Supporting Information to

Unexpected thermal characteristics of aqueous poly(2-isopropyl-2-oxazoline) solutions

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Materials. Chemicals and solvents were purchased from various suppliers and used, unless otherwise noted, as received. Sigma–Aldrich: isobutyronitrile (99.6%), 2-aminoethanol (99+%), cadmium acetate dihydrate (98%), methyl *p*-tosylate (98%), CaH_2, NaCl, NaOH; Acros Organics: 4-(*N*-Boc-amino)-piperidine (98%), trifluoroacetic acid (99%); Merck: ethyl acetate (>99.5%), hexane (≥99%), acetonitrile (99.9%); Fluka–Riedel-deHaën: CH_2Cl_2 (>99.9%). 2-Isopropyl-Δ^2-oxazoline, IPOX, was synthesized from 2-aminoethanol (3.34 mol) and isobutyronitrile (3.16 mol) in the presence of cadmium acetate dihydrate (0.16 mol) at 130 °C. The mixture was stirred for 24 hours at that temperature and then fractionated by vacuum distillation. Physiological saline solution was obtained by dissolving NaCl (0.94 g) in bi-distilled water (100 ml); the solution was adjusted to neutral pH by the addition of 1N aqueous NaOH.

Polymers. Poly(2-isopropyl-2-oxazoline), PIPOX, was prepared by cationic polymerization of IPOX (41 mmol; twice distilled and dried over CaH_2) using methyl *p*-tosylate (0.4 mmol) as the initiator and acetonitrile (10 ml; freshly distilled from CaH_2) as the solvent. The solution was stirred for 2 days at 80 °C under an argon atmosphere. 4-(*N*-Boc-amino)-piperidine (1.2 mmol) was then added at room temperature, and the mixture was stirred for another 3 days at 80 °C. After evaporation of the solvent in vacuum, the solid residue was dissolved in water, dialyzed against bi-distilled water (molecular weight cut-off: 3.5 kDa), and freeze-dried ($\rightarrow$ $PIPOX_{147}^{+}$). The polymer (2.8 g) was then dissolved in CH_2Cl_2 (22 ml) and stirred with trifluoroacetic acid (5.4 ml) for 50 minutes at room temperature. The reaction mixture was partially neutralized with aqueous NaOH, and the polymer was extracted with CH_2Cl_2. After evaporation of the solvent, the polymer was dissolved in water, dialyzed against bi-distilled water, and freeze-dried ($\rightarrow$ $PIPOX_{147}^{++}$). Poly(*N*-isopropylacrylamide) (PNiPAM) was synthesized in the labs of A. Laschewsky (Fraunhofer IAP, Potsdam, Germany).

Analytical instrumentation and methods. (*i*) ^1H NMR spectra were recorded at room temperature on a Bruker DPX–400 spectrometer operating at 400.1 MHz; the solvent used was $CDCl_3$. (*ii*) Size-exclusion chromatography (SEC) was performed at room temperature using THF as the eluent at a flow rate of 1.0 mL/min. The column set consisted of two 300 x 8 mm PSS SDV 10^3 and 10^5 Å, 5 μm (PSS GmbH, Mainz, Germany); calibration was done with polystyrene standards. (*iii*) Light scattering apparatus consisted of a HeNe laser (Polytec, 34 mW) with a wavelength of 633 nm, a goniometer with a fixed scattering angle of $\Theta = 90°$, a photon detector (ALV/SO-SIPD), and a digital correlator (ALV 5000). Heating/cooling of polymer samples in a thermostat was done in 0.5 °C steps at a heating rate of 2.5 °C/h. At every temperature, the first of three measurements of scattering intensity was started after 180 s; data were accumulated for 3×180 s. (*iv*) Transmission electron microscopy (TEM) was done with a Zeiss Omega 912 operating with an acceleration voltage of 120 kV. A drop of dispersed aqueous sample solution was placed on a copper grid, which was steamed with carbon, and the solvent was allowed to evaporate in air.

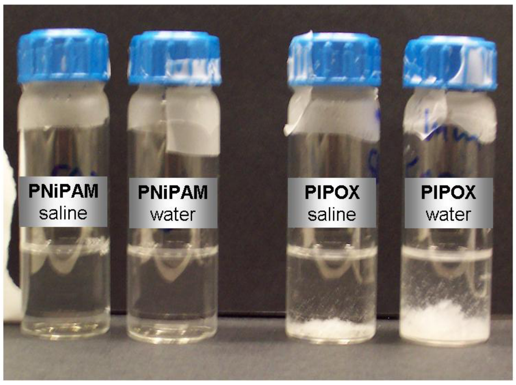

Fig. SI-1 Appearance of the 0.05 wt % polymer solutions of PNiPAM (left) and PIPOX (right) in water and in saline solution after annealing for 24 h at 65 °C. Solutions were kept for 2 h at room temperature before taking the photograph.

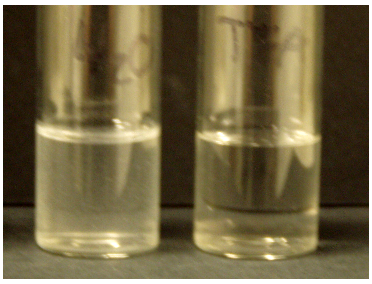

Fig. SI-2 Appearance of PIPOX coagulate, dispersed in 2 mL of water, after addition of 10 mL of water (left) or of 10 mL of TFA (right).

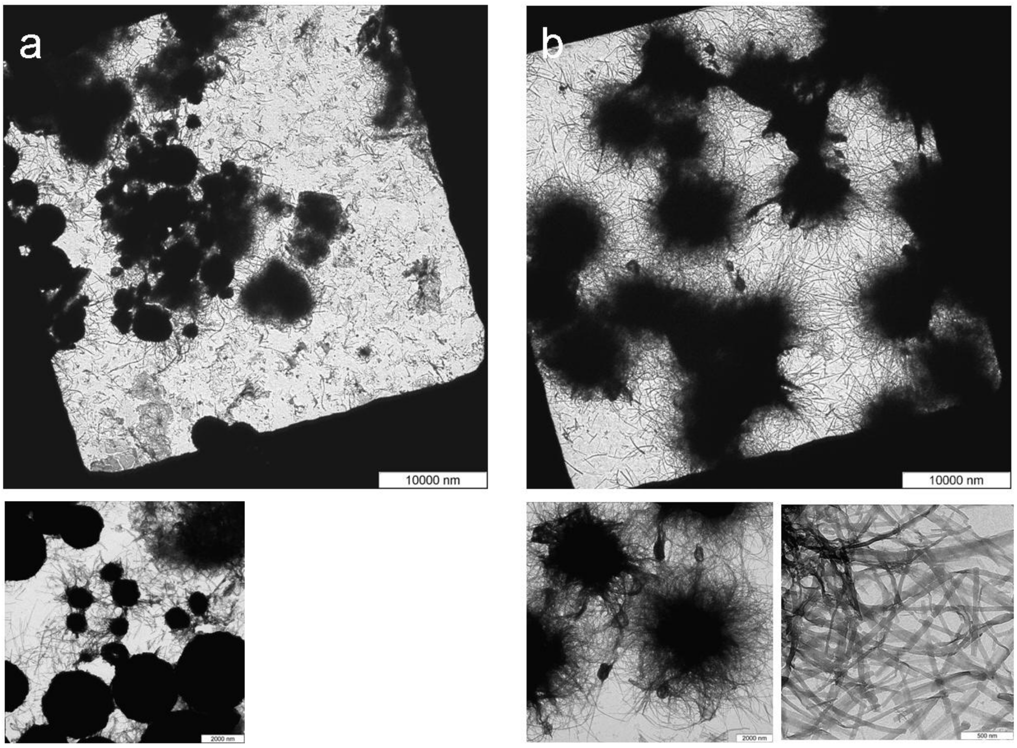

Fig. SI-3 TEM images of dried coagulate particles formed by (a) PIPOX$_{47}^{+}$ in saline solution and by (b) PIPOX$_{47}^{++}$ in water (0.05 wt % polymer) through annealing for 24 h at 65 °C.

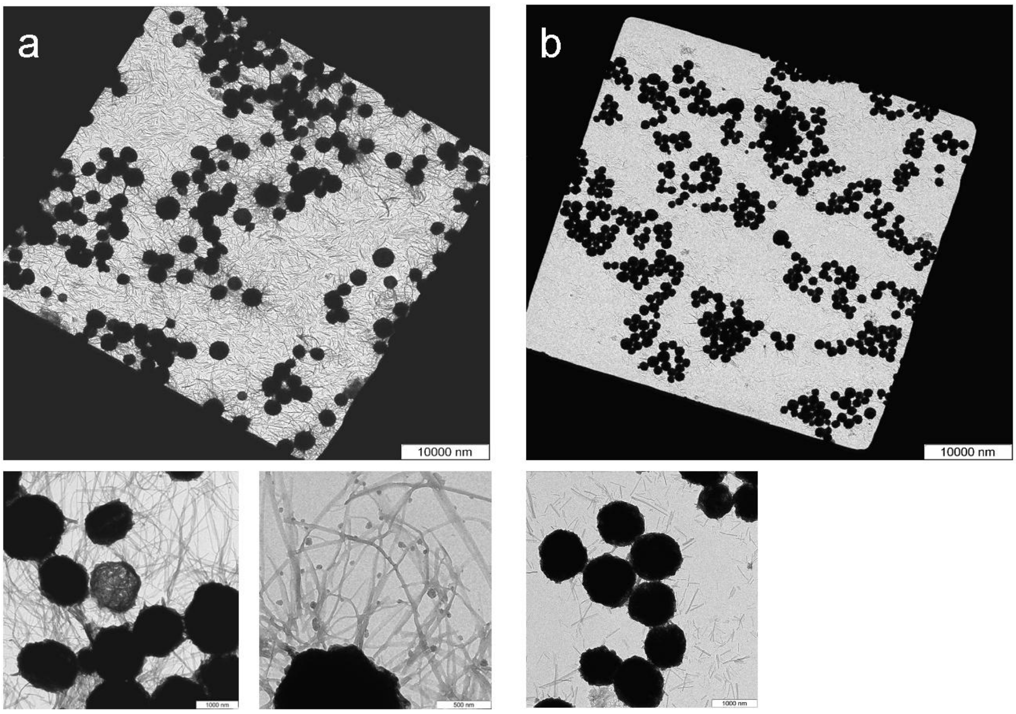

Fig. SI-4 TEM images of dried coagulate particles formed by (a) PIPOX$_{47}^{+}$ and by (b) PIPOX$_{117}^{+}$ in water (0.05 wt % polymer) through annealing for 24 h at 65 °C.

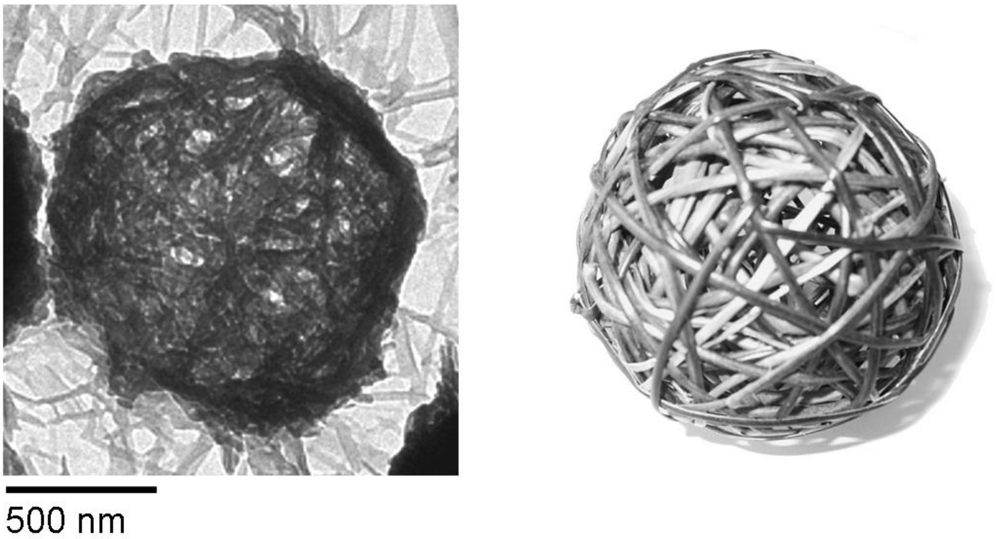

Fig. SI-5 TEM image of a dried "premature" coagulate particle of PIPOX$_{47}^{+}$ (left, see Fig. SI-4) and an image of a decoration ball made of rattan (right).