pc-AFM

- phase contrast AFM
  large areas of higher phase
  values



phase contrast AFM,
injection moulded sample

PMMA64 **RS**06 **MAG**30

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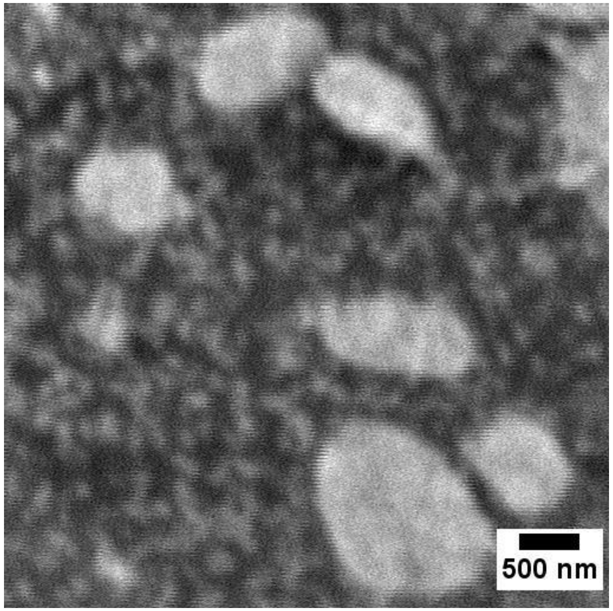
Investigations broad field pc-AFM and BSE-SEM

- phase contrast AFM
  large areas of higher phase values

- similar „clusters“ for BSE-SEM



back scattering electron SEM, sample as before

PMMA64 **RS**06 **MAG**30

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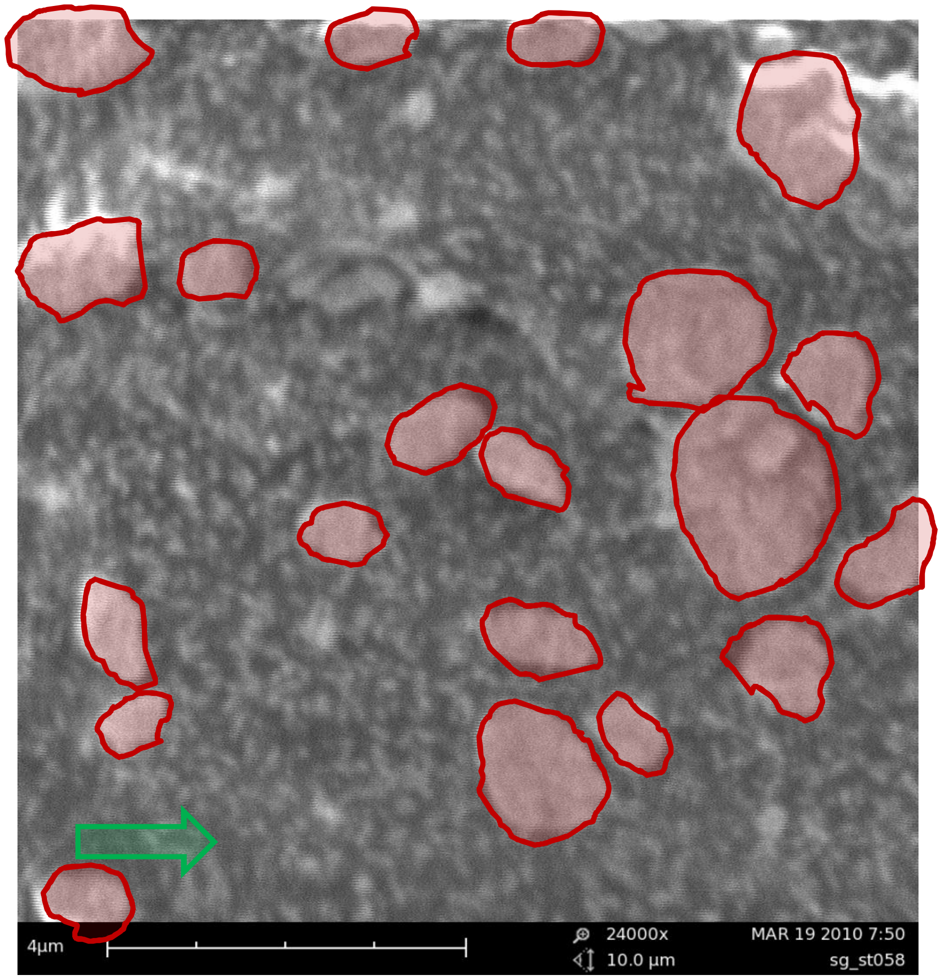
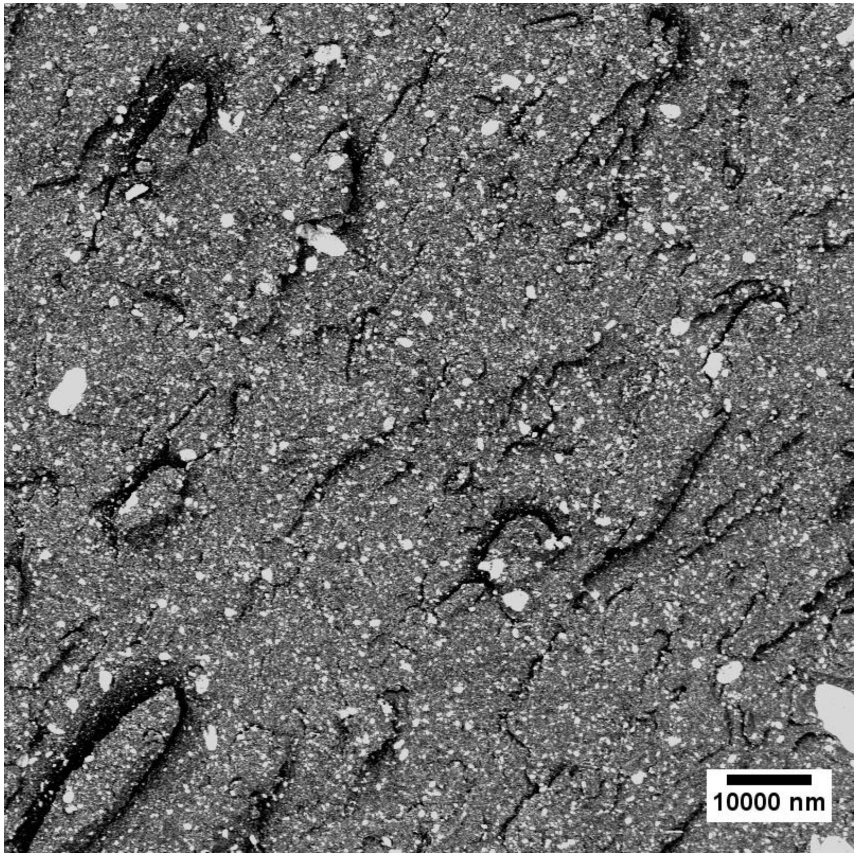
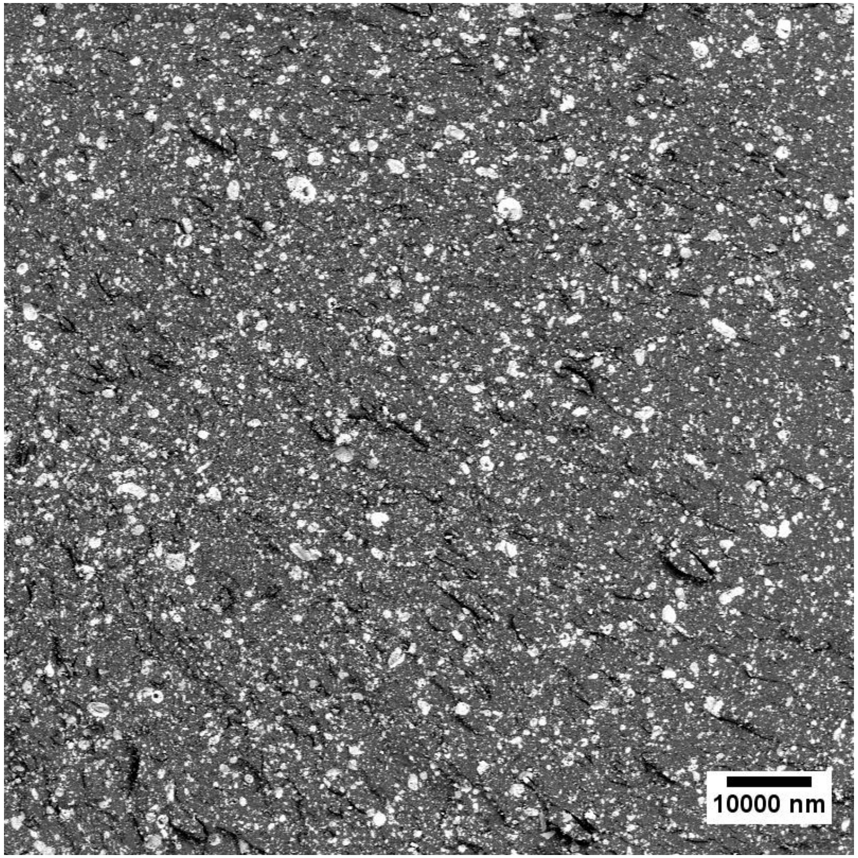
Agglomerates? / Primary Particles?



Investigations broad field pc-AFM and BSE-SEM



PMMA61 – RS09 – MAG30



PMMA40 – RS10 – MAG50

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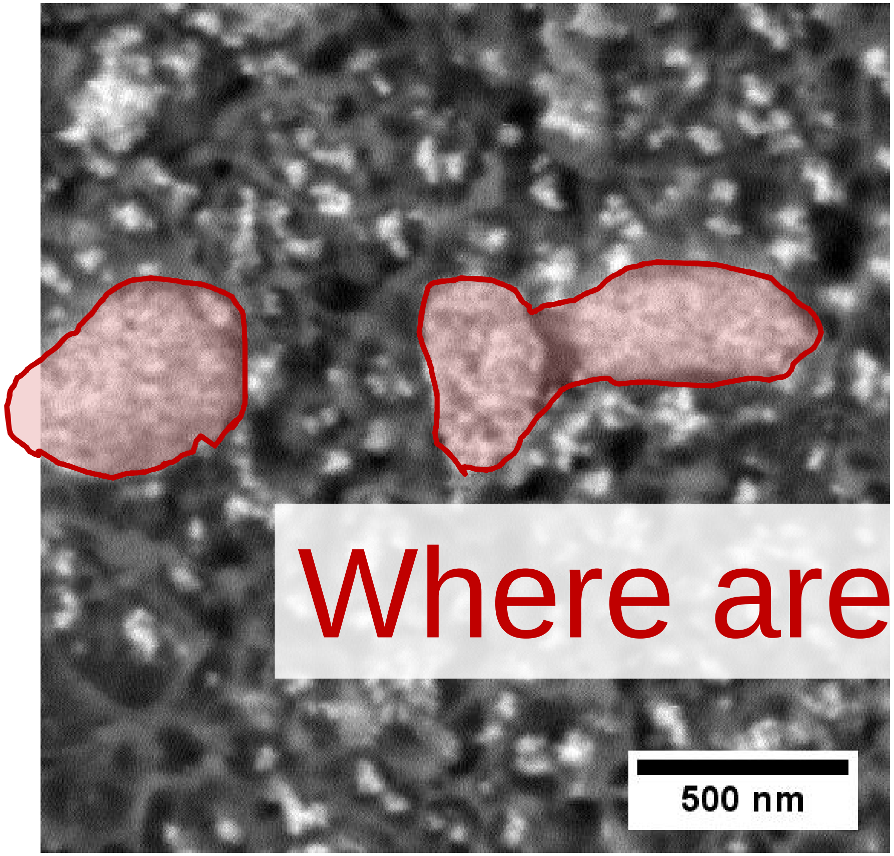

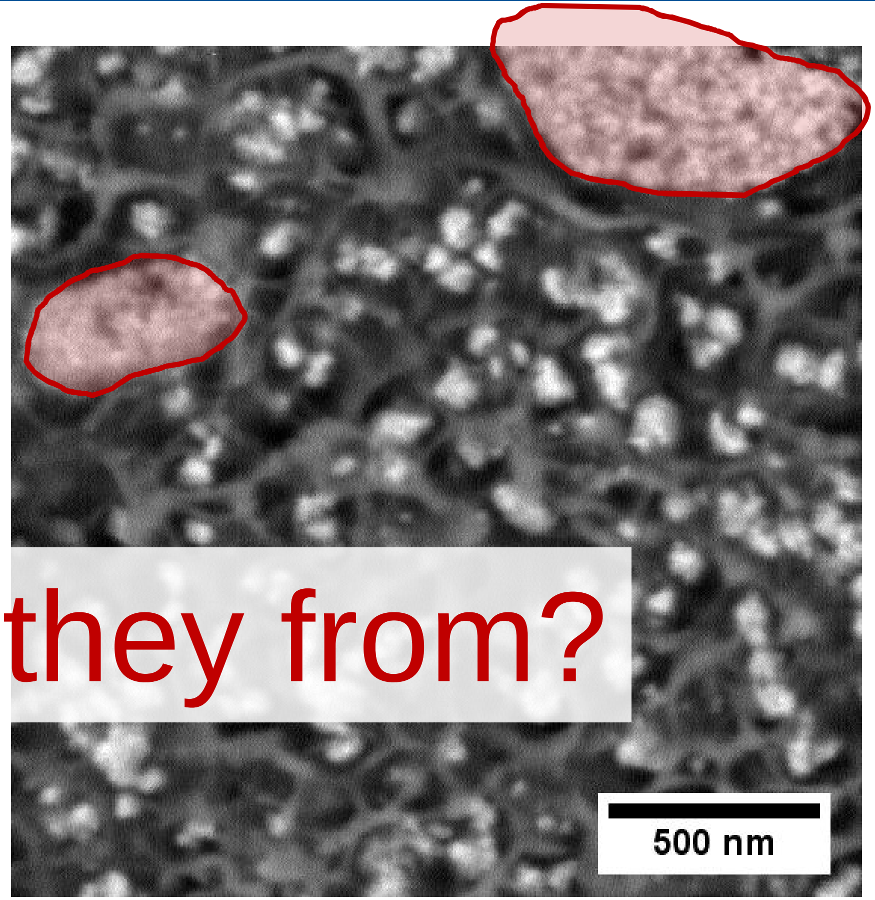

Where are they from?

PMMA61 – RS09 – MAG30

PMMA40 – RS10 – MAG50

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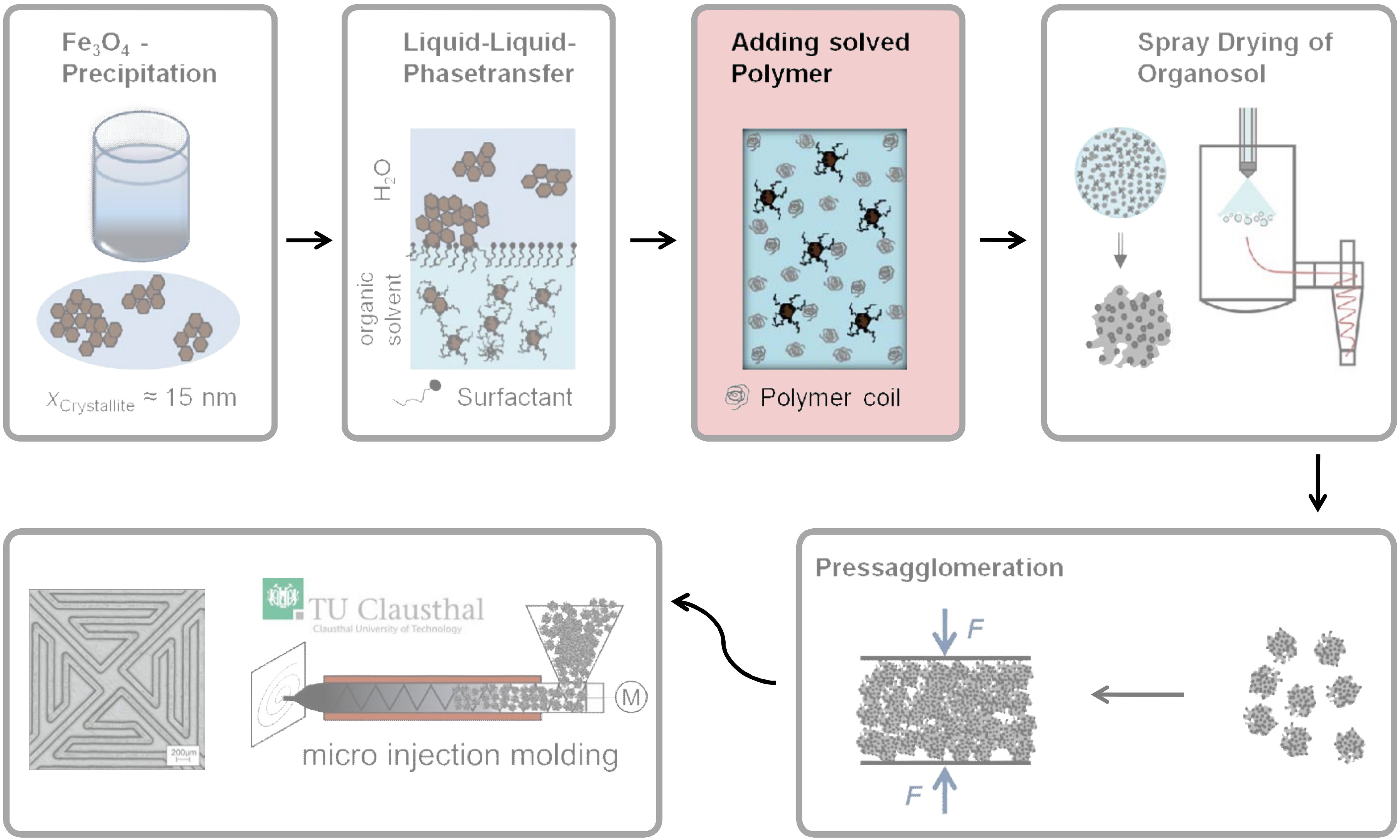

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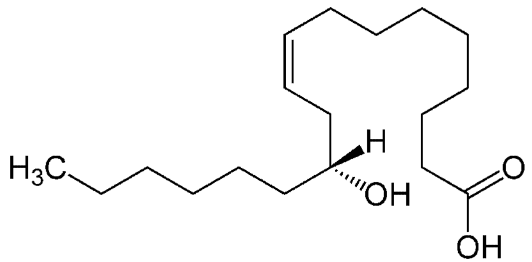
- strong VAN DER WAALS attraction leads to agglomeration

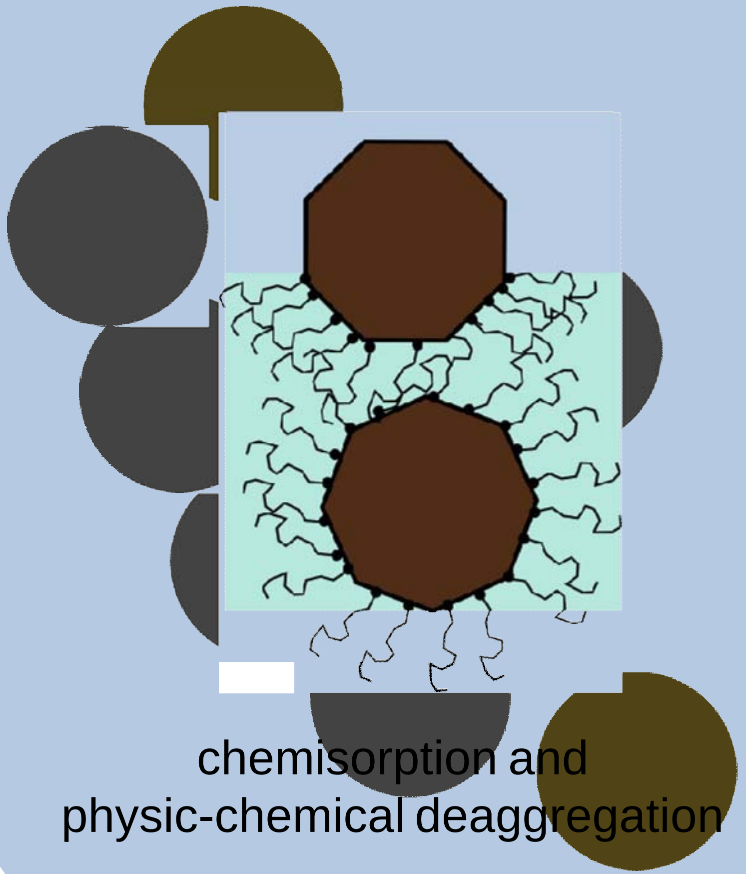
- stabilization against agglomeration with surfactants by liquid-liquid phase-transfer

Machunsky, S. *Coll & Surf A,* 348, 186 (2009)



surfactant of choice: ricinoleic acid

Gyergyek, S. *J Coll Interf Sci,* 354, 498 (2011)



chemisorption and physic-chemical deaggregation

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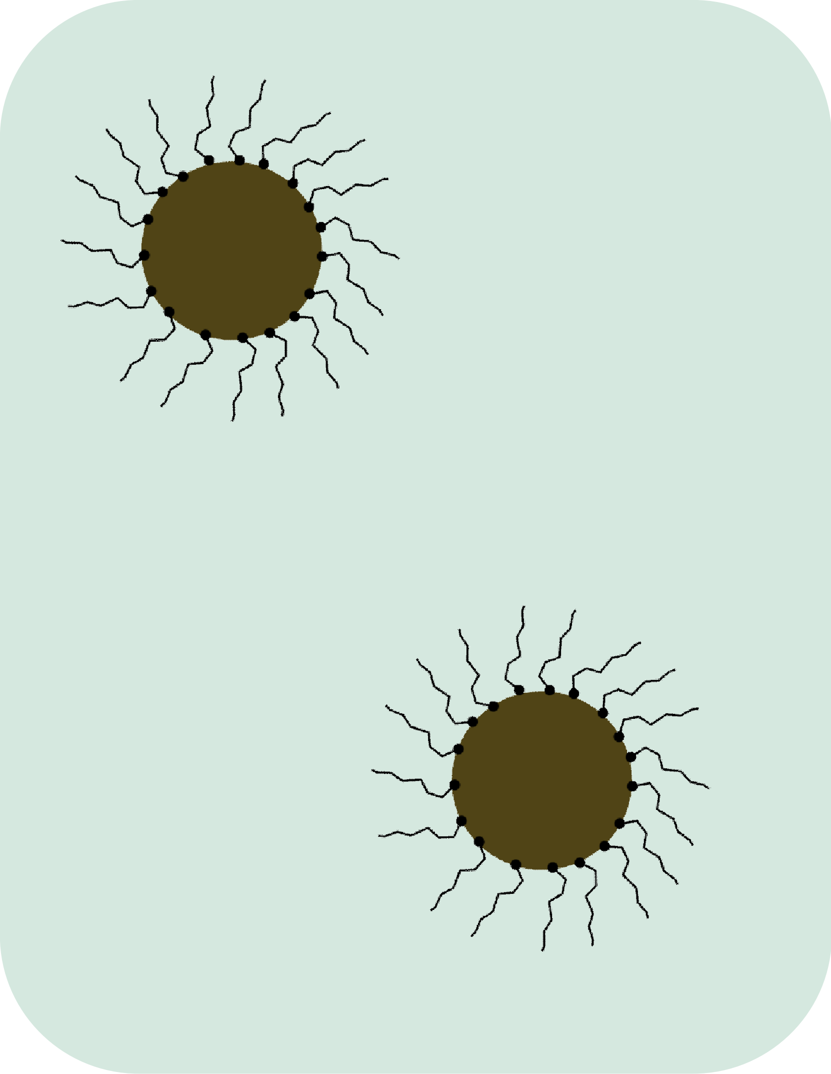
- strong VAN DER WAALS attraction leads to agglomeration

- stabilization against agglomeration with surfactants by liquid-liquid phase-transfer



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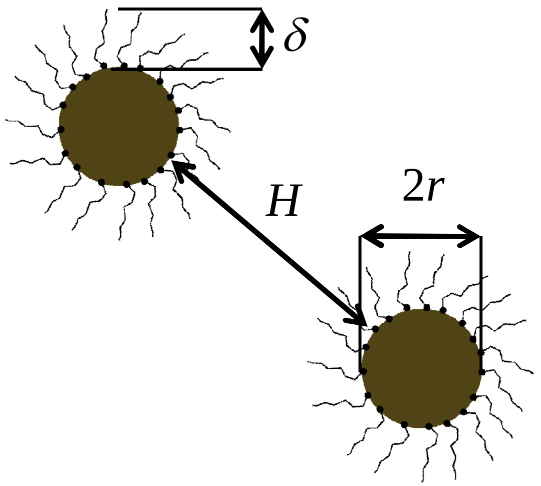
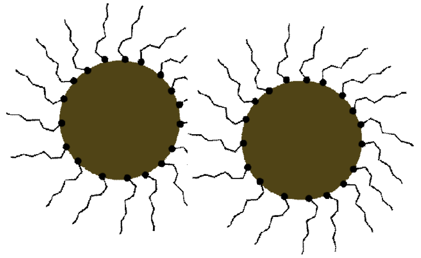
$$h = \frac{H}{r}$$



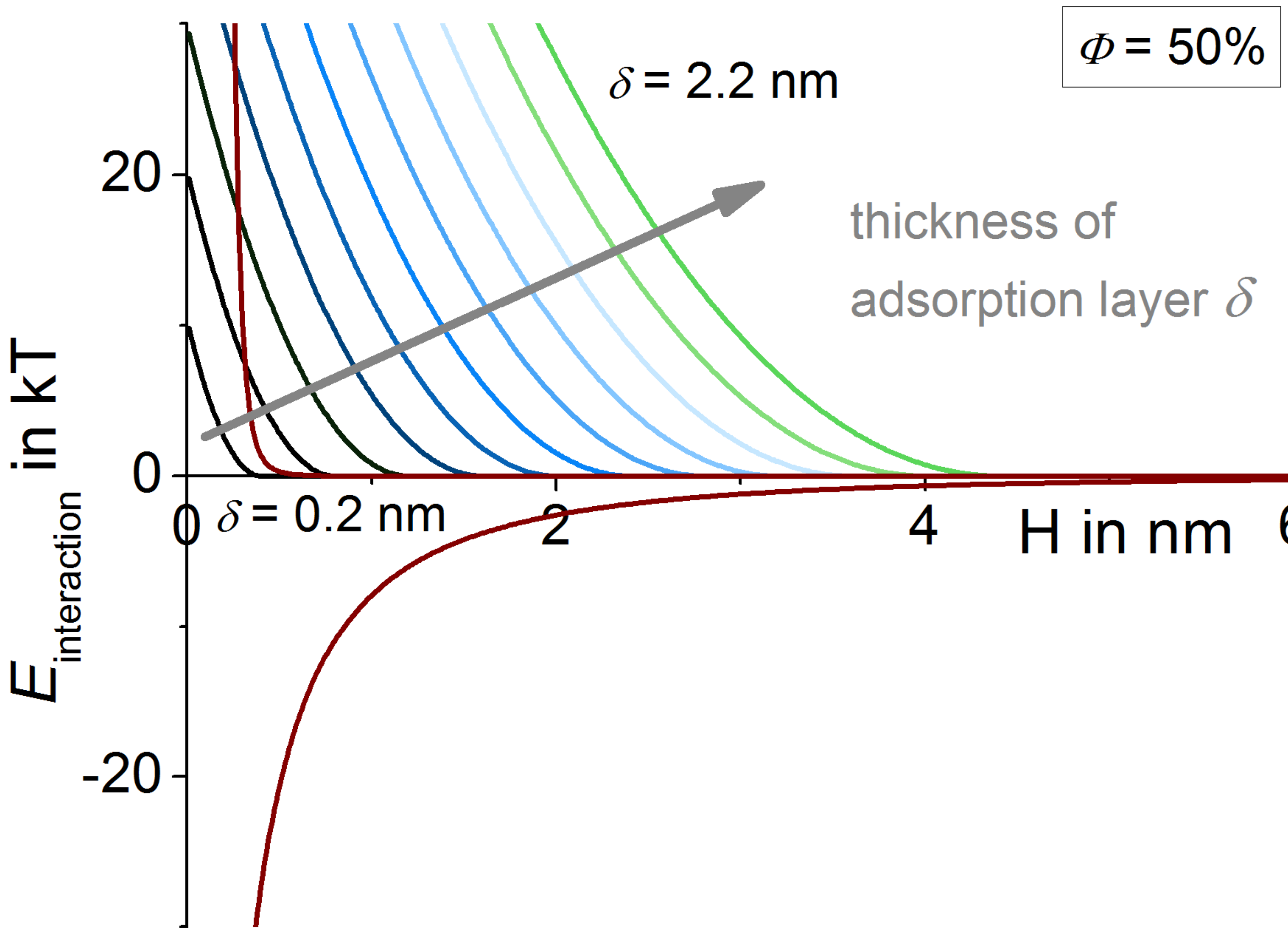
$$E_{\text{vdW Attraction}} = -\frac{C_{\text{H}}}{6}\left[\frac{2}{h^2+4\cdot h} + \frac{2}{(h+2)^2} + \ln\frac{h^2+4\cdot h}{(h+2)^2}\right]$$

$$E_{\text{entrop Repulsion}} = \begin{cases} 2\cdot\pi\cdot r^2\cdot\frac{\Phi}{A_{\text{FattyAcid}}}\cdot k\cdot T\cdot\left(2-\frac{(h+2)\cdot r}{\delta}\cdot\ln\left(\frac{1+\delta/r}{1+h/2}\right)-\frac{h\cdot r}{\delta}\right) & ,\frac{h\cdot r}{2\cdot\delta}<1 \\ 0 & ,\frac{h\cdot r}{2\cdot\delta}>1 \end{cases}$$



$$E_{\text{interaction}} = E_{\text{vdW Attraction}} + E_{\text{entrop Repulsion}} + E_{\text{Born}}$$

Rosensweig,R.E. *A.I.Ch.E.Symp.Ser.*, 5, 104 (1965)



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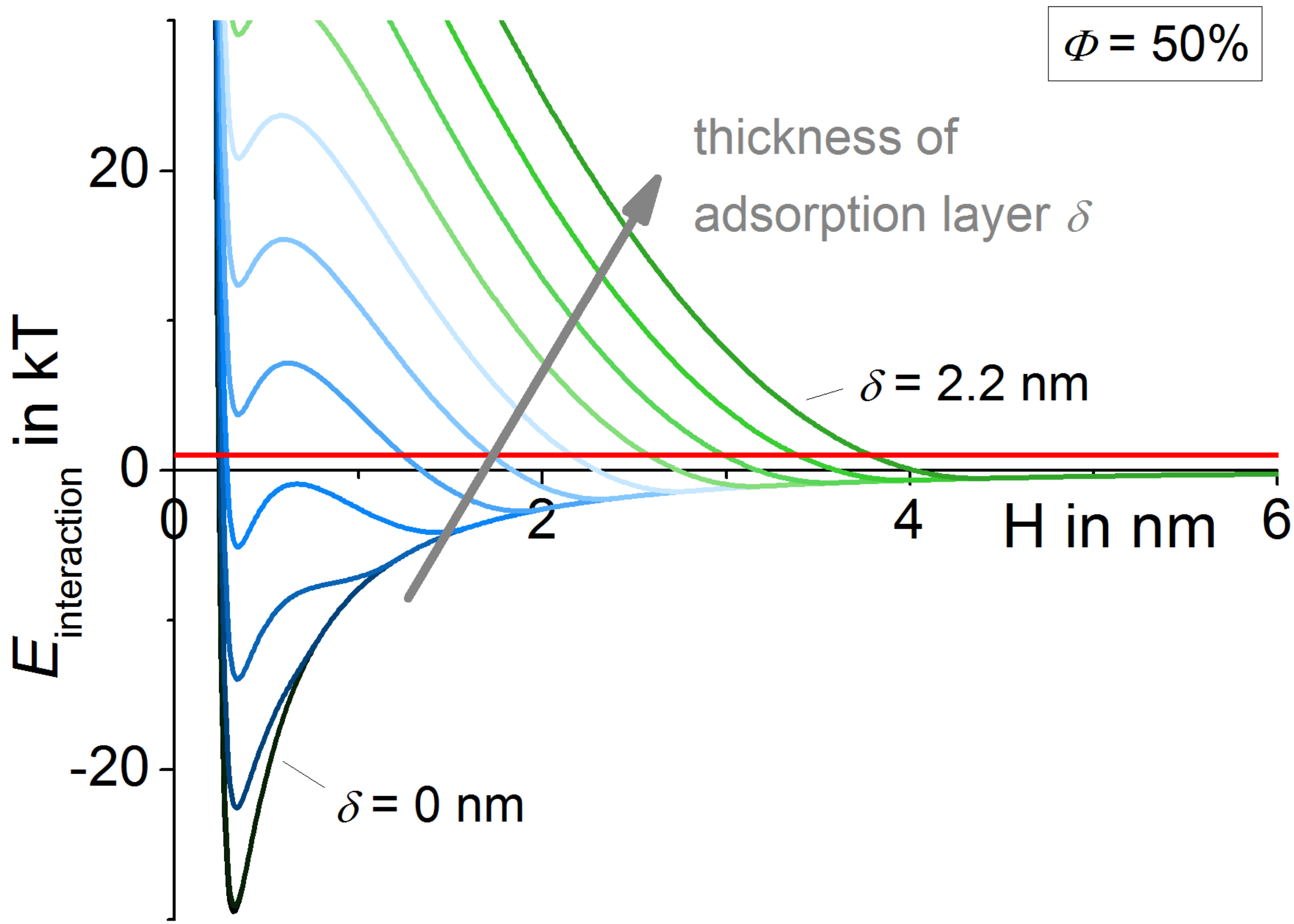
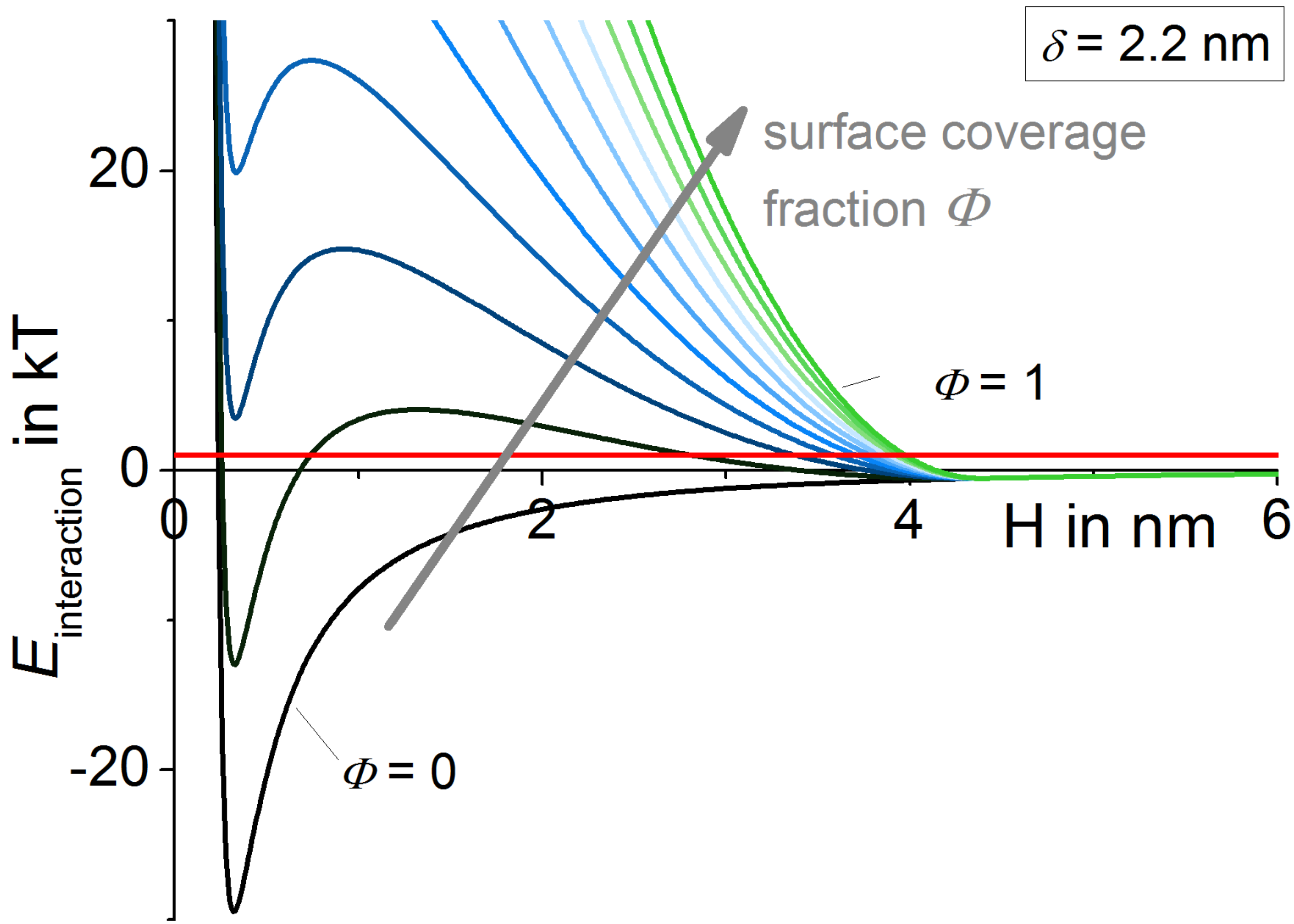
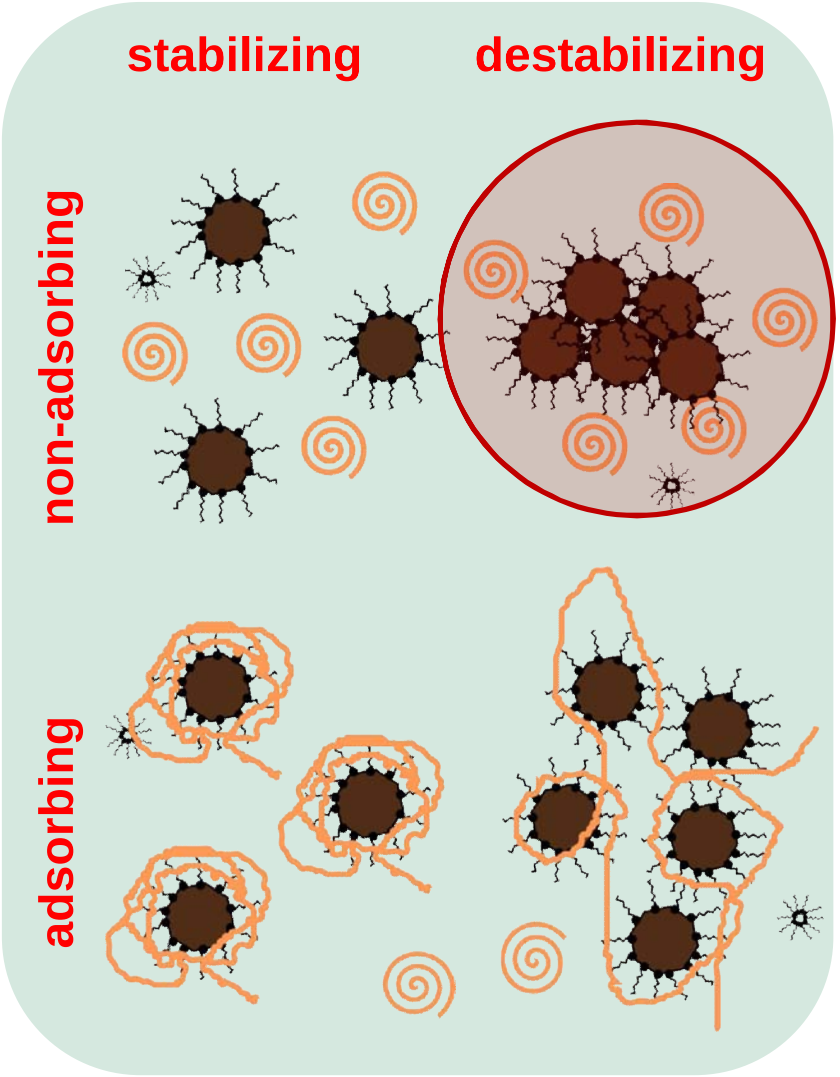

Φ = 50%
thickness of
adsorption layer δ
δ = 2.2 nm
δ = 0 nm
E interaction in kT
20
0
-20
0
2
4
6
H in nm



δ = 2.2 nm
surface coverage
fraction Φ
Φ = 1
Φ = 0
$E_{interaction}$ in kT
20
0
-20
0
2
4
6
H in nm

- strong VAN DER WAALS attraction leads to agglomeration
- stabilization against agglomeration with surfactants by liquid-liquid phase-transfer
- stability effects by polymer addition



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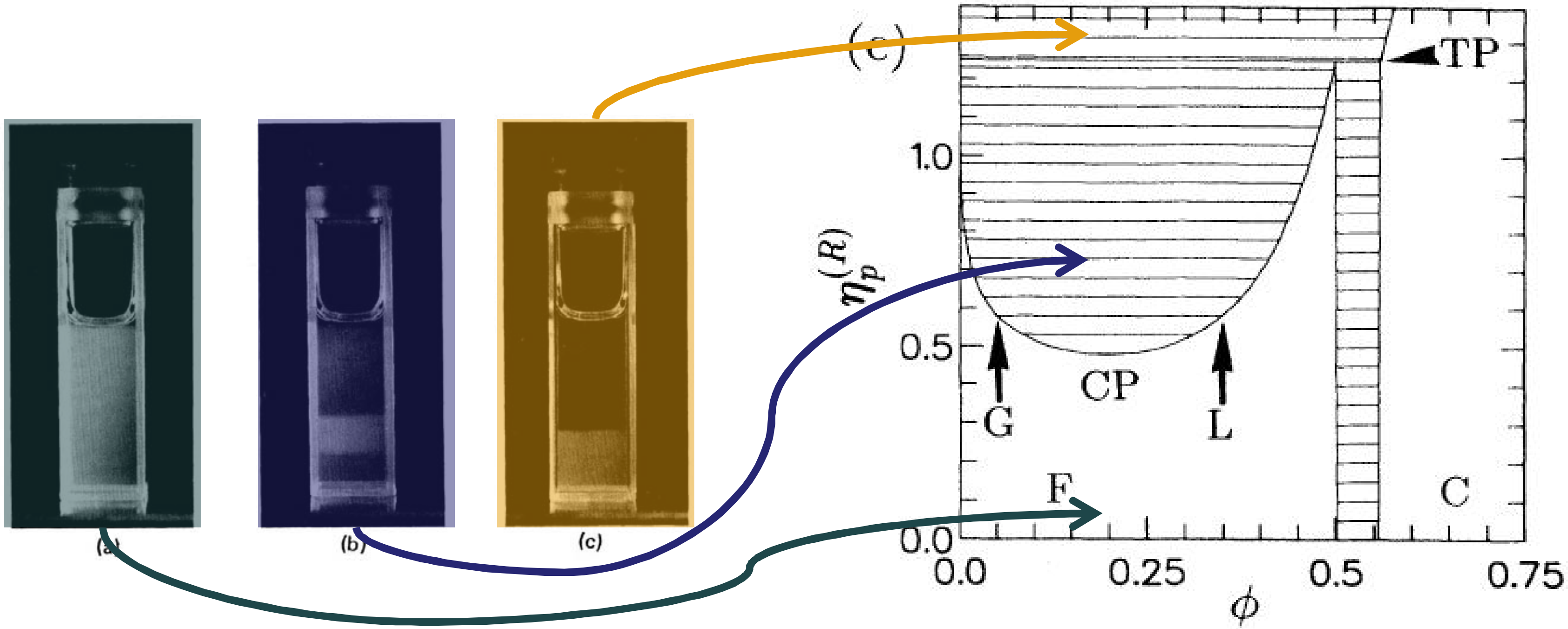
Depletion interaction – Phase diagrams



Ilett,S.M. *PhysRevE,* 51, 1344 (1995)

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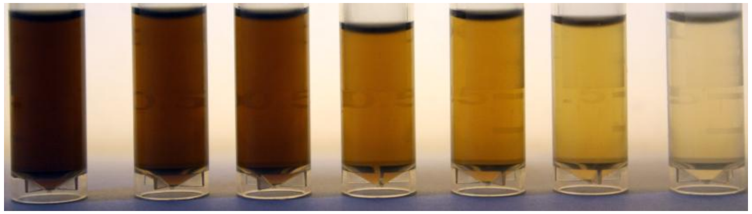
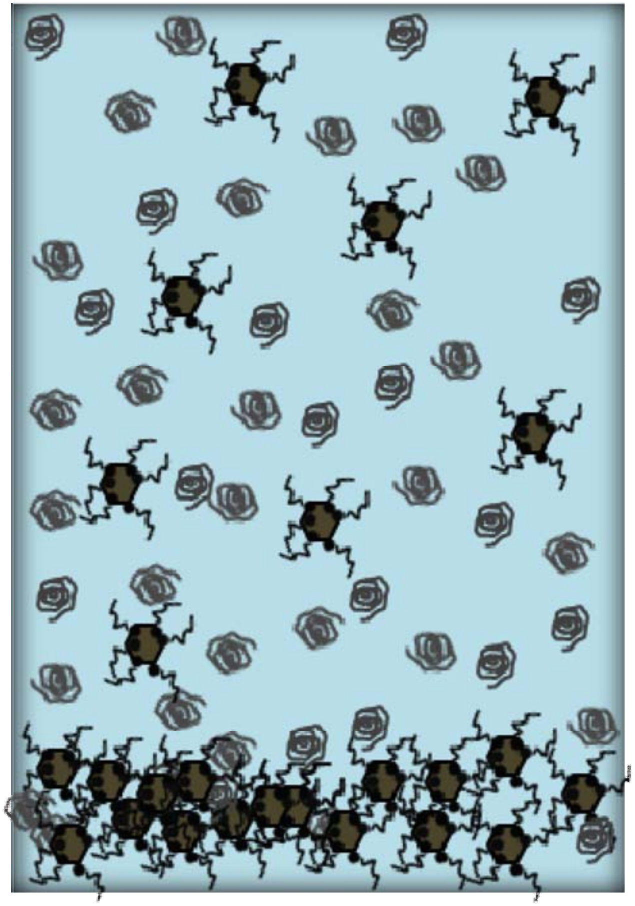
- assessment of the mass concentration of primary particles w_{primary}
- centrifugation and determination of the concentration with TGA, Photospectrometer

increasing c_{Poly} ⟶



diluted supernatant after centrifugation,



centrifugation

$x_{\mathrm{primary,\ supernatant}} < 40$ nm

Rudolph,M. *J Coll Interf Sci,* 357, 292 (2011)

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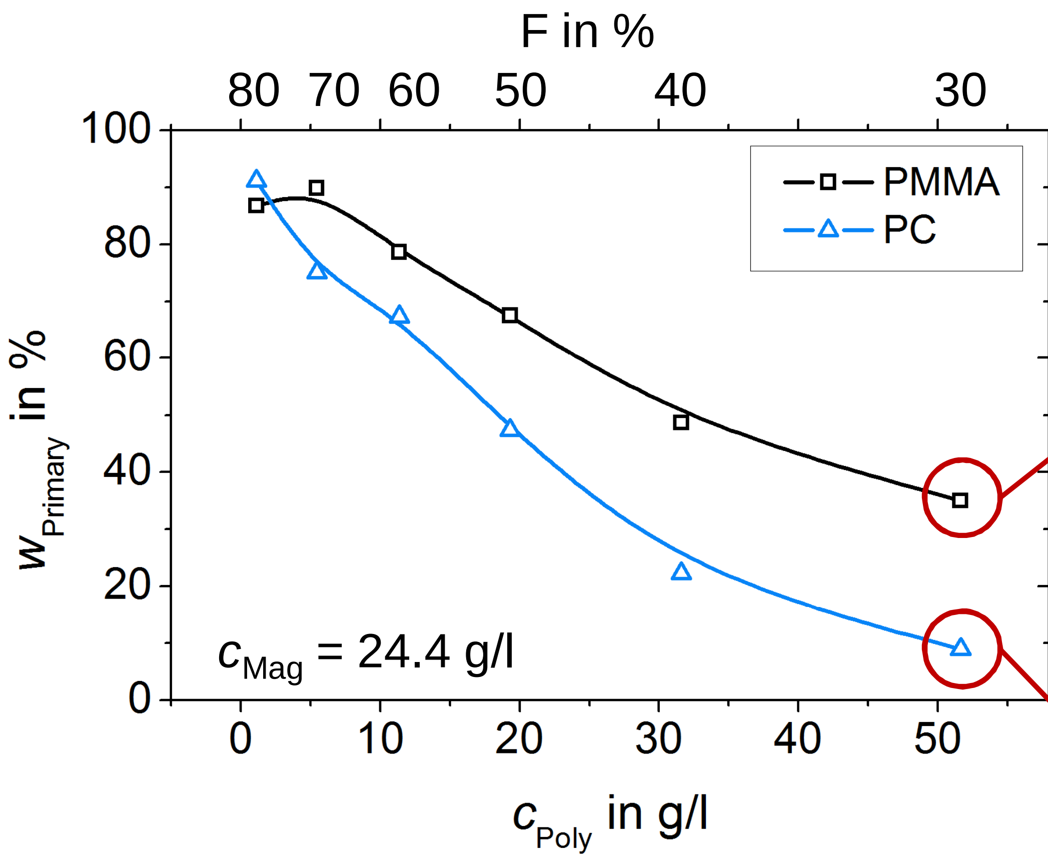

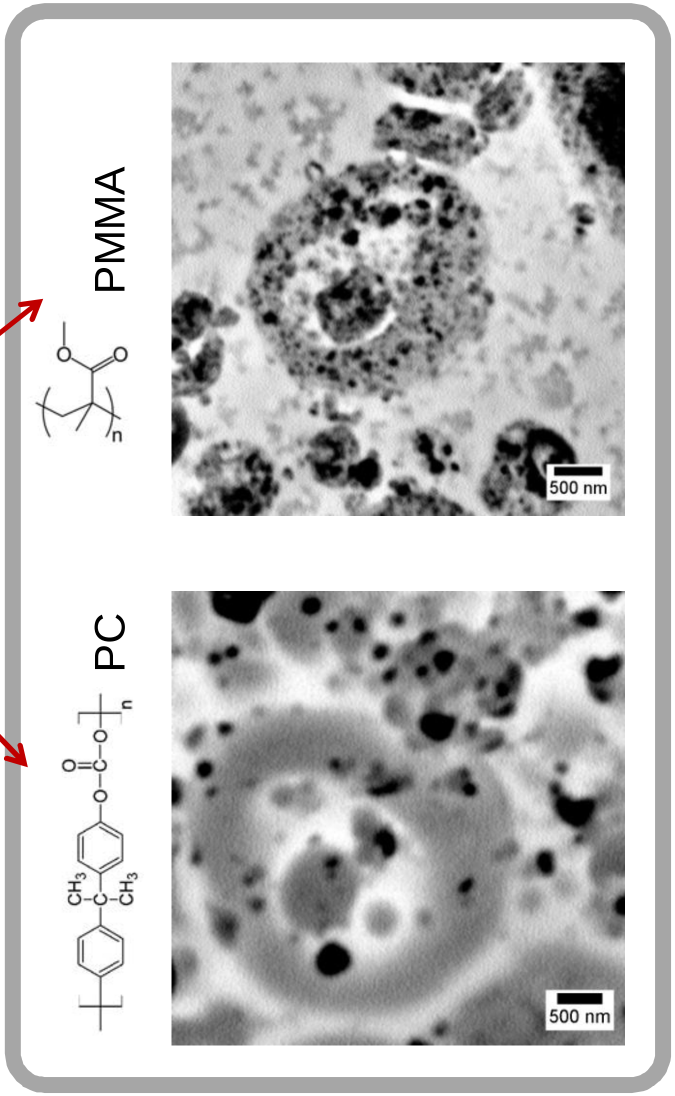

destabilization: decreasing primary particle concentration with increasing polymer concentration

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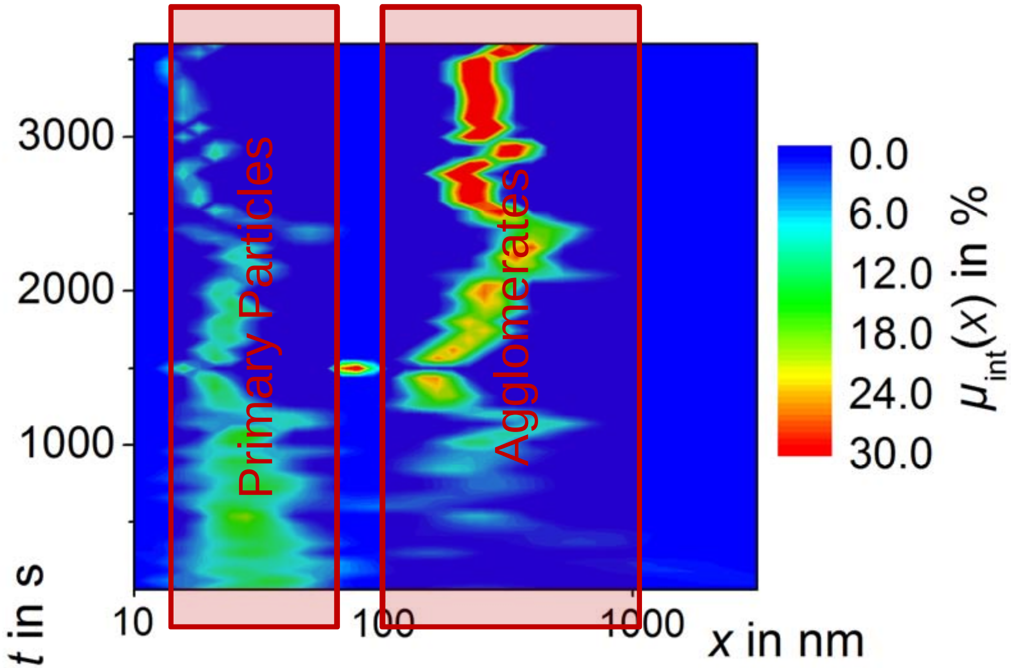
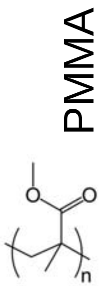
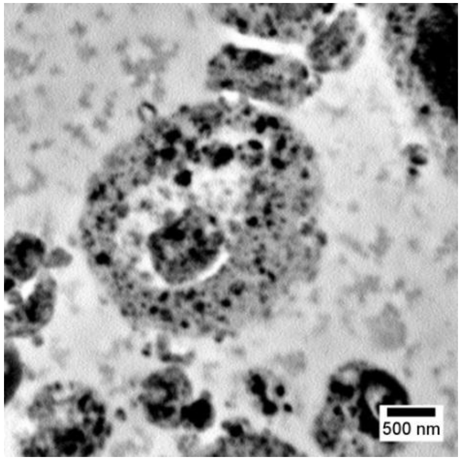


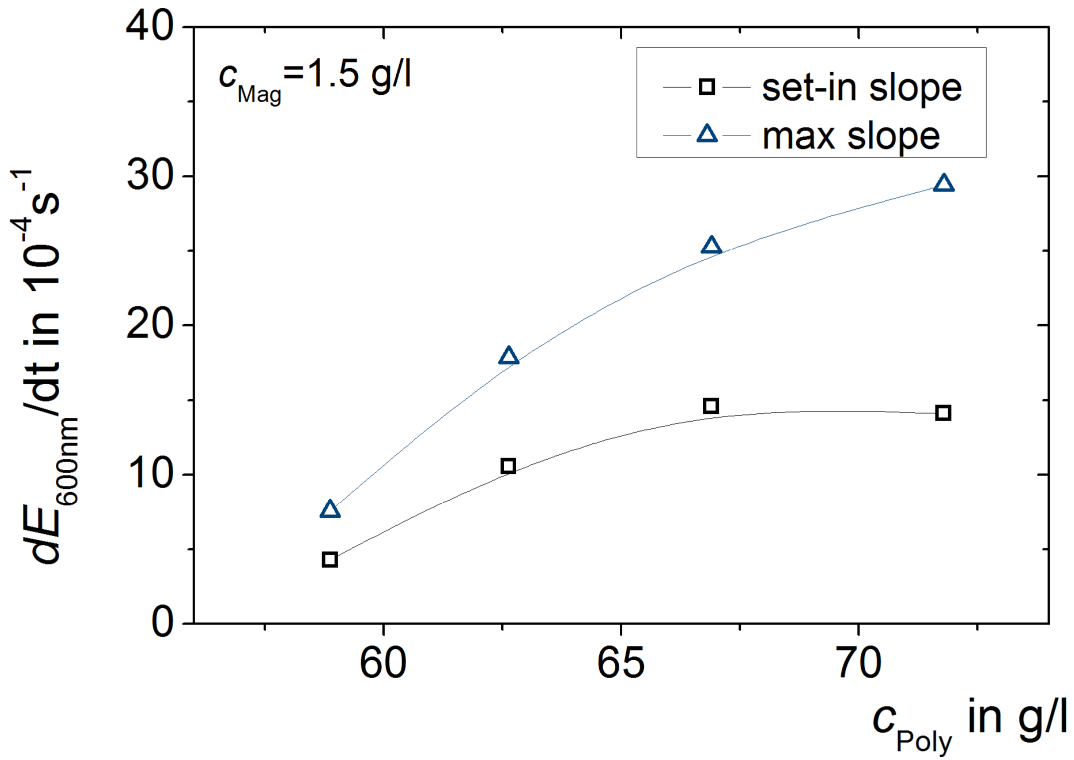


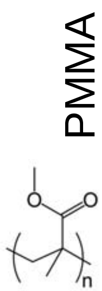


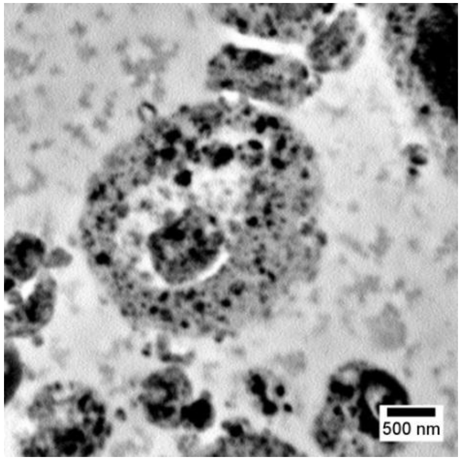
kinetics measured with DLS
Sympatec Nanophox

$c_{Mag} = 1.2$ g/l
$c_{Poly} = 58.9$ g/l

kinetics of coagulation: not rapid → fast
drying after mixing should reduce large amount of agglomerates







kinetics measured with UVVIS at 600nm

c_{Mag} = 1.2g/l
c_{Poly} = 58.9 g/l

kinetics of coagulation: problem of comparability to stability investigation due to very low colloid concentration

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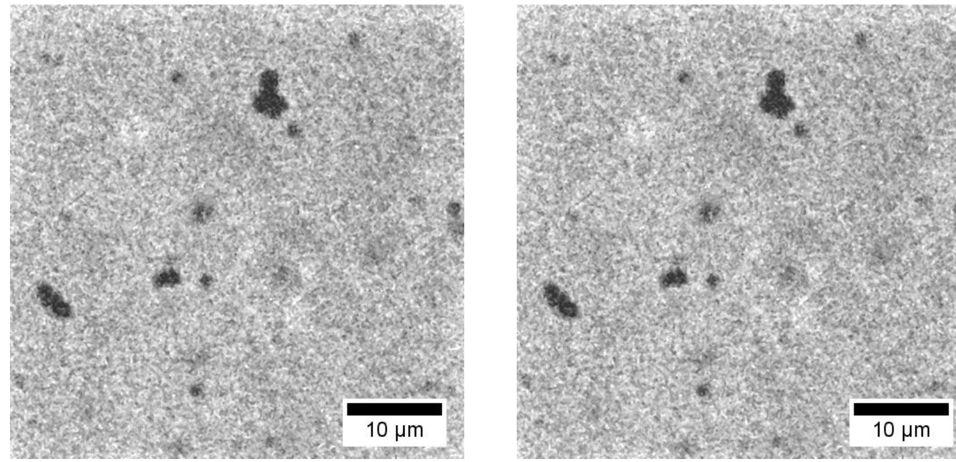
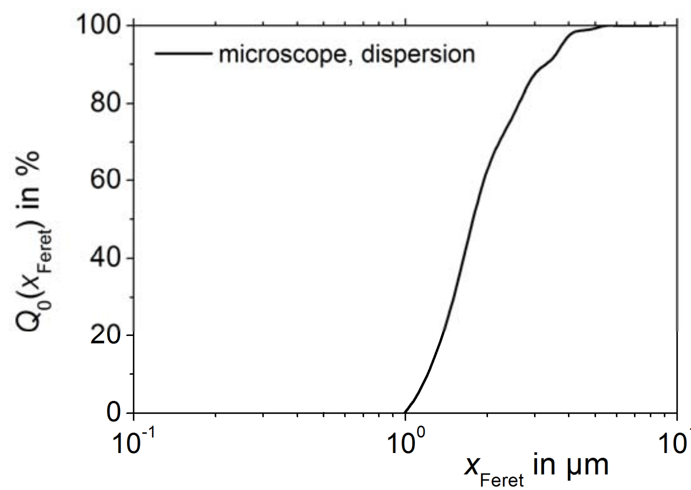
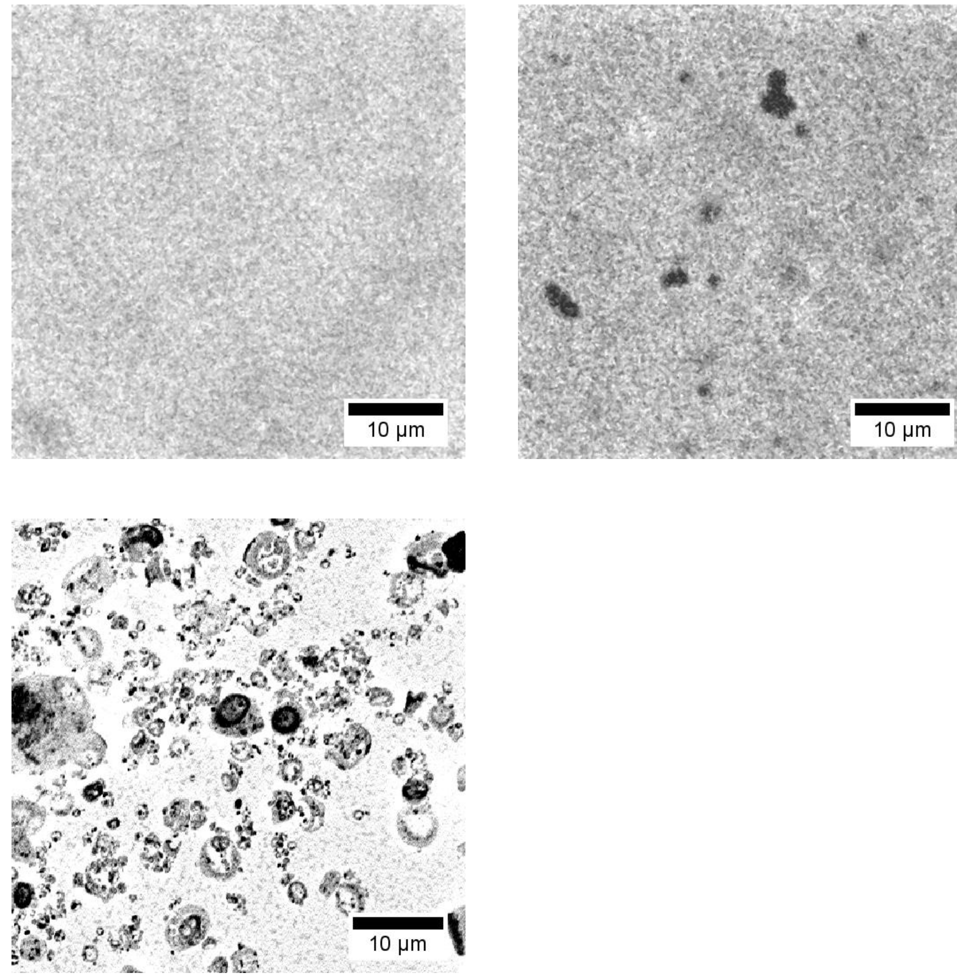
- Nano-Fe_3O_4 dispersion under microscope with c_{Mag} = 1.5 g/l
- addition of PMMA leads to larger light-optically visible agglomerates, τ = 15 min





- Nano-Fe_3O_4 dispersion under microscope with c_{Mag} = 1.5 g/l
- addition of PMMA leads to larger light-optically visible agglomerates
- inverted BSE-SEM of spray dried particles **PMMA64-RS06-MAG30** show agglomerates as well



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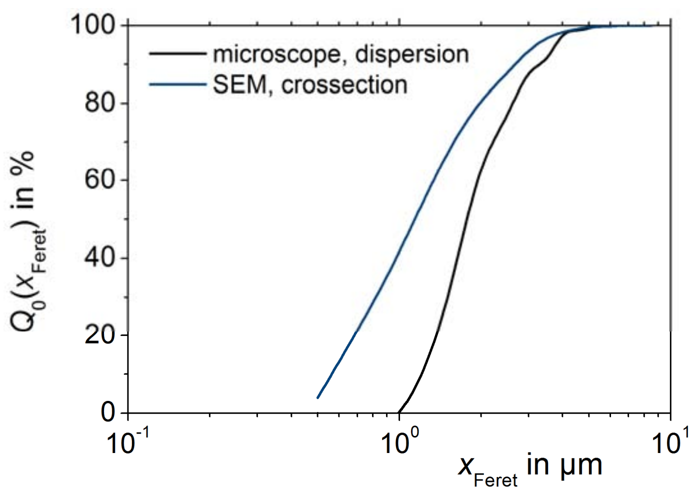
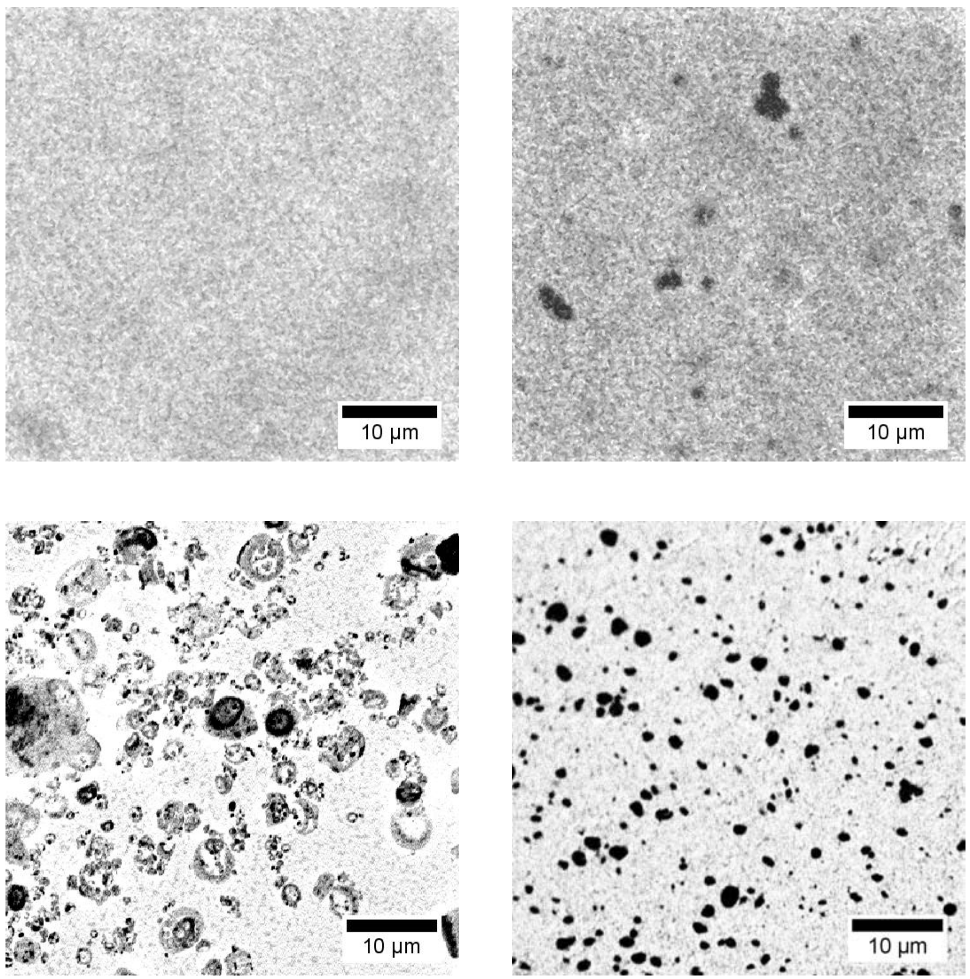
- similar agglomerate sizes for dispersion and moulded BSE-SEM crossection





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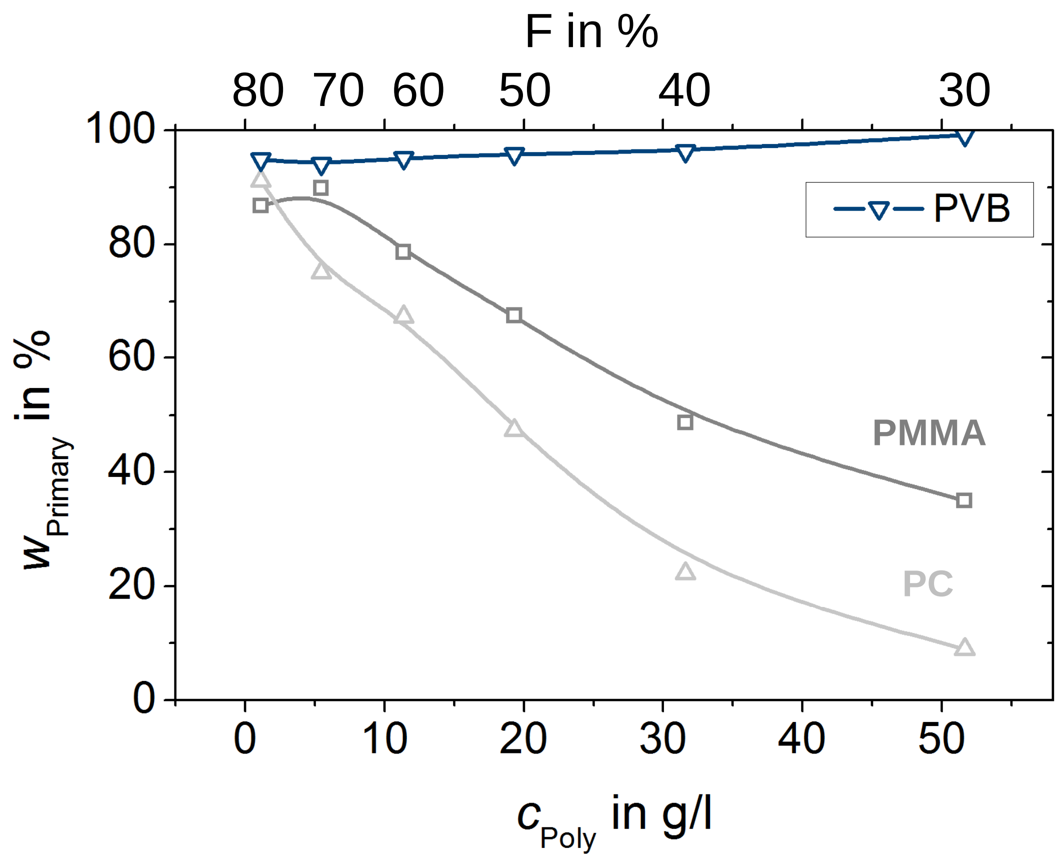

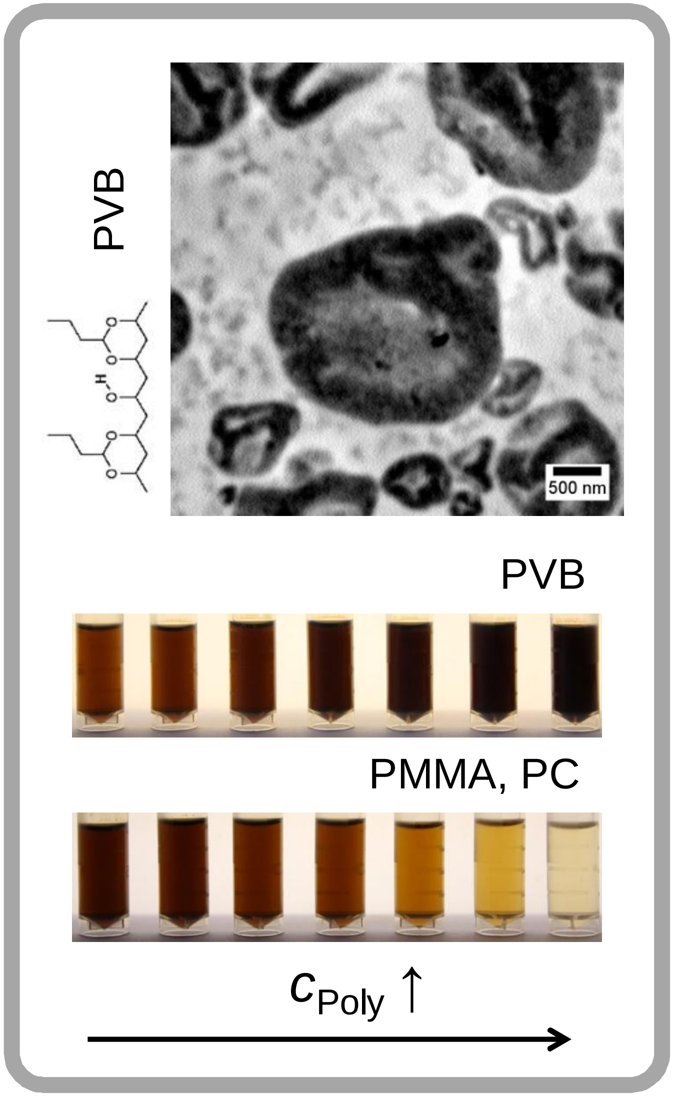

stabilization: increasing primary particle concentration with increasing polymer concentration

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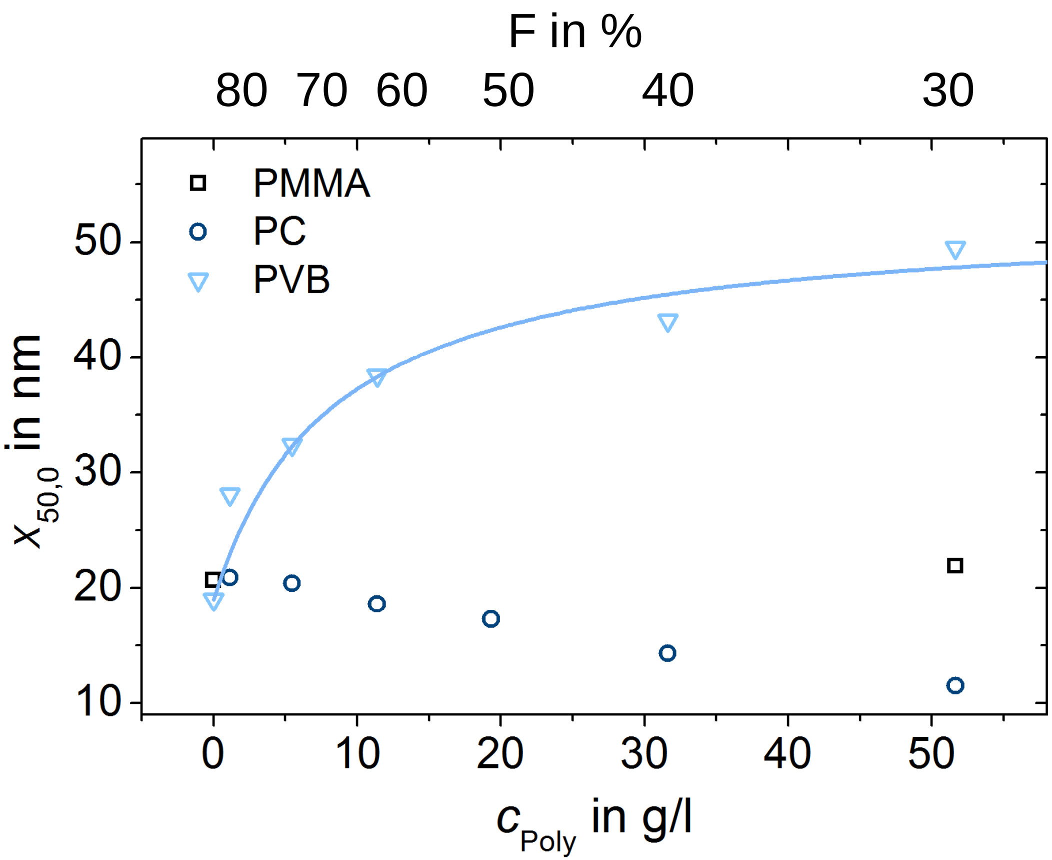
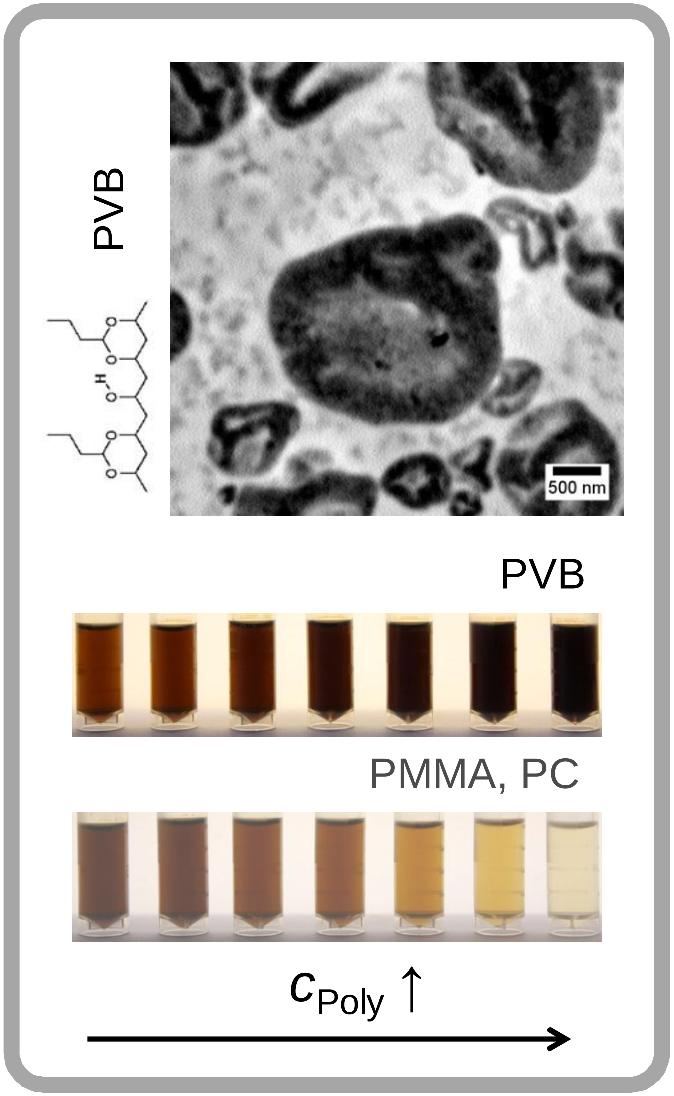
5b Stabilization with adsorbing polymer





particle size: increase in particle size with adsorbing polymer layer forming, of Langmuir type (line)

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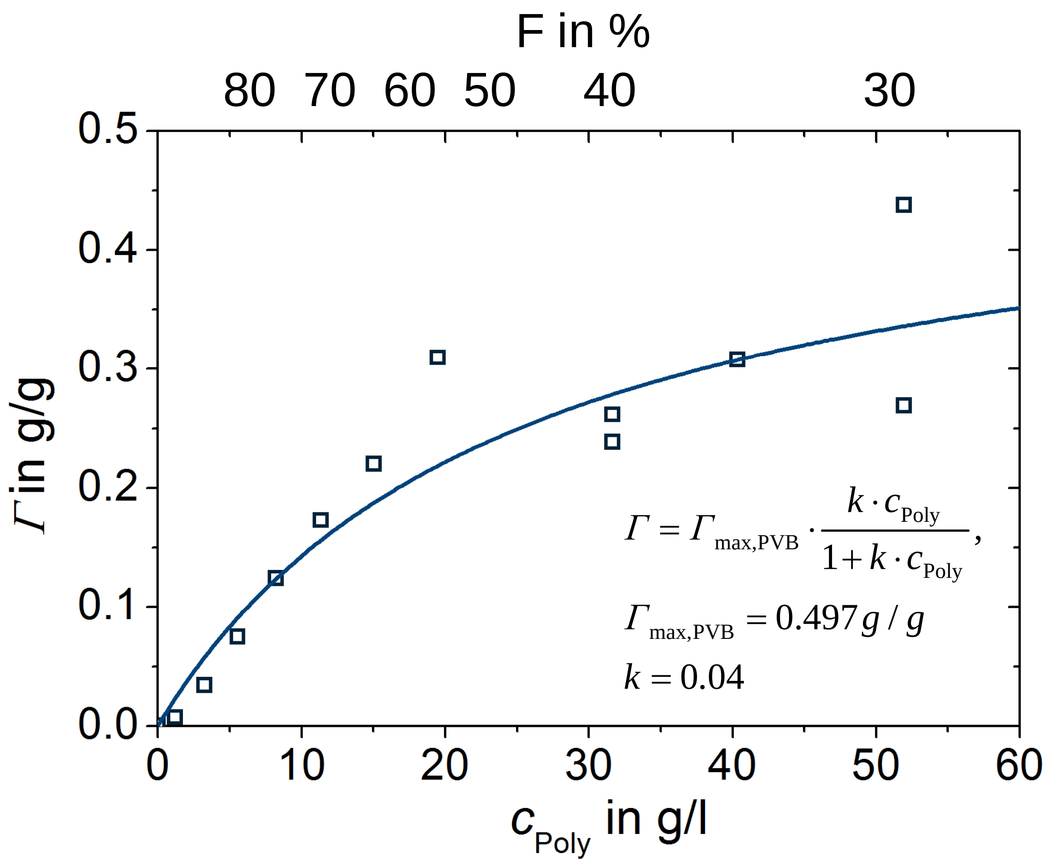

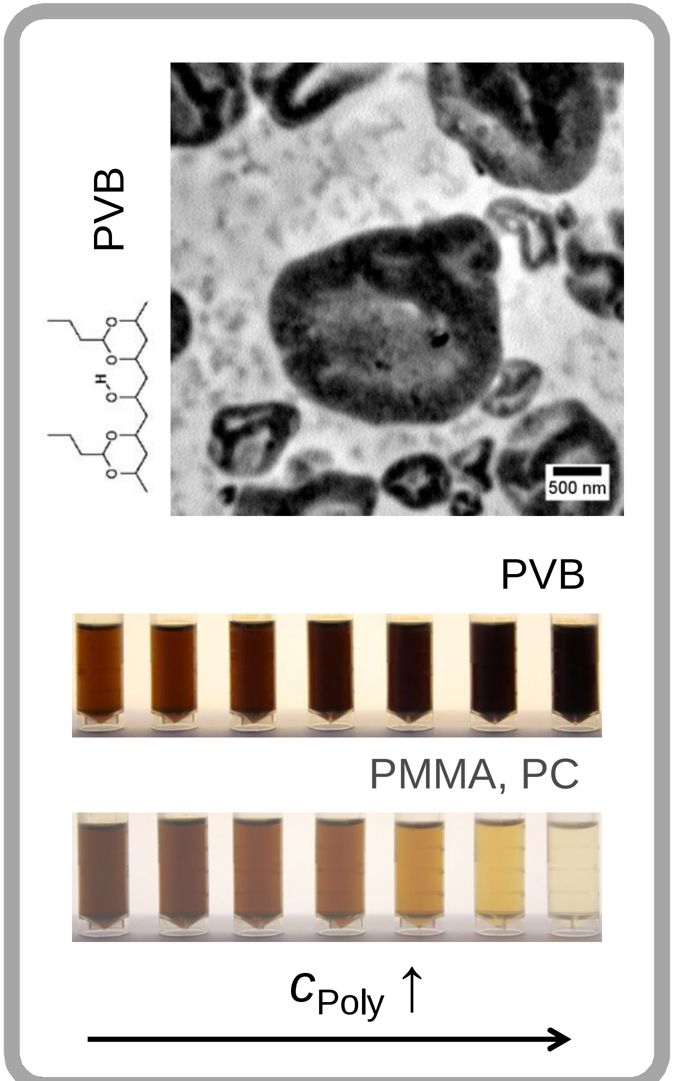

adsorption isotherm: Langmuir type
adsorption of PVB on sterically stabilized nanomagnetite

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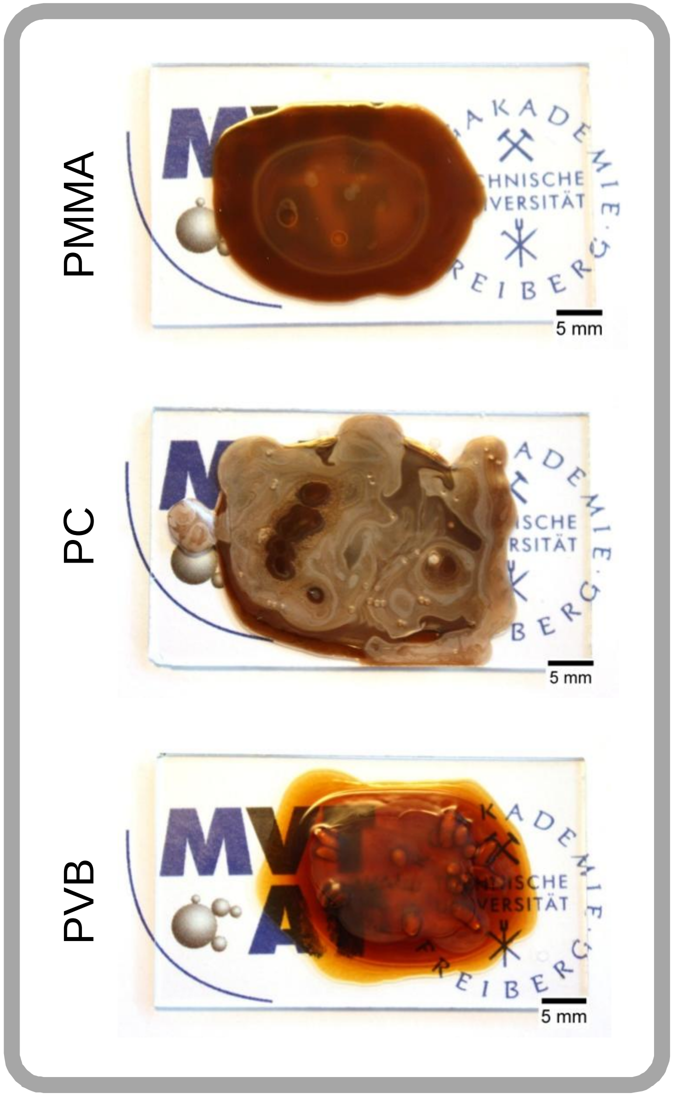
- ✓ Solution and spray drying process is suitable for nanocomposite synthesis
- ✓ HOWEVER: nanoparticle interactions have to be considered
- ✓ Added, solved polymers will influence nanoparticle interaction
- ✓ Stabilization through adsorbing polymers reveals suitability of the solution method



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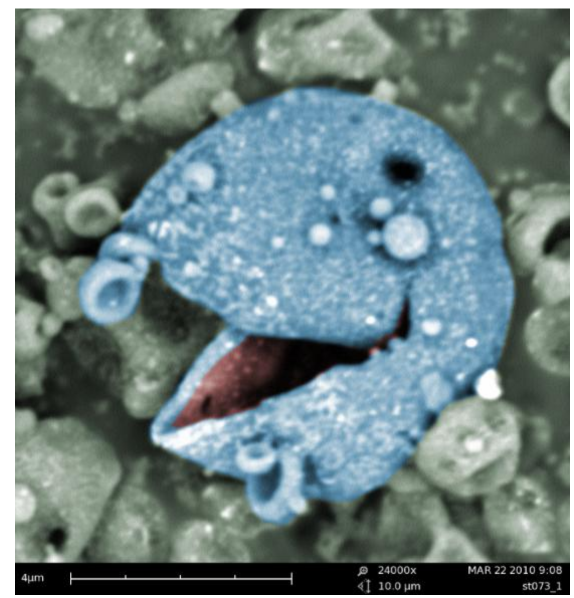
Deutsche Forschungsgemeinschaft

Thanks for your interest!



Meet me at poster **D-PO3-20**

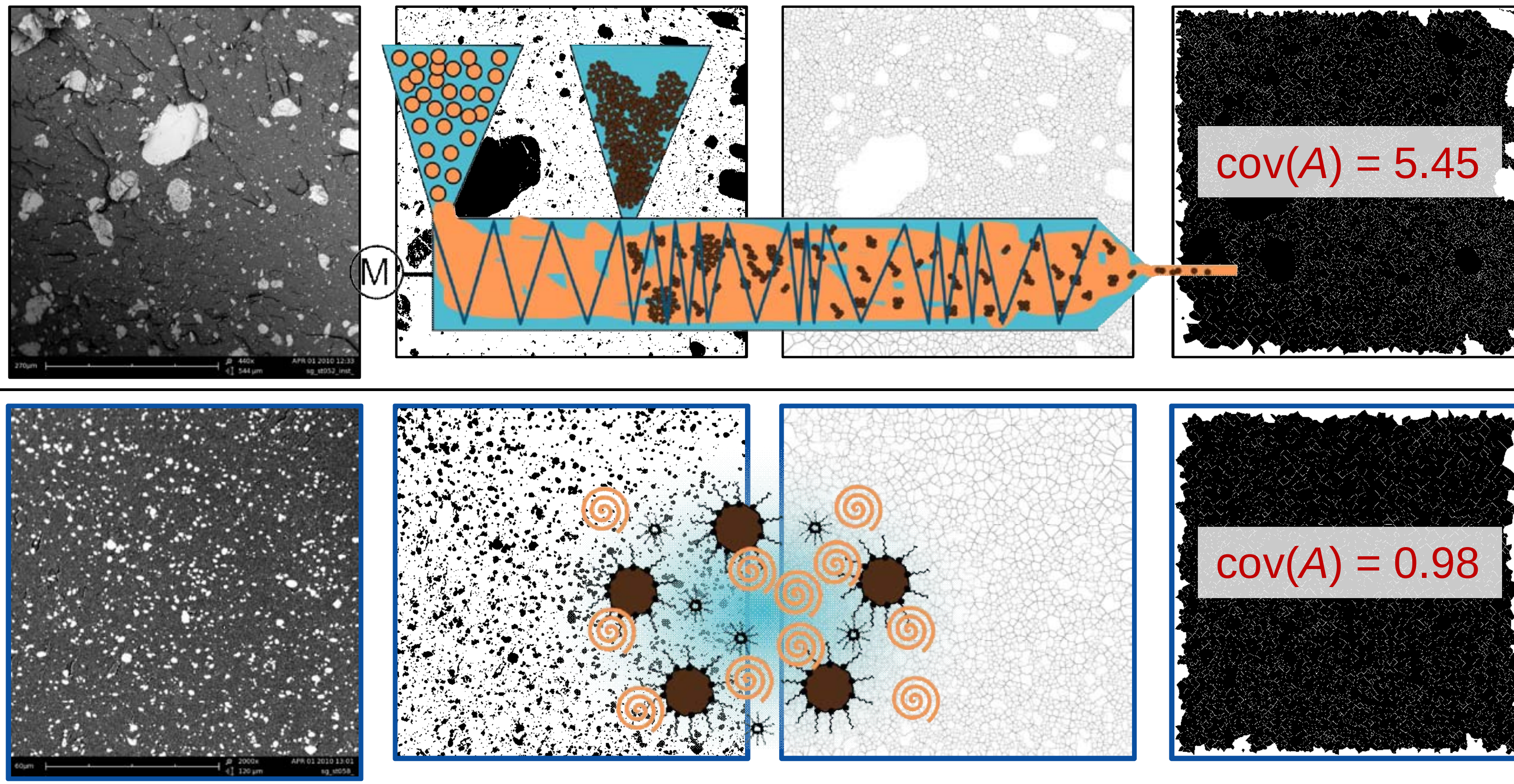
» Nanofix – Nanoparticle-wax-formulations as Additives for Extruder Compounding«

Filler Homogeneity – SEM Analysis (F = 30 %)

B-SEM cross section → Binary → Voronoi → coefficient of variance - cov

Compounding

Solution/Drying



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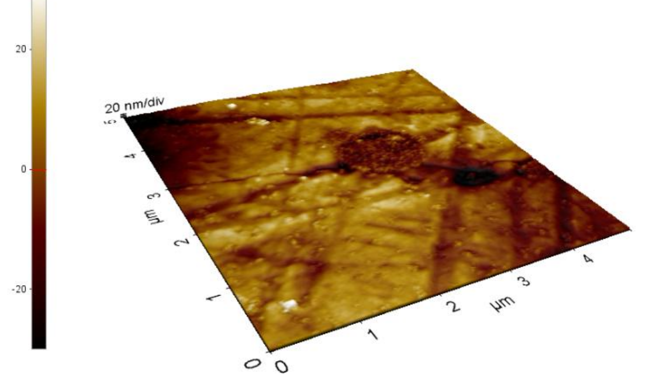
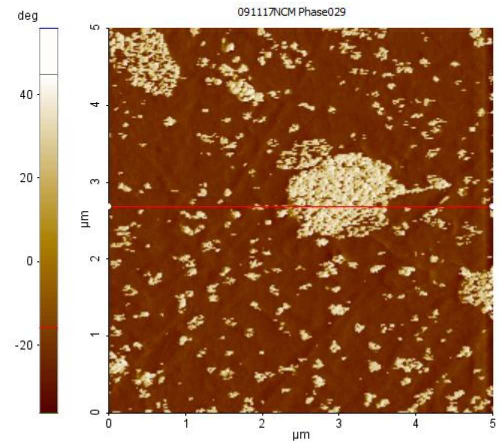
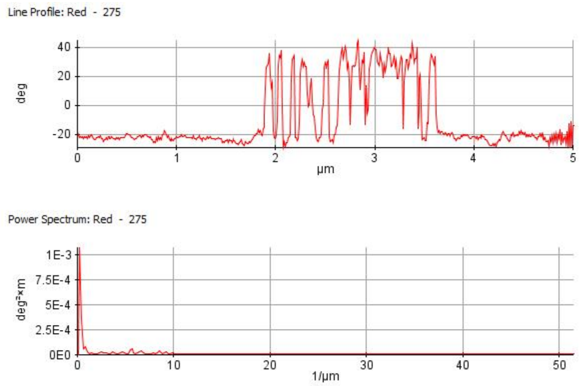
Phase contrast AFM analysis

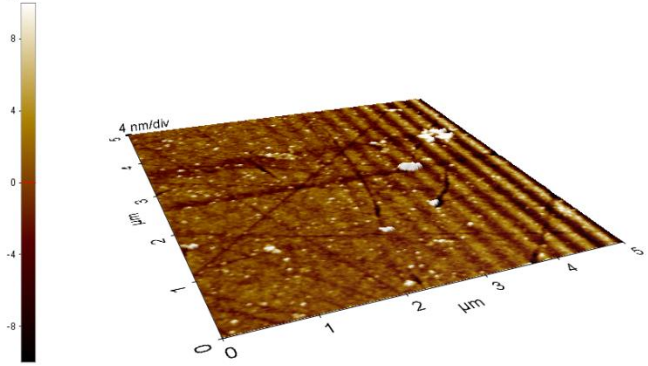
PMMA61 – RS09 – MAG30

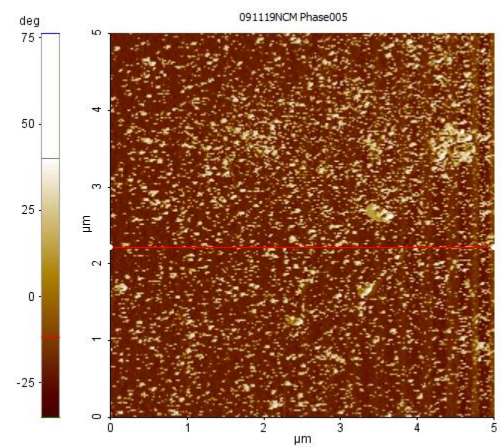


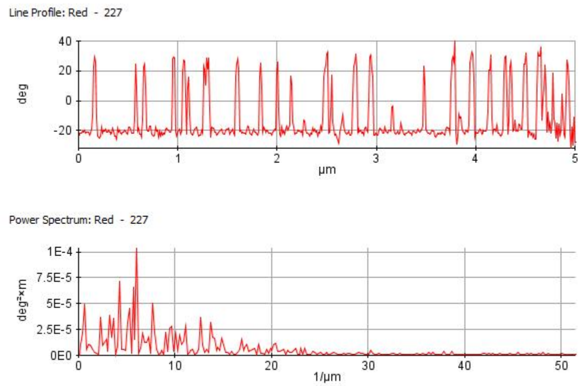




PMMA49 – RS21 – MAG30

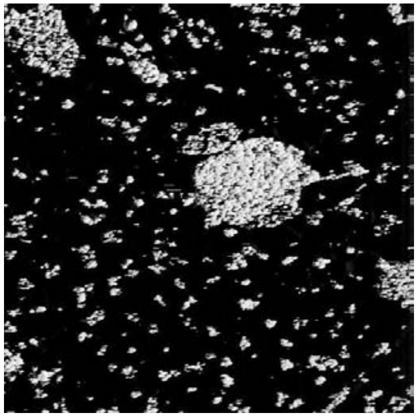


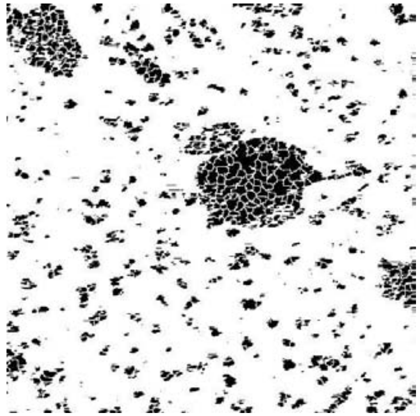


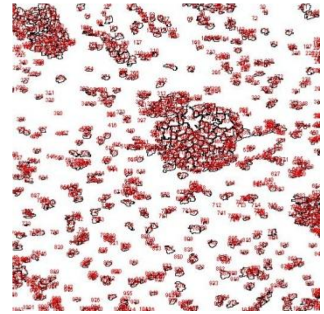


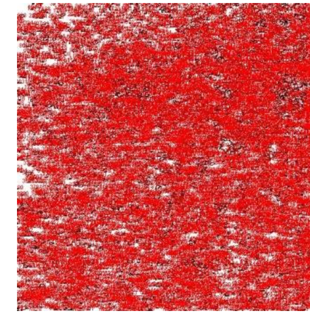
Rudolph,M. CIT, 82, 2189 (2010)

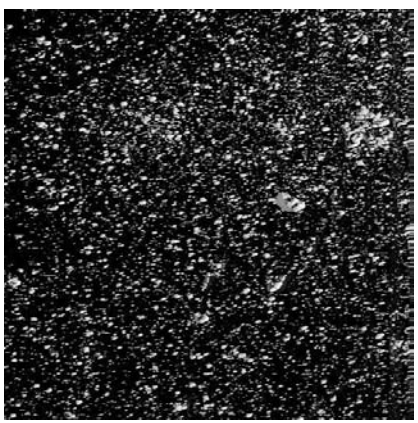
Phase contrast AFM analysis

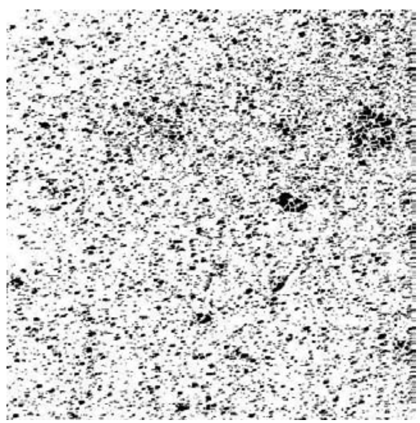


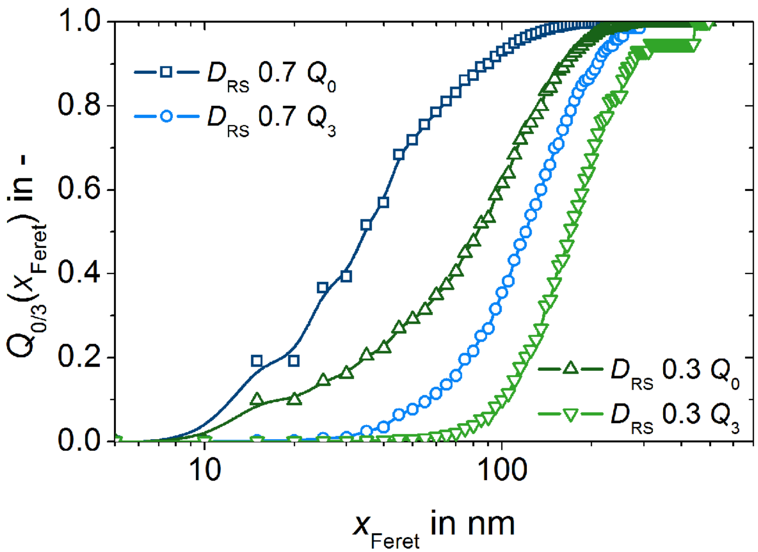












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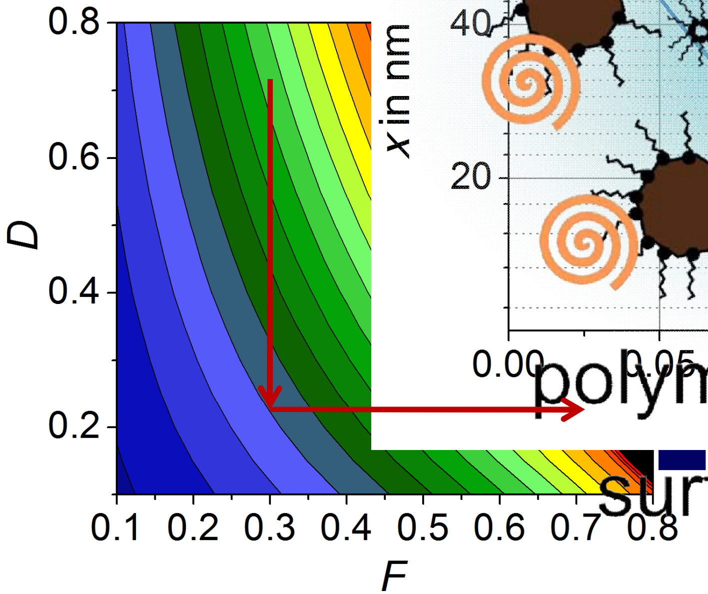
- Composition

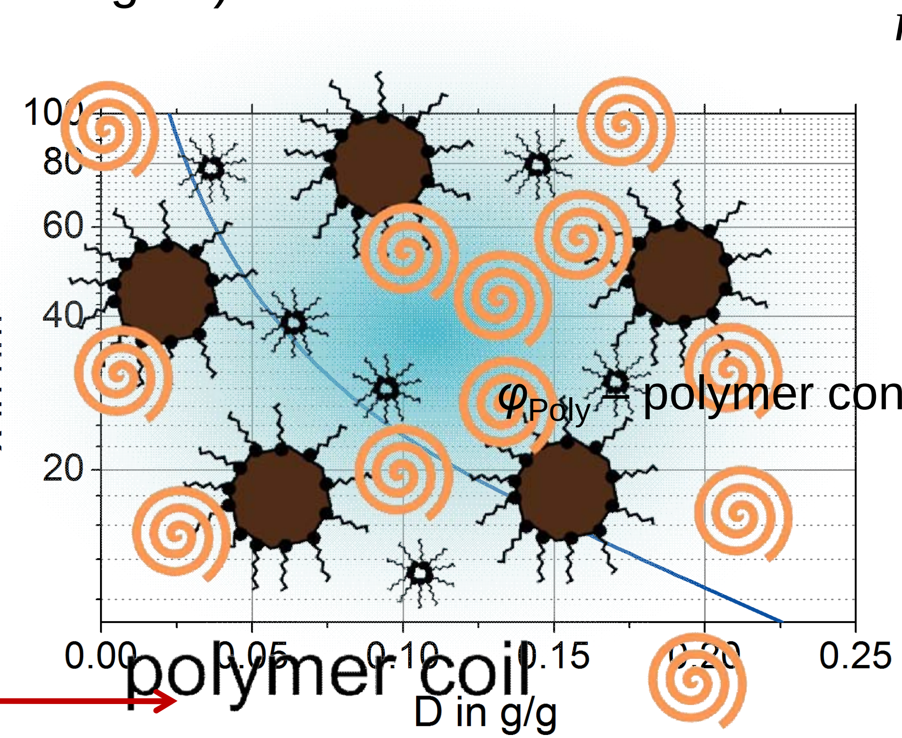
D – surfactant (detergent) ratio

$$D = \frac{m_{\text{surfactant}}}{m_{\text{nano}}}$$

F – filler conce

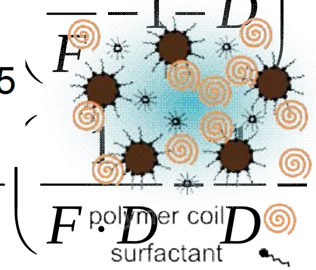
$$\frac{m_{\text{nano}}}{\ldots\text{rfactant} + m_{\text{polymer}}}$$



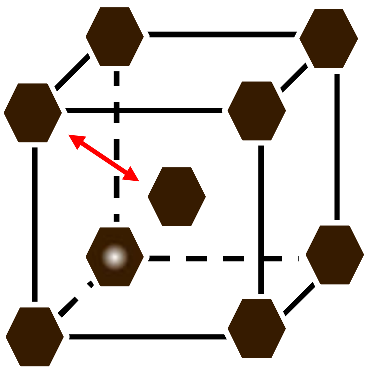


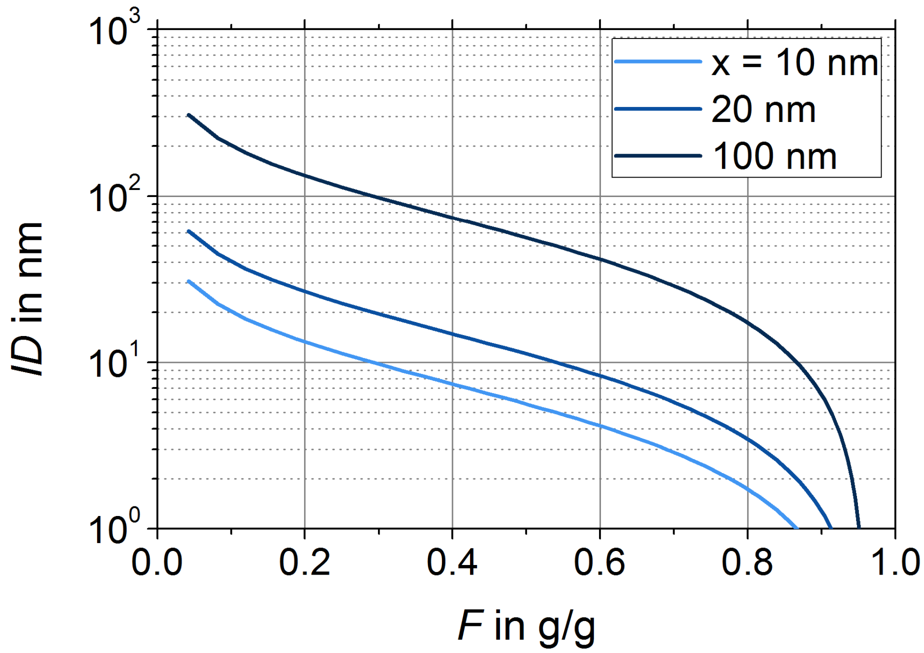
φ_{Poly} = polymer concentration

$$\left[\left(\frac{1}{F} - 1 - D \right)^{-1} + \frac{\varphi_{\text{polymer}}}{\varphi_{\text{surfactant}}} \left(\frac{1}{F \cdot D} - \frac{1}{D} - 1 \right)^{-1} \right]^{-1}$$



- Interparticle Distance





$$ID = x \cdot \left[\left(\frac{\pi}{3 \cdot \varphi_{\mathrm{nano}}} \right)^3 \cdot \sqrt{3/4} - 1 \right]$$

$$\varphi_{\mathrm{nano}} = \frac{\rho_{\mathrm{polymer}}}{\rho_{\mathrm{nano}}} \left[\frac{1}{F} + D \left(\frac{\rho_{\mathrm{polymer}}}{\rho_{\mathrm{surfactant}}} - 1 \right) - 1 \right]^{-1}$$

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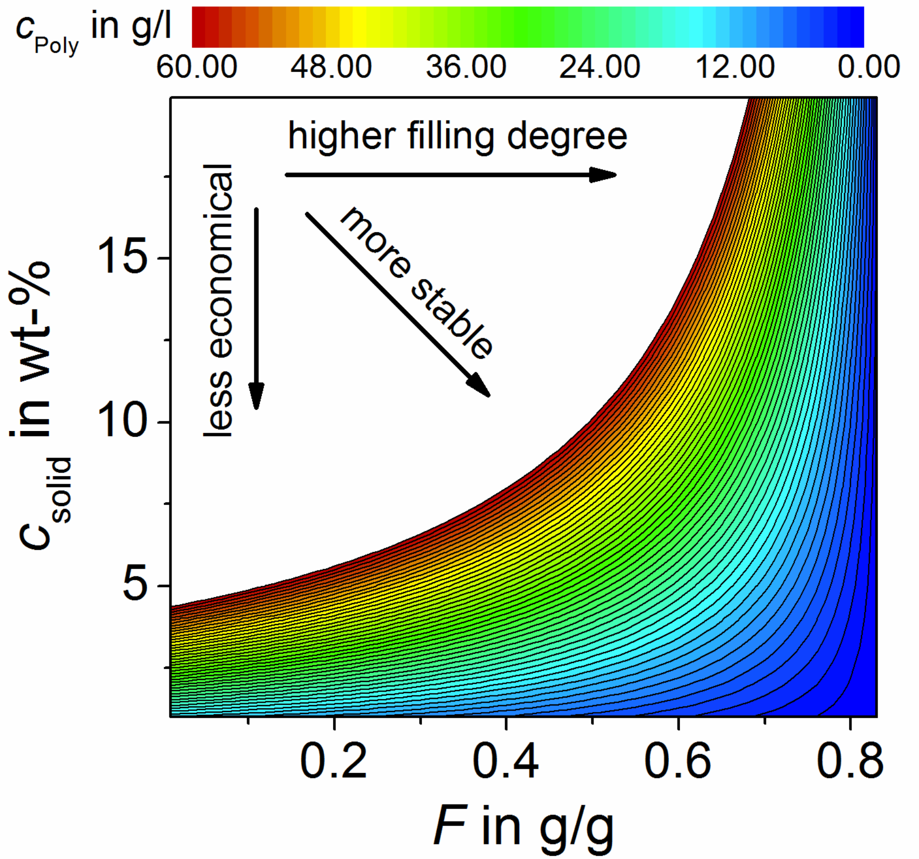

$$c_{\mathrm{Poly}} = \frac{\rho_{\mathrm{DCM}} \cdot \left[c_{\mathrm{solid}} - c_{\mathrm{solid}} \cdot F \cdot (1 + D) \right]}{1 - c_{\mathrm{solid}}}$$

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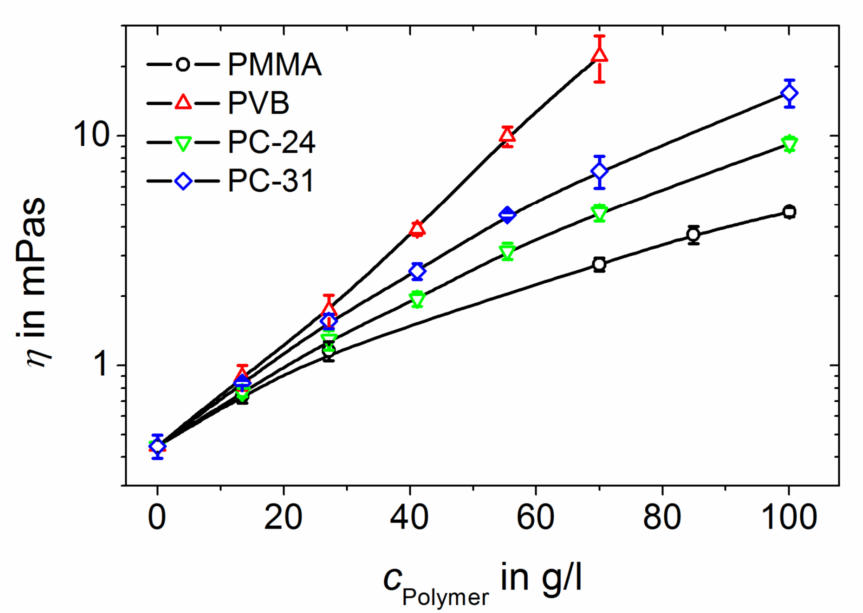
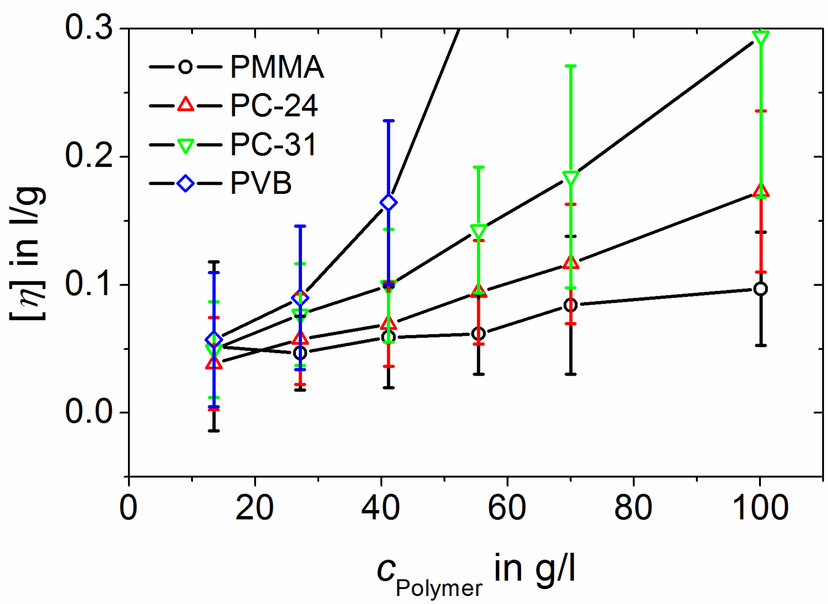
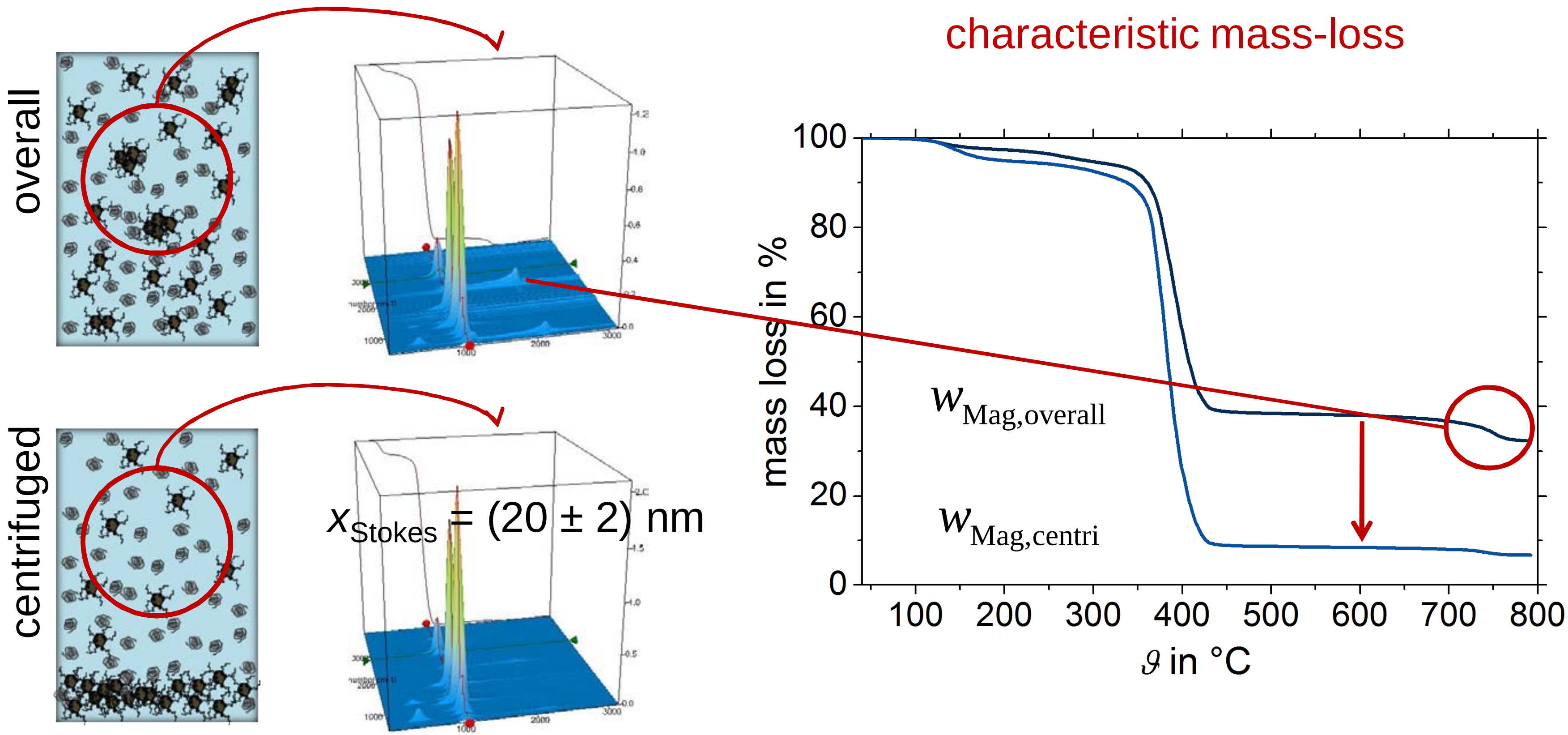

PMMA
PVB
PC-24
PC-31
η in mPas
10
1
0
20
40
60
80
100
c Polymer in g/l


PMMA
PC-24
PC-31
PVB
[η] in l/g
0.3
0.2
0.1
0.0
0
20
40
60
80
100
c Polymer in g/l

- Gravimetric Characterisation with TGA/FTIR



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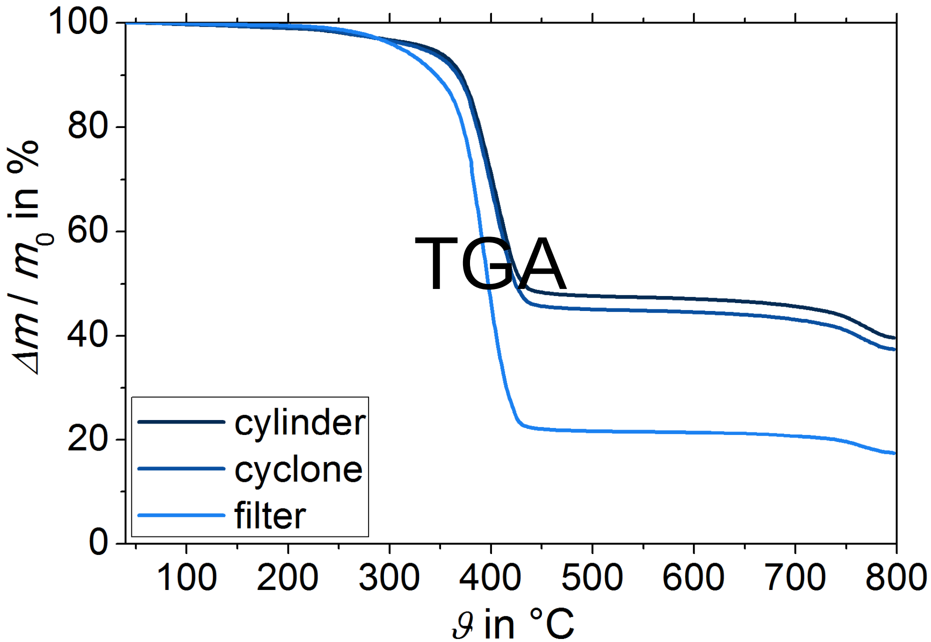
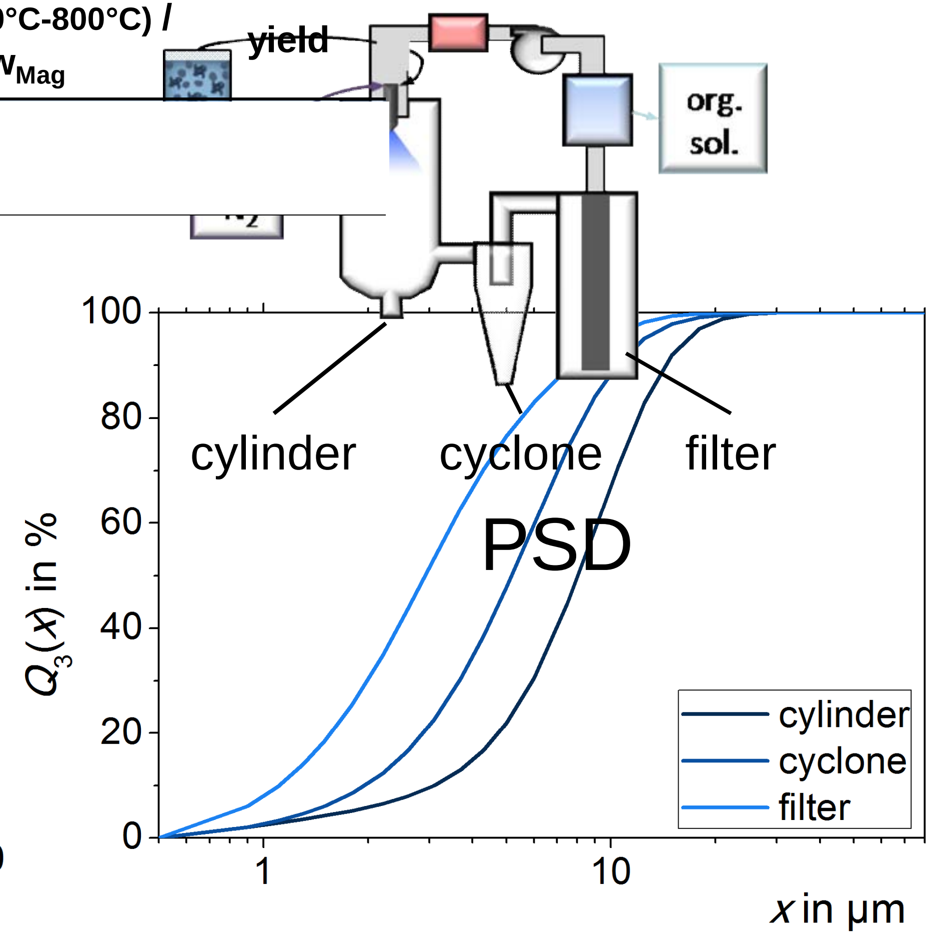
- Segregation Effects with Spray Drying

fraction	$x_{50,3}$	w_{Mag}	$\Delta m(600°C\text{-}800°C)$ / w_{Mag}	yield
cylinder				
cyclone				
filter				





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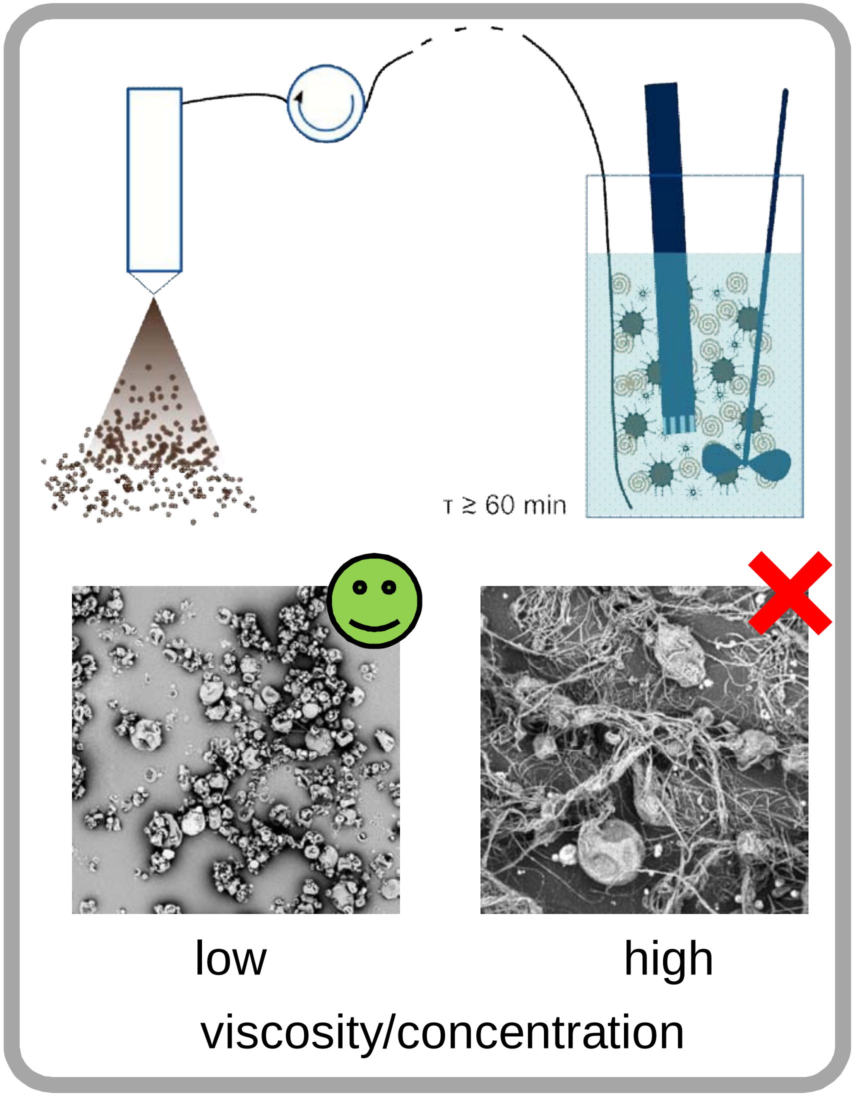
- Spray Drying
- Büchi lab scale spray dryer co-current, inert-loop
- $x_{50,\ \mathrm{composite}} \approx 4\ \mu m$
- up to 100g/h composites



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