Supporting Information

Accelerating the acidic degradation of a novel thermoresponsive polymer by host-guest interaction

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Synthesis of Compounds and Characterizations

\[
\begin{align*}
\text{HOOC-S-S-} & + \text{Br-} \text{OH} & \xrightarrow{\text{DCC, DMAP, rt}} & \text{OOC-S-S-} \\
\end{align*}
\]

\[85^\circ \text{C} \]

Scheme S1 Synthetic route of CTA 4.

Synthesis of 3

Compound 1 (1 g), DMAP (62.16 mg), and compound 2 (825 µL) were dissolved in anhydrous dichloromethane (20 mL). The flask was cooled to 0 °C in ice-water bath. Then DCC (1.2 g) in 10 mL of anhydrous dichloromethane was added dropwise and stirred for 24 h at room temperature. After filtration, the filtrate was concentrated and further purified by silica gel column chromatography using dichloromethane:n-hexane (2:1, v/v). After evaporating solvent in vacuum, a yellow liquid 3 was obtained (1.3 g, yield: 81.3%). \(^1\)H NMR (300 MHz, chloroform-\(d\)) \(\delta \) 4.83 (q, \(J = 7.4 \text{ Hz, 1H}\)), 4.27 – 4.04 (m, 2H), 3.41 (dt, \(J = 14.1, 7.1 \text{ Hz, 4H}\)), 1.87 (dt, \(J = 8.1, 6.6 \text{ Hz, 2H}\)), 1.78 – 1.55 (m, 7H), 1.53 – 1.35 (m, 6H), 0.96 (t, \(J = 7.3 \text{ Hz, 3H}\)).

Synthesis of 4

Compound 3 (800 mg) and 4-methylpyridine (792 µL) were added into a flask and reacted at 85 °C for 24 h, then purified by silica gel column chromatography using dichloromethane:methanol (10:1, v/v). After evaporating solvent under vacuum, a yellow syrupy liquid 4 was obtained (600 mg, yield: 60.7%). \(^1\)H NMR (300 MHz, chloroform-\(d\)) \(\delta \) 9.47 – 9.17 (m, 2H), 7.87 (d, \(J = 6.3 \text{ Hz, 2H}\)), 4.98 (t, \(J\)
$J = 7.4 \text{ Hz, 2H}$, 4.79 (q, $J = 7.4 \text{ Hz, 1H}$), 4.26 – 4.02 (m, 2H), 3.37 (td, $J = 7.2, 2.6 \text{ Hz, 2H}$), 2.70 (s, 3H), 2.22 – 1.92 (m, 2H), 1.77 – 1.56 (m, 7H), 1.51 – 1.35 (m, 6H), 0.94 (t, $J = 7.3 \text{ Hz, 3H}$).

Figure S1 $^1\text{H NMR (CDCl}_3, 300 \text{ MHz) spectrum of 3.}$
Figure S2 $^1$H NMR (CDCl$_3$, 300 MHz) spectrum of CTA 4.
Figure S3 $^1$H NMR (DMSO-$d_6$, 300 MHz) spectrum of P2.
Figure S4 SEC measurement of P1, P2 and P3.
**Figure S5** Transmittance changes of polymer P2 with or without H1 and H2 by heating and cooling down temperature. Heating and cooling rate: 0.2 °C min⁻¹.
**Figure S6** Transmittance changes of polymer **P2** without addition of **H2** and with different ratios of **H2** (1 eq., 1.5 eq. and 2 eq.). Heating rate: 0.2 °C min⁻¹.
Complexation between P2 and H1 or H2 at different temperatures in D$_2$O

Figure S7 $^1$H NMR (D$_2$O, 300 MHz) spectrum of complexation at 23 °C. A) 1 eq. H1, B) mixture of H1 and P2, C) P2 (5 mg mL$^{-1}$).
Figure S8 \(^1\)H NMR (D\(_2\)O, 300 MHz) spectrum of complexation at 37 °C. A) 1 eq. H1, B) mixture of H1 and P2, C) P2 (5 mg mL\(^{-1}\)).
Figure S9 $^1$H NMR (D$_2$O, 300 MHz) spectrum of complexation at 45 °C. A) 1 eq. H1, B) mixture of H1 and P2, C) P2 (5 mg mL$^{-1}$).
Figure S10 $^1$H NMR (D$_2$O, 300 MHz) spectrum of complexation at 23 °C. A) 1 eq. H2, B) mixture of H2 and P2, C) P2 (5 mg mL$^{-1}$).
Figure S11 $^1$H NMR (D$_2$O, 300 MHz) spectrum of complexation at 37 °C. A) 1 eq. H$_2$, B) mixture of H$_2$ and P$_2$, C) P$_2$ (5 mg mL$^{-1}$).
Figure S12 $^1$H NMR (D$_2$O, 300 MHz) spectrum of complexation at 45 °C. A) 1 eq. H$_2$, B) mixture of H$_2$ and P$_2$, C) P$_2$ (5 mg mL$^{-1}$).
Hydrolysis measurement of polymers or complexation between polymer and pillar[5] arene in D$_2$O at different pH at 37 °C.

Figure S13 $^1$H NMR (D$_2$O, 300 MHz) spectrum of hydrolysis of P2 (5 mg mL$^{-1}$) at pH 7.4. A) 0 h, B) 3 h, C) 24 h, D) 48 h, E) 96 h, F) 120 h, G) 168 h, H) 216 h, and I) 264 h.
Figure S14 $^1$H NMR (D$_2$O, 300 MHz) spectrum of hydrolysis of P2 (5 mg mL$^{-1}$) with 1 eq. H1 at pH 7.4. A) 0 h, B) 3 h, C) 24 h, D) 48 h, E) 96 h, F) 120 h, G) 168 h, H) 216 h, and I) 264 h.
Figure S15 $^1$H NMR (D$_2$O, 300 MHz) spectrum of hydrolysis of P2 (5 mg mL$^{-1}$) with 1 eq. H2 at pH 7.4. A) 0 h, B) 24 h, C) 48 h, D) 96 h, E) 120 h, F) 168 h, G) 216 h, and H) 264 h.
Figure S16 $^1$H NMR (D$_2$O, 300 MHz) spectrum of hydrolysis of P2 (5 mg mL$^{-1}$) with 5 eq. G1 at pH 7.4. A) 0 h, B) 24 h, C) 48 h, D) 96 h, E) 120 h, F) 168 h, G) 216 h, and H) 264 h.
Figure S17 $^1$H NMR (D$_2$O, 300 MHz) spectrum of hydrolysis of P2 (5 mg mL$^{-1}$) at pH 5.2. A) 0 h, B) 3 h, C) 24 h, D) 48 h, E) 96 h, F) 120 h, G) 168 h, H) 216 h, and I) 264 h.
Figure S18 $^1$H NMR (D$_2$O, 300 MHz) spectrum of hydrolysis of P2 (5 mg mL$^{-1}$) with 1 eq. H1 at pH 5.2. A) 0 h, B) 3 h, C) 24 h, D) 48 h, E) 96 h, F) 120 h, G) 168 h, H) 216 h, and I) 264 h.
Figure S19 $^1$H NMR (D$_2$O, 300 MHz) spectrum of hydrolysis of P1 (5 mg mL$^{-1}$) at pH 5.2 A) 0 h, B) 24 h, C) 48 h, D) 96 h, E) 120 h, F) 168 h, G) 216 h, and H) 264 h.
Figure S20 $^1$H NMR (D$_2$O, 300 MHz) spectrum of hydrolysis of P1 (5 mg mL$^{-1}$) with 1 eq. H1 at pH 5.2. A) 0 h, B) 24 h, C) 48 h, D) 96 h, E) 120 h, F) 168 h, G) 216 h, and H) 264 h.
Figure S21 $^1$H NMR (D$_2$O, 300 MHz) spectrum of hydrolysis of P3 (5 mg mL$^{-1}$) at pH 5.2. A) 0 h, B) 24 h, C) 48 h, D) 96 h, E) 120 h, F) 168 h, G) 216 h, and H) 264 h.
Figure S22 $^1$H NMR (D$_2$O, 300 MHz) spectrum of hydrolysis of P3 (5 mg mL$^{-1}$) with 1 eq. H1 at pH 5.2. A) 0 h, B) 24 h, C) 48 h, D) 96 h, E) 120 h, F) 168 h, G) 216 h, and H) 264 h.
Figure S23 $^1$H NMR (D$_2$O, 300 MHz) spectrum of hydrolysis of P2 (5 mg mL$^{-1}$) with 1 eq. H$_2$ at pH 5.2. A) 0 h, B) 24 h, C) 48 h, D) 96 h, E) 120 h, F) 168 h, G) 216 h, and H) 264 h.
Figure S24 $^1$H NMR (D$_2$O, 300 MHz) spectrum of hydrolysis of P2 (5 mg mL$^{-1}$) with 5 eq. G1 at pH 5.2. A) 0 h, B) 24 h, C) 48 h, D) 96 h, E) 120 h, F) 168 h, G) 216 h, and H) 264 h.
Association constant measurement between P2 and H1 or P2 and H2 by ITC

**Figure S25** Association constant between P2 and H1.
Figure S26 Association constant between P2 and H2.