Supporting information

Water-Soluble Copolymers and Their Hydrogels with pH-Tunable

Diverse Thermoresponsive Behaviors Enabled by Hydrogen Bonding

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1 Materials and Characterization

1.1 Materials

All reagents were purchased from Sigma-Aldrich. N-vinylcaprolactam (NVCL) and acrylic acid (AA) were purified by distillation under vacuum. Dimethyl acrylamide (DMA) was purified by passing through a column filled with basic Al_2O_3 powder. 2, 2-Azoisobutyronitrile (AIBN) was purified through recrystallization from 95% ethanol. Acrylamide (AAm), N,N'-methylenebis(acrylamide) (MBA), 2-hydroxy-4'-(2-hy-droxyethoxy)-2-methylproplophenone (I2959), hydrochloric acid (38 wt % in water) and dimethyl sulfoxide (DMSO, anhydrous) were used without further purification.

1.2 Characterizations

¹H-NMR spectra were recorded on a 400 MHz Bruker spectrometer with DMSO-d6 or D₂O as solvent. The temperature-dependent ¹H-NMR spectra of the copolymers (2.0 mg/mL, 0.5 mL) were taken over a temperature range of 20-60 °C, with intervals of 10 degrees. Size-exclusion chromatograph (SEC) measurements were performed using a Waters system equipped with a refractive index and a photodiode array detector. The temperature-dependent transmittance measurements of the copolymers in aqueous solution were carried out on an Agilent Cary Series UV-Vis-NIR spectrophotometer with a temperature controller by recording the transmittance at 621 nm every 2.0 K over the 6–80 °C temperature range. Dynamic light scattering (DLS) measurements were performed on a Malvern Zetasizer Nano ZS ZEN3600 system with a helium–neon laser (wavelength, $\lambda = 633$ nm). All measurements were carried out at a scattering angle of 173°.

2 Experimental Procedures

2.1 Copolymerization of Acrylic Acid and N-vinylcaprolactam

As an example, the synthesis of P(AA-*co*-NVCL) (PAN) with an NVCL feed content of 10 mol % was conducted as follows. To a 25 mL ampoule, AIBN (0.0073 g, 0.044 mmol), AA (0.6 g, 8.33 mmol), NVCL (0.13 g, 0.93 mmol) and DMSO (7.27 mL) were quickly added. Then, the mixture was degassed and filled with nitrogen. After 30 min stirring at room temperature, the ampoule was placed in a preheated oil bath (80 °C) for 24 h. In order to completely remove DMSO and non-reacted water-soluble monomers, the polymer solution was dialyzed against ultrapure water (Spectrum, MW cut off 3,500); water was frequently refreshed (every 6 h during day time).). The polymer sample was finally recovered by freeze-drying.



Figure S1. The ¹H-NMR spectrum of PAN_{11.6%} in DMSO-d6.



Figure S2. The ¹H-NMR spectrum of PAN_{5.3%} in DMSO-d6.



Figure S3. The ¹H-NMR spectrum of PAN_{4.4%} in DMSO-d6.



Figure S4. The ¹H-NMR spectrum of PAN_{3.7%} in DMSO-d6.

2.2 Copolymerization of Acrylic Acid, N-vinylcaprolactam and Dimethyl Acrylamide

As an example, the synthesis of P(AA-*co*-NVCL-*co*-DMA) (PAND) with an DMA feed content of 50 mol % was conducted as follows. To a 25 mL ampoule, AIBN (0.018 g, 0.11 mmol), AA (0.65 g, 9.08 mmol), NVCL (0.14 g, 1.01 mmol), DMA (1.0g, 10.09 mmol) and DMSO (9.0 mL) were quickly added. Then, the reaction mixture was degassed and filled with nitrogen. After 30 min stirring at room temperature, the ampoule was placed in a preheated oil bath (80 °C) for 24 h. To remove DMSO and water-soluble monomers remained in the mixture, the polymer solution was dialyzed against ultrapure water (Spectrum, MW cut off 3,500), with water refreshed every 6 h during day time. The polymer was then recovered by freeze-drying.



Figure S5. The ¹H-NMR spectrum of PAND_{52.6%} in DMSO-d6.



Figure S6. The ¹H-NMR spectrum of PAND_{58.1%} in DMSO-d6.



Figure S7. The ¹H-NMR spectrum of PAND_{64.5%} in DMSO-d6.



Figure S8. The ¹H-NMR spectrum of PAND_{68.5%} in DMSO-d6.

2.3 Preparation of UCST and LCST hydrogels

PAN/PAND hydrogel: 2.0 g of NVCL and AA monomers (total), and 2.0% molar ratio of crosslinker MBA were dissolved in 8.5 ml of DMSO. After adding 0.02 g AIBN, the solution was quickly transferred into a homemade glass mold sealed using silicone rubber. The reaction was kept in an oven at 80 °C for 12 h. After polymerization, the as-prepared gel was soaked in water for solvent exchange. A flat and uniform single-network hydrogel of P(AA-*co*-NVCL) (PAN) was obtained after 5 days by exchanging water every 12 h. The P(AA-*co*-NVCL-*co*-DMA) (PAND) hydrogel was prepared with the same procedure.

PAN-IPN hydrogel: A piece of PAN hydrogel was first swollen in an aqueous solution (50 mL) of acrylamide (AAm, 1.0 mol/L), I2959 (1.0 mg/mL, photoinitiator) and MBA (3.0 mg/mL, crosslinker), and then exposed to UV light (320-480 nm filter, 90 mW cm⁻²) through a photomask for 15 min. The photomask was achieved by cutting the black paper. Afterward, the as-prepared hydrogels were then soaked in deionized water for another 2 days to remove unreactive monomers, to yield the PAN/PAAm interpenetrating network hydrogels (denoted as PAN-IPN).

3 Study of The Thermo- and pH-Sensitive Solubility of The Copolymers



Figure S9. (a) Plots of solution transmittance vs temperature and (b) cloud point as a function of pH for PAN_{5.3%} aqueous solution (5.0 mg/mL; heating or cooling rate: 1.0 °C/min). Solid lines and dotted lines represent the heating and cooling curves, respectively.



Figure S10. Plots of solution transmittance vs temperature for (a) $PAN_{5.3\%}$ with different concentrations at pH 2.0, and (b) PAN of different compositions at pH 2.0 (5.0 mg/mL). For all measurement, heating or cooling rate: 1.0 °C/min. Solid lines and dotted lines represent the heating and cooling curves, respectively.



Figure S11. (a) Plots of solution transmittance vs temperature and (b) cloud point as a function of pH for PAND_{52.6%} aqueous solution (5.0 mg/mL; heating or cooling rate: 1.0 °C/min). Solid lines and dotted lines represent the heating and cooling curves, respectively.



Figure S12. Plots of solution transmittance vs temperature for (a) $PAND_{52.6\%}$ with different concentrations at pH 2.0, and (b) PAND of different compositions in aqueous solution (5.0 mg/mL; heating or cooling rate: 1.0 °C/min) at pH 2.0. Solid lines and dotted lines represent the heating and cooling curves, respectively.



Figure S13. The DLS-determined size distribution of the polymer solutions at different temperatures: (a) $PAN_{5.3\%}$ in deionized water (5 mg/mL, pH 3.0, no thermoresponsive behavior), (b) $PAN_{5.3\%}$ solutions (5 mg/mL) at room temperature with various pH from 3.0 to 1.3. (c) $PAND_{52.6\%}$ in deionized water (5 mg/mL, pH 3.5, no thermoresponsive behavior). (d) $PAND_{52.6\%}$ solutions (5 mg/mL) at room temperature with various pH from 3.5 to 1.4.



Figure S14. The zeta potential changes in solutions of $PAN_{5.3\%}$ (5 mg/mL, black line) and $PAND_{52.6\%}$ (5 mg/mL, red line) as a function of measured pH value.

4 The Morphology Analysis of Polymer Self-Assemblies

Figure S15 shows the TEM image of the PAND_{52.6%} prepared in water at room temperature with pH 2.0. Additionally, the average diameter (D_H) of the nano-particles can be estimated as ~10 nm, indicating that small micellar aggregates are formed due to the amphiphilic character of PAND.



Figure S15. TEM images of PAND52.6% were prepared in water at room temperature with pH 2.0.

5 Study of The Thermo and pH Sensitivity of The Hydrogels

As shown in Figure S16, the phase transition temperature for PAN (UCST) and PAND (LCST) hydrogels is roughly 40 °C and 35 °C, respectively. It should be noted that before monitoring, the hydrogels were treated with acid (HCl, 2.0 mol/L).



Figure S16. Photos showing the hydrogels of (a) PAN and (b) PAND upon heating from 25 to 50 $^\circ\mathrm{C}.$