

## Supplemental Material

All reagents and solvents were obtained from commercial sources without further purification unless otherwise specified.  $^1\text{H}$  NMR spectra were obtained on Varian VXR-300 and Unity p300 spectrometers at 300 MHz. Chemical shifts are reported in ppm with chloroform (7.27 ppm) as an internal standard. Gel Permeation Chromatography was performed using a Ranin SD-200 HPLC system equipped with a Dynamax UV-C detector (at 254 nm). A TOSOH BIOSEP column (7  $\mu\text{m}$ ) was used. Differential scanning calorimetry (DSC) was performed using a Perkin Elmer Differential Scanning Calorimeter Pyris 1.

**Synthesis of poly(*N*-isopropylacrylamide) (PNIPAM) from poly(*N*-acryloxysuccinimide) (pNASI).<sup>1</sup>** 1.69 g of pNASI were dissolved in DMF. Then 0.85 mL of isopropylamine were added to the solution. The mixture was stirred for 12 h, filtered, and added dropwise to an excess amount of diethyl ether. The precipitate that formed was filtered, redissolved in THF and precipitated from hexanes.  $^1\text{H}$  NMR:  $\delta$ 4.0 (br, s, 1H), 2.4 – 1.4 (br, m, 3H), 1.1 (br, 6H). IR ( $\text{cm}^{-1}$ ): 1648. The polymers molecular weight was determined by GPC:  $M_w = 340,000$ ,  $M_n = 180,000$  (polydispersity 1.89).

**Synthesis of *N*, *N*-diethylacrylamide.** A solution of acryloyl chloride (4.67 mL, 0.0574 mol) in  $\text{CH}_2\text{Cl}_2$  (3 mL) was added dropwise to distilled diethylamine (20.8 mL, 0.20 mol) previously dissolved in  $\text{CH}_2\text{Cl}_2$  (45 mL) at 0°C under  $\text{N}_2$  atmosphere. The reaction mixture was stirred for 4h, filtered, and washed with HCl, concentrated at reduced pressure using a rotary evaporator, and then vacuum dried. Distillation yielded

the desired monomer as a colorless oil in 75% yield.  $^1\text{H}$  NMR:  $\delta$ 6.6 (dd, 1H), 6.4 (dd, 1H), 5.6 (dd, 1H), 3.4 (q, 4H), 1.2 (q, 6H).

**Polymerization of *N, N*-diethylacrylamide.** *N, N*-Diethylacrylamide (1.27 g, 10 mmol) was added to an oven-dried, 3-necked, 50-mL flask and then condensed with 1.5 mL of methanol under  $\text{N}_2$ . The flask was evacuated first and flushed with  $\text{N}_2$  three times. Then it was placed in an oil bath and heated to 60 °C. A solution of AIBN (8 mg, 0.05 mmol) in methanol was placed in a separate vial, evacuated first and flushed with  $\text{N}_2$  three times. Once the solution of starting material had reached the desired temperature (the mixture was allowed to equilibrate at 60 °C for an hour), the  $\text{N}_2$ -purged AIBN solution was added and stirred at 60 °C for 6 hours. The reaction mixture was cooled and 5 mL of acetone was added. The product polymer was then precipitated by pouring the reaction mixture into 50 mL of hexane. The product polymer was characterized by IR spectroscopy (IR ( $\text{cm}^{-1}$ ): 1631) and by GPC ( $M_w = 230,000$ ,  $M_n = 110,000$  (polydispersity of 2.09)).

**Measurements of lower critical solution temperature (LCST).** A temperature gradient device similar to the ones described in previous work<sup>2</sup> was fabricated using two square brass tubes (O. D. 1/8 inch, K & S Engineering, Chicago, IL) placed parallel to each other 3 mm apart. After applying a small amount of vacuum grease to the surface of each brass tube to ensure uniform thermal contact, a piece of borosilicate cover glass (VWR Scientific, Inc., Media, PA), that served as a sample stage, was placed over these two tubes. Rectangular borosilicate capillary tubes with a high aspect ratio ( $100\ \mu\text{m} \times 1\ \text{mm} \times 2\ \text{cm}$ ) were placed parallel to the direction of the thermal gradient. The capillary

tubes were sealed with vacuum grease at both ends to prevent leakage of the polymer solution inside. The temperature gradient was regulated via two water circulators (Fisher Scientific, Pittsburgh, PA) by pumping hot and cold antifreeze fluid, respectively, through the two brass tubes. The temperature gradient device was placed under a dark field condenser of an inverted microscope (Nikon, Eclipse TE 2000-U) and dark field images of capillary tubes containing various polymer solutions at different temperatures were recorded using a CCD camera. Each CCD image can fit 6 capillary tubes under a 2× objective. Two capillary tubes containing 10 mg/mL PNIPAM in DI water (LCST 30.5°C) and 10 mg/mL PNIPAM in 0.7 M KCl solution (LCST 26.3 °C), respectively, were used as internal standards.

**Differential scanning calorimetry (DSC) measurements.** PNIPAM and poly-(N,N-diethylacrylamide) (PDEAM) polymers were dissolved separately in DI water to a concentration of 10 mg/mL. DSC was performed immediately after mixing of these two polymer solutions to a desired molar ratio. The DSC scanning range was set from 20.00 °C to 45.00 °C and the scan rate was 5.00 °C/min. The DSC data were analyzed using Thermal Analysis Instrument Control and Data Analysis: Pyris Thermal Analysis System Version 3.70. The initial onset point of the heat flow curve was used as the nascent LCST of the polymer mixture, which is plotted in Figure 1. The solid line represents a fit to the data.

Reference:

- 1) Wang, J. Q.; Chen, X., Zhang, W.; Zacharek, S.; Chen, Y; and Wang, P. G. *J. Am. Chem. Soc.*, **1999**, 121, 8174-8181.

- 2) (a) Mao, H.; Yang, T.; Cremer, P. S. *J. Am. Chem. Soc.* 2002, 124, 4432-4435. (b) Mao, H.; Holden, M. A.; You, M.; Cremer, P. S. *Anal. Chem.* **2002**, 74, 5071-5075.

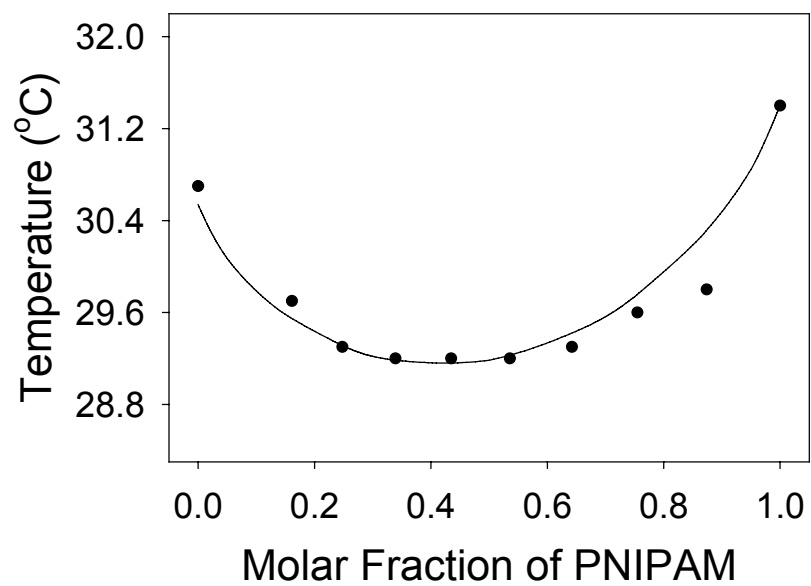


Fig. 1 Onset temperature for phase transition measurements made by differential scanning calorimetry. The solid line represents a fit to the data.

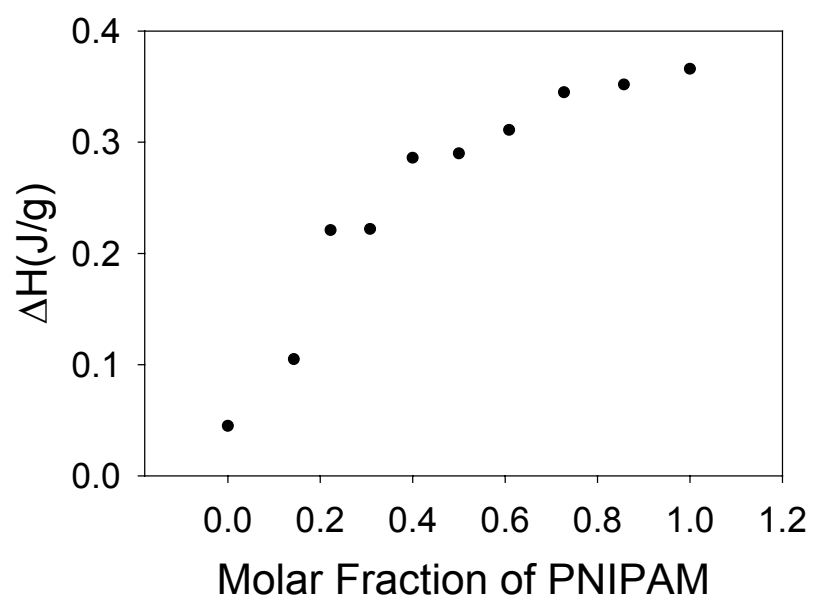


Fig. 2 The enthalpy change *vs.* molar fraction of PNIPAM in PNIPAM/PDEAM mixtures.