Characterization of Concentrated Nano-Scaled Droplets, Soft and Hard Particles by Fiber-Optical Photon Density Wave Spectroscopy

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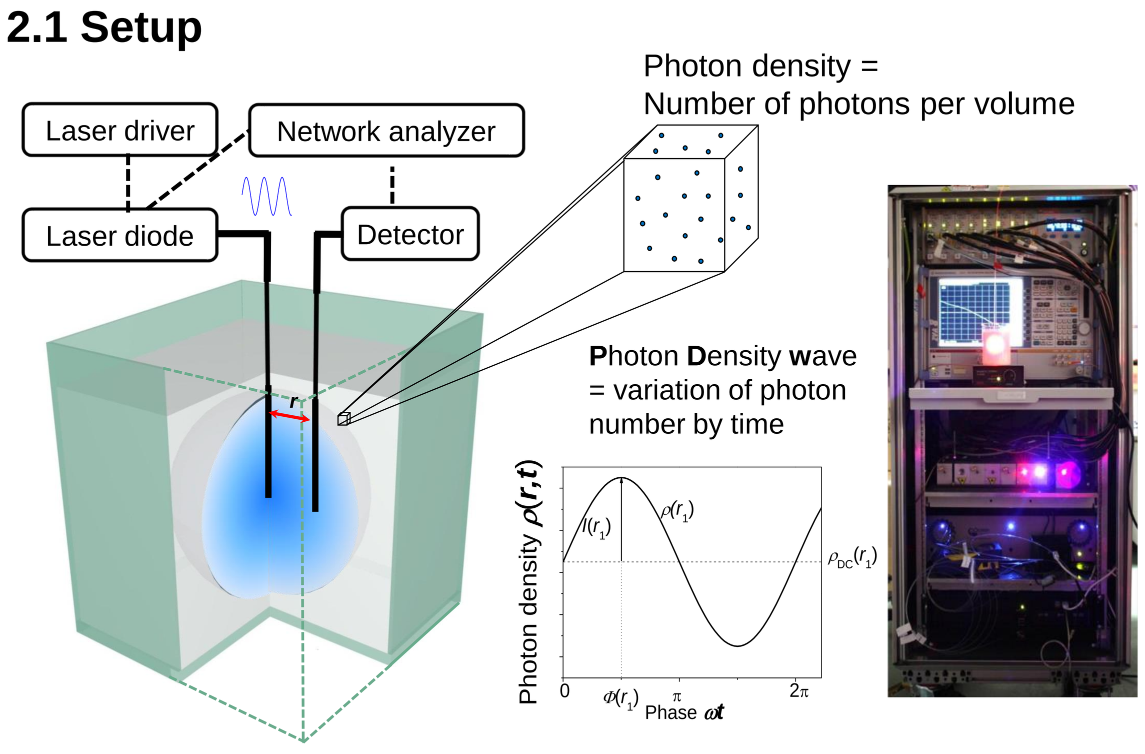
1 Photon density wave spectroscopy

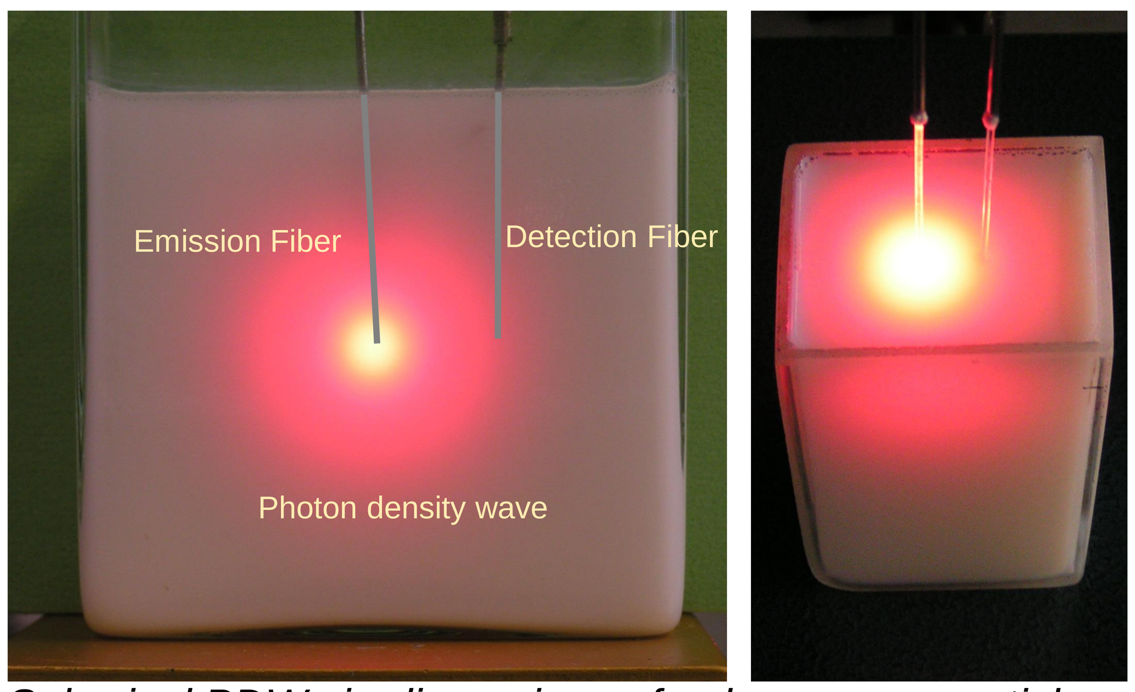
- In-line Process Analytic Technology (PAT) for concentrated and strongly scattering dispersions
- Dilution and calibration free
- Based on multiple-light scattering
- Independent characterization of reduced scattering coefficient μ_s' (linked to particle size) and absorption coefficient μ_a

2 Experimental

2.1 Setup



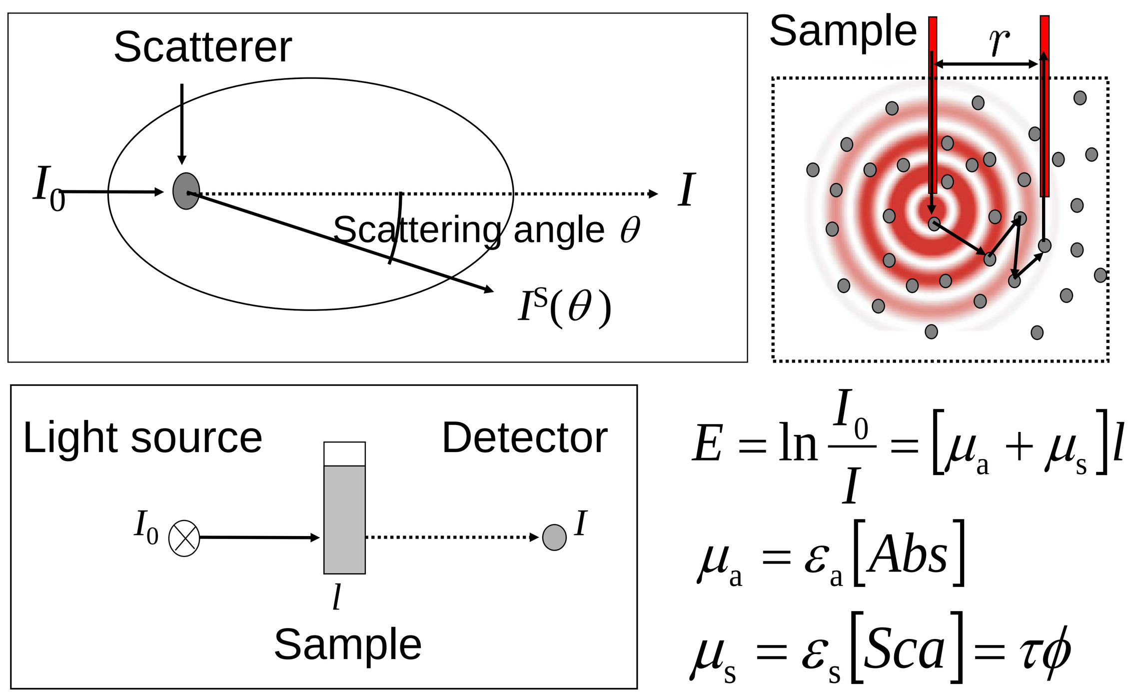
2.2 Snapshots of PDWs



Spherical PDWs in dispersions of polymer nanoparticles.

3 Theory

3.1 Single scattering & absorption



$$E = \ln\frac{I_0}{I} = [\mu_a + \mu_s]l$$

$$\mu_a = \varepsilon_a[Abs]$$

$$\mu_s = \varepsilon_s[Sca] = \tau\phi$$

3.2 Multiple scattering & absorption

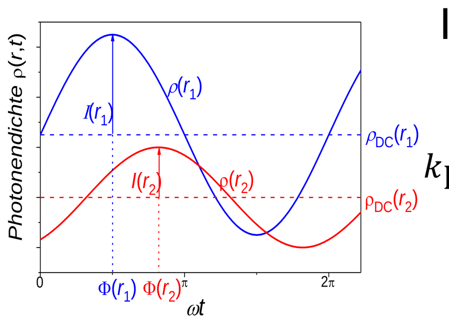
Reduced Scattering coefficient: $\mu_s' = \mu_s[1-g] = \tau'\phi$

Anisotropy factor: $g = \langle\cos\theta\rangle = \dfrac{\int I^S(\theta)\cos\theta \,\mathrm{d}\cos\theta}{\int I^S(\theta)\,\mathrm{d}\cos\theta}$

Photon density:

$$\rho(r,t) = \frac{\rho_{DC}^0}{r}\exp[-k_{DC}r] + \frac{\rho_{AC}^0}{r}\exp[-k_I r]\cos[\omega t - k_\Phi r]$$

Time constant — Intensity $I(r,f)$ — Phase $\Phi(r,f)$



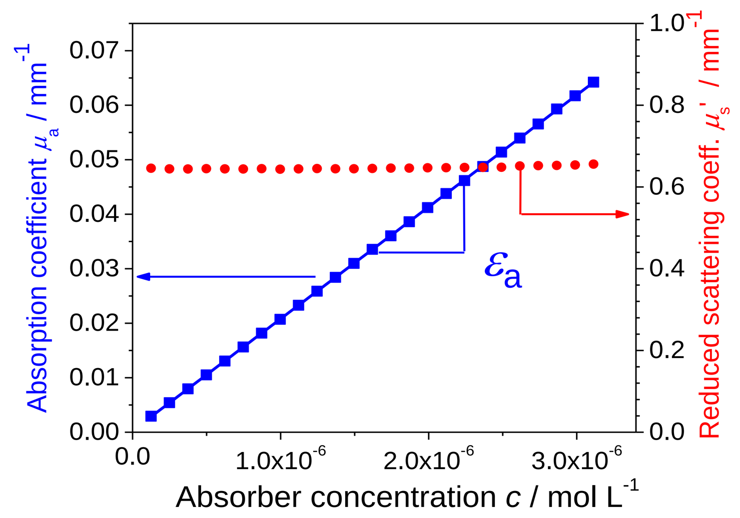
Intensity- and phase coefficient:

$$k_{I/\Phi} = \left[\frac{3}{2}\left[\left\{\left(\left(\frac{\mu_a}{3}+\mu_s'\right)^2 + \frac{\omega^2}{c^2}\right)\left(\mu_a^2 + \frac{\omega^2}{c^2}\right)\right\}^{\frac{1}{2}} \pm \mu_a\left(\frac{\mu_a}{3}+\mu_s'\right) \mp \frac{\omega^2}{c^2}\right]\right]^{\frac{1}{2}}$$

Absorption and scattering properties can be determined independently!

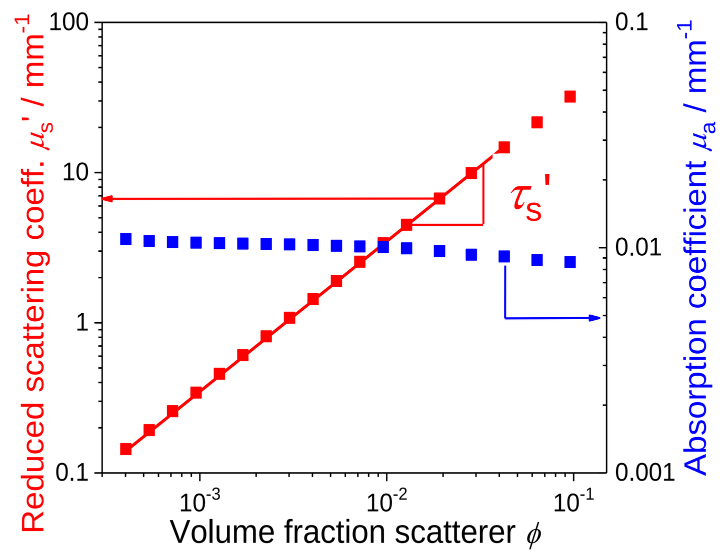
4 Fundamentals of particle sizing

4.1 Variable absorber concentration



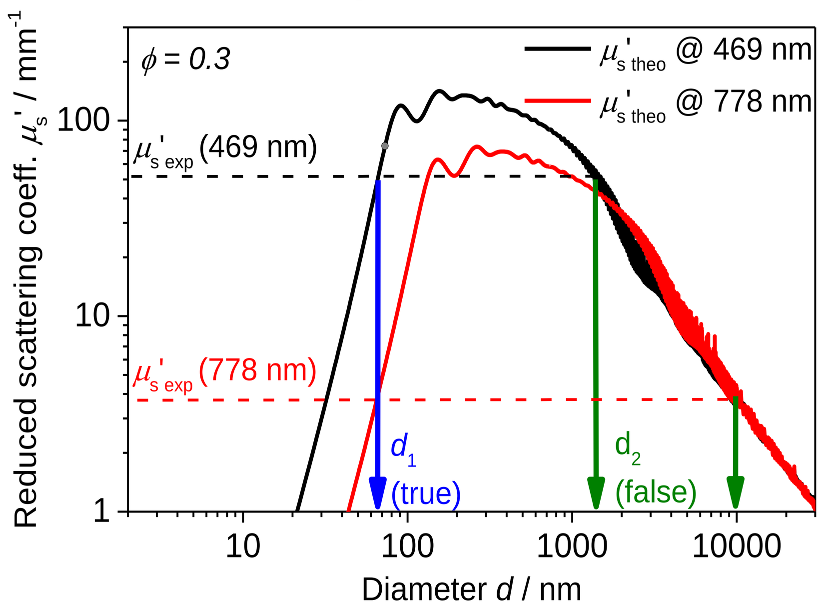
- μ_a analogous to Lambert-Beer -> slope = ε_a(Absorber)
- μ_s' constant
- Allows determination of absorber concentration

4.2 Variable scatterer concentration



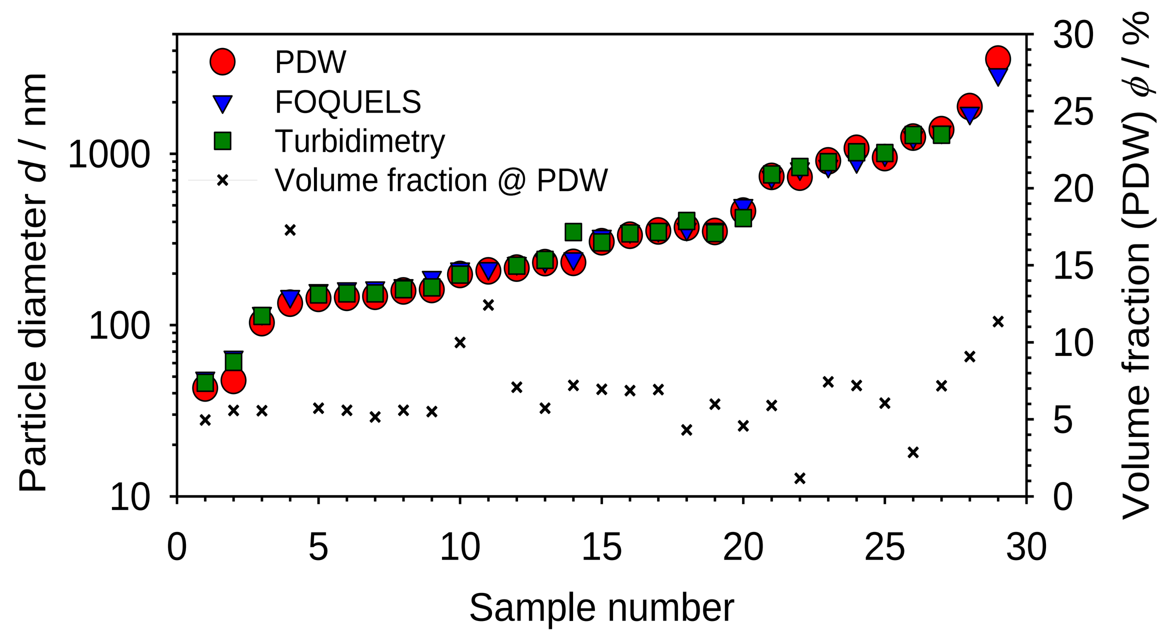
- μ_s' increases linearly with slope τ_s'
- μ_a decreases due to reduced water content
- Allows determination of particle size or volume fraction ϕ

4.3 Determination of particle sizes

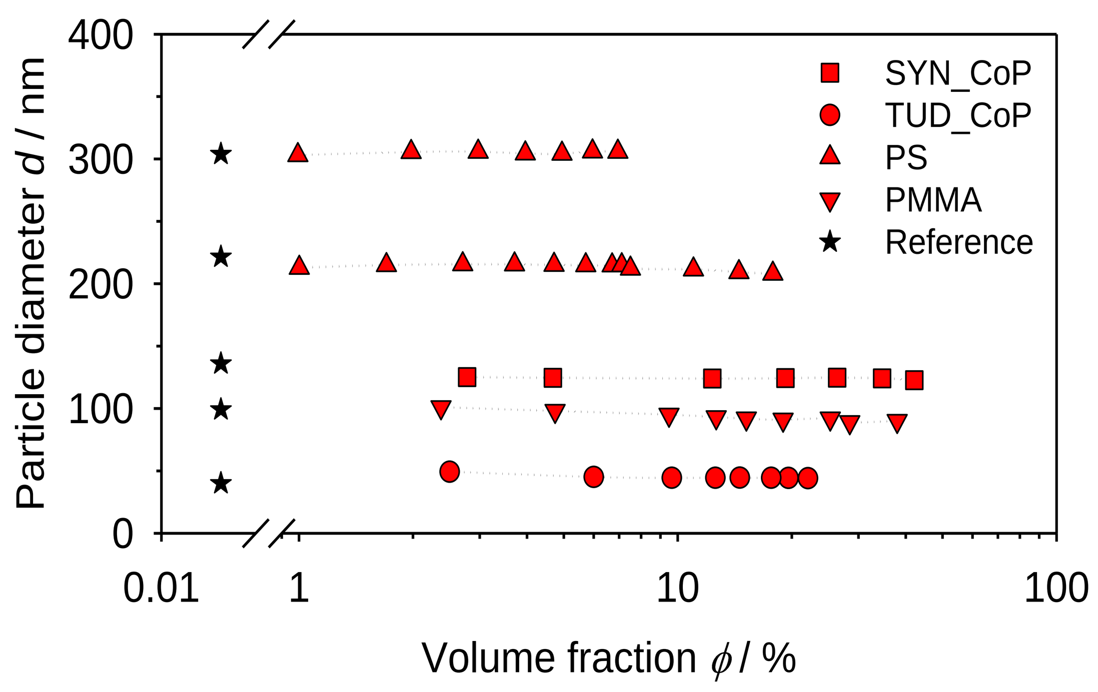


- Ambiguity in particle size at one measurement wavelength
- Measurements at different wavelengths solves ambiguity

4.4 High level of agreement with reference techniques



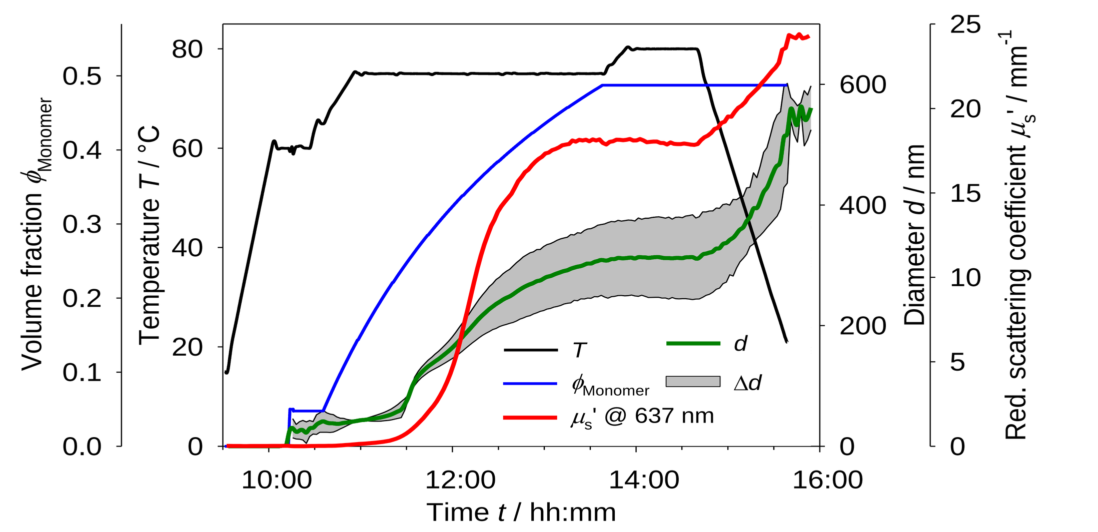
4.5 High Volume fraction



- Different polymer dispersions with volume fractions up to 60% measurable

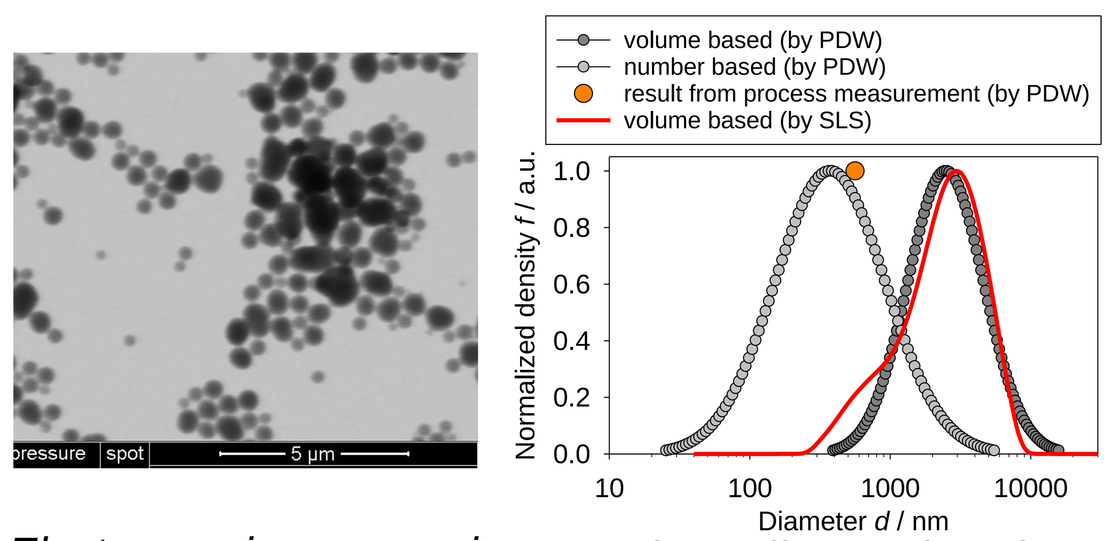
5 PDW for PAT

5.1 Radical fed-batch polymerization of vinyl acetate in water in 1 L scale



Temperature T, monomer volume fraction ϕ, reduced scattering coefficient μ_s' at 637 nm, mean diameter d and its distribution width Δd as function of time t for the polymerization of vinyl acetate.

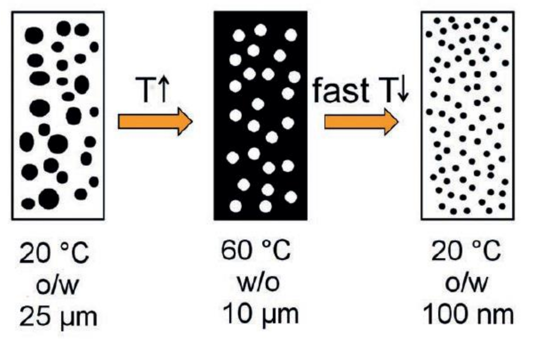
Nano particle size characterization of PVAc



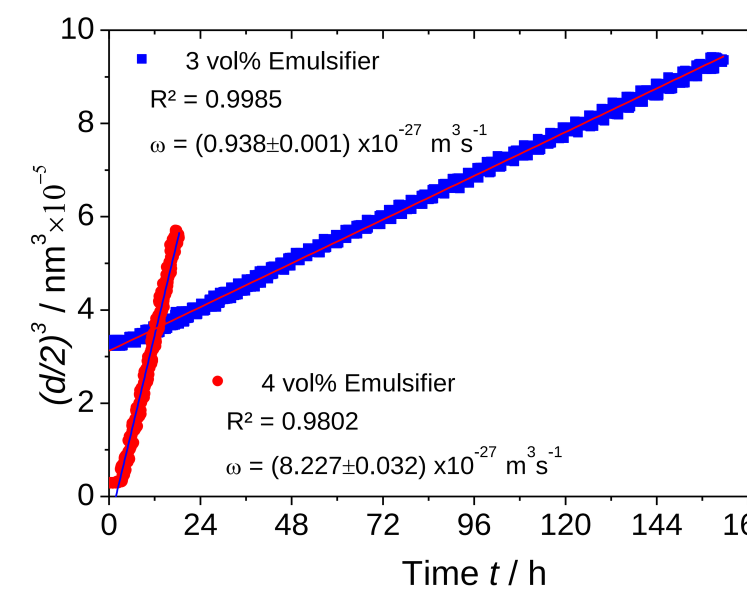
Electron microscope image of synthesized polyvinyl acetate particles (left) and particle size distributions from PDW spectroscopy and static light scattering (right).

- Good agreement with electron microscopy
- Result from process measurement reflects number based particle size distribution by PDW spectroscopy, reference analysis by static light scattering agrees well with volume based distribution from PDW spectroscopy

5.2 Ostwald ripening of nano emulsions



Principle of Phase Inversion Temperature (PIT) emulsification with typical temperatures, phases (o/w – oil-in-water, w/o – water-in-oil) and typical droplet diameter



Cubic nanodroplet radius as function of time for two different emulsifier concentrations (points) and linear fit (lines) to obtain the according Ostwald ripening rates ω.

- Ostwald ripening rates can be determined without dilution, shown here for nano droplets generated by the PIT emulsification method

6 Conclusions

- Unique **in-line** process analytic technology to characterize **highly turbid** materials
- **Optical properties and sizing** of nano- and micrometer-scaled droplets / particles
- **Dilution-free** measurement technique
- Size distribution measurements require **multi-wavelength experiments**

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