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Aqueous RAFT (co)polymerization of *N*-isopropylacrylamide above lower critical solution temperature of poly(*N*-isopropylacrylamide) and stimuli-responsive properties of the polymers formed

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Experimental part

Polymer synthesis

The calculated amounts of NIPA or NIPA and DMAEMA, the RAFT agent (10^{-2} –10^{-3} mol/L) and the ammonium persulfate (PSA) initiator ((1.0– 1.8)×10^{-3} mol/L) were dissolved in 5 mL of water. The mixture was then poured into an ampoule and degassed to a residual pressure of ~ 5×10^{-3} Torr by repeating the freeze-thaw cycles three times. The ampoules were sealed and placed in a thermostat, where they were kept for 24 h at 60 °C with constant stirring. Upon completion of the polymerization, the ampoules were opened, the polymer was dissolved in excess water; then the polymer was dialyzed to remove monomer residues and low molecular weight fractions, and freeze-dried until the solvent was completely removed.

Methods

The SEC measurements were performed in DMF at 50 ºC containing 0.1 wt% of LiBr at 50 °C using a chromatograph GPC-120 “PolymerLabs” equipped with a refractive index detector and two PLgel 5 μm MIXED B columns for the MM range from 5×10^2 to 1×10^7 g mol^{-1}. The SEC system was calibrated using narrow-dispersed linear poly(methyl methacrylate) (PMMA) standards.

NMR spectra were recorded on a Bruker Avance III HD (400 MHz ^{1}H) in DMSO-d_6 for PNIPA and PEG-*b*-PNIPA and $CDCl_3$ for copolymers of NIPA and DMAEMA.

DLS measurements of 1 wt. % aqueous polymer solutions were performed by a static/dynamic compact goniometer (DLS/SLS-5000, ALV, Langen, Germany) at a scattering angle of 90°. A HeNe laser with a power of 22 mW emitting a polarized light at λ = 633 nm was used as the incident beam. At each temperature, the samples were left for 30 min to equilibrate. Distributions over decay times were obtained using a nonlinear regularized inverse Laplace transformation method (CONTIN).

Turbidimetry was performed on a Shimadzu UV-2401PC spectrophotometer. An 1 wt.% aqueous polymer solution was poured into the cuvette. The cuvette was placed in a spectrophotometer and the absorbance of the solution was recorded at a wavelength of 550 nm. The solution was heated using additional equipment based on Arduino Uno in increments of 1 °C. Upon reaching the set temperature, the solution was kept for 1 – 2 min and the turbidity of the solution was recorded.

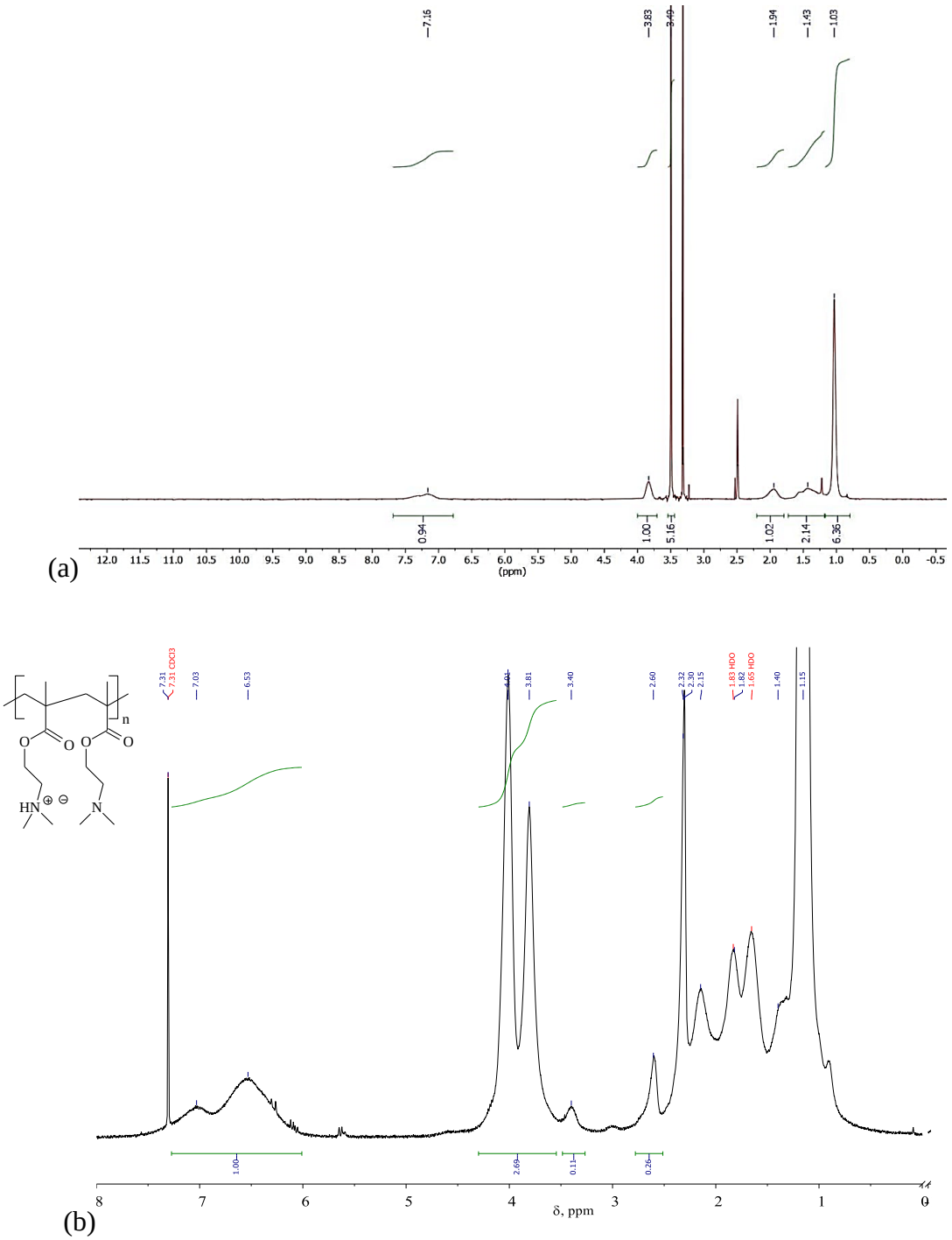

Figure S1 ^{1}H NMR spectra of the PEG1-*b*-PNIPA in DMSO-d_6 (*a*) and copolymer of DMAEMA and NIPA (f_{DMAEMA} = 9.4 mol. %) in $CDCl_3$ (*b*).