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 \( ^1\)H 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, Styrage 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 Et\(_3\)N (45.3 mmol) and 45 mL of dry diethyl ether (Et\(_2\)O) 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 Et\(_2\)O 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 MgSO\(_4\) 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%; \( ^1\)H NMR (CDCl\(_3\)): 1.96 (6H, (C\(_\text{H}_3\)\(_2\)C-), 2.52 (1H, CΗ≡C), 4.78 (2H, -CH\(_2\)-).

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

The synthetic scheme for azide-terminated PNIPAAm (N\(_3\)-PNIPAAm) is shown in Scheme 2. CuCl (16 mg, 16.6 × 10\(^{-2}\) mmol), Me\(_6\)TREN (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 interval was checked until the conversion reached to 78%. PNIPAAm, $M_n,_{\text{NMR}} = 13,240 \text{ g mol}^{-1}$. After exposing the reaction mixture to the air and diluting with THF, the mixture was passed through a neutral Al$_2$O$_3$ column to remove the catalyst. The light yellow filtrate was concentrated and reprecipitated into ether. N$_3$-PNIPAAm$_{117}$, $M_n,_{\text{GPC(DMF)}} = 23,000 \text{ g mol}^{-1}$; $M_w/M_n = 1.19$.

S4. Synthesis of N$_3$-PNIPAAm-b-PNMA (4b-c)

The preparation of N$_3$-PNIPAAm$_{117}$-b-PNMA$_{43}$ (4b) is taken as an example as follows: CuCl (16 mg, $16.6 \times 10^{-2} \text{ mmol}$), N$_3$-PNIPAAm macroinitiator (2.2 g, $16.6 \times 10^{-2} \text{ mmol}$) and NMA (1.7 g, $1.66 \times 10^{-2} \text{ mol}$) were mixed in 8.3 mL of H$_2$O. The mixture was degassed by three freeze-pump-thaw cycles. Me$_6$TREN (46 μl, $16.6 \times 10^{-2} \text{ mmol}$) 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$_3$-PNIPAAm$_{117}$-b-PNMA$_{43}$ (4b) as a white solid (2.34 g, 70% yield).

$^1$H NMR in DMSO-$d_6$, δ (ppm) $0.85$-$1.17$ (6H, -CH(CH$_3)_2$), $1.26$-$1.77$ (4H, -CH$_2$CH-, -CH$_2$CH$_2$-), $1.81$-$2.23$ (2H, -CH$_2$CH-, -CH$_2$CH$_2$-), $3.72$-$3.96$ (1H, -CH(CH$_3)_2$), $4.36$-$4.68$ (2H, -CONHCH$_2$-), $5.36$-$5.62$ (H, -NHCH$_2$OH), $6.95$-$7.58$ (1H, -CONHCH-), $7.96$-$8.40$ (1H, -NHCH$_2$OH). N$_3$-PNIPAAm-b-PNMA, $M_n,_{\text{NMR}} = 17,500 \text{ g mol}^{-1}$; $M_n,_{\text{GPC(DMF)}} = 27,500 \text{ g mol}^{-1}$; $M_w/M_n = 1.15$. (Figure S1).
S5. Characterization of N\textsubscript{3}-PNIPAAm-b-PNMA (4a-c)

Diblock copolymers, N\textsubscript{3}-PNIPAAm\textsubscript{100}-b-PNMA\textsubscript{10} (4a), N\textsubscript{3}-PNIPAAm\textsubscript{117}-b-PNMA\textsubscript{43} (4b) and N\textsubscript{3}-PNIPAAm\textsubscript{117}-b-PNMA\textsubscript{103} (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 \textit{d} at 4.0 ppm) and methylene protons due to PNMA (signal \textit{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.)

\textbf{Table S1.} Polymerization conditions and molecular weights of N\textsubscript{3}-PNIPAAm-b-PNMA (5a and 5b) diblock copolymers.

<table>
<thead>
<tr>
<th>Polymer composition</th>
<th>NIPAAm Conv. (%)</th>
<th>NMA Conv. (%)</th>
<th>(M_n) NMR (^a) (g/mol)</th>
<th>(M_n) GPC (g/mol) ((M_w/M_n)) (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{3}-PNIPAAm\textsubscript{117} ((3))</td>
<td>78</td>
<td>-</td>
<td>13,200</td>
<td>23,000 (1.19)</td>
</tr>
<tr>
<td>N\textsubscript{3}-PNIPAAm\textsubscript{100}-b-PNMA\textsubscript{10} ((4a))</td>
<td>99.6</td>
<td>98.4</td>
<td>12,300</td>
<td>25,400 (1.31)</td>
</tr>
<tr>
<td>N\textsubscript{3}-PNIPAAm\textsubscript{117}-b-PNMA\textsubscript{43} ((4b))</td>
<td>60</td>
<td>-</td>
<td>17,600</td>
<td>27,500 (1.15)</td>
</tr>
<tr>
<td>N\textsubscript{3}-PNIPAAm\textsubscript{117}-b-PNMA\textsubscript{103} ((4c))</td>
<td>52</td>
<td>-</td>
<td>23,700</td>
<td>41,500 (1.25)</td>
</tr>
</tbody>
</table>

\(^a\) Determined by \(^1\)H NMR. \(^b\) Determined by GPC with DMF as the eluent.
Figure S1. (a) $^1$H NMR spectrum of alkynyl-terminated PPy (2) in CDCl$_3$ 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) PPy_{18-b}-PNIPAAm_{100-b}-PNMA_{10} (5a), (b) PPy_{18-b}-PNIPAAm_{117-b}-PNMA_{43} (5b), and (c) PPy_{18-b}-PNIPAAm_{117-b}-PNMA_{103} (5c), together with their N3-PNIPAAm-b-PNMA precursors.
Figure S3. (a) IR spectra of N$_3$-PNIPAAm$^{100}$-b-PNMA$_{10}$ (4a) and PPy$_{18}$-b-PNIPAAm$^{100}$-b-PNMA$_{10}$ (5a) and $^1$H NMR spectra of PPy$_{18}$-b-PNIPAAm$_{100}$-b-PNMA$_{10}$ (5a): (b) in CDCl$_3$ and (c) in $d$-DMSO.
Figure S4 (a) IR spectra of $N_3$-PNIPAAm$_{117}$-b-PNMA$_{103}$ (4c) and PPy$_{18}$-b-PNIPAAm$_{117}$-b-PNMA$_{103}$ (5c) and $^1$H NMR spectra of PPy$_{18}$-b-PNIPAAm$_{117}$-b-PNMA$_{103}$ (5c): (b) in CDCl$_3$ and (c) in d-DMSO.
Figure S5. (a) $^1$H NMR spectra of $N_3$-PNIPAm$_{100}$-$b$-PNMA$_{10}$ (4a), $N_3$-PNIPAm$_{117}$-$b$-PNMA$_{43}$ (4b), and $N_3$-PNIPAm$_{117}$-$b$-PNMA$_{103}$ (4c) in $d$-DMSO; (b) GPC profiles of $N_3$-PNIPAm$_{117}$ (3), $N_3$-PNIPAm$_{117}$-$b$-PNMA$_{43}$ (4b), and $N_3$-PNIPAm$_{117}$-$b$-PNMA$_{103}$ (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; I₀: 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)