

Supplementary Materials: Modified Flory-Rehner Theory Describes Thermotropic Swelling Transition of Smart Copolymer Microgels

Simon Friesen, Sergej Kakorin and Thomas Hellweg *

1. ¹H-NMR analysis

Quantification of the comonomer content was carried out using ¹H-NMR spectra. A three-fold quantification was performed. The results are listed in Table S1. For the calculation of the comonomer content in p(NNPAM-co-NIPAM) and p(NIPAM-co-NNPAM) microgels, the signal of the isopropyl H atom ($\delta = 3.93$ ppm $\text{NHCH}(\text{CH}_3)_2$, 1H) and the signal of the H atoms of the secondary carbon ($\delta = 3.14$ ppm $\text{NHCH}_2\text{CH}_2\text{CH}_3$, 2H) were used. From the ratios of the intensity integrals of the signals, the comonomer content was calculated. Since all signals overlap in p(NIPAM-co-NIPMAM) microgels, the signals from the H atoms of the methyl groups ($\delta \approx 1.15$ ppm) of the homopolymer microgels p(NIPAM) and p(NIPMAM) and copolymer microgels p(NIPAM-co-NIPMAM) were normalized to the signal of the isopropyl H atom ($\delta \approx 3.93$ ppm). Linear combination of the normalized values of the homopolymers were used to calculate the comonomer content in the copolymer microgels.

Table S1. Nominal comonomer content and measured comonomer content of p(NNPAM-co-NIPAM), p(NIPAM-co-NIPMAM) and p(NIPMAM-co-NNPAM). The copolymerization ratio was calculated from the ¹H-NMR spectra.

nominal comonomer content / mol%	p(NNPAM-co-NIPAM) measured comonomer content / mol%	p(NIPAM-co-NIPMAM) measured comonomer content / mol%	p(NIPMAM-co-NNPAM) measured comonomer content / mol%
30.0	30.2	36.9	26.2
	30.0	33.6	26.2
	30.0	31.4	26.5
50.0	55.1	51.1	44.9
	54.3	50.4	45.7
	53.5	50.7	46.5
70.0	74.9	72.3	69.8
	74.9	73.3	70.0
	74.9	73.7	70.0

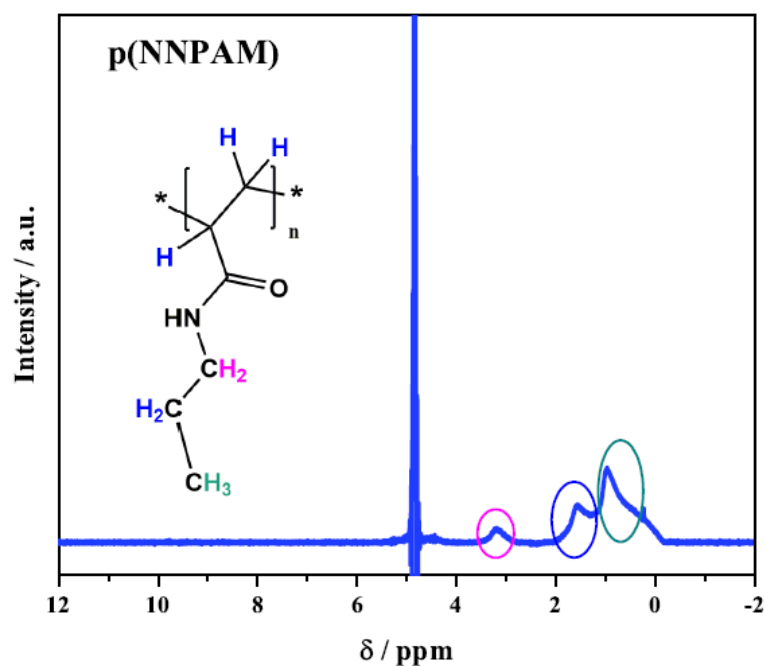


Figure S1. ^1H -NMR spectrum of microgel p(NNPAM) and the chemical structural formula with the H atoms highlighted in color. $\delta = 0.91$ ppm ($\text{NHCH}_2\text{CH}_2\text{CH}_3$, 3H) (green); $\delta \approx 1.50$ ppm ($\text{NHCH}_2\text{CH}_2\text{CH}_3$, 2H) (blue); $\delta \approx 1.50$ ppm (CHCH_2 , 1H) (blue); $\delta \approx 1.50$ ppm (CHCH_2 , 2H) (blue); $\delta = 3.14$ ppm ($\text{NHCH}_2\text{CH}_2\text{CH}_3$, 2H) (pink).

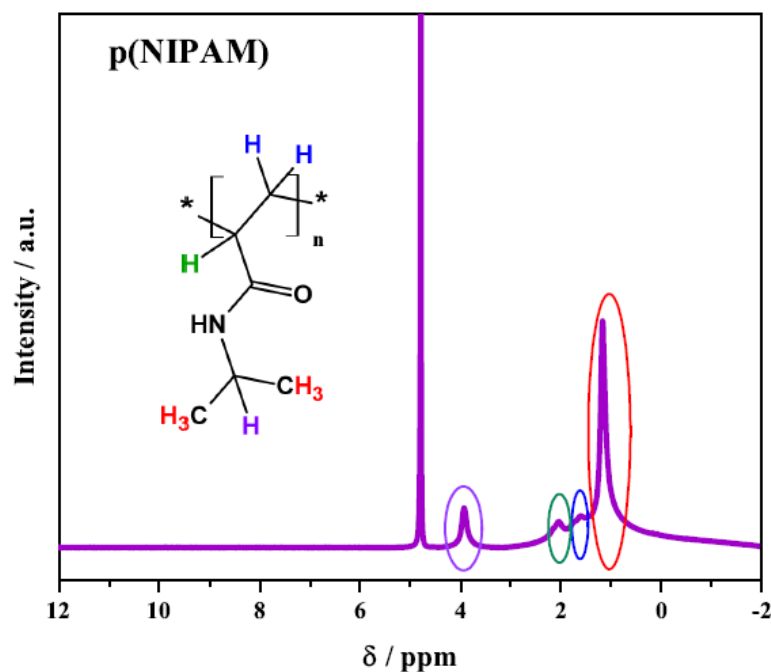


Figure S2. ^1H -NMR spectrum of microgel p(NIPAM) and the chemical structural formula with the H atoms highlighted in color. $\delta = 1.17$ ppm ($\text{NHCH}(\text{CH}_3)_2$, 6H) (red); $\delta = 1.61$ ppm (CHCH_2 , 2H) (blue); $\delta = 2.05$ ppm (CHCH_2 , 1H) (green); $\delta = 3.93$ ppm ($\text{NHCH}(\text{CH}_3)_2$, 1H) (purple).

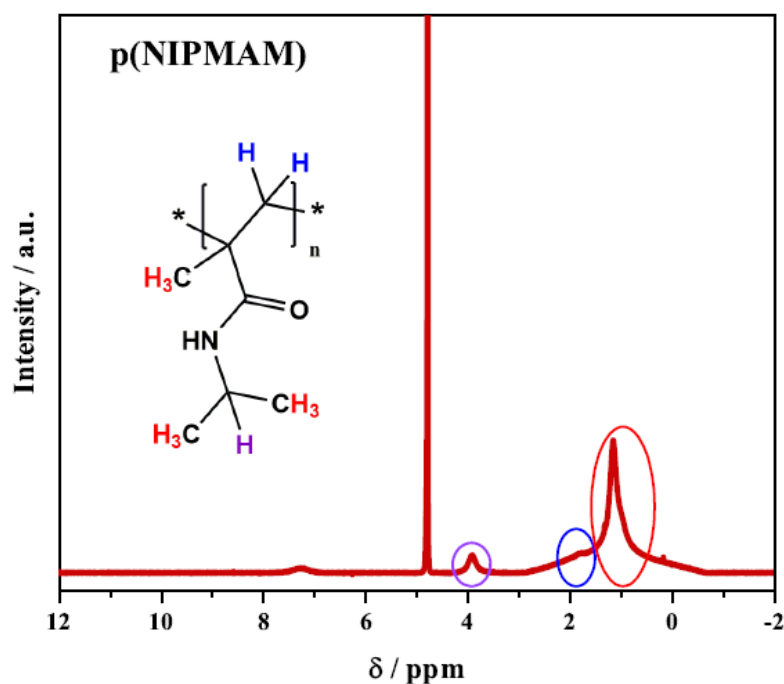


Figure S3. ^1H -NMR spectrum of microgel p(NIPMAM) and the chemical structural formula with the H atoms highlighted in color. $\delta \approx 1.15$ ppm (NHCH(CH₃)₂, 6H) (red); $\delta \approx 1.15$ ppm (CCH₃CH₂, 3H) (red); $\delta \approx 1.78$ ppm (CCH₃CH₂, 2H) (blue); $\delta = 3.92$ ppm (NHCH(CH₃)₂, 1H) (purple).

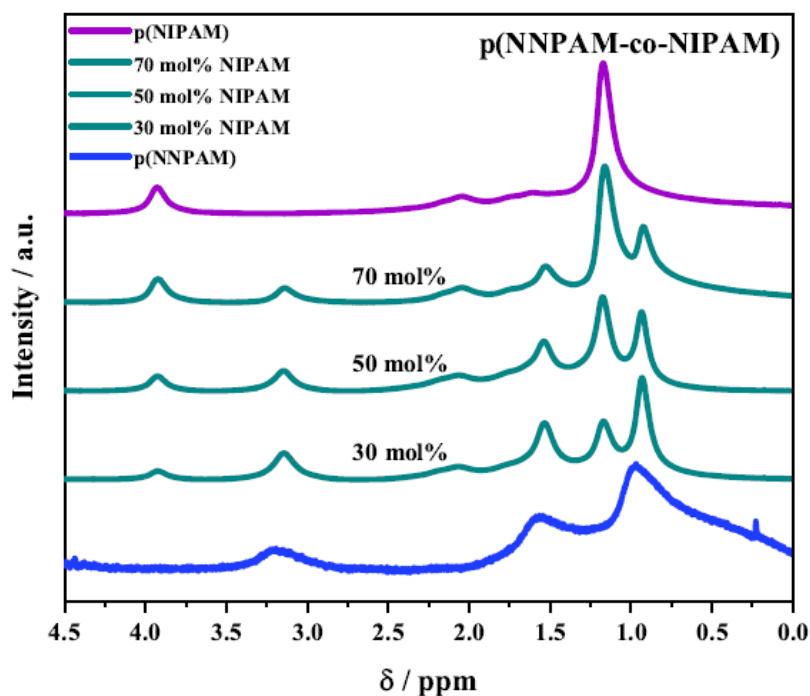


Figure S4. ^1H -NMR spectrum of microgel p(NNPAM), p(NIPAM) and p(NNPAM-co-NIPAM) with different comonomer contents.

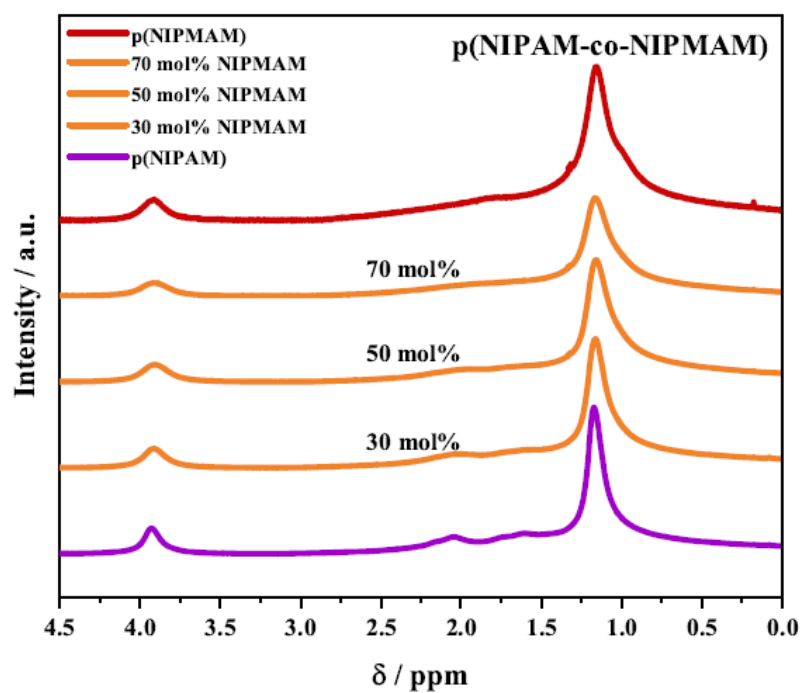


Figure S5. ^1H -NMR spectrum of microgel p(NIPAM), p(NIPMAM) and p(NIPAM-co-NIPMAM) with different comonomer contents.

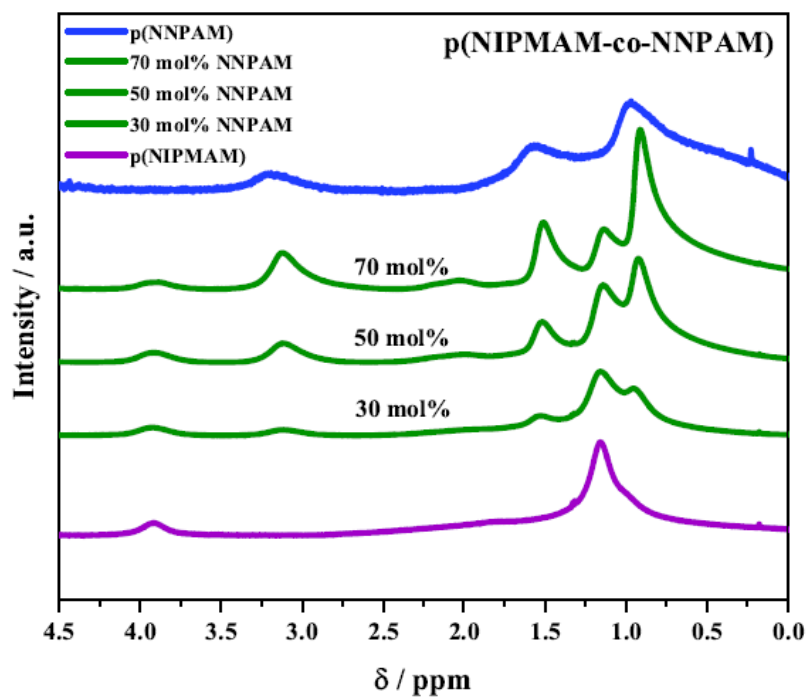


Figure S6. ^1H -NMR spectrum of microgel p(NIPMAM), p(NNPAM) and p(NIPMAM-co-NNPAM) with different comonomer contents.