

# Revisiting differences in the thermoresponsive behavior of PNIPAAm and PMEO<sub>2</sub>MA aqueous solutions

## Supporting Information

Ye Li, Jianhai Yang, Jingqing Li, Yuan Liu, Wei Wang, Wenguang Liu\*

*School of Materials Science and Engineering, Tianjin Key Laboratory of Composite and Functional Materials, Tianjin University, Tianjin 300072, PR China; E-mail: wgliu@tju.edu.cn*

### Experimental Section

#### Material

2-(2-Methoxyethoxy)ethyl methacrylate (MEO<sub>2</sub>MA, 95%, Aldrich Chemical Co.), copper(I) chloride (99%, Aldrich Chemical Co.), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me<sub>4</sub>Cyclam, 98%, Fluka Co.), *N,N,N',N',N'*-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich Chemical Co.), diethyl-meso-2,5-dibromoadipate (DEDBA, Aldrich Chemical Co.) were used as received. N-Isopropylacrylamide (NIPAAm, Aldrich Chemical Co.) was purified by recrystallization in hexane and dried under vacuum at 25 °C. Pyrene (99%, Aldrich Chemical Co.) was recrystallized five times from spectroscopic grade toluene. All solvents were analytical grade.

#### Syntheses of PNIPAAm and PMEO<sub>2</sub>MA homopolymers

DEDBA (9.1 mg, 0.025 mmol), CuCl (4.9 mg, 0.05 mmol) and NIPAAm (1.1315 g, 10 mmol, target degree of polymerization= 400) dissolved in 6 mL of methanol were placed into a Schlenk tube and degassed by three freeze-thaw cycles. Me<sub>4</sub>Cyclam (12.8 mg, 0.050 mmol) dissolved in 2 mL of methanol was then added by a syringe under nitrogen and the reaction mixture was degassed by another three freeze-thaw cycles. The mixture was heated at 60 °C in a water bath for 4 h. Then, the experiment

was stopped by opening the flask and exposing the catalyst to air. The solvent was then evaporated off, and the polymer was dissolved in deionized water followed by dialysis in a Cellu SepH1 membrane (MWCO=3000) to remove the impurities and unreacted monomers. Finally, the PNIPAAm homopolymer powder was collected by freeze-drying.

Similarly, PMEO<sub>2</sub>MA homopolymer with the same target DP as that of PNIPAAm was synthesized using PMDETA as a ligand. The absolute molecular weights were determined by GPC (Viscotek TDAmx GPC/SEC) equipped with a multi-angle light scattering detector (GPC/MALS) at 30 °C. THF was used as the eluent with a flow rate of 1.0 mL/min. Detectors: UV-PDA detector and RALS (90° angle)/LALS(7° angle) light scattering detector with a temperature controlled 3 mW laser diode operating at 670nm.

GPC analysis results (polystyrene standards):  $M_{n, GPC}$  of PNIPAAm = 34249 g/mol; polydispersity (PDI) = 1.31,  $DP_n=303$ .  $M_{n, GPC}$  of PMEO<sub>2</sub>MA = 51461 g/mol; polydispersity (PDI) = 1.17,  $DP_n = 273$ .

### **Determination of phase diagram**

The phase diagrams of PNIPAAm and PMEO<sub>2</sub>MA solutions were determined by a microtube inversion method over a temperature range from 14 to 43 °C at 2 °C intervals. Glass microtubes (4 mL) containing polymer solutions with varied concentrations were kept in a thermostated water bath for 30 min prior to each inversion. The gelation temperature was determined visually when the polymer solutions did not flow by inverting the microtubes.

### **Rheological properties**

The oscillatory shear measurements were performed on a stress-controlled rheometer RELOGICA INSTRUMENTS AB using a Bob-Cup geometry. In each measurement, 1.2 ml of a polymer solution was loaded into the bob-cup by a micropipette. The rate of temperature increase was controlled at 1 °C·min<sup>-1</sup> by a computer-programmable circulator with a precision of 0.5 °C. The viscosity, storage moduli ( $G'$ ) and loss

moduli ( $G''$ ) of the polymer solutions were measured as a function of temperature, at a constant angular frequency of  $0.2 \text{ rad}\cdot\text{s}^{-1}$  and shear strain of 0.2.

### Fluorescence Measurements

100  $\mu\text{L}$  of pyrene in THF solution ( $1.0 \times 10^{-3} \text{ mol/L}$ ) was added into a 100 mL volumetric flask, and the solvent was evaporated under a nitrogen flow. Then the polymer solution was added with the final concentration of pyrene in PNIPAAm or PMEO<sub>2</sub>MA solutions being set at  $10^{-6} \text{ mol/L}$ . Steady-state spectra were recorded with FLS920 fluorometer (Edinburgh Instruments, Britain). The excitation wavelengths were set at 334 nm and 338 nm for PNIPAAm and PMEO<sub>2</sub>MA, respectively. The emission spectra were recorded from 360 to 550 nm. All fluorescence decays were taken by using the time-correlated single-photon counting (TCSPC) technique equipped with a 1.5 ns pulse-width H<sub>2</sub> flash lamp. Temperature was controlled by a water-jacketed cell holder connected to a circulating bath. The data were analyzed by reconvolution fit analysis with the instrument response function using the software package provided by Edinburgh Instruments. The average lifetime is calculated from Eq. (1):<sup>1</sup>

$$\langle\tau_f\rangle = \frac{\sum \alpha_i \tau_i^2}{\sum \alpha_i \tau_i} \quad (1)$$

Where  $\alpha_i$  and  $\tau_i$  are the amplitude and time component, respectively, of the  $i$ th decay. Each sample was repeated three times.

---

<sup>1</sup> C. D. Grant, M. R. DeRitter, K. E. Steege, T. A. Fadeeva and E. W. Castner, *Langmuir*, 2005, **21**, 1745–1752.