Direct monitoring of microgel formation during precipitation polymerization of N-isopropylacrylamide using in situ SANS

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1 Supporting Information

1.1 Effect of cross-linker bisacrylamide on particle growth rate

Total volume growth rate in dependence of BIS concentration was calculated from Eq. 12 and are shown in Figure S1.

![Figure S1: Total volume growth rate during the precipitation polymerization of NIPAM with increasing BIS concentration.](image)

\[ y(x) = y_0 + A_1 \exp\left(\frac{x}{t_1}\right) + A_2 \exp\left(\frac{x}{t_2}\right) \]  

(S1)

To calculate the initial reaction rate from this fit, the first derivative has to be calculated:

\[ \frac{dy}{dx} = \frac{A_1}{t_1} \exp\left(\frac{x}{t_1}\right) + \frac{A_2}{t_2} \exp\left(\frac{x}{t_2}\right) \]  

(S2)

At a reaction time of 0 this equation simplifies to:

1.2 Effect of cross-linker bisacrylamide on initial reaction rate

To determine the initial reaction rate \( r_{\text{initial}} \) of the NIPAM precipitation polymerization in dependence of the cross-linker concentration, the conversion is plotted against the reaction time (Figure S2). This plot is then fitted with the following two exponential equation:
\[
\frac{dy}{dx}_{(t=0)} = \frac{A_1}{t_1} + \frac{A_2}{t_2}
\]  

**Figure S2:** Conversion of the precipitation polymerization of NIPAM in dependence of reaction time, fitted with the single exponential Eq. 11 and the two exponential Eq. S1.

With this equation the initial reaction rate in dependence of the cross-linker concentration can be calculated using the fitting parameters found in Table S3 (see Table S1).

**Table S1:** Initial reaction rate in dependence of BIS concentration

| \(c_{\text{BIS}} \times 10^{-3}\) | \(r_{\text{initial}}\) |
|---------------------------------|-----------------|
| 1.8                            | 0.6120          |
| 1.5                            | 0.5356          |
| 0                              | 0.4537          |
**Table S2**: Conversion fit with Eq. 11

| $c_{BIS} \times 10^{-3}$ | $V_M/np$ | $t$ | $\chi^2$ | $r^2$ | cor. $r^2$ |
|-------------------------|----------|-----|----------|------|------------|
| 1.8                     | 74.3502  | 150.9645 | 0.3415 | 0.9975 | 0.9975     |
|                         | ±0.0174  | ±0.2933 |          |       |            |
| 1.5                     | 70.6655  | 160.0966 | 0.7553 | 0.9969 | 0.9969     |
|                         | ±0.0500  | ±0.5559 |          |       |            |
| 0                       | 69.4449  | 164.2591 | 0.4485 | 0.9982 | 0.9982     |
|                         | ±0.0390  | ±0.4456 |          |       |            |

**Table S3**: Conversion fit with two exponential Eq. S1

| $c_{BIS} \times 10^{-3}$ | $y_0$    | $A_1$   | $t_1$    | $A_2$   | $t_2$    | $\chi^2$ | $r^2$ | cor. $r^2$ |
|-------------------------|----------|---------|----------|---------|----------|----------|------|------------|
| 1.8                     | 74.5264  | -40.7241| -93.9698 | -37.6271| -210.6464| 0.1262   | 0.9991| 0.9991     |
|                         | ±0.0125  | ±1.9407 | ±2.4102  | ±1.9872 | ±4.1741  |          |       |            |
| 1.5                     | 72.1159  | -47.2412| -106.2111| -27.2607| -300.1492| 0.1347   | 0.9989| 0.9989     |
|                         | ±0.0141  | ±0.8615 | ±1.4974  | ±0.8983 | ±4.9010  |          |       |            |
| 0                       | 73.4011  | -68.1594| -151.2669| -6.5663 | -2090.4057| 0.2782   | 0.9976| 0.9976     |
|                         | ±0.2223  | ±0.1562 | ±0.7051  | ±0.1249 | ±173.1407|          |       |            |