Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

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

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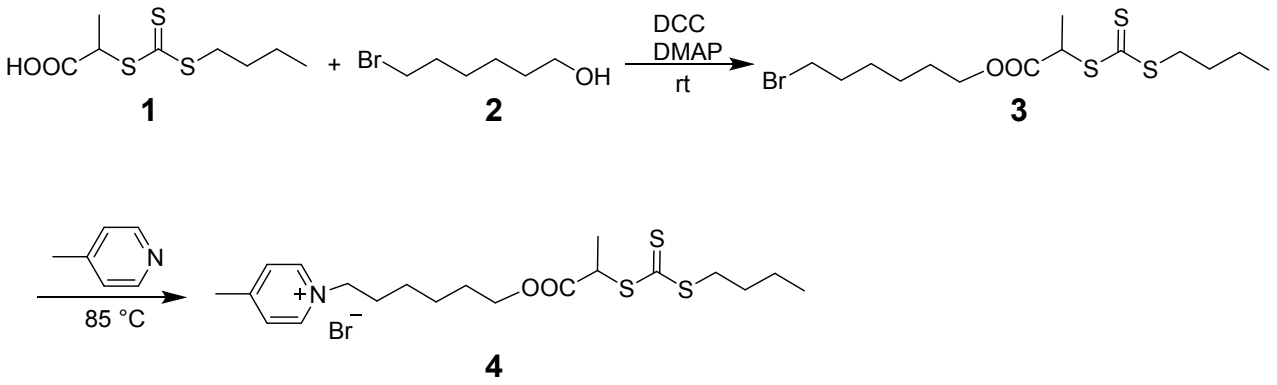
Synthesis of Compounds and Characterizations



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*) δ 4.83 (q, J = 7.4 Hz, 1H), 4.27 – 4.04 (m, 2H), 3.41 (dt, J = 14.1, 7.1 Hz, 4H), 1.87 (dt, J = 8.1, 6.6 Hz, 2H), 1.78 – 1.55 (m, 7H), 1.53 – 1.35 (m, 6H), 0.96 (t, J = 7.3 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*) δ 9.47 – 9.17 (m, 2H), 7.87 (d, J = 6.3 Hz, 2H), 4.98 (t, J

= 7.4 Hz, 2H), 4.79 (q, *J* = 7.4 Hz, 1H), 4.26 – 4.02 (m, 2H), 3.37 (td, *J* = 7.2, 2.6 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 Hz, 3H).

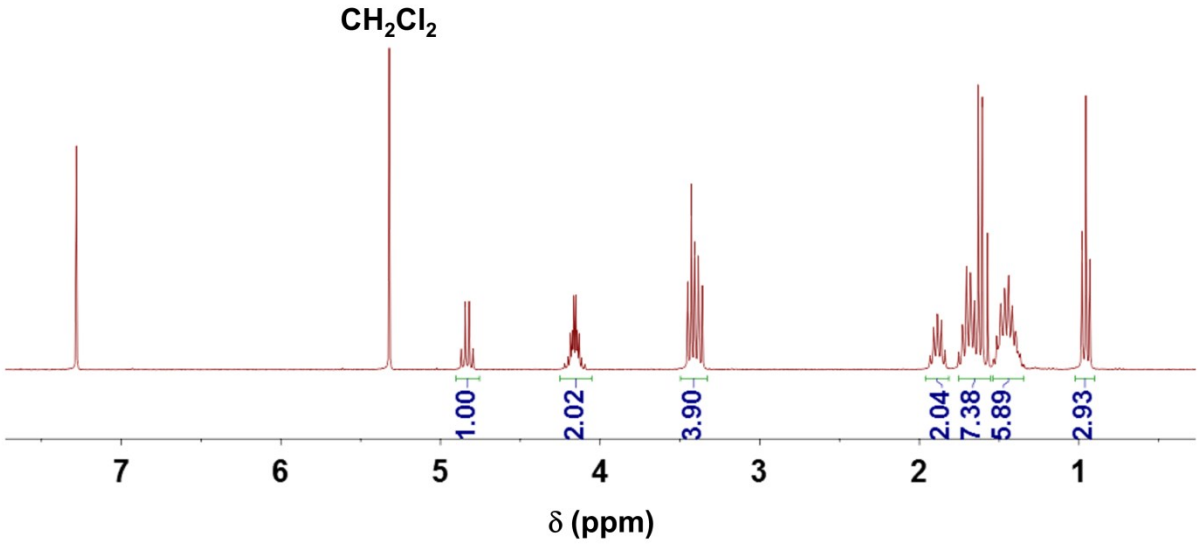


Figure S1 ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **3**.

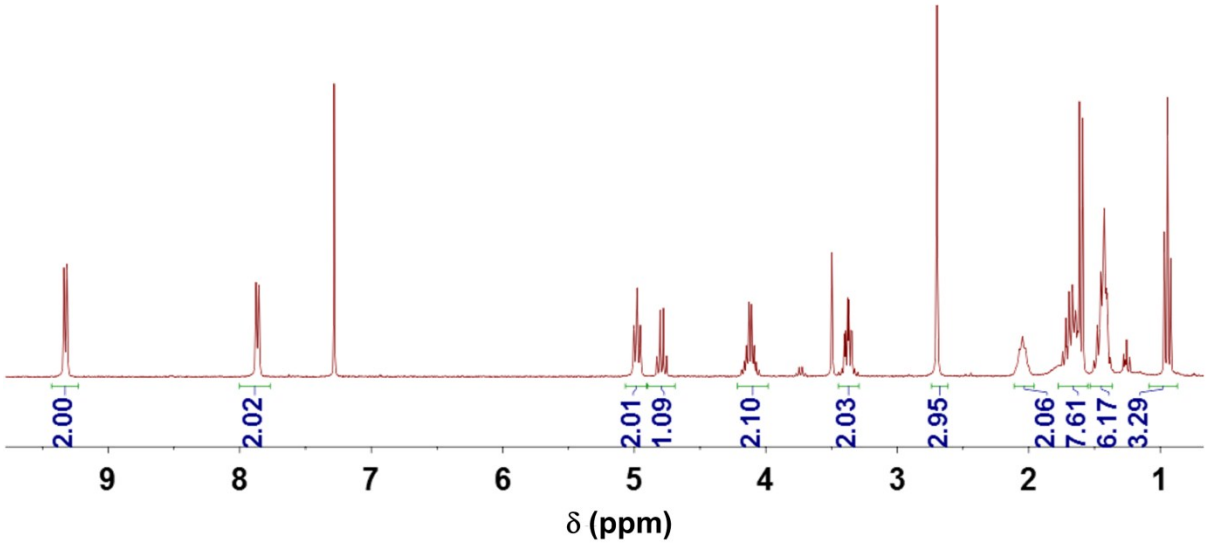


Figure S2 ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of CTA **4**.

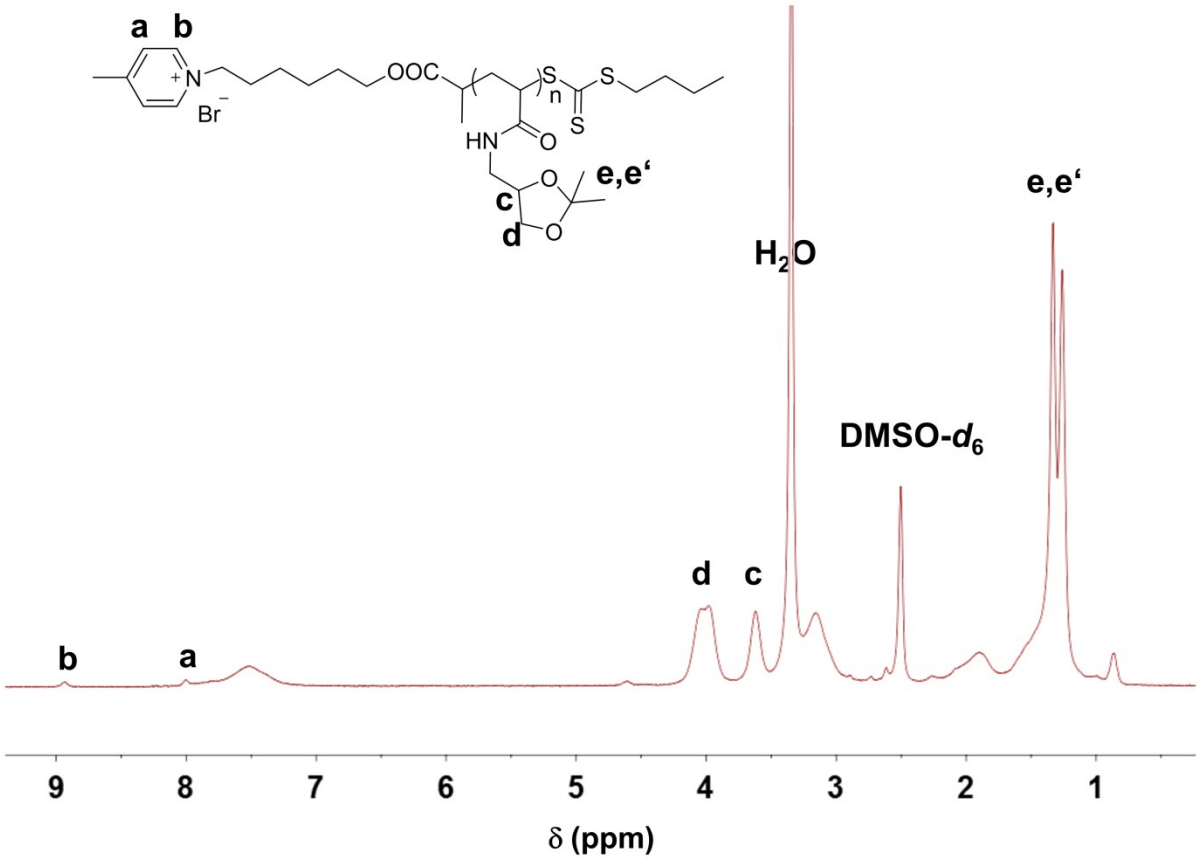


Figure S3 ^{1}H NMR (DMSO-d_6, 300 MHz) spectrum of **P2**.

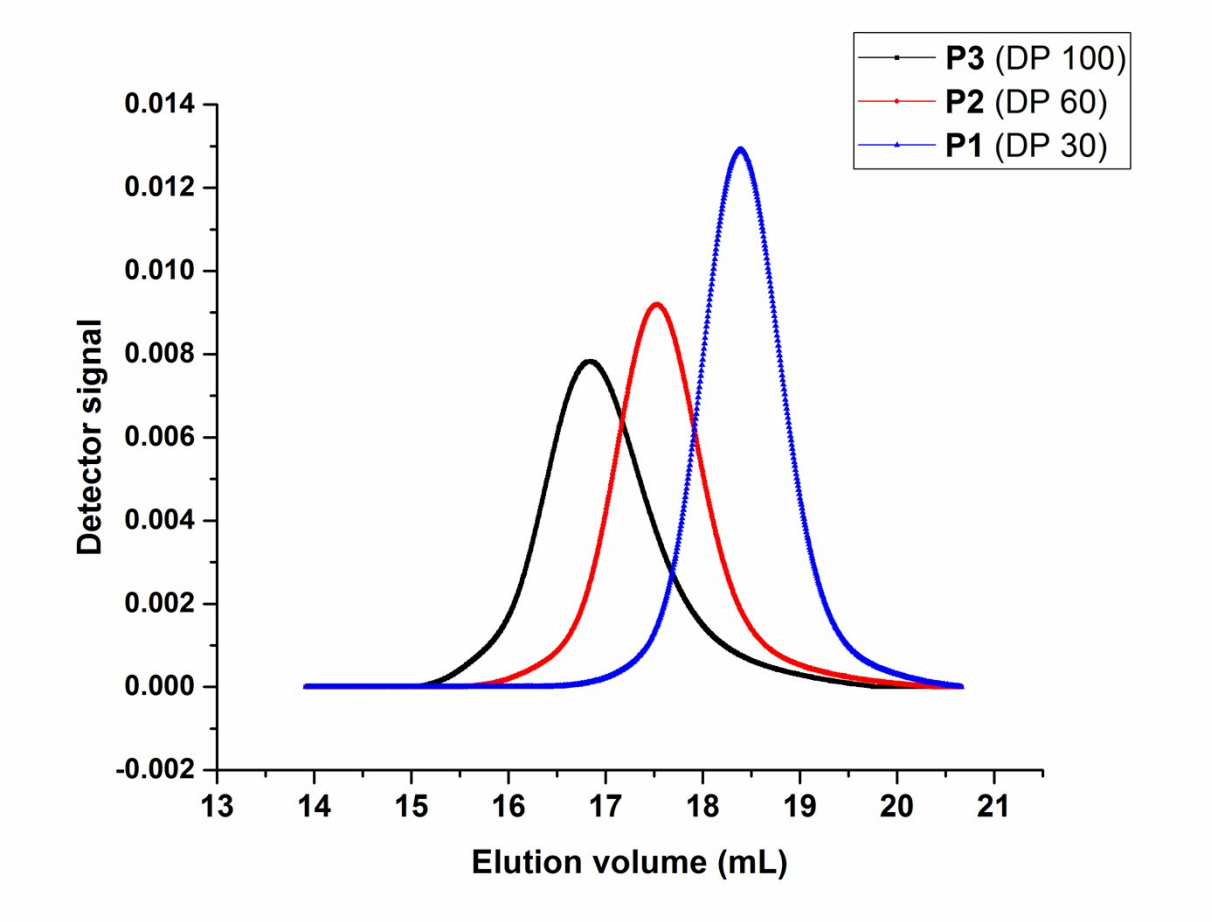


Figure S4 SEC measurement of **P1**, **P2** and **P3**.

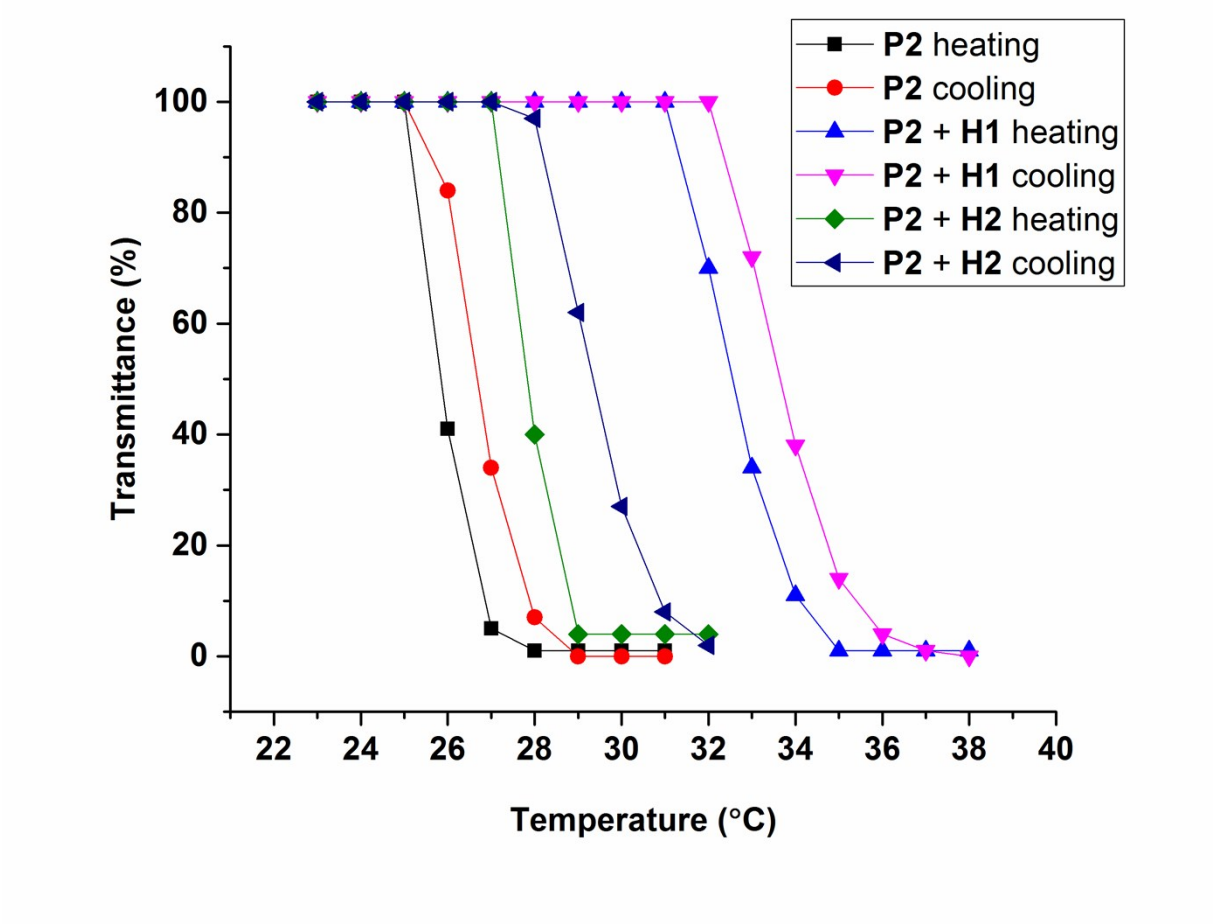


Figure S5 Transmittance changes of polymer **P2** with or without **H1** and **H2** by heating and cooling down temperature. Heating and cooling rate: 0.2 °C min^{-1}.

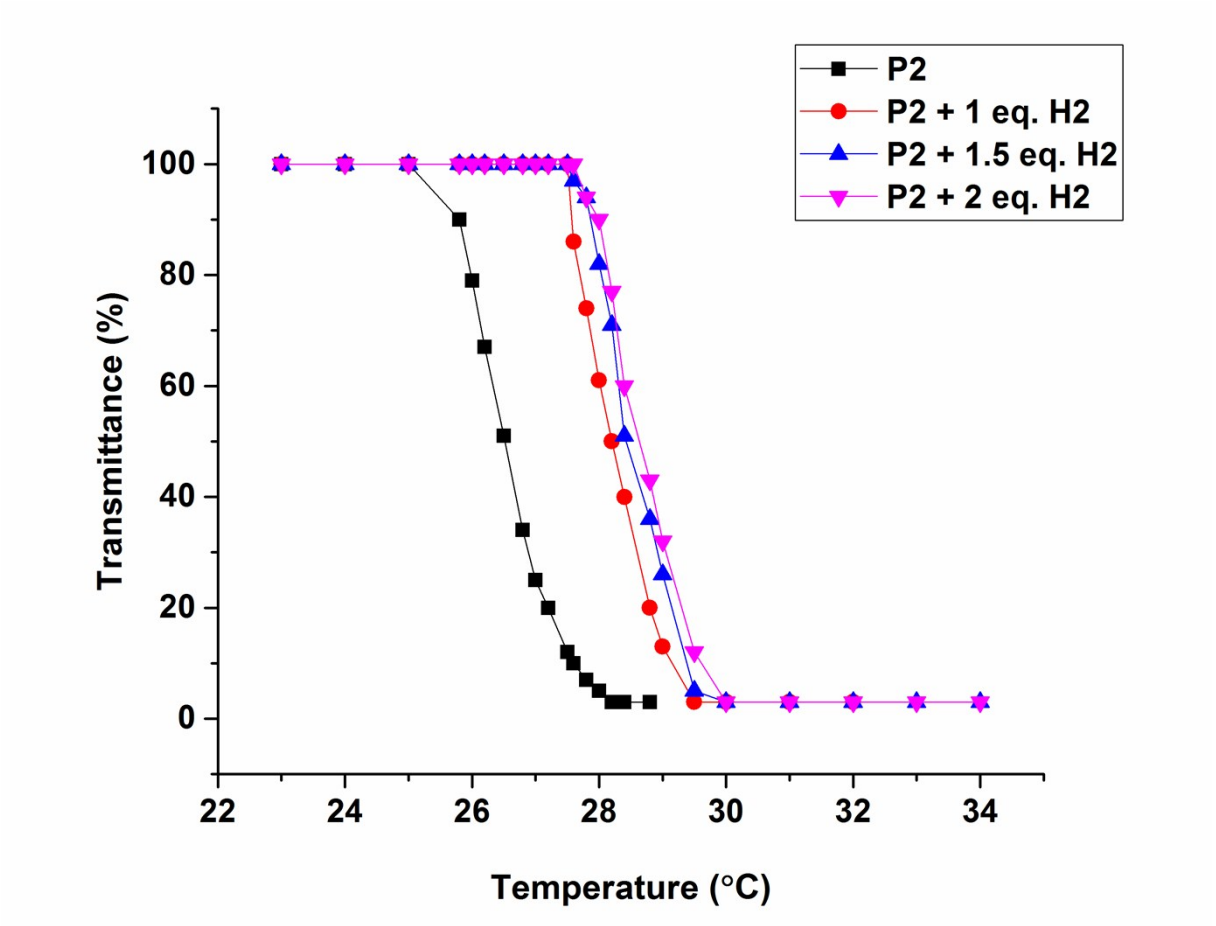


Figure S6 Transmittance changes of polymer **P2** without addition of **H2** and with different ratios of **H2** (1 eq., 1.5 eq. and 2 eq.). Heating rate: 0.2 °C min^{-1}.

Complexation between P2 and H1 or H2 at different temperatures in D_2O

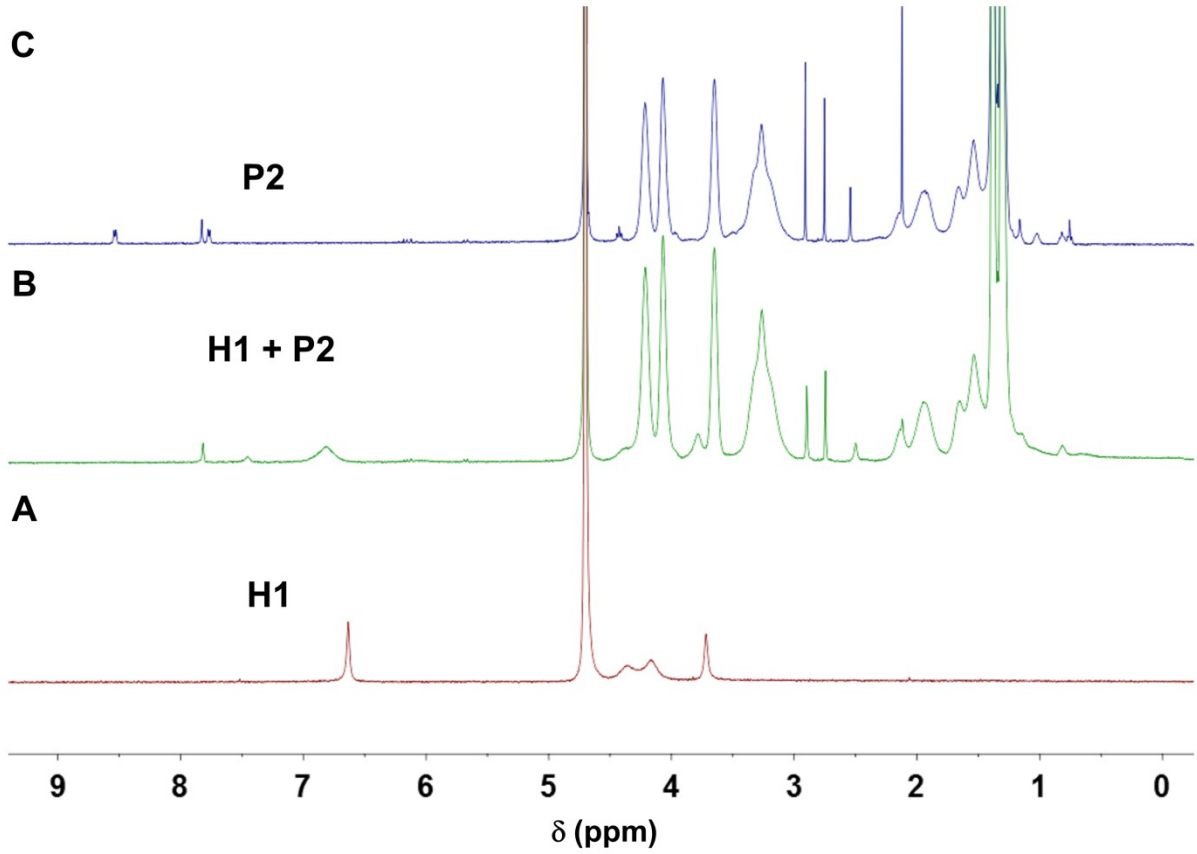


Figure S7 ^{1}H NMR (D_2O, 300 MHz) spectrum of complexation at 23 ℃. A) 1 eq. **H1**, B) mixture of **H1** and **P2**, C) **P2** (5 mg mL^{-1}).

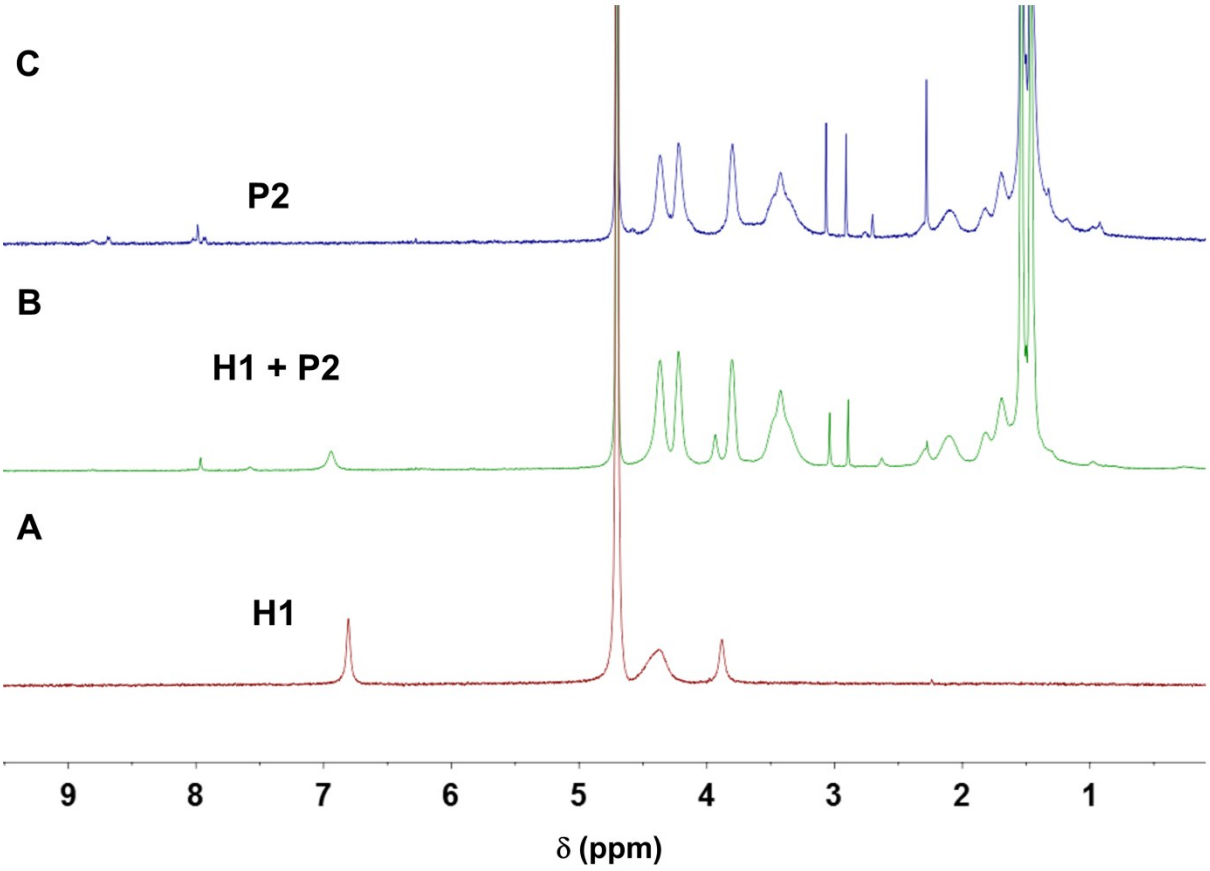


Figure S8 ^{1}H NMR (D_2O, 300 MHz) spectrum of complexation at 37 ℃. A) 1 eq. **H1**, B) mixture of **H1** and **P2**, C) **P2** (5 mg mL^{-1}).

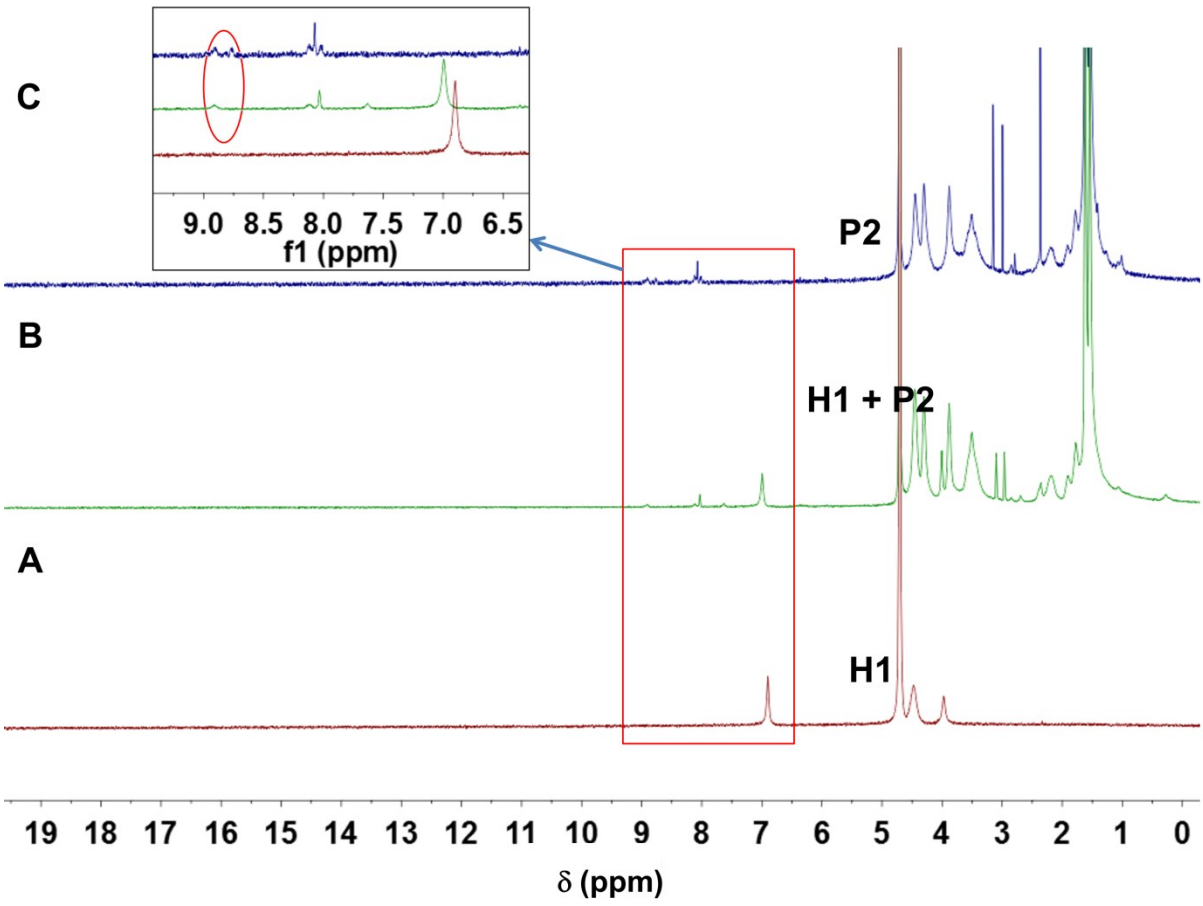


Figure S9 ^{1}H NMR (D_2O, 300 MHz) spectrum of complexation at 45 ℃. A) 1 eq. H1, B) mixture of H1 and P2, C) P2 (5 mg mL^{-1}).

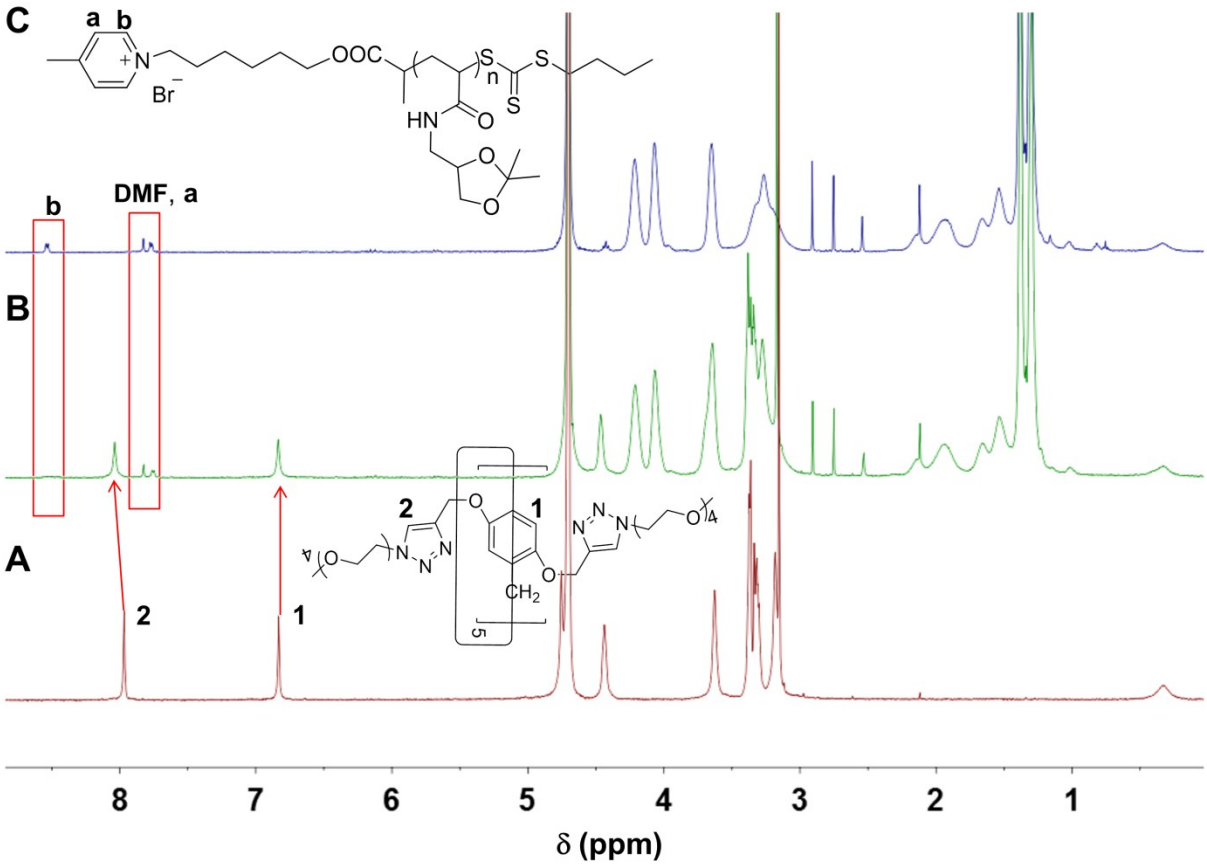


Figure S10 ^{1}H NMR (D_2O, 300 MHz) spectrum of complexation at 23 ℃. A) 1 eq. **H2**, B) mixture of **H2** and **P2**, C) **P2** (5 mg mL^{-1}).

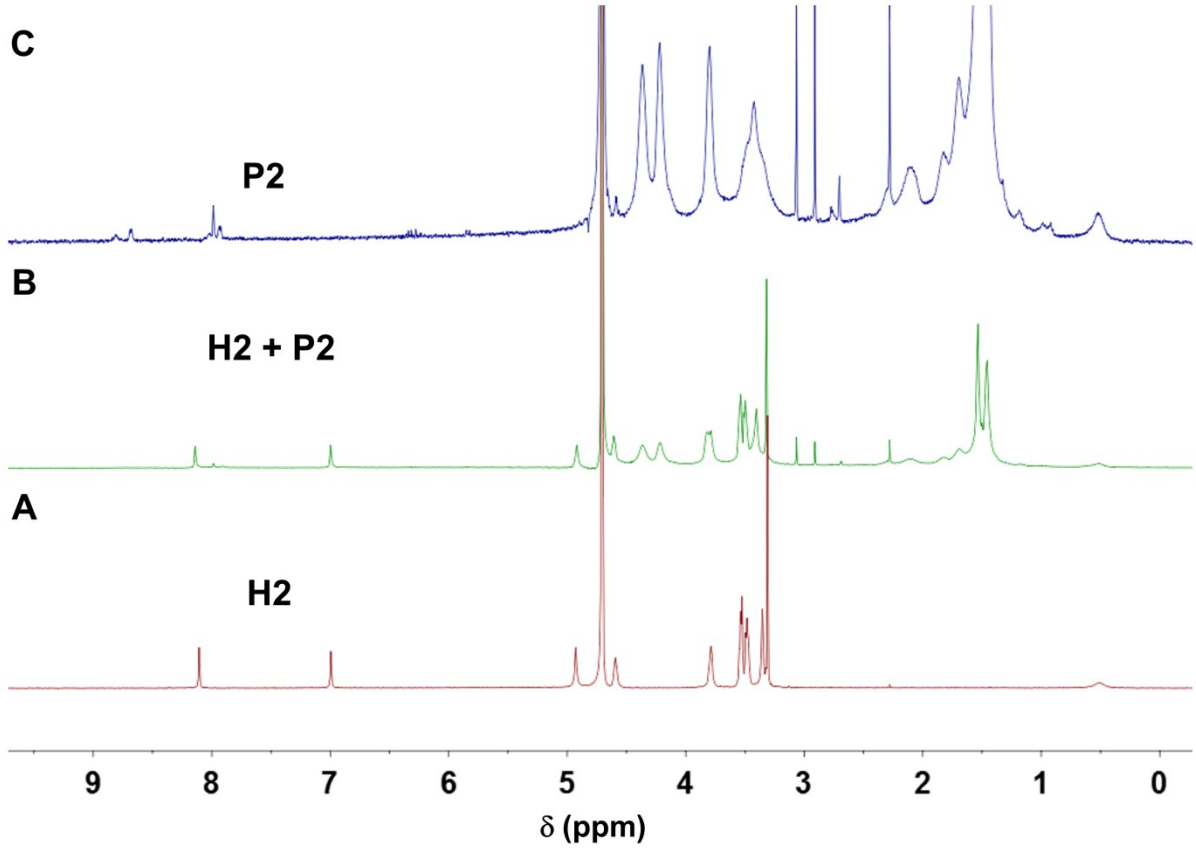


Figure S11 ^{1}H NMR (D_2O, 300 MHz) spectrum of complexation at 37 ℃. A) 1 eq. **H2**, B) mixture of **H2** and **P2**, C) **P2** (5 mg mL^{-1}).

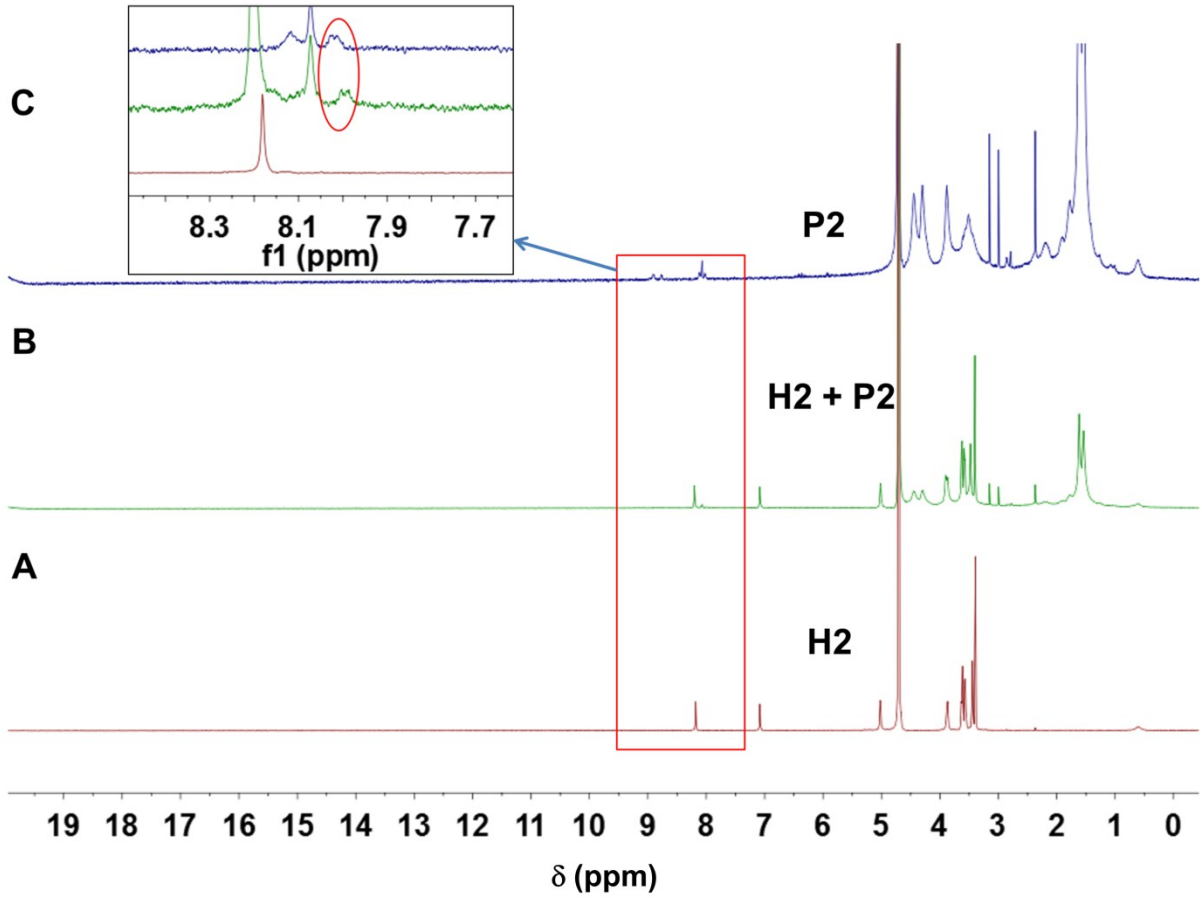


Figure S12 ^{1}H NMR (D_2O, 300 MHz) spectrum of complexation at 45 ℃. A) 1 eq. **H2**, B) mixture of **H2** and **P2**, C) **P2** (5 mg mL^{-1}).

Hydrolysis measurement of polymers or complexation between polymer and pillar[5] arene in D_2O at different pH at 37 ℃

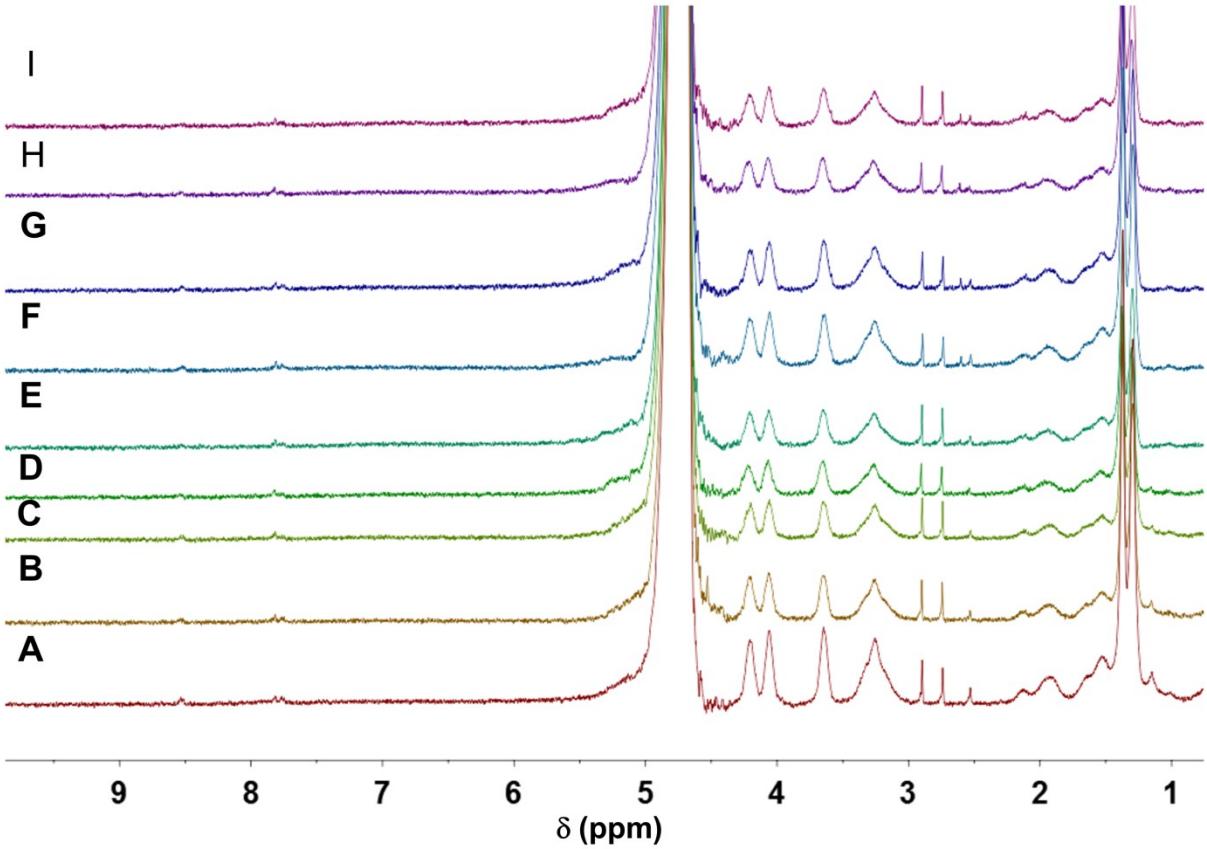


Figure S13 ^{1}H NMR (D_2O, 300 MHz) spectrum of hydrolysis of **P2** (5 mg mL^{-1}) at pH 7.4. A) 0 h, B) 3 h, C) 24 h, D) 48 h, E) 96 h, F) 120 h, G) 168 h, H) 216 h, and I) 264 h.

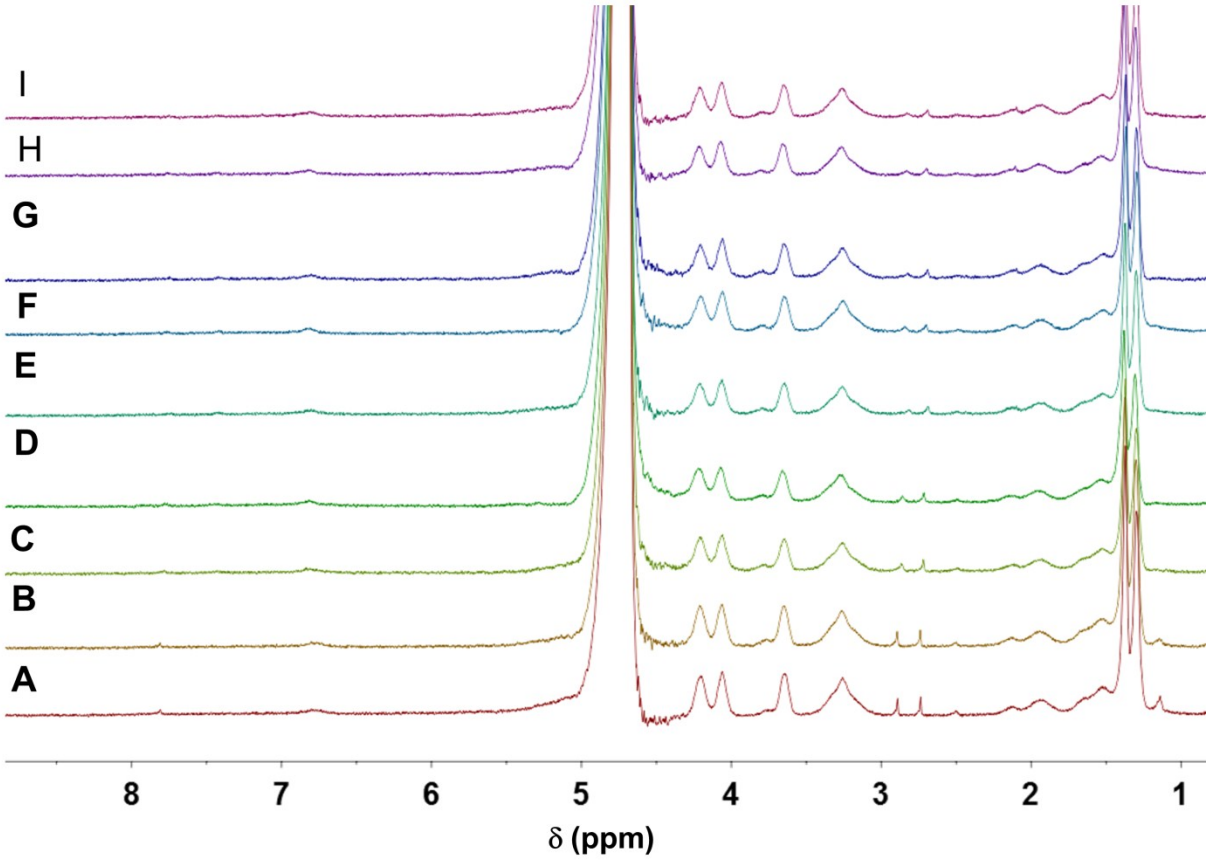


Figure S14 ^{1}H NMR (D_2O, 300 MHz) spectrum of hydrolysis of **P2** (5 mg mL^{-1}) with 1 eq. **H1** at pH 7.4. A) 0 h, B) 3 h, C) 24 h, D) 48 h, E) 96 h, F) 120 h, G) 168 h, H) 216 h, and I) 264 h.

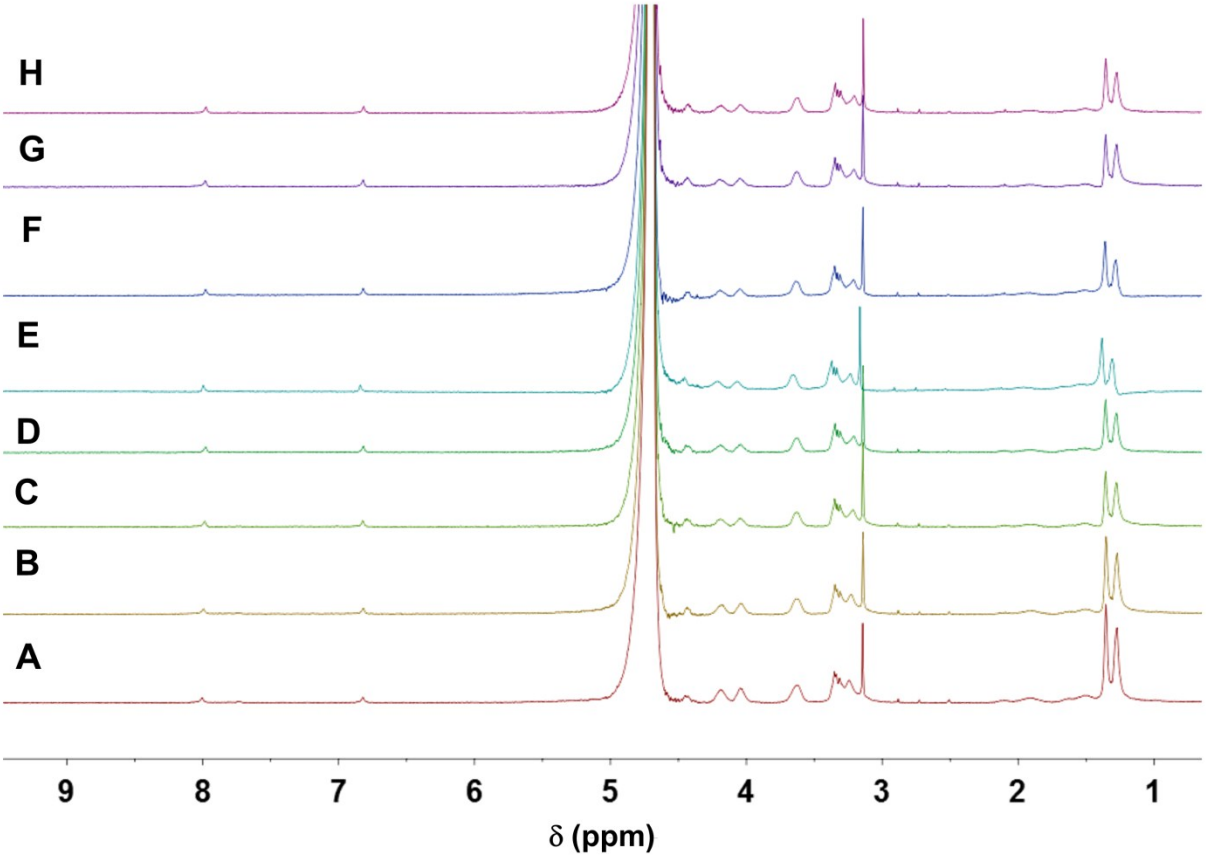


Figure S15 ^{1}H NMR (D_2O, 300 MHz) spectrum of hydrolysis of **P2** (5 mg mL^{-1}) with 1 eq. **H2** at pH 7.4. A) 0 h, B) 24 h, C) 48 h, D) 96 h, E) 120 h, F) 168 h, G) 216 h, and H) 264 h.

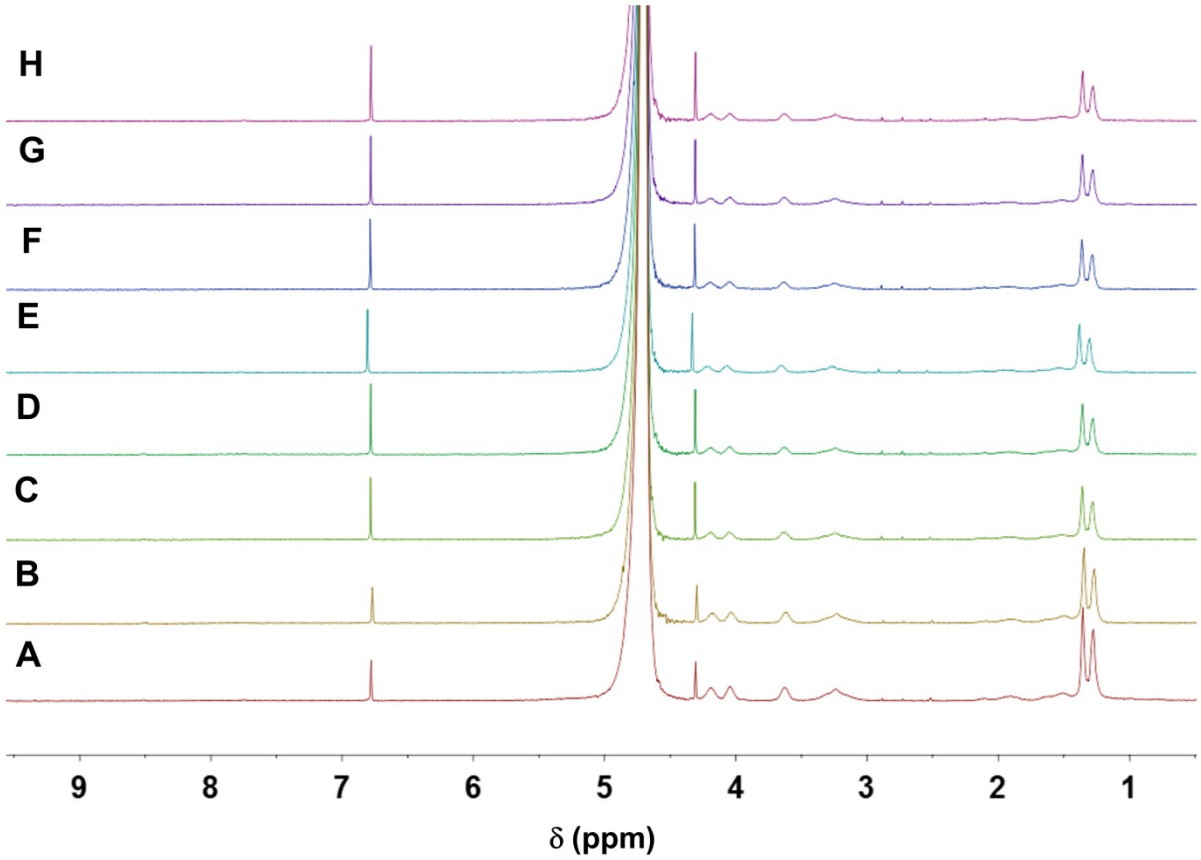


Figure S16 ^{1}H NMR (D_2O, 300 MHz) spectrum of hydrolysis of **P2** (5 mg mL^{-1}) with 5 eq. **G1** at pH 7.4. A) 0 h, B) 24 h, C) 48 h, D) 96 h, E) 120 h, F) 168 h, G) 216 h, and H) 264 h.

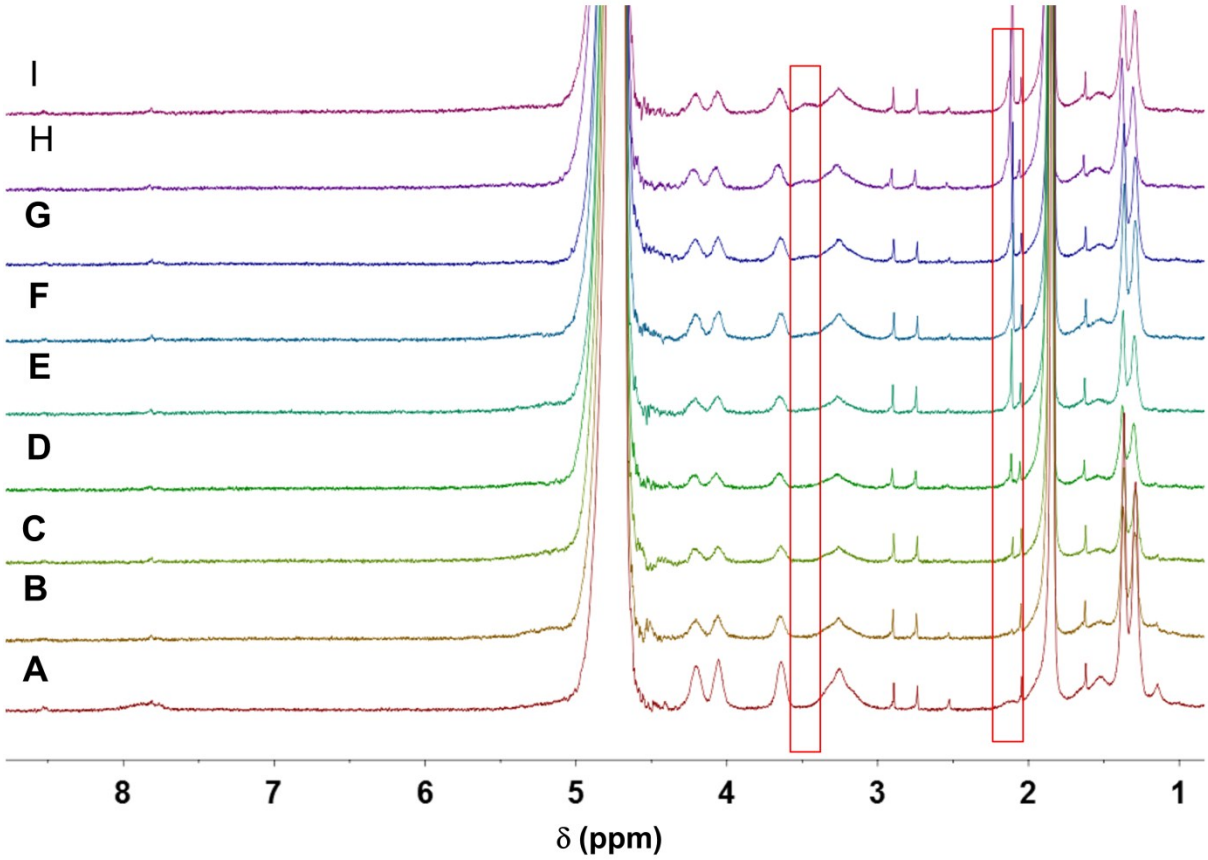


Figure S17 ^{1}H NMR (D_2O, 300 MHz) spectrum of hydrolysis of **P2** (5 mg mL^{-1}) at pH 5.2. A) 0 h, B) 3 h, C) 24 h, D) 48 h, E) 96 h, F) 120 h, G) 168 h, H) 216 h, and I) 264 h.

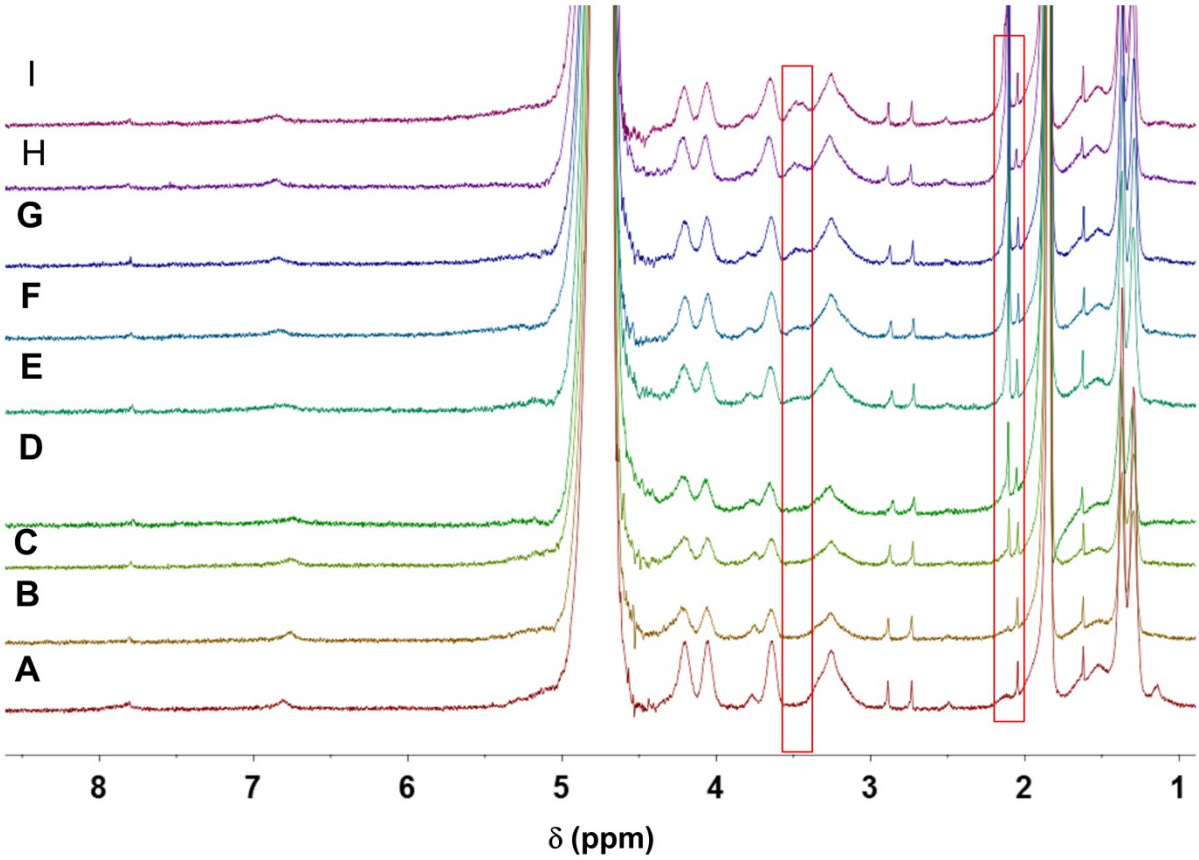


Figure S18 ^{1}H NMR (D_2O, 300 MHz) spectrum of hydrolysis of **P2** (5 mg mL^{-1}) with 1 eq. **H1** at pH 5.2. A) 0 h, B) 3 h, C) 24 h, D) 48 h, E) 96 h, F) 120 h, G) 168 h, H) 216 h, and I) 264 h.

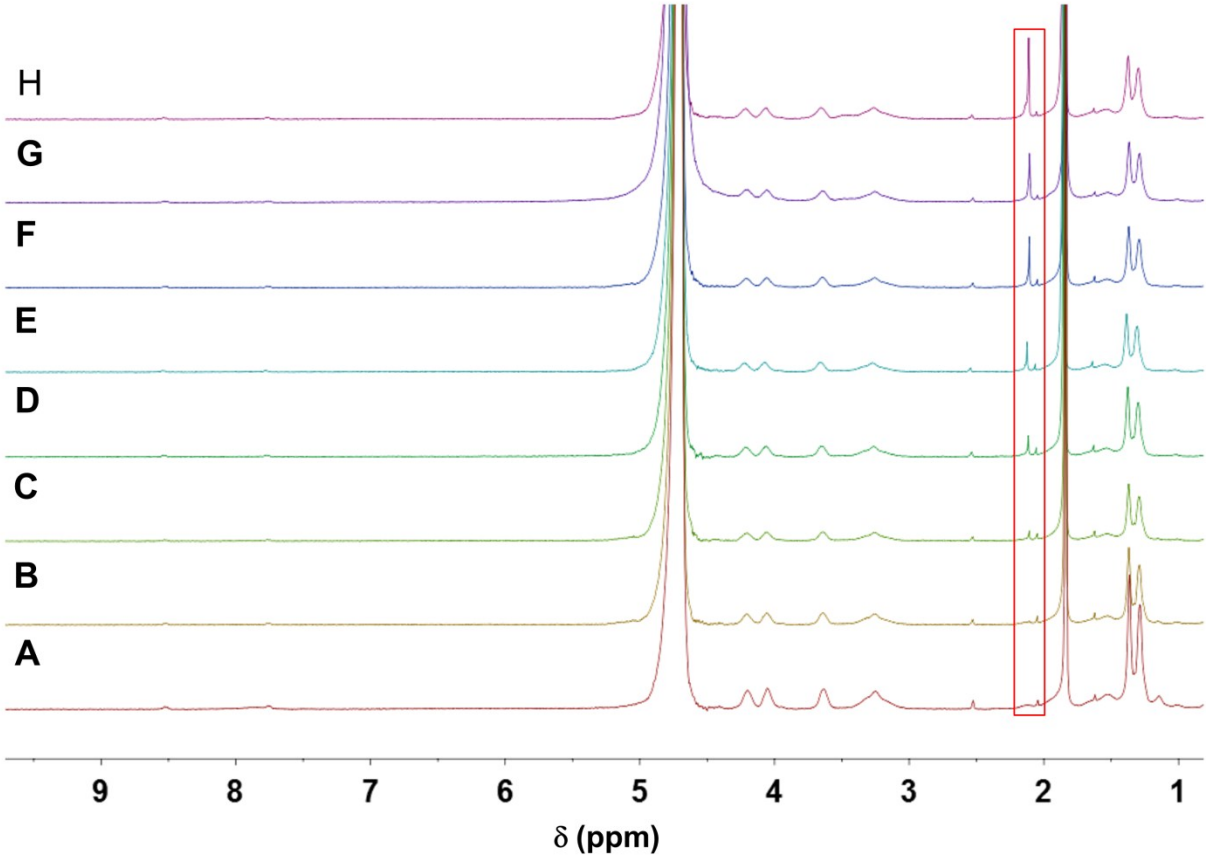


Figure S19 ^{1}H NMR (D_2O, 300 MHz) spectrum of hydrolysis of **P1** (5 mg mL^{-1}) at pH 5.2 A) 0 h, B) 24 h, C) 48 h, D) 96 h, E) 120 h, F) 168 h, G) 216 h, and H) 264 h.

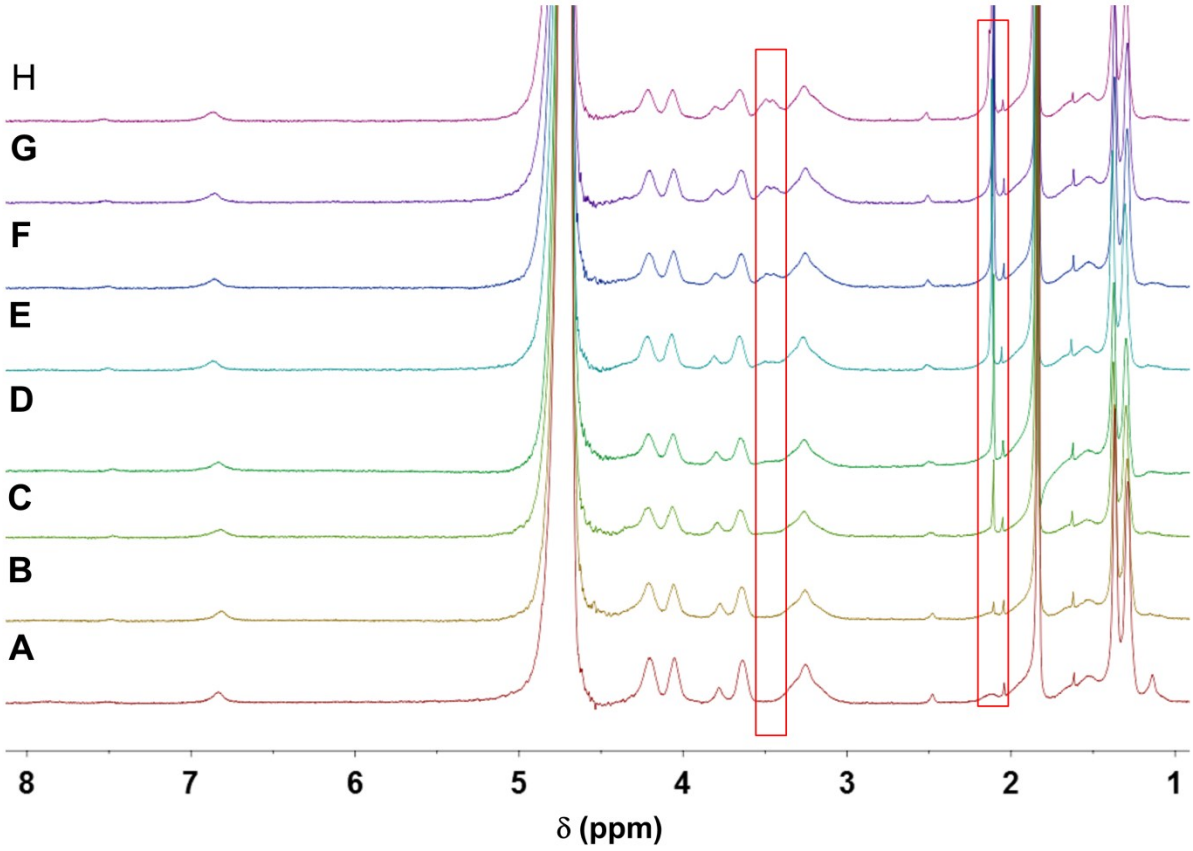


Figure S20 ^{1}H NMR (D_2O, 300 MHz) spectrum of hydrolysis of **P1** (5 mg mL^{-1}) with 1 eq. **H1** at pH 5.2. A) 0 h, B) 24 h, C) 48 h, D) 96 h, E) 120 h, F) 168 h, G) 216 h, and H) 264 h.

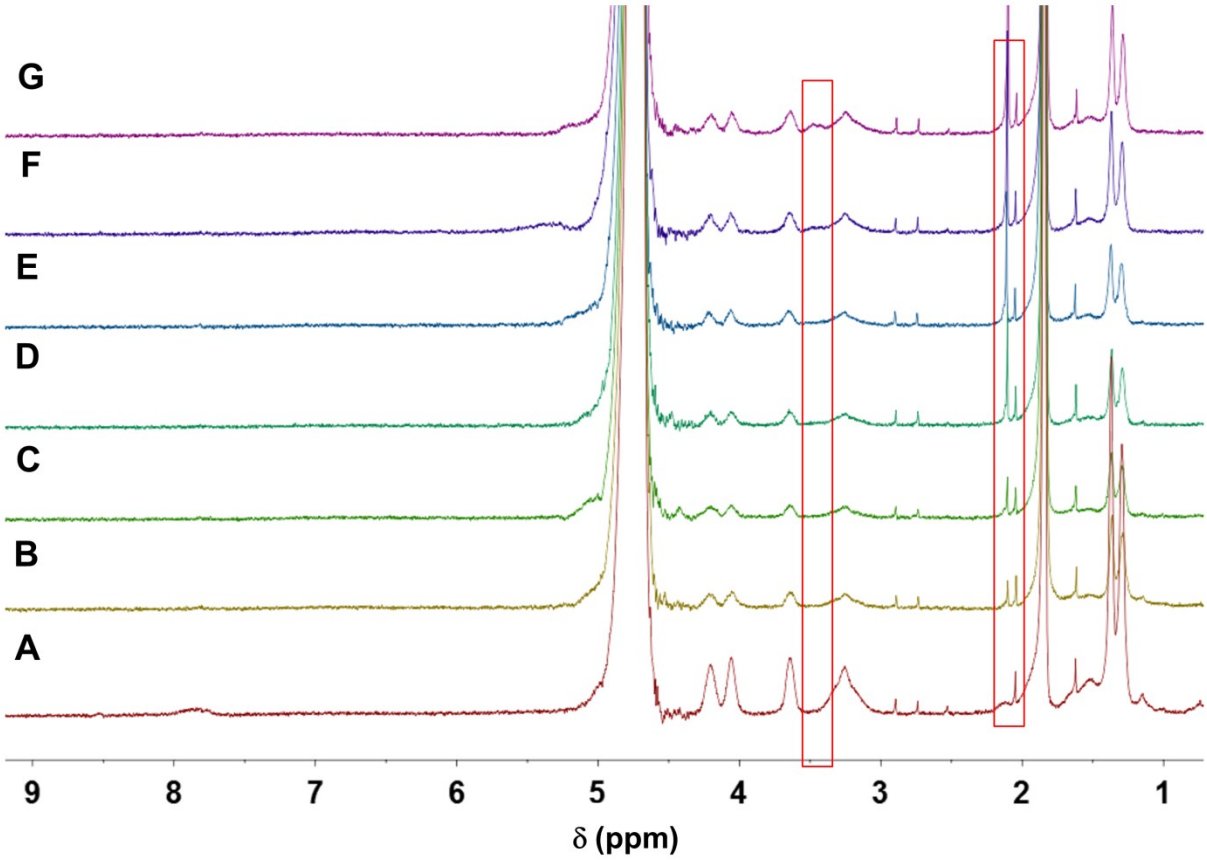


Figure S21 ^{1}H NMR (D_2O, 300 MHz) spectrum of hydrolysis of **P3** (5 mg mL^{-1}) at pH 5.2. A) 0 h, B) 24 h, C) 48 h, D) 96 h, E) 120 h, F) 168 h, G) 216 h, and H) 264 h.

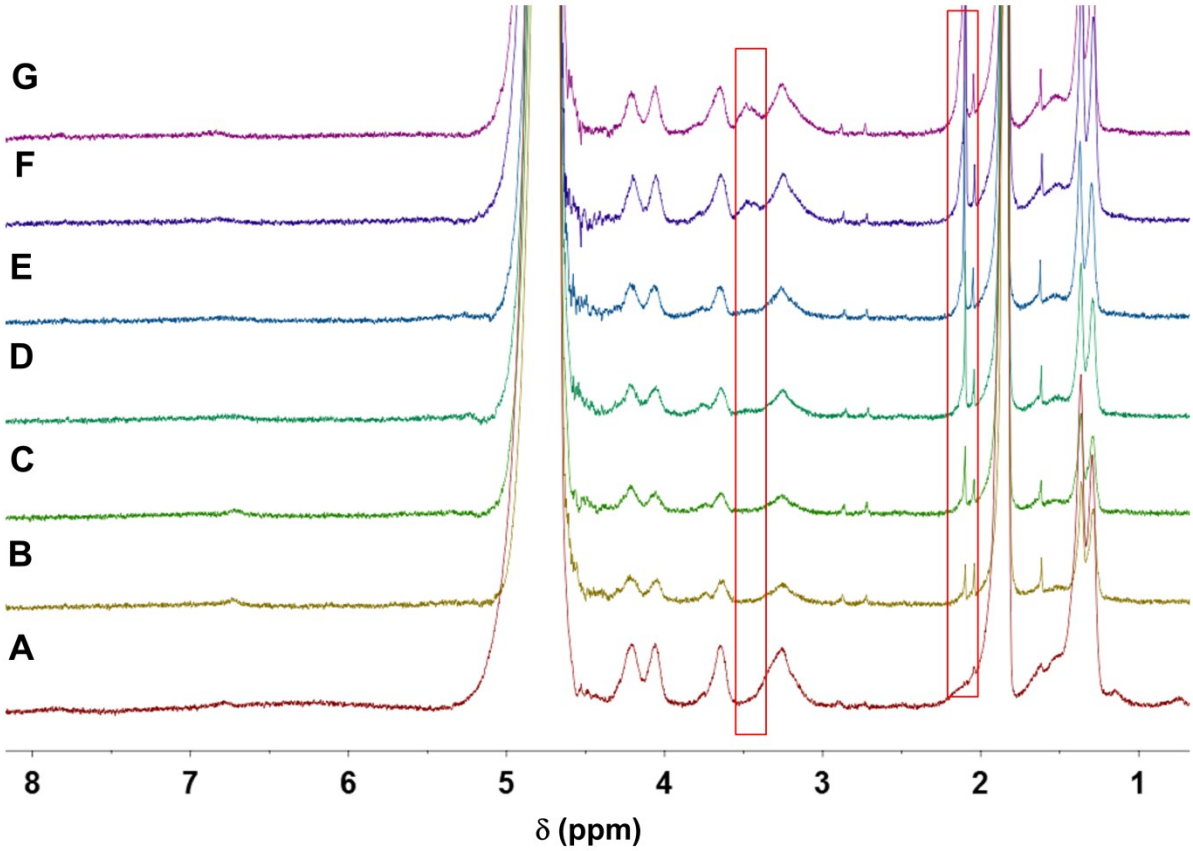


Figure S22 ^{1}H NMR (D_2O, 300 MHz) spectrum of hydrolysis of **P3** (5 mg mL^{-1}) with 1 eq. **H1** at pH 5.2. A) 0 h, B) 24 h, C) 48 h, D) 96 h, E) 120 h, F) 168 h, G) 216 h, and H) 264 h.

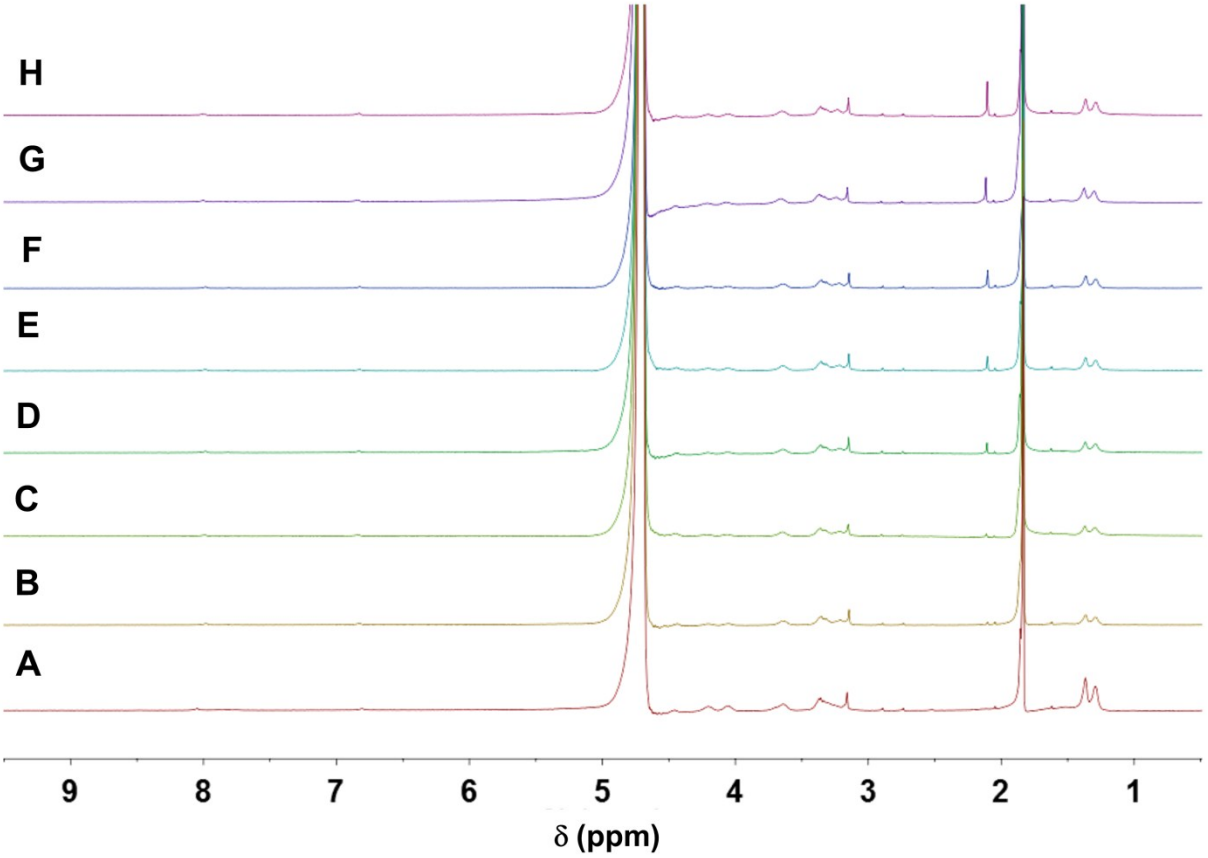


Figure S23 ^{1}H NMR (D_2O, 300 MHz) spectrum of hydrolysis of **P2** (5 mg mL^{-1}) with 1 eq. **H2** at pH 5.2. A) 0 h, B) 24 h, C) 48 h, D) 96 h, E) 120 h, F) 168 h, G) 216 h, and H) 264 h.

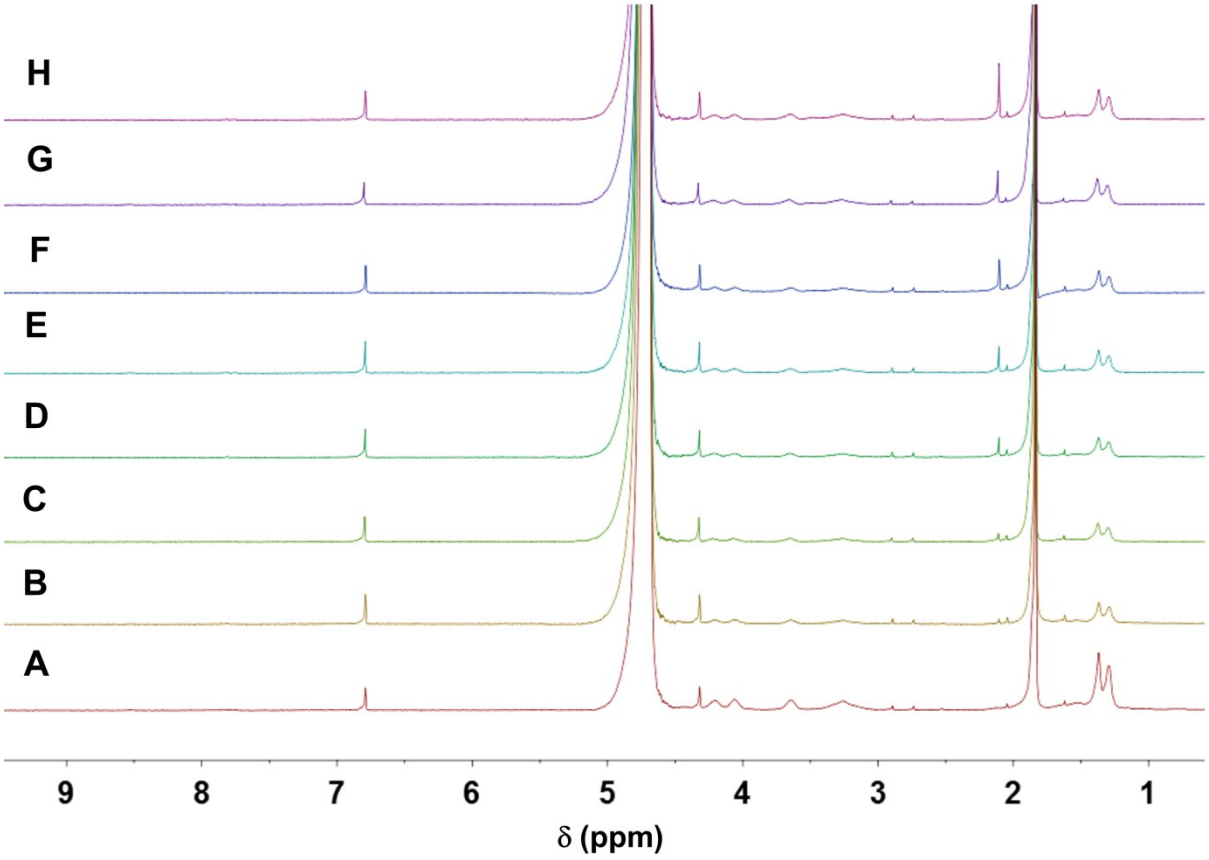


Figure S24 ^{1}H NMR (D_2O, 300 MHz) spectrum of hydrolysis of **P2** (5 mg mL^{-1}) with 5 eq. **G1** at pH 5.2. A) 0 h, B) 24 h, C) 48 h, D) 96 h, E) 120 h, F) 168 h, G) 216 h, and H) 264 h.

Association constant measurement between P2 and H1 or P2 and H2 by ITC

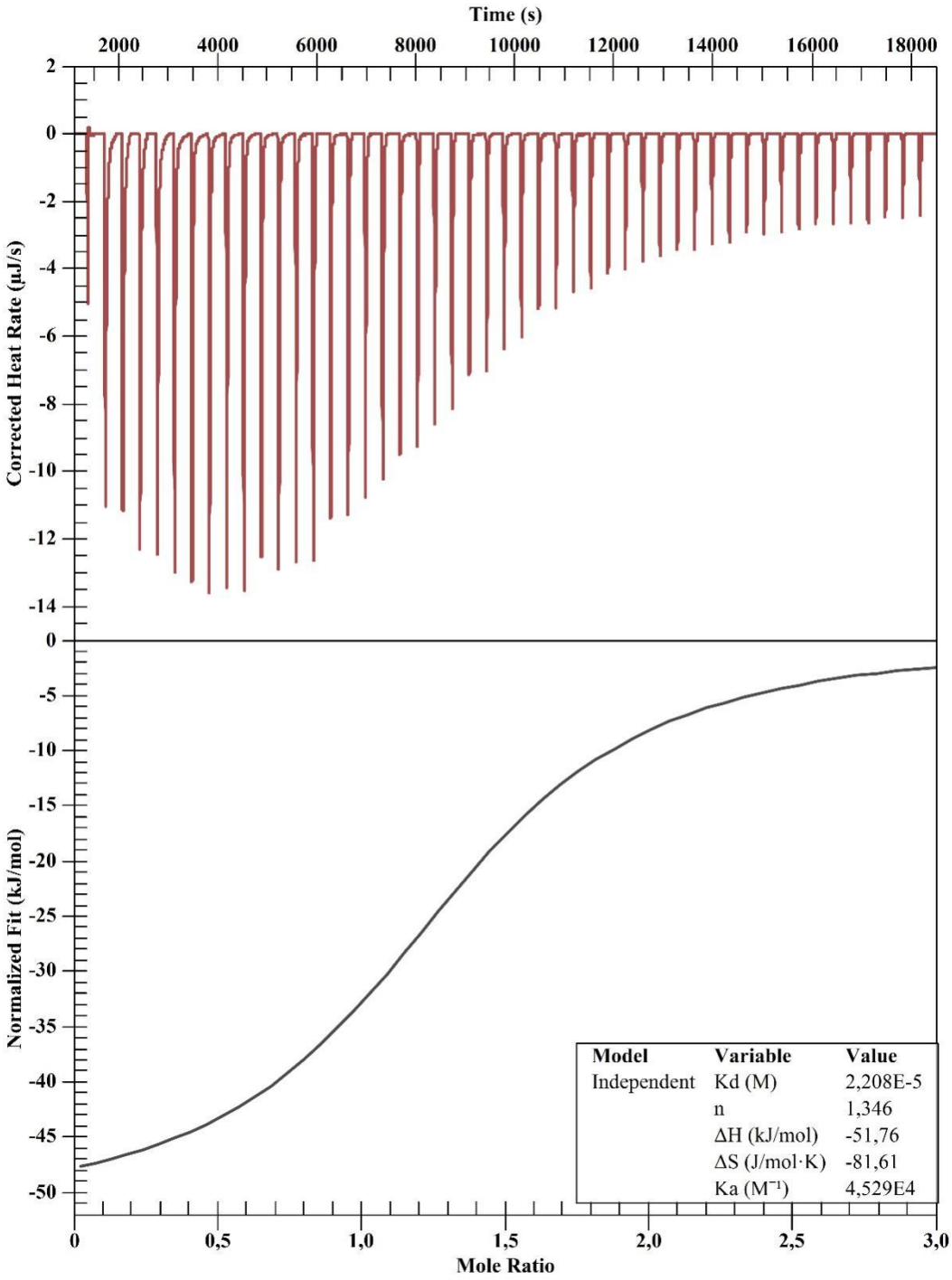


Figure S25 Association constant between **P2** and **H1**.

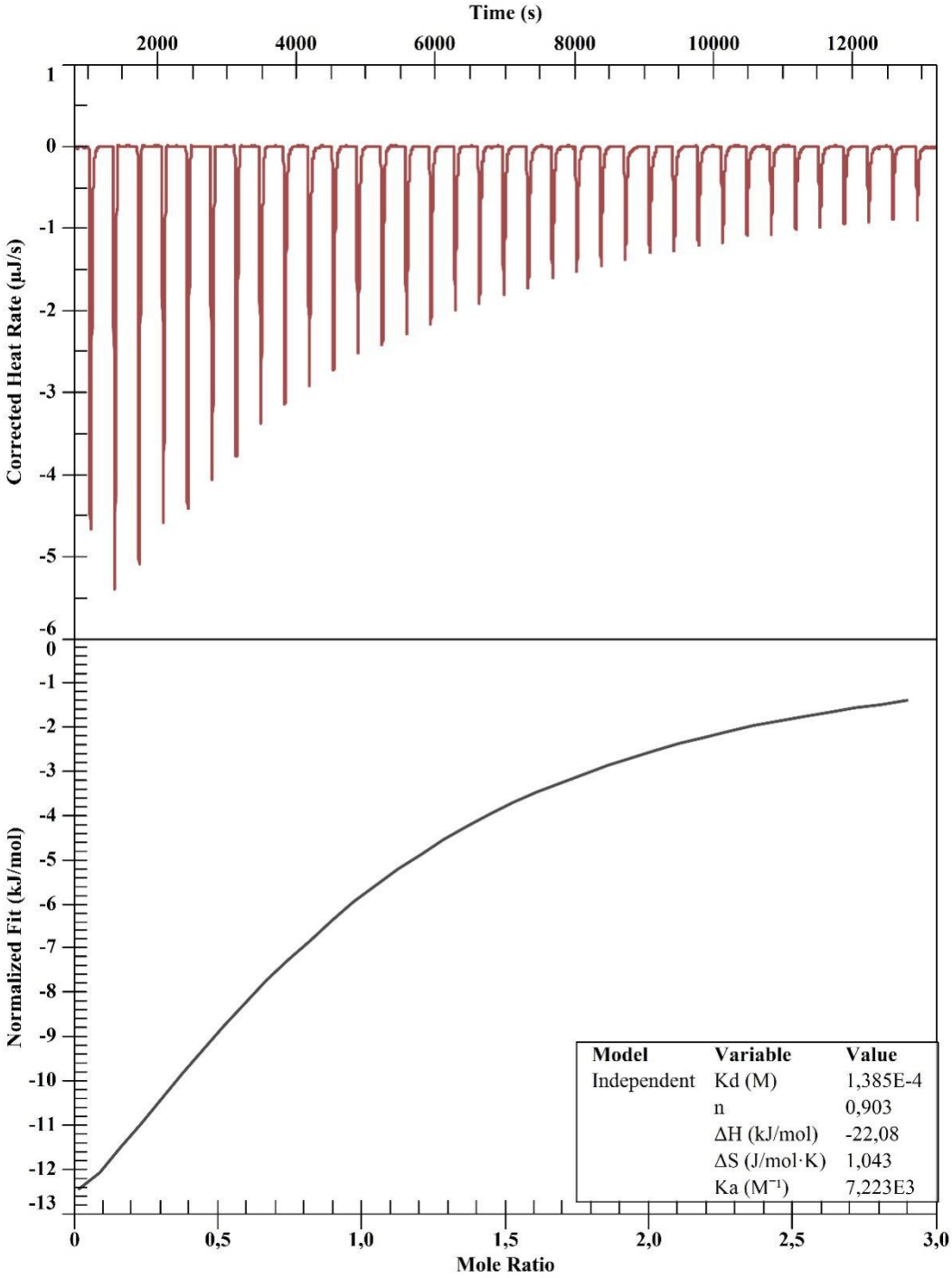


Figure S26 Association constant between **P2** and **H2.**