## Electronic Supplementary Information

## Effect of heterogeneous and homogeneous polymerisation on the structure of pNIPAm nanogels

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**Figure S1**. NMR spectrum of nanogels isolated after purification in comparison to spectra of SDS, measured in  $D_2O$  (residual solvent peak at 4.8 ppm)



**Figure S2**. DLS data by intensity, number and volume distribution, measured for NG 1-5 at 0.5 mg/mL solutions in deionized water at 20 °C.



**Figure S3**. DLS data by intensity, number and volume distribution, measured for NG 6-10 at 0.5 mg/mL solutions in deionized water at 20 °C.



**Figure S4**. Changes in transmittance of aqueous solution of nanogel NG2, synthesized at 30 °C, due to heating of the sample determined at different concentrations.



**Figure S5**. Changes in transmittance of aqueous solution of nanogel NG1, synthesized at 80 °C, due to heating of the sample determined at different concentrations.



**Figure S6**. Z-average size of NG1 determined by DLS measurements of aqueous solutions at different concentrations.



**Figure S7**. Changes in steady-state surface tension of air/water interface due to adsorption of aqueous solutions of NG1 and NG2 at the concentration range between 0.01 and 0.5 mg/ml, measured at room temperature.



Figure S8. TEM images of NG1, scale bars on top pictures are presented in nm.



Figure S9. TEM images of NG2, scale bars on top pictures are presented in nm.



**Figure S10**. Changes in particle size upon volume phase transition measured by DLS for diluted solutions of NGs (0.5 mg/ml for NG1 and NG3, 0.1 mg/ml for NG4), error bars are below 1%.



Figure S11. TEM images of NG3, scale bars are presented in nm.



Figure S12. TEM images of NG4, scale bars are presented in nm.



Figure S13. Liquid AFM images of NGs adsorbed at hydrophobic interface, scale bar is 400 nm.



**Figure S14**. Changes in transmittance of aqueous solution of nanogel NG5, synthesized at 30 °C, due to heating of the sample determined at different concentrations.



Figure S15. TEM images of NG5.