Supporting information

Synthesis of Multifunctional Poly(1-pyrenemethyl methacrylate)-*b*-Poly(*N*isopropylacrylamide)-*b*-Poly(*N*-methylolacrylamide)s and Their Electrospun Nanofibers for Metal Ion Sensory Applications

Jau-Tzeng Wang,¹ Yu-Cheng Chiu,¹ Han-Sheng Sun,¹ Kohei Yoshida,² Yougen Chen³ Toshifumi Satoh,⁴ Toyoji Kakuchi^{*,2,3,4}, and Wen-Chang Chen^{*,1}

¹ Department of Chemical Engineering, National Taiwan University, Taipei, 10617,

Taiwan

² Graduate School of Chemical Sciences and Engineering, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan, ³ Frontier Chemistry Center, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan, and ⁴ Division of Biotechnology and Macromolecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

*To whom all correspondence should be addressed:

W. C. Chen (chenwc@ntu.edu.tw), T. Kakuchi (kakuchi@poly-bm.eng.hokudai.ac.jp)

S1. Characterization

The ¹H spectra were recorded using a JEOL JNM-A400II instrument. The IR spectra were recorded using a PerkinElmer Paragon 1000 FT-IR instrument. Gel permeation chromatographic analysis was performed on a Lab Alliance RI2000 instrument (tandem two columns, Styragel HR2 and HR4 from Waters) connected with one refractive index detector from Schambeck SFD GmbH. GPC analyses were performed on polymer/THF or DMF solution at the flow rate of 1 ml/min at 40 °C or 70 °C and calibrated with polystyrene standards.

S2. Synthesis of propargyl 2-bromoisobutyrate (PBiB, 1).

2.40 g (42.8 mmol) of propargyl alcohol, 6.7 ml of Et₃N (45.3 mmol) and 45 mL of dry diethyl ether (Et₂O) were introduced into a 250 ml three-neck round-bottom flask equipped with a condenser, a dropping funnel, and a nitrogen inlet/outlet. After cooling to 0 °C, 10.4 g of 2-bromoisobutyryl bromide (45.0 mmol) in 5ml dry Et₂O was added into the flask slowly under stirring for 1 h. The reaction temperature was then allowed to rise to room temperature and the mixture was stirred for another 24 h. After that insoluble salts were removed by filtration. The filtrate was then dried over MgSO₄ for 10 h. After removal of the solvent by rotary evaporation and further purification by distillation under reduced pressure, a colorless liquid were obtained. Yield = 70%; ¹H NMR (CDCl₃): 1.96 (6H, (CH₃)₂C-), 2.52 (1H, CH=C), 4.78 (2H, -CH₂-).

S3. Synthesis of azide-terminated PNIPAAm macroinitiator (3)

The synthetic scheme for azide-terminated PNIPAAm (N₃-PNIPAAm) is shown in **Scheme 2**. CuCl (16 mg, 16.6×10^{-2} mmol), Me₆TREN (46 µl, 16.6×10^{-2} mmol), and NIPAAm (2.82 g, 24.9 mmol) were mixed in 12.5 mL of IPA. The mixture was degassed by three freeze -pump-thaw cycles. AHCP (38.8 mg, 16.6×10^{-2} mmol) was then added to the mixture under an argon flow. The mixture was degassed once again, back-filled with

argon, and sealed. The polymerization was kept at 20 °C and the NIPAAm conversion at different polymerization time internal was checked until the conversion reached to 78%. PNIPAAm, $M_{n,(NMR)} = 13,240$ g mol⁻¹. After exposing the reaction mixture to the air and diluting with THF, the mixture was passed through a neutral Al₂O₃ column to remove the catalyst. The light yellow filtrate was concentrated and reprecipitated into ether. N₃-PNIPAAm₁₁₇, $M_{n,GPC(DMF)} = 23,000$ g mol⁻¹; $M_w/M_n = 1.19$.

S4. Synthesis of N₃-PNIPAAm-*b*-PNMA (4b-c)

The preparation of N_3 -PNIPAAm₁₁₇-b-PNMA₄₃ (4b) is taken as an example as follows: CuCl (16 mg, 16.6×10^{-2} mmol), N₃-PNIPAAm macroinitiator (2.2 g, 16.6×10^{-1} ² mmol) and NMA (1.7 g, 1.66×10^{-2} mol) were mixed in 8.3 mL of H₂O. The mixture was degassed by three freeze-pump-thaw cycles. Me₆TREN (46 μ l, 16.6 \times 10⁻² mmol) was then added to the mixture under an argon flow. The mixture was degassed once again, back-filled with argon, and sealed under argon flow. The mixture was further stirred for 24 h for the second polymerization. The polymerization was stopped by bubbling air into the crude solution. Subsequently, the mixture was diluted with methanol and passed through a silica column to remove the copper catalyst. In order to remove unreacted monomer, the resulting solution was dialyzed against water with a Spectra/Por 6 dialysis membrane (molecular-weight cutoff: 1,000 g mol⁻¹) for 48 h, with replacement of the deionized water at regular time intervals. The obtained aqueous solution was freeze-dried overnight to form N_3 -PNIPAAm₁₁₇-b-PNMA₄₃ (4b) as a white solid (2.34 g, 70% yield). ¹H NMR in DMSO-d₆, δ (ppm) 0.85-1.17 (6H, -CH(CH₃)₂), 1.26-1.77 (4H, -CH₂CH-, -CH₂CH-), 1.81-2.23 (2H, -CH₂CH-, -CH₂CH-), 3.72-3.96 (1H, -CH(CH₃)₂), 4.36-4.68 (2H, -CONHCH₂-), 5.36-5.62 (H, -NHCH₂OH), 6.95-7.58 (1H, -CONHCH-), 7.96-8.40 (1H, -NHCH₂OH). N₃-PNIPAAm-b-PNMA, $M_{n,NMR} = 17,500$ g mol⁻¹; $M_{n,GPC(DMF)} =$ 27,500 g mol⁻¹; $M_w/M_n = 1.15$. (Figure S1).

S5. Characterization of N₃-PNIPAAm-*b*-PNMA (4a-c)

Diblock copolymers, N₃-PNIPAAm₁₀₀-*b*-PNMA₁₀ (**4a**), N₃-PNIPAAm₁₁₇-*b*-PNMA₄₃ (**4b**) and N₃-PNIPAAm₁₁₇-*b*-PNMA₁₀₃ (**4c**), were characterized by the NMR spectra. The coil length of **4b** and **4c** were determined by comparing the integrated peak areas of methine protons due to PNIPAAm (signal *d* at 4.0 ppm) and methylene protons due to PNMA (signal *e* at 4.5 ppm). The estimated (M_n , PDI)s of **4a-4c** are (25,400 g mol⁻¹, 1.31), (27,500 g mol⁻¹, 1.15), and (31,500 g mol⁻¹, 1.25), respectively (see Figure **S5(a-b)** and Table **S1** in the Supporting information.)

Table S1. Polymerization conditions and molecular weights of N₃-PNIPAAm-*b*-PNMA (**5a** and **5b**) diblock copolymers.

Polymer composition	NIPAAm	NMA	M _{n NMR} ^a (g/mol)	$\frac{M_{\rm n GPC}(\rm g/mol)}{(\rm M_w/M_n)^{b}}$
	Conv.(%)	Conv.(%		
N_3 -PNIPAAm ₁₁₇ (3)	78	-	13,200	23,000 (1.19)
N_3 -PNIPAAm ₁₀₀ -b-PNMA ₁₀ (4a)	99.6	98.4	12,300	25,400 (1.31)
N_3 -PNIPAAm ₁₁₇ - <i>b</i> -PNMA ₄₃ (4b)		60	17,600	27,500 (1.15)
N_3 -PNIPAAm ₁₁₇ - <i>b</i> -PNMA ₁₀₃ (4c)		52	23,700	41,500 (1.25)

^{*a*} Determined by ¹H NMR. ^{*b*} Determined by GPC with DMF as the eluent.



Figure S1. (a) ¹H NMR spectrum of alkynyl-terminated PPy **(2)** in CDCl₃ and (b) GPC profile of the alkynyl-terminated PPy using THF as the eluent.



Figure S2. GPC profiles of the synthesized triblock copolymers after click reaction (a) PPy₁₈-*b*-PNIPAAm₁₀₀-*b*-PNMA₁₀ (**5a**), (b) PPy₁₈-*b*-PNIPAAm₁₁₇-*b*-PNMA₄₃ (**5b**), and (c) PPy₁₈-*b*-PNIPAAm₁₁₇-*b*-PNMA₁₀₃ (**5c**), together with their N₃-PNIPAAm-*b*-PNMA precursors.



Figure S3. (a) IR spectra of N₃-PNIPAAm₁₀₀-*b*-PNMA₁₀ (4a) and PPy₁₈-*b*-PNIPAAm₁₀₀*b*-PNMA₁₀ (5a) and ¹H NMR spectra of PPy₁₈-*b*-PNIPAAm₁₀₀-*b*-PNMA₁₀ (5a): (b) in CDCl₃ and (c) in *d*-DMSO.



Figure S4 (a) IR spectra of N₃-PNIPAAm₁₁₇-*b*-PNMA₁₀₃ (**4c**) and PPy₁₈-*b* - PNIPAAm₁₁₇-*b*-PNMA₁₀₃ (**5c**) and ¹H NMR spectra of PPy₁₈-*b*-PNIPAAm₁₁₇-*b*-PNMA₁₀₃ (**5c**): (b) in CDCl₃ and (c) in *d*-DMSO.



Figure S5. (a) ¹H NMR spectra of N₃-PNIPAAm₁₀₀-*b*-PNMA₁₀ (4a), N₃-PNIPAAm₁₁₇-*b*-PNMA₄₃ (4b), and N₃-PNIPAAm₁₁₇-*b*-PNMA₁₀₃ (4c) in *d*-DMSO; (b) GPC profiles of N₃-PNIPAAm₁₁₇ (3), N₃-PNIPAAm₁₁₇-*b*-PNMA₄₃ (4b), and N₃-PNIPAAm₁₁₇-*b*-PNMA₁₀₃ (4c).



Figure S6. DSC curves of PPy-*b*-PNIPAAm-*b*-PNMA triblock copolymers at a heating rate of 10 °C /min under a nitrogen atmosphere.



Figure **S7**. FE-SEM images of **5c** crosslinked nanofibers treated by water at temperatures of: (a) 20 °C and (b) 50 °C.



Figure S8. The variation of relative fluorescence intensity recorded for crosslinked **5b** nanofibers (I: the PL intensity at different temperatures; I_0 : the PL intensity at 50 °C).



Figure **S9**. PL dependence of drop-cast **5b** thin films on temperature: (a) with increasing temperature from 20 to 50 °C and (b) with decreasing temperature from 50 to 20 °C; PL dependence of crosslinked **5c** ES nanofibers on temperature: (c) with increasing temperature from 20 to 50 °C and (d) with decreasing temperature from 50 to 20 °C; and PL dependence of drop-cast **5c** thin films on temperature: (e) with increasing temperature from 20 to 50 °C and (f) with decreasing temperature from 50 to 20 °C; $\lambda_{ex} = 360$ nm)