Inline monitoring of particle size in emulsion polymerization processes by Photon Density Wave (PDW) Spectroscopy

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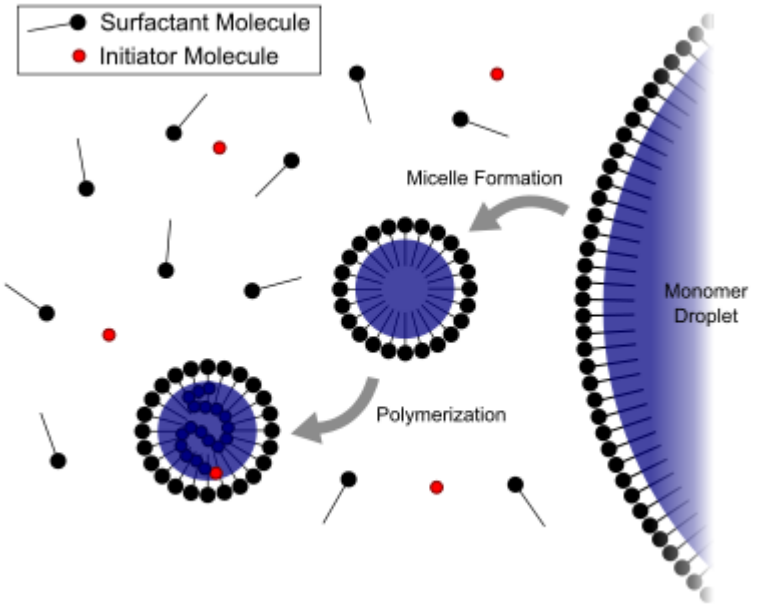

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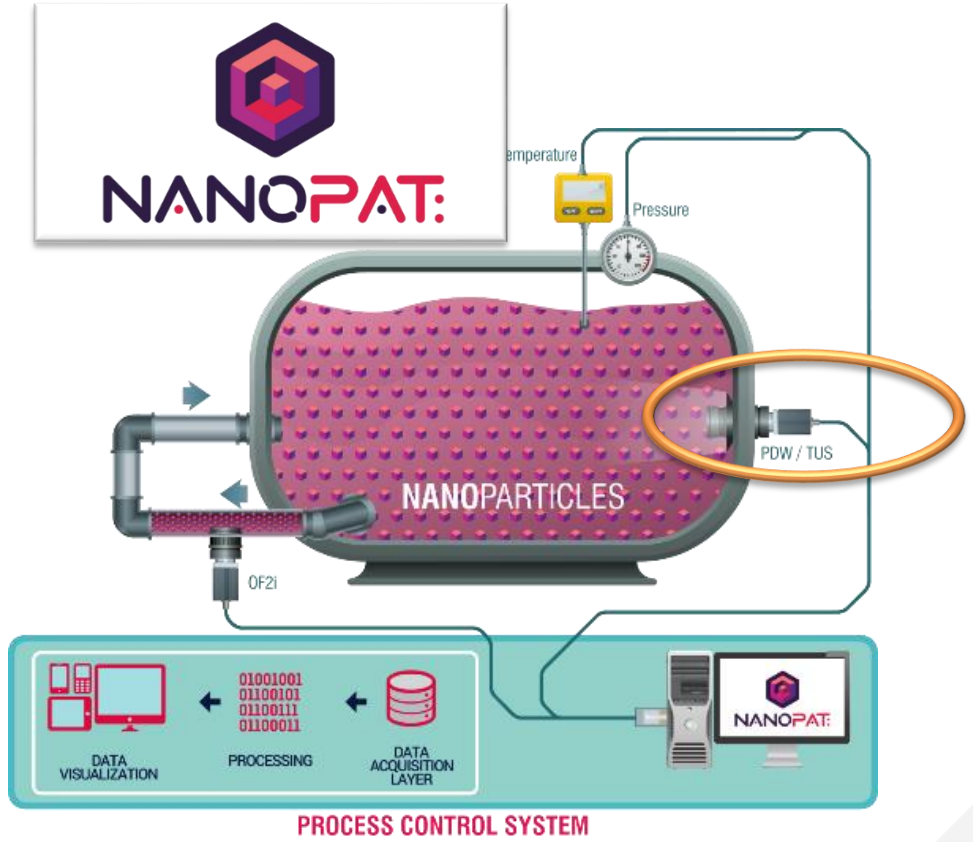
1 i) Introduction.

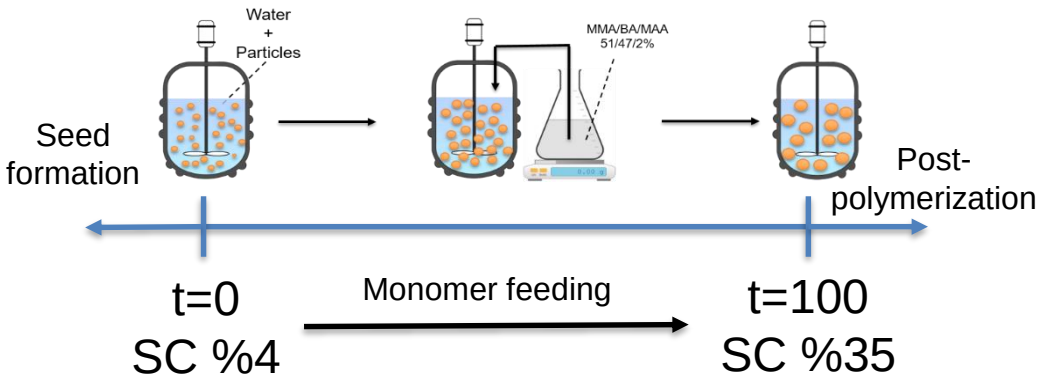
NanoPAT European Project: Application of three new real-time analytical tools for particle size (dp) and particle size distribution (PSD) in-line or on-line monitoring.

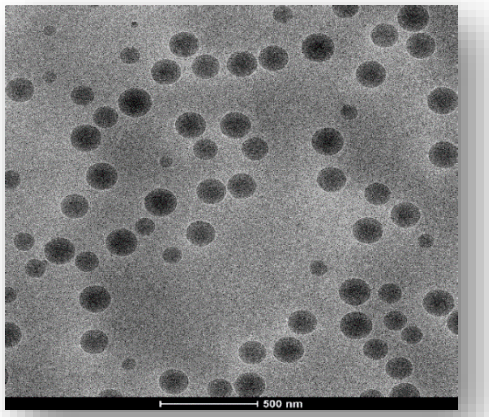
Present Work objective: Assessing Photon Density Wave (PDW) spectroscopy analysis method as in-line monitoring technique in emulsion polymerization processes.



Polyacrylate latex synthesis

Emulsion polymerization process





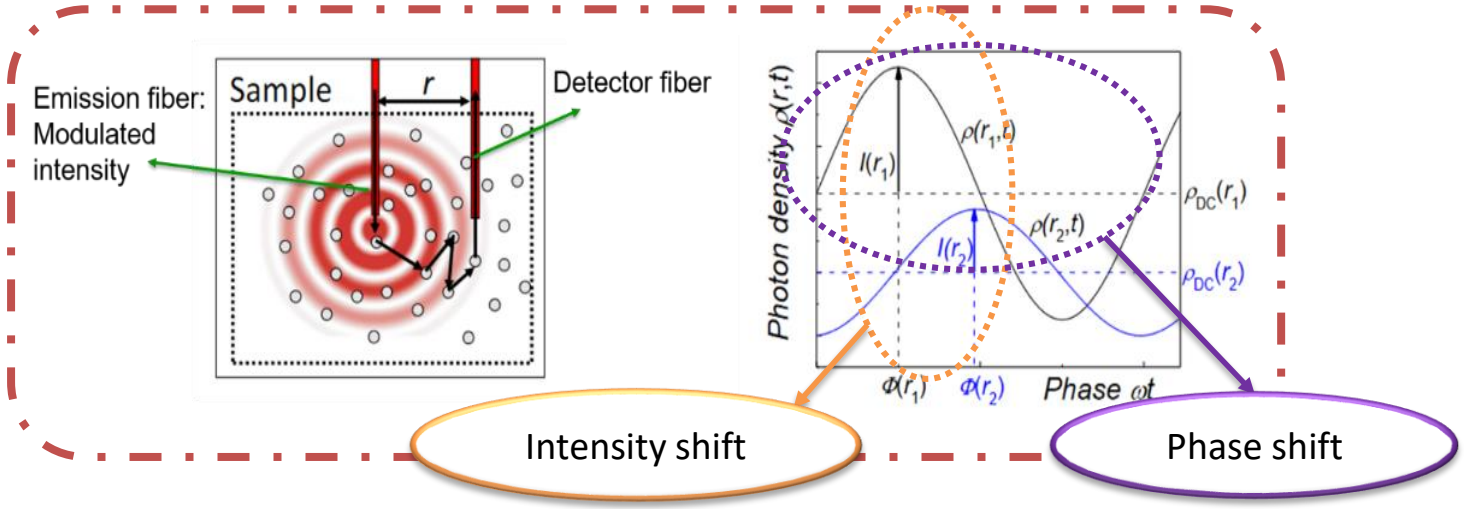
CryoTEM image for final latex (t=130min). Scale: white line in the base of the figure=500nm

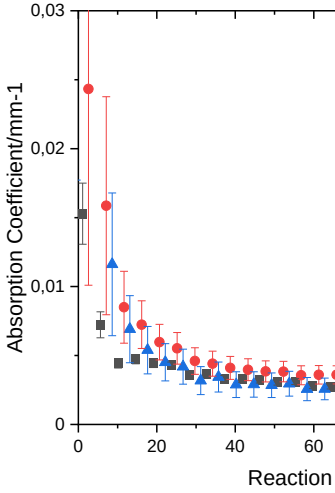
1 ii) PDW background

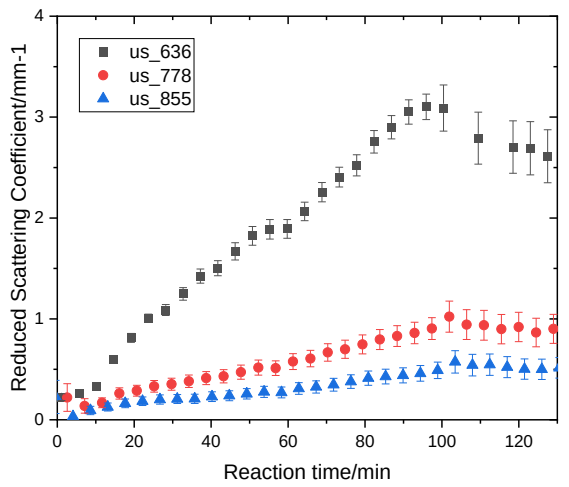
Phase shift (k_ϕ)
Intensity shift (k_I)

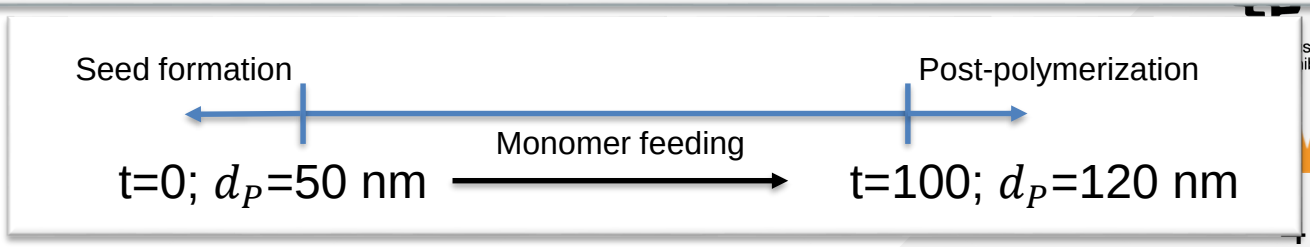
Absorption Coefficient (μ_a)
Reduced Scattering Coefficient (μ_s')

Particle diameter (d_P)
(Particle size distribution. PSD)









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(Particle size distribution. PSD)

$$\mu_s' = \frac{3\phi_1 Q_s}{2d_p}\int_{-1}^{1} f(\cos(\theta))S(\theta,\phi)[1-\cos(\theta)]dcos(\theta)$$

*Hass, Bressel, Münzberg, Reich, Appl. Opt. 52, p. 1423-1431 (2013)

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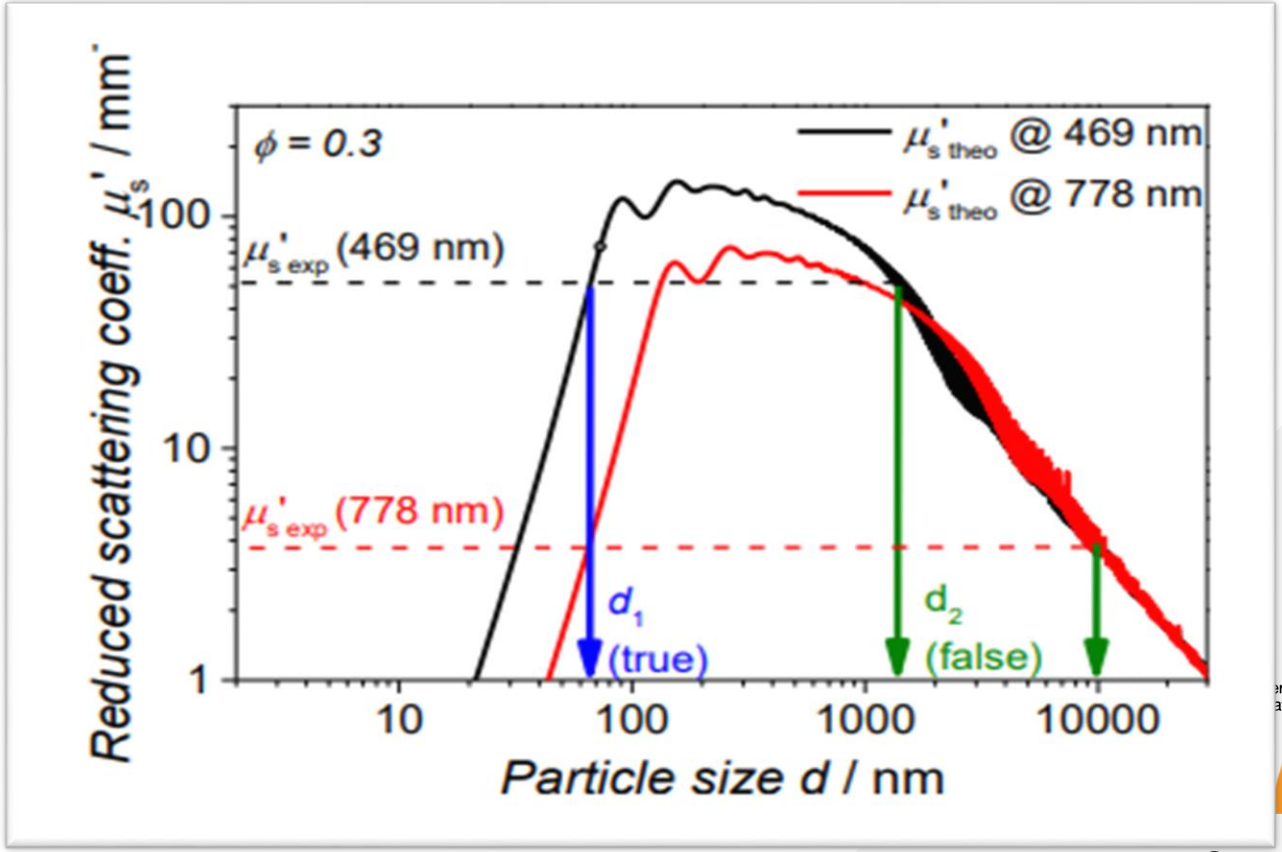
2 potential solutions

Which is the correct one?

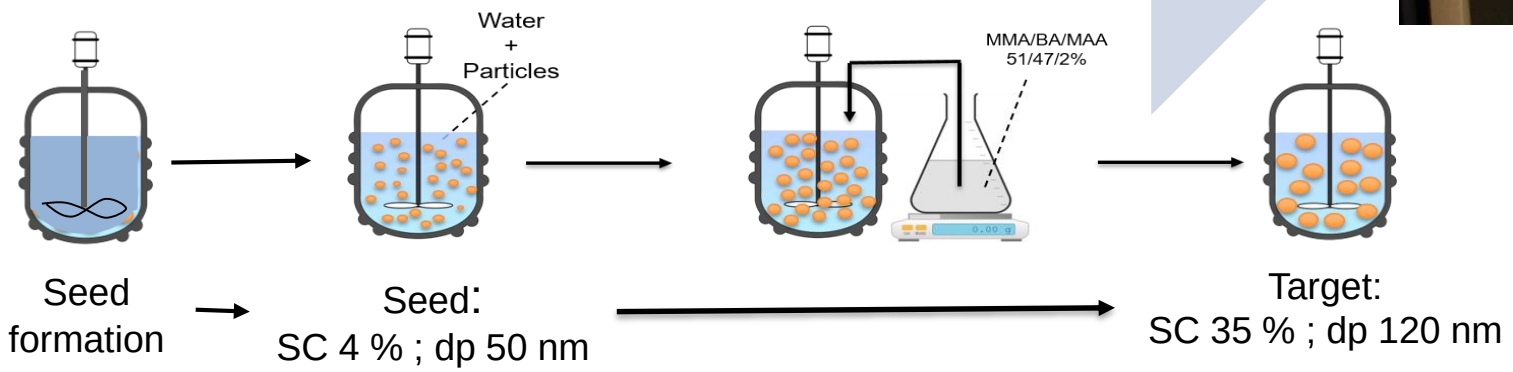
Comparison of data obtained with different λ



2. Analysed process

All acrylic latex synthesis

In-situ seed formation (30 min)	Particle growth (100 min)	Postpolymerization (30 min)

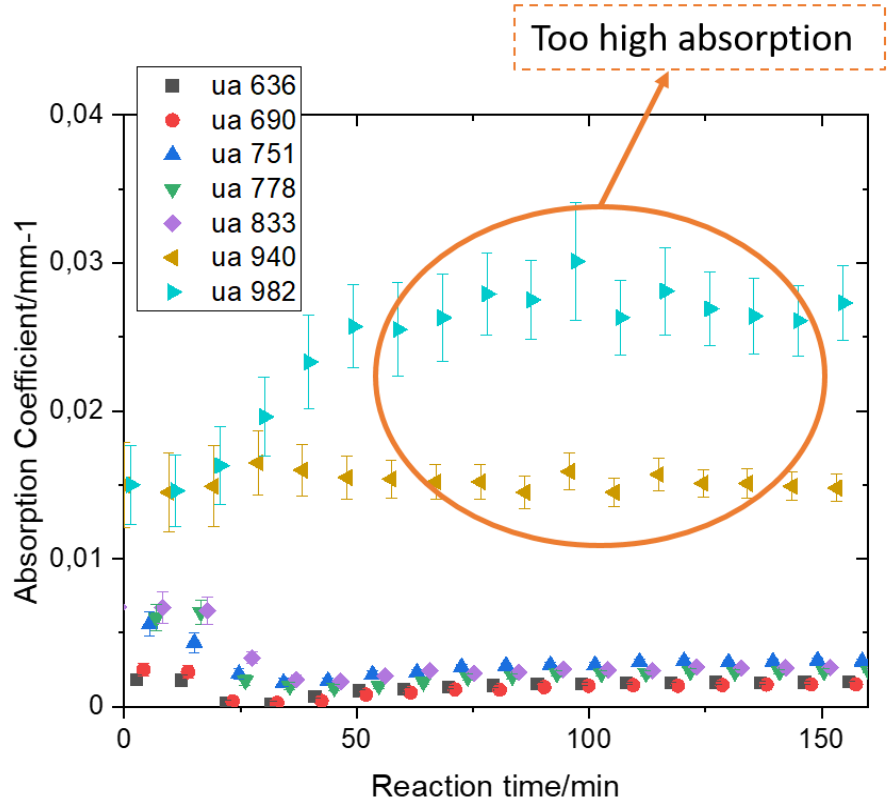


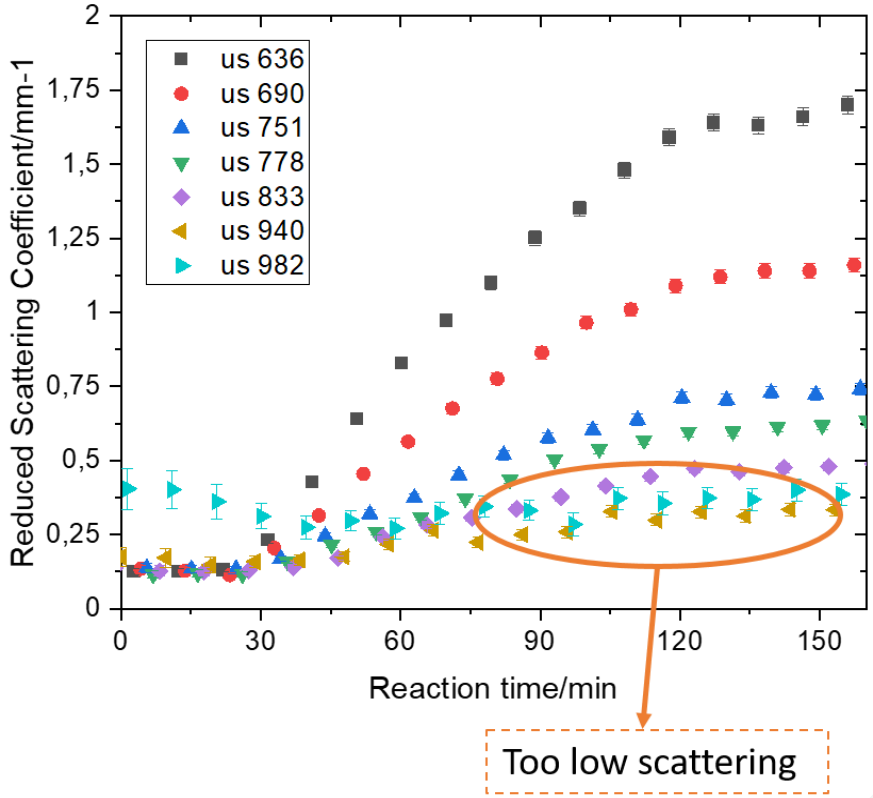
Recipe:

- Monomer (w/w)
  - MMA 51 %
  - BA 47 %
  - MAA 2 %
- Initiator: APS
- Surfactant: SDS
- Water

3. Results. Inline analysis

Effect of laser wavelength





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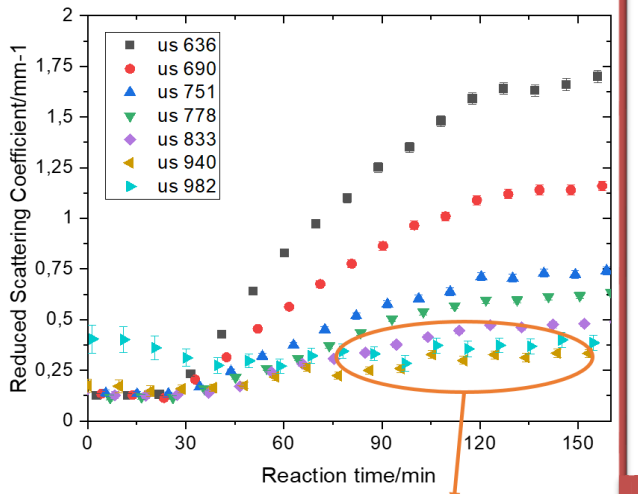
3. Results. Inline analysis

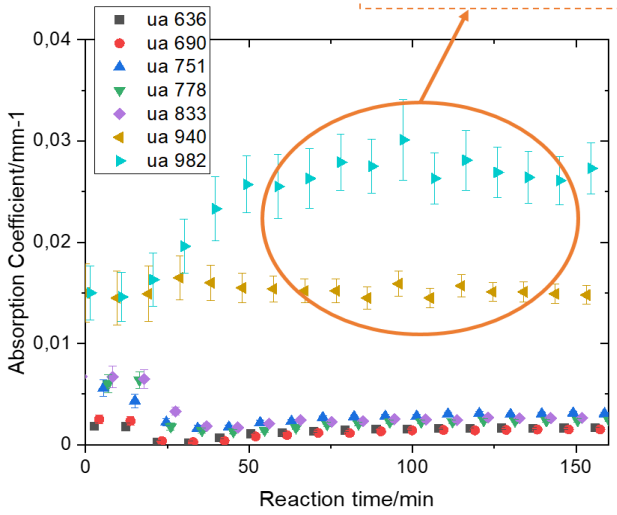
Good agreement between inline PDW and offline DLS results

For the range 50-120 nm and up to 35 % SC:
the smaller the wavelengths, the better the inline analysis.



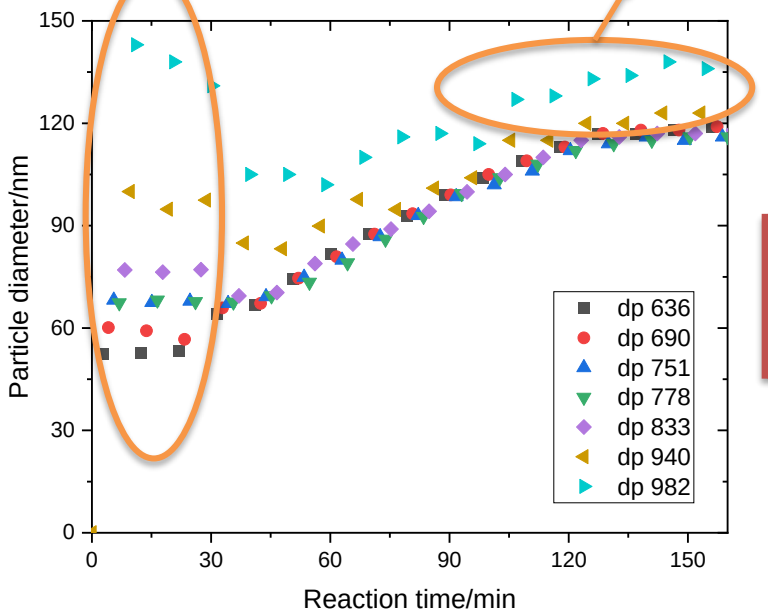
Too low scattering

Too high absorption



Too low SC for multiple scattering

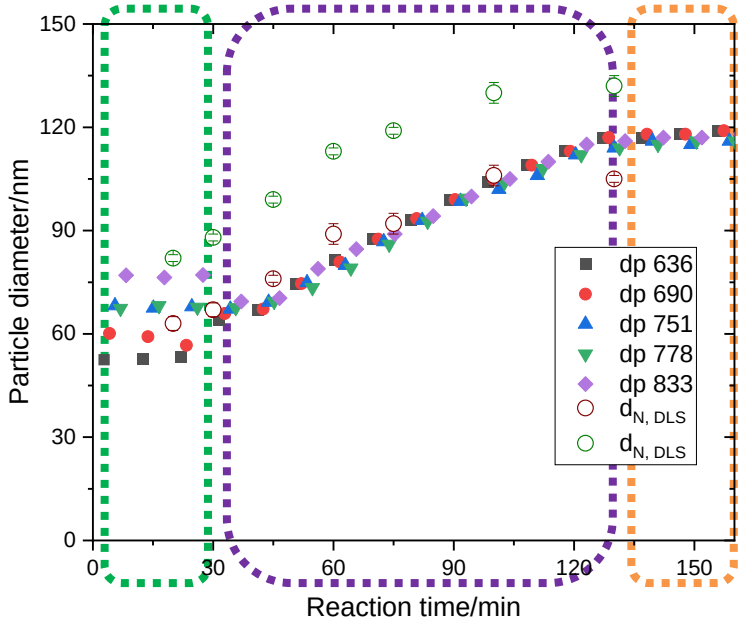
Too high wavelength



Seed formation

Particle growth

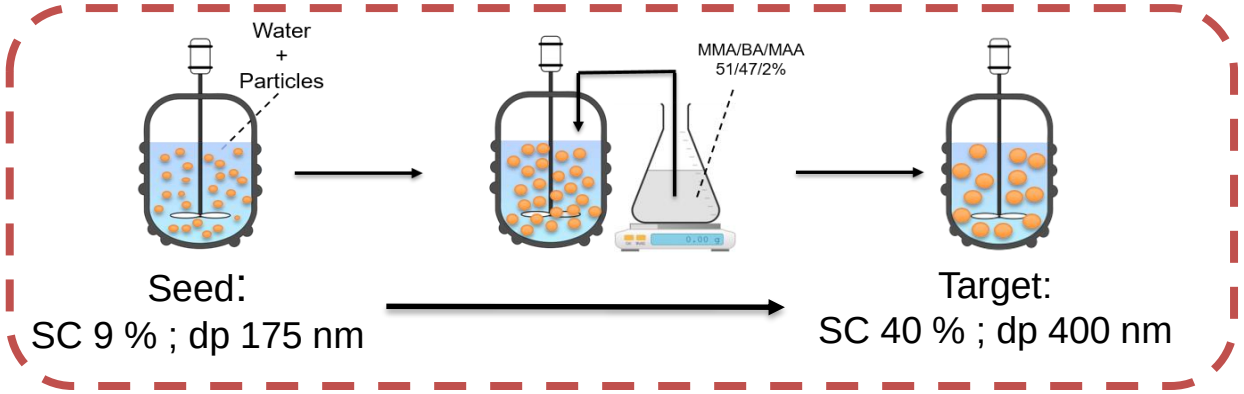
Postpolymerization

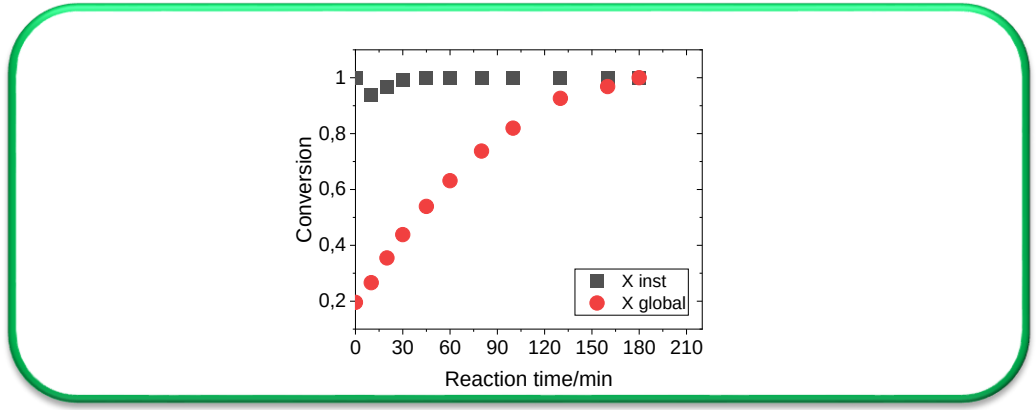


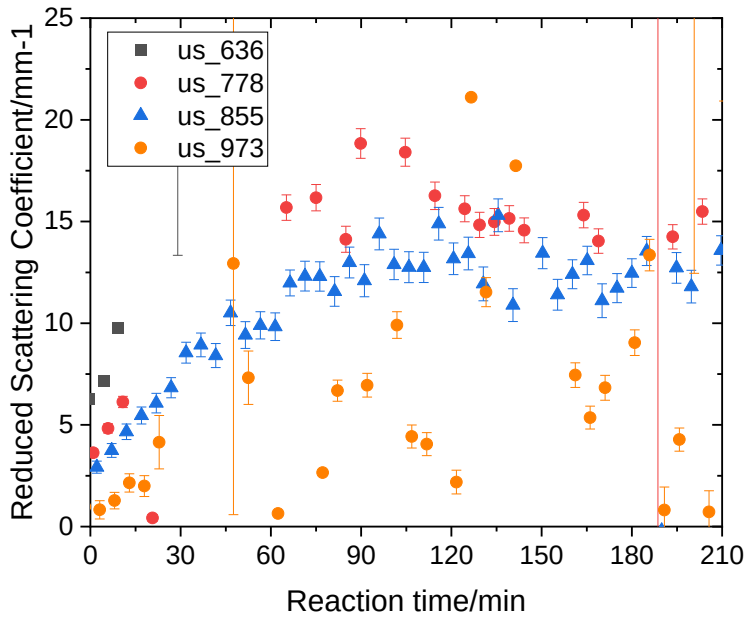
Analysis of broader dp and SC range
Coagulation detection
Bimodal latex analysis

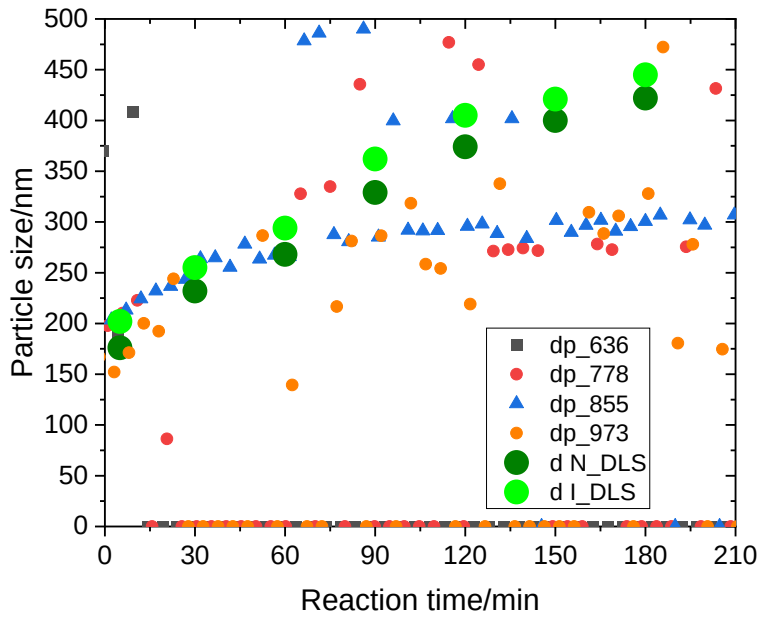
3. Results. Particle size range analysis

SC40 %; monomodal; dp 175→400 nm









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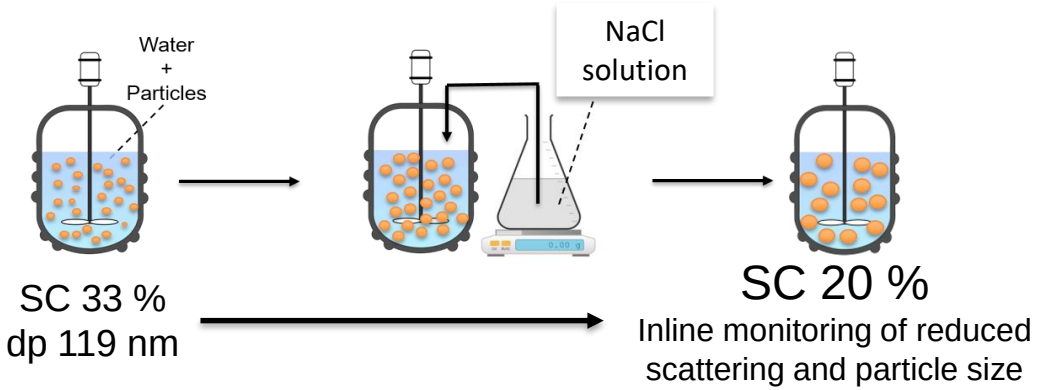
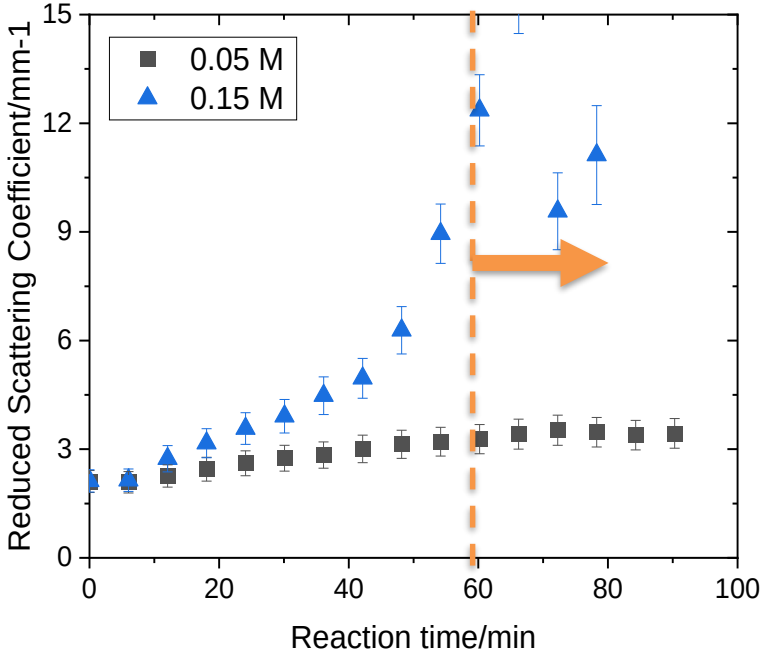
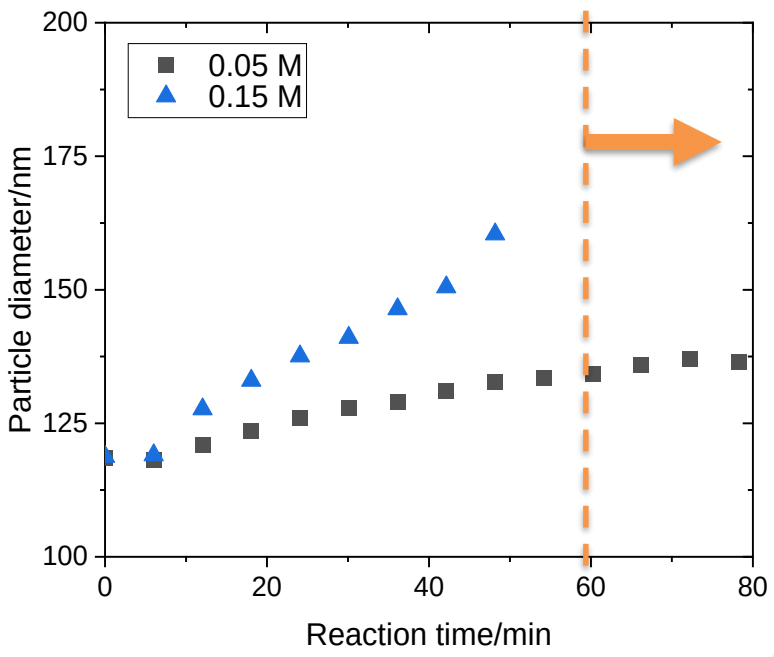
3. Results. Coagulation detection



Feeding rate: 1 g/min
Feeding time: 65 min
Final solution concentration: 0.05-0.15 M

* Wavelength used for the analysis: λ = 636 nm





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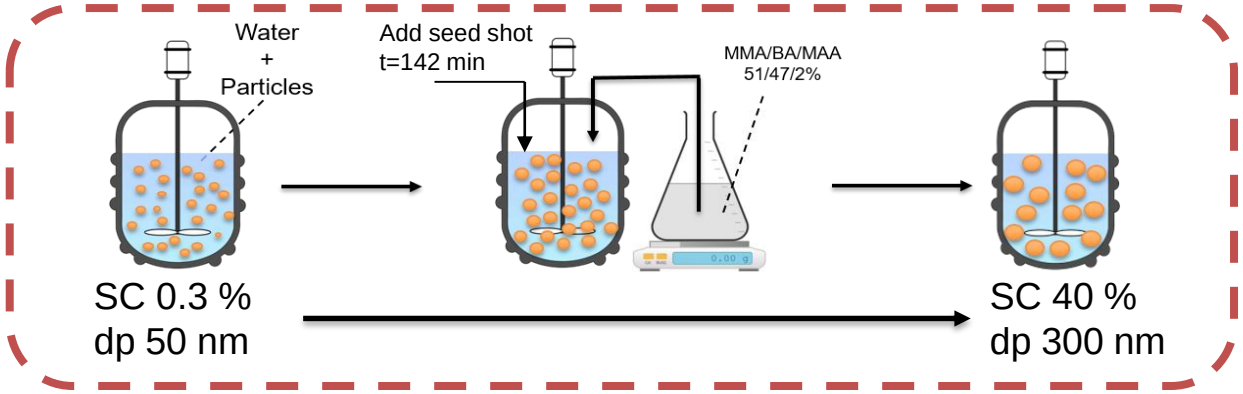
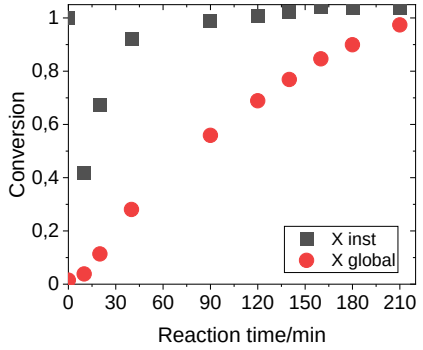
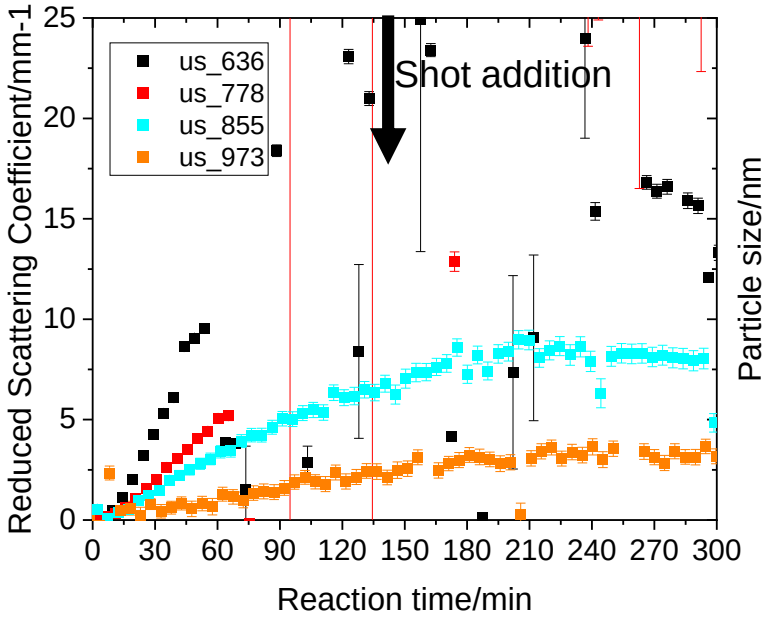
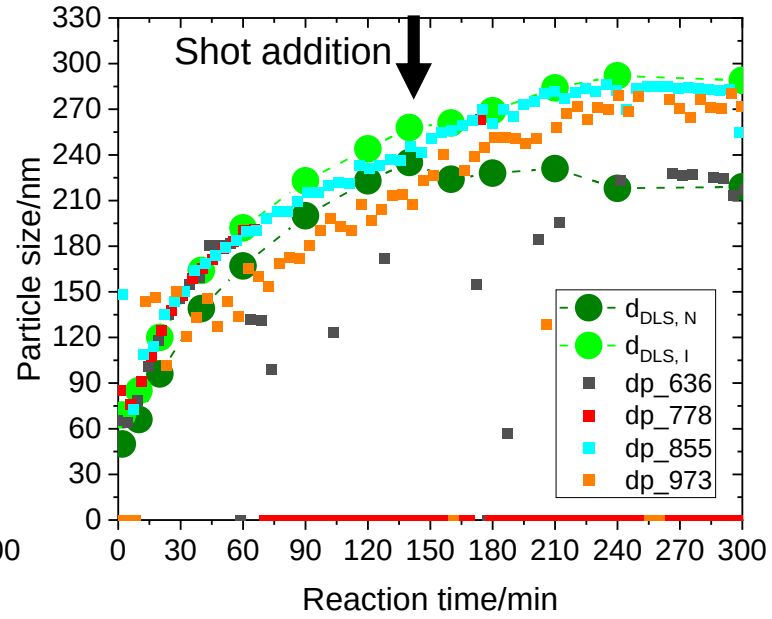
3. Results. Detection of bimodal latex formation

SC40 %; bimodal; dp 45→80/300 nm (Post-process)

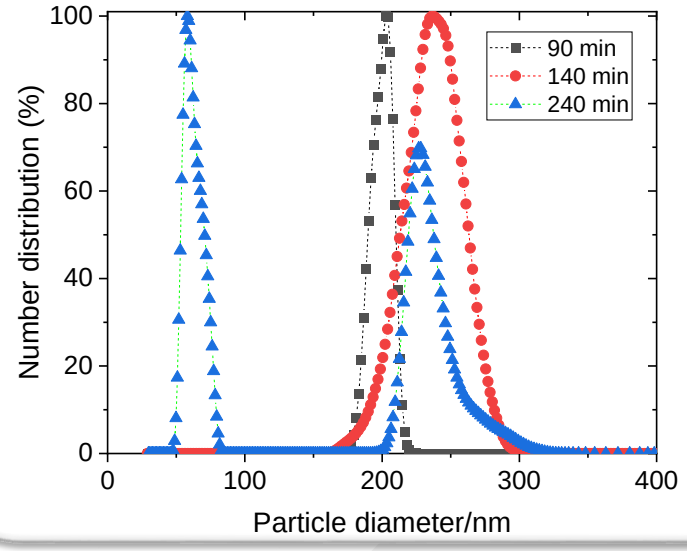








CHDF analysis of PSD



4. Conclusions

- ✓ Accurate monitoring of particle size during seeded semibatch emulsion polymerization processes (SC of 40 % and particle size range 50-300 nm).
- ✓ PDW particle size is within number and intensity average DLS particle sizes (closer to dp,N).
- ✓ Aggregation of polymer particles can be detected. Reduced scattering is more sensitive than particle size.
- ✓ The detection of new nucleations is challenging due to the big influence of the existing large polymer particles in the light scattering.

Acknowledgement

Thank you for your attention

NANOPAT:

PDW ANALYTICS

covestro

innoFSPEC
Innovative faseroptische Spektroskopie
und Sensorik

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