ESI: Core-shell microgels synthesized in continuous flow: Deep insight into shell growth by temperature-dependent FTIR

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1 Time deviation caused by a non-temperatured outlet

Table 1 Time of residence t inside the continuously heated reactor at corresponding flow rates f and additional residence time t_{output} of the solution in the finite, unheated output between the outlet of the reactor and the quenching vial (length: 5 cm, time deviation: 1.8 %)

t / min	f / mL min^{-1}	t_{output} / s
1	412.0	1
3	137.3	3
5	82.4	5
7	58.9	7
10	41.2	11
30	13.7	32

2 ^{1}H-NMR on stock solution stability in presence of the initiator

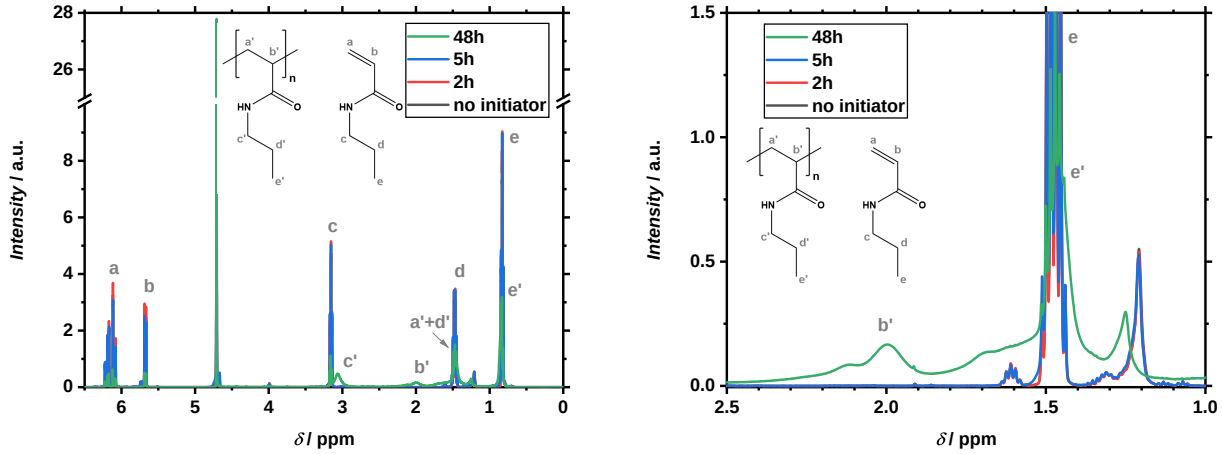

Figure 1 (left) ^{1}H-NMR spectra of a cooled NnPAM solution in D_2O (<5 °C) with premixed ammonium persulfate show the characteristic signals of the monomer and evolving signals of the polymer. (b) A closer look between 1 and 2.5 ppm does not show any significant changes in the monomer signals, even after 5 h. After 48 h, polymer signals evolved to significant intensity. The spectra show that no unwanted self initiation is observable during the typical duration of a continuous flow experiment.

3 Preheating time in the continuous flow reactor

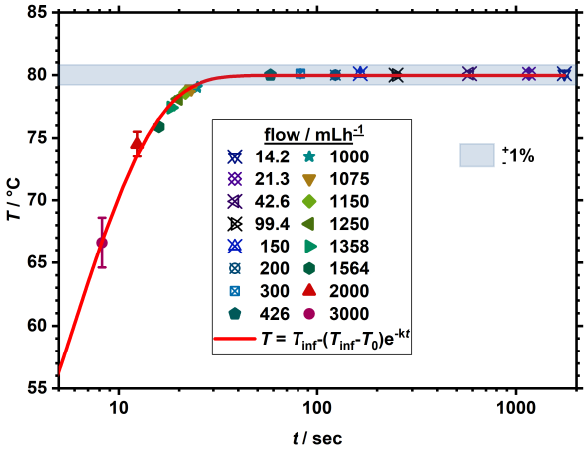

Figure 2 The temperature T of water was measured inside the tubing at different flow rates, resulting in corresponding residence times t from the entrance of the reactor to the position of the thermometer (GMH3210, Greisinger, Regenstauf, Germany). The data was fitted with an approach of Newton's law of heating.[1] The final region at 79 °C (blue) is reached after 23 s. T_0 describes the initial temperature of water (22.4 °C), T_{inf} the setpoint (80.0 °C) and k the rate of heating.

4 Comparison of batch and flow reactor

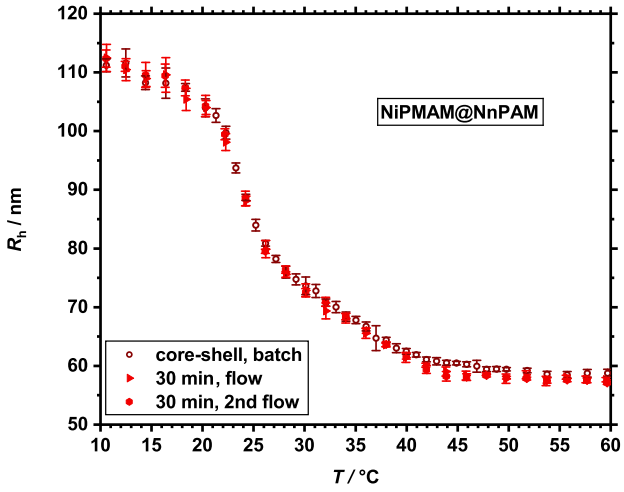

Figure 3 Swelling curves of fully grown PNiPMAM@PNnPAM core-shell microgels from batch syntheses in comparison to two independent flow syntheses after 30 min. The swelling curves are identical with respect to the error, demonstrating the excellent repeatability of continuous flow syntheses.

5 Normalized swelling curves from photon correlation spectroscopy

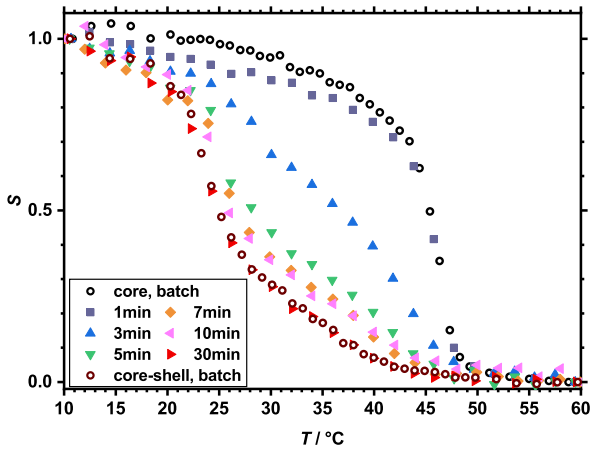

Figure 4 Normalized swelling curves of PNiPMAM@PNnPAM core-shell microgels from batch and continuous flow syntheses after residence times between 1 min and 30 min are shown.[2] The normalized swelling curves highlight the emerging shell swelling and the linear phase transition.

6 Angle-dependent PCS measurements

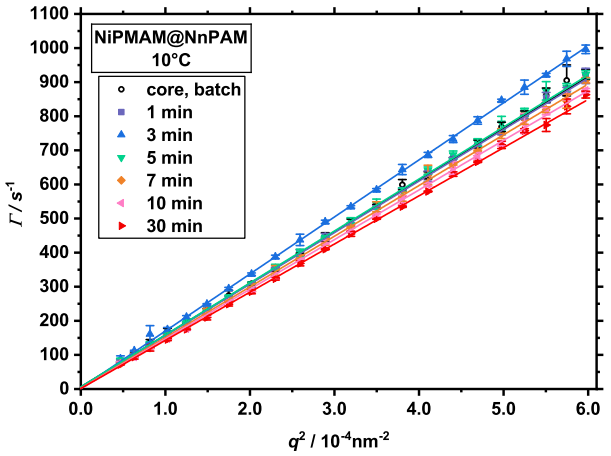

Figure 5 Angle-dependent PCS measurements of PNiPMAM@PNnPAM core-shell microgels, quenched after different residence times t. The data were analyzed using a linear fit and they perfectly match the prediction of eq. (1). All fits cross the origin, confirming that only translational diffusion occurs.

7 AFM height profiles

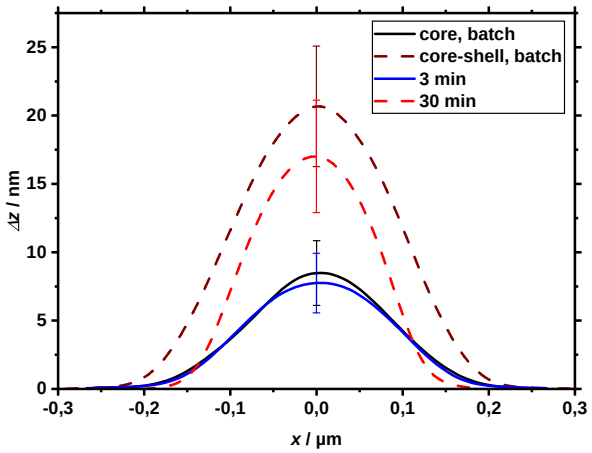

Figure 6 Averaged height profiles of PNiPMAM@PNnPAM core-shell microgels and the used PNiPMAM core at different synthesis times. The height profiles were extracted from their respective AFM height images with the standard deviation as error bars. The incorporation of shell monomer is clearly visible by an increase in height for batch synthesis and after 30 min.

8 Correlation between the hydrodynamic volume in the collapsed state and the wavenumber of the amide II vibration

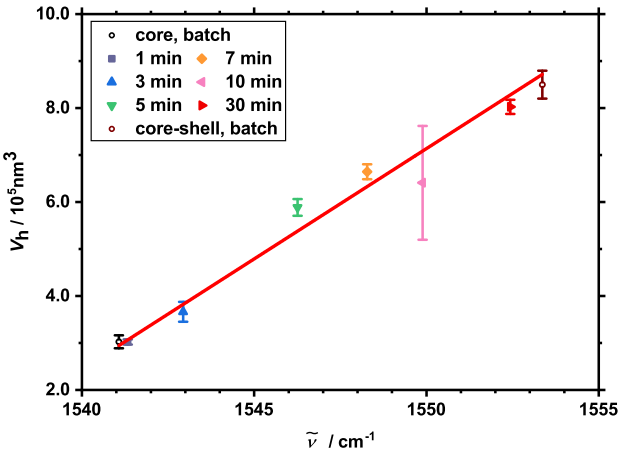

Figure 7 The hydrodynamic volume V_h from PCS measurements (angle: 60°, temperature: 60 °C) is plotted against the wavenumber ν of the maximum from FTIR measurements (11 °C), showing a direct contribution of shell material to the volume increase.

Notes and references

[1] M. Gockenbach and K. Schmidtke, *Involve*, 2009, **2**, 419–437.

[2] M. Cors, L. Wiehemeier, J. Oberdisse and T. Hellweg, *Polymers*, 2019, **11**, 620.