Mechanistic study of the phase separation/crystallization process of poly(2-isopropyl-2-oxazoline) in hot water

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Polymer synthesis and characterization

2-Isopropyl-2-oxazoline (IPOX) was synthesized as described elsewhere [H. Witte and W. Seeliger, *Liebigs Annalen der Chemie*, 1974, 996]. Acetonitrile (≥99.5%) and methyl *p*-tosylate (MeTos, ≥97%) were received from Sigma-Aldrich and Fluka-Riedel-deHaën, respectively.

Poly(2-isopropyl-2-oxazoline) (PIPOX) was synthesized by cationic isomerization polymerization of IPOX using MeTos as the initiator; the polymerization was quenched with water introducing a neutral hydroxyl group at the ω-chain end: A solution of IPOX (11.4 g, 0.1 mol; distilled from CaH_2) in acetonitrile (50 ml; distilled from CaH_2) was prepared and heated to 70 °C under a dry argon atmosphere. MeTos (100 µl, 0.66 mmol; distilled from CaH_2) was then added via microsyringe, and the mixture stirred for 3 days at 70 °C. After evaporation of the solvent, the PIPOX was dissolved in H_2O, dialyzed against 3x500 ml H_2O for 3 days (Spectra/Por membrane of regenerated cellulose, MWCO 1kDa), and isolated by freeze-drying. ^1H NMR (400.1 MHz, $CDCl_3$): δ/ppm = 1.05-1.15 (bs, 6H), 2.5-3.0 (m, 1H), 3.05-3.08 (s, 3H), 3.35-3.55 (bs, 4H). M_n^{app} = 15.4 kg/mol, PDI = 1.04 (SEC, PS calibration). $T_g \sim$ 68 °C (DSC). $T_{CP} \sim$ 38°C (1 wt.% PIPOX in H_2O) (phototurbidimetry). Specific density, ρ = 1.226 g/ml (H_2O) (density meter).
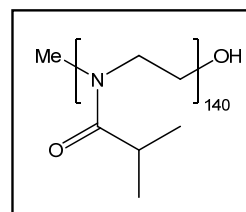
^1H NMR measurements were carried out at room temperature using a Bruker DPX-400 spectrometer operating at 400.1 MHz. $CDCl_3$ (99.8% D, Sigma-Aldrich) was used as the solvent. Size exclusion chromatography (SEC) with simultaneous UV and RI detection was performed in *N*-methyl-pyrrolidone (+ 5 g/L LiBr) at 70 °C, flow rate: 0.8 ml/min. The column set consisted of two PSS-GRAM columns, 300 x 8 mm, 7 µm, 10^2 and 10^3 Å. Calibration was done with polystyrene standards (PSS, Mainz, Germany). Differential scanning calorimetry (DSC) was performed on a Netzsch DSC Phoenix® in an inert nitrogen atmosphere at a heating rate of 10 K/min. Melting and glass transition temperatures were determined from the first and second heating curves, respectively. Photo turbidimetry was conducted with a turbidimetric photometer TP1 (Tepper Analytik, Wiesbaden, Germany) operating at λ = 670 nm; the heating/cooling rate was 1 K/min. The T_{CP} was taken as the temperature at 80% transmission. Measurement of the specific polymer density was carried out on a density meter DMA5000 (Anton Paar, Graz, Austria).
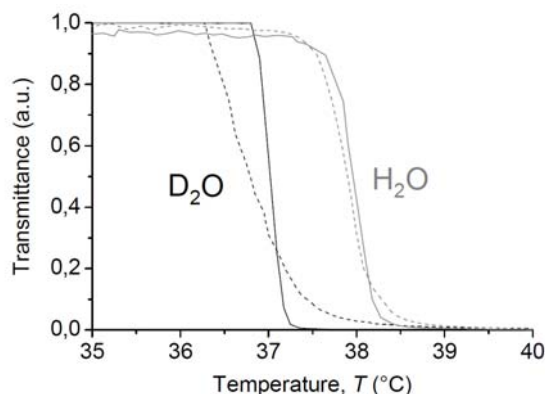

Figure S1. Turbidity curves of PIPOX (15.4 kDa) at a concentration of 1 wt.% in H_2O (grey) and in D_2O (black); —— heating curve, ---- cooling curve.
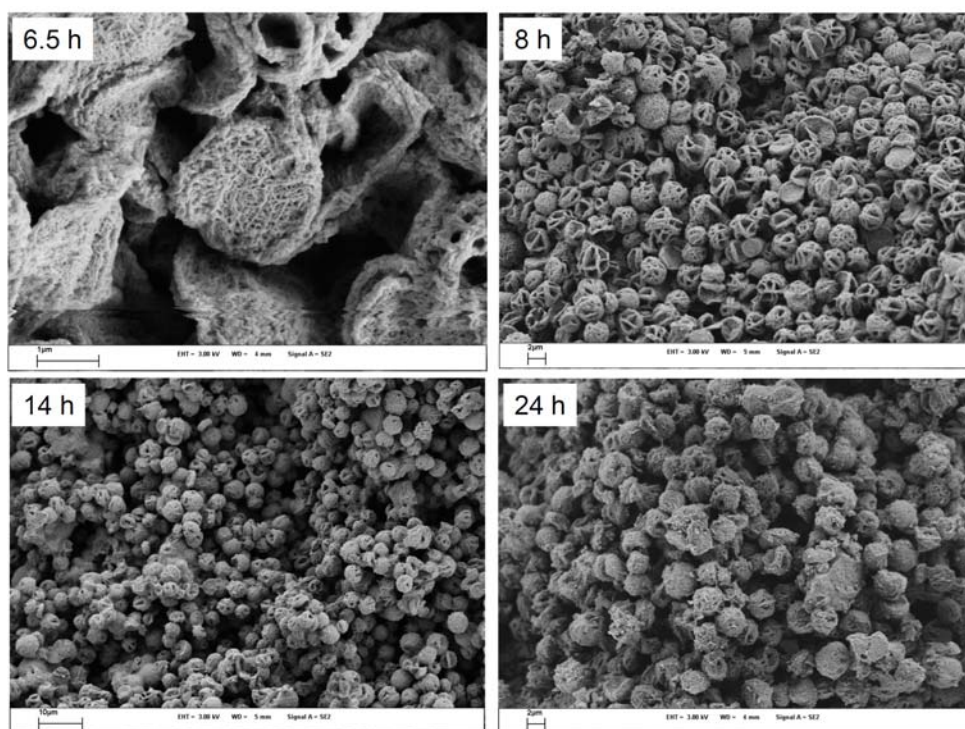
Figure S2. Scanning electron micrographs of freeze-dried PIPOX (15.4 kDa) samples annealed for 6.5 h, 8 h, 14 h, and 24 h at 60 °C in H_2O (1 wt.%).
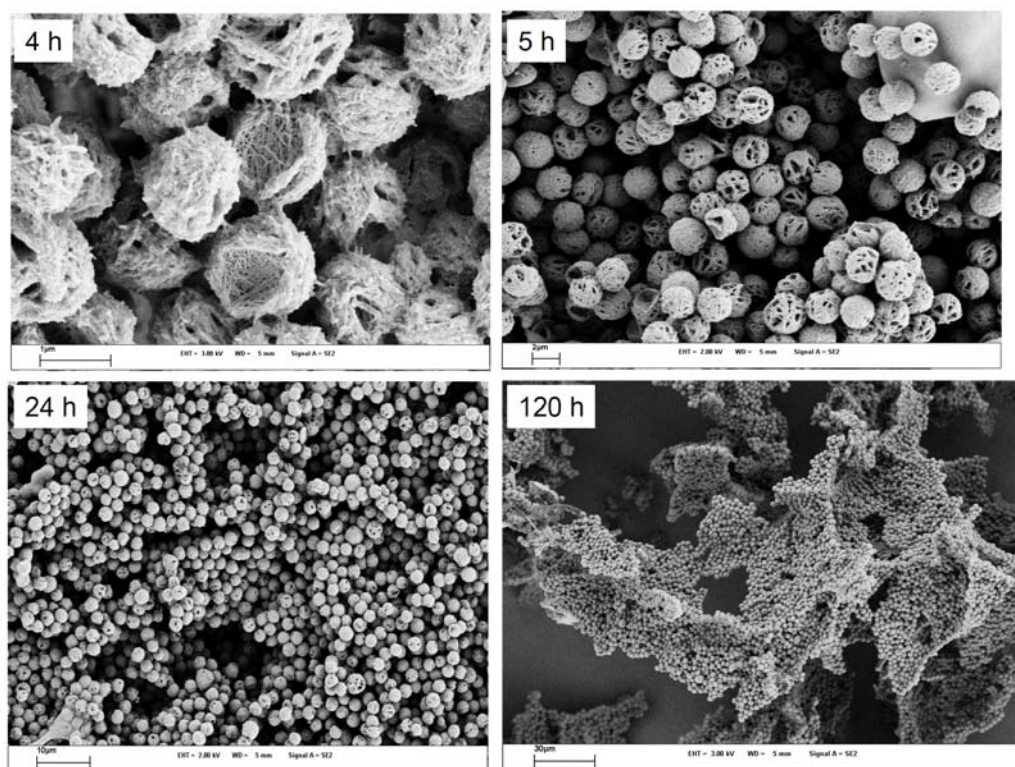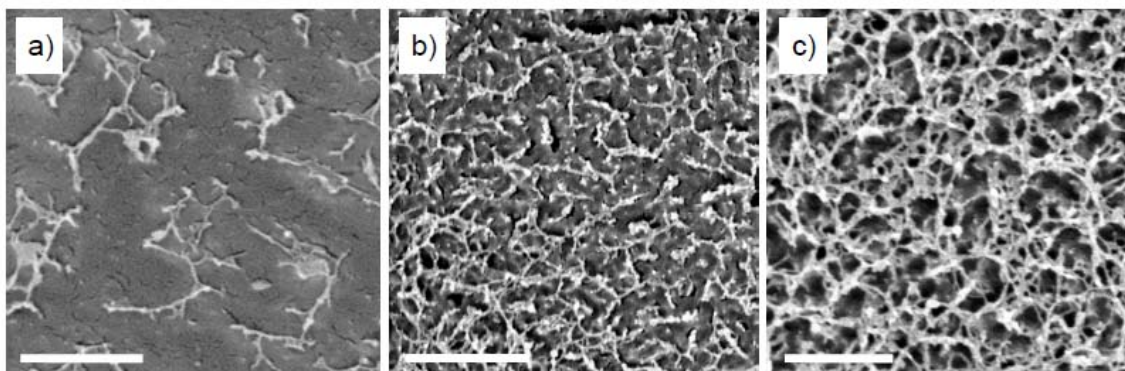

Figure S3. Scanning electron micrographs of freeze-dried PIPOX (15.4 kDa) samples annealed for 4 h, 5 h, 24 h, and 120 h at 60 °C in D_2O (1 wt.%).
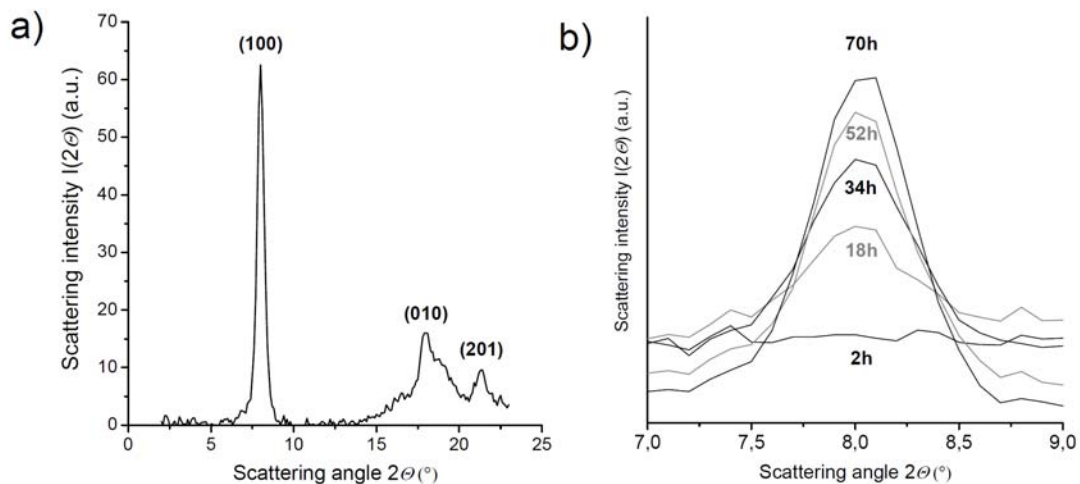
Figure S4. *In situ* WAXS measurements of 10 wt.% solution of PIPOX (15.4 kDa) in D_2O at 60 °C: (a) Scattering curve measured after 84 h. (b) Evolution of the (100) reflection with time (2-70 h)
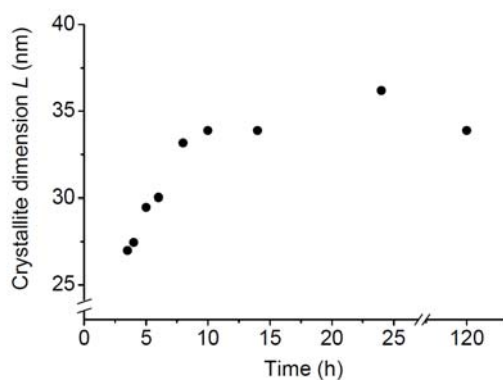
Figure S5. *In situ* WAXS measurements of 10 wt.% solution of PIPOX (15.4 kDa) in D_2O at 60 °C: Evolution of the mean crystallite dimension L with time, determined by the Debye Scherrer equation, $L = K\lambda/\beta\cos\theta$, with K as the Scherrer constant (typical value for polymers ~0.9), $\lambda = 0.154$ nm as the wavelength of CuKα radiation, β as the line broadening at half the maximum intensity in radians, and θ as the Bragg angle [N. Kasai, M. Kakudo: X-ray diffraction by macromolecules, Springer, 2005].

Figure S6. Cryogenic scanning electron micrographs of a) 0.01, b) 0.1, c) 1 wt.% solutions of PIPOX (15.4 kDa) in D_2O annealed for 30 min at 75, 65, and 60 °C, respectively. Scale bars = 500 nm.
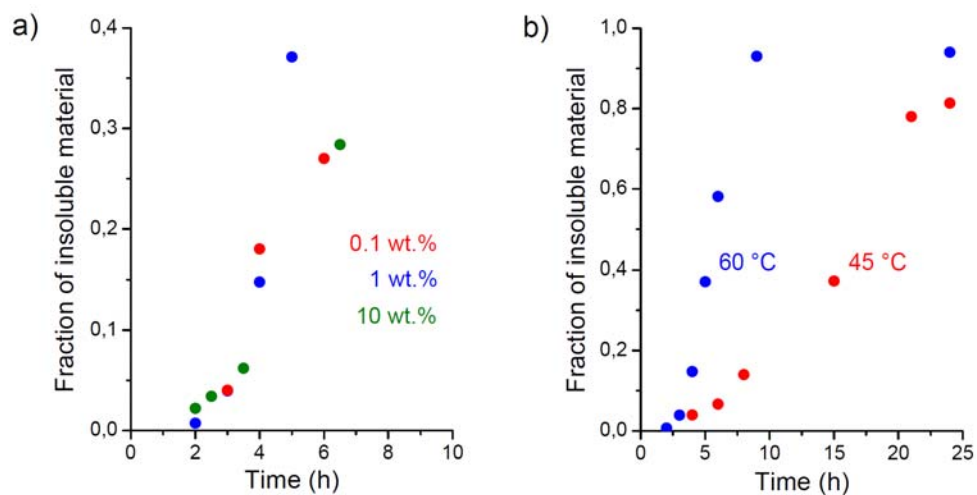
Figure S7. Time-dependent evolution of the fraction of insoluble material in dependence of a) concentration (PIPOX 15.4 kDa) and b) temperatue (PIPOX 18.3 kDa) (gravimetric analysis).