Supporting Information

Self-Association of the Thermosensitive Block Copolymer Poly(2-isopropyl-2-oxazoline)-*b*-Poly(*N*- isopropylacrylamide) in Water-Methanol Mixtures

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Materials

All chemicals were purchased from Sigma-Aldrich Chemicals Co. and used as received unless otherwise stated. 2-Isopropyl-2-oxazoline was prepared from isobutyric acid and 2-aminoethanol following a known procedure.¹ Diethylene glycol di(*p*-toluenesulfonate) was synthesized according to a reported procedure and purified by recrystallization from methanol.² Acetonitrile was dried by reflux over CaH₂ under dry nitrogen atmosphere and distilled prior to use. Water was deionized with a Millipore Milli-Q system.

Preparation of α, ω -diazido poly(2-isopropyl-2-oxazoline) (N₃-PIPOZ-7K). A round-bottom flask equipped with a N_2 filled condenser and a rubber stopper was charged with 2-isopropyl-2-oxazoline (5 mL, 44 mmol), acetonitrile (20 mL), and diethylene glycol di(*p*-toluenesulfonate) (248 mg, 0.6 mmol) via oxygen-free syringes at room temperature. The reaction flask was immersed in an oil bath pre-heated to 65 °C. The mixture was kept at 65 °C for 72 hrs while stirring. In order to monitor the kinetics of the polymerization, during the polymerization process, small amounts of the polymerization mixture were withdrawn at various times and analysed by

for NMR spectroscopy. The monomer conversion was calculated by comparing the resonances of the methylene groups at 4.22 and 3.80 ppm of the monomer with the resonances at 3.40 ppm of the polymer backbone methylene groups. At the end of the polymerization, the solution was cooled to room temperature and sodium azide (0.40 g, 6.0 mmol) was added to quench the oxazolinium ions. The termination reaction was conducted at 65 °C for 8 hrs. After that, the solution was diluted with water to 100 mL and dialyzed against water for 3 days with a membrane MWCO of 3500 Dalton. The purified polymer was recovered by freeze-drying. Yield 4.0 g, 80%. ¹H NMR (CDCl₃, δ) ppm: 1.1 (br, (CH₃)₂CH-), 2.66 and 2.89 (br, (CH₃)₂CH-), 3.45 (br, -NCH₂CH₂-). FT-IR, 2976, 2934, 2873, 2105, 1646, 1474, 1431, 1205, 1160, 1089, and 755 cm⁻¹.

References

1. Seeliger, W.; Aufderhaar, E.; Diepers, W.; Feinauer, R.; Nehring, R.; Thier, W.; Hellmann, H., Recent Syntheses and Reactions of Cyclic Imidic Esters. *Angew. Chemie Int. Ed. Engl.* **1966**, *5* (10), 875-888.

2. Schwabacher, A. W.; Lane, J. W.; Schiesher, M. W.; Leigh, K. M.; Johnson, C. W., Desymmetrization Reactions: Efficient Preparation of Unsymmetrically Substituted Linker Molecules. *J. Org. Chem.* **1998**, *63* (5), 1727-1729.



Figure S1. ¹H NMR spectrum of PIPOZ-7k in CDCl₃



Figure S2. FTIR spectrum of PIPOZ-7K with azide end groups



Figure S3. GPC traces of PIPOZ-7K and PIPOZ-7K-b-PNIPAM-9K in DMF at 40 °C.



Figure S4. Temperature dependence of transmittance of PIPO7k-b-PNIPAM9k (1.0×10^{-3} g/cm³) in the mixture of MeOH/water. (heating rate 0.2 °C/min)



Figure S5. Temperature dependence of transmittance of PNIPAM-10k $(1.0 \times 10^{-3} \text{ g/cm}^3)$ in the mixture of MeOH/water. (heating rate 0.2 °C/min)