Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

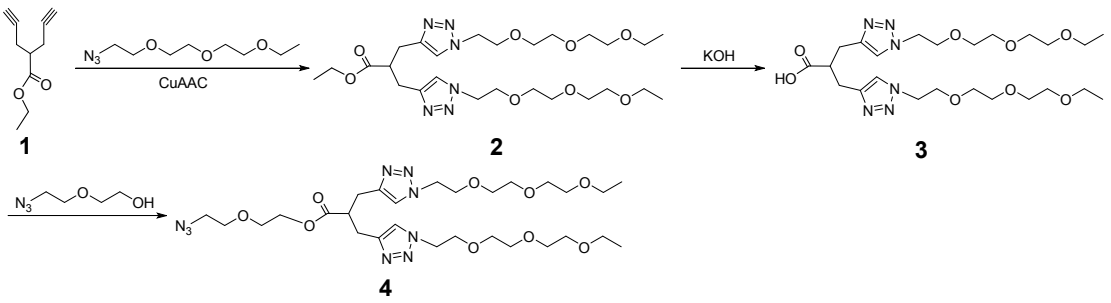
Hyperbranched poly(triazole) with thermal and metal ion dual stimuli-responsiveness

Jianhua Wu, Wenmei Liu, Huijing Han, Ruyi Sun, Meiran Xie* and Xiaojuan Liao*

School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200241, China

E-mail: *mrxie@chem.ecnu.edu.cn; Tel: +86 21 54340058; Fax: +86 21 54340058*

E-mail: xjliao@chem.ecnu.edu.cn; Tel: +86 21 54340105; Fax: +86 21 54340105



Scheme S1. Synthesis of model compound **4**.

Synthesis of 2

To a solution of **1** (4.92 g, 30 mmol) and azido-2-(2-(2-methoxyethoxy)ethoxy)ethane (15.3 g, 75 mmol) in DMF (40 mL) was added $CuSO_4 \cdot 5H_2O$ aqueous solution (1.5 mmol in 1.5 mL of H_2O), after bubbled nitrogen for 30 min, fresh sodium ascorbate aqueous solution (3.0 mmol in 1.5 mL of H_2O) was added. The resulting mixture was stirred at room temperature for 12 h. The mixture was poured into H_2O, then extracted with CH_2Cl_2, and the organic layer was washed with EDTA aqueous solution, H_2O and saturated brine aqueous solution until the aqueous phase became colorless. Combined and concentrated the organic layer, a pale yellow viscous oil **2** (14.3 g) was obtained, and used without purification.

Synthesis of 3

To the solution of **2** (12 g) in CH_3OH (100 mL) and H_2O (10 mL) was added KOH (7.4 g, 42 mmol), and the mixture was refluxed for 8 h. After the removal of the most solvent, it was poured into HCl (6 mol/L), and exacted with CH_2Cl_2. The organic layer was washed with saturated brine aqueous solution, followed by concentrating the organic layer to obtain **3** as a pale yellow viscous oil (10.1 g), and used without purification.

Synthesis of 4

To the solution of **3** (8.13 g) and 2-(2-azidoethoxy)ethanol (2.95 g, 22.5 mmol) in CH_2Cl_2 (60 mL) were added EDCI (3.44 g, 18 mmol) and DMAP (0.37 g, 3 mmol) at 0 ^oC, the resulting mixture was warmed to room temperature and stirred for 24 h. The mixture was diluted with CH_2Cl_2 (100 mL), the organic layer was washed with water and saturated brine, and dried over anhydrous $MgSO_4$. After removal of solvent, the crude product was purified using column chromatography (ethyl acetate/methanol = 30:1 to 10:1) to yield a pale yellow liquid (7.8 g, 93.6%). ^1H NMR (500 MHz, D_2O, ppm): δ 7.79 (s, triazole-*H*), 4.51 (t, =N-NC*H*$_2$CH$_2$O), 4.11 (t, -C*H*$_2$C=O), 3.87 (t, =N-NCH$_2$C*H*$_2$O), 3.49 (m, -OC*H*$_2$-), 3.34, 2.78 (t, N$_3$C*H*$_2$-), 3.18 (m, O=CC*H*CH$_2$), 3.02-2.97(m, -OC*H*$_2$-), 1.08 (t, -C*H*$_3$). ^{13}C NMR (125 MHz, D_2O) δ 175.7, 144.6, 124.3, 69.7, 69.6, 69.44, 69.3, 68.9, 68.8, 68.3, 66.5, 64.25, 50.1, 49.9, 45.6, 26.8, 14.1. IR (cm^{-1}): 3145 (triazole), 2960-2870 (-CH_2), 2100 (-N_3), 2115 (C≡C), 1730 (C=O).

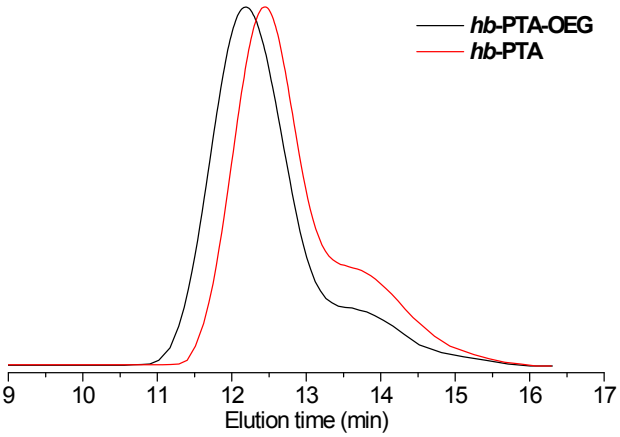


Fig. S1 GPC curves of (a) ***hb*-PTA** and (b) ***hb*-PTA-OEG**.

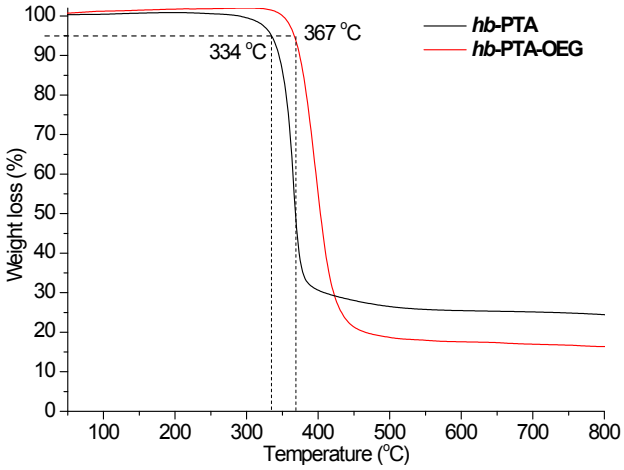


Fig. S2 TGA curves of (a) ***hb*-PTA** and (b) ***hb*-PTA-OEG**.

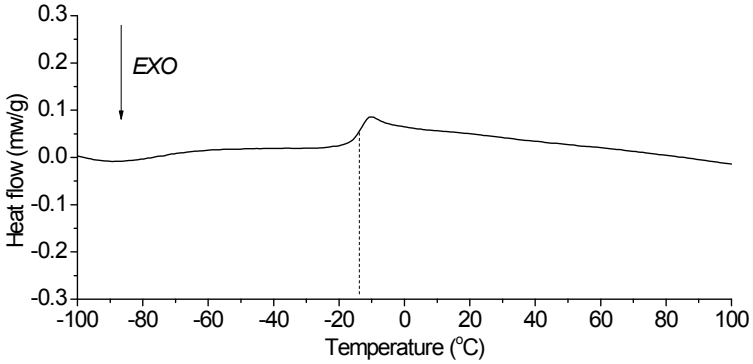


Fig. S3 DSC curve of ***hb*-PTA-OEG**.

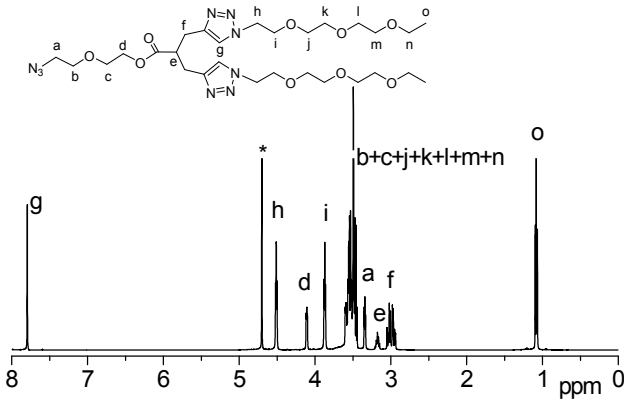


Fig. S4 ^{1}H NMR spectrum of **4** in D_2O.

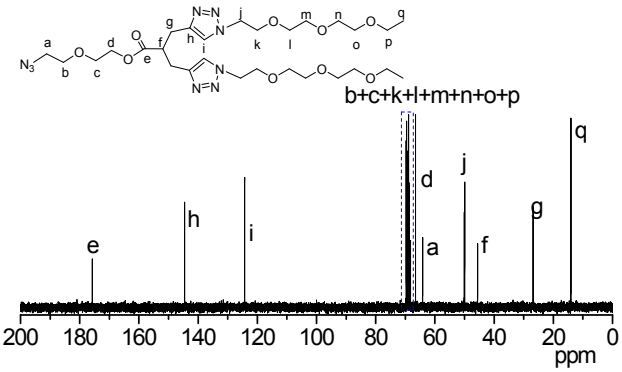


Fig. S5 ^{13}C NMR spectrum of **4** in D_2O.

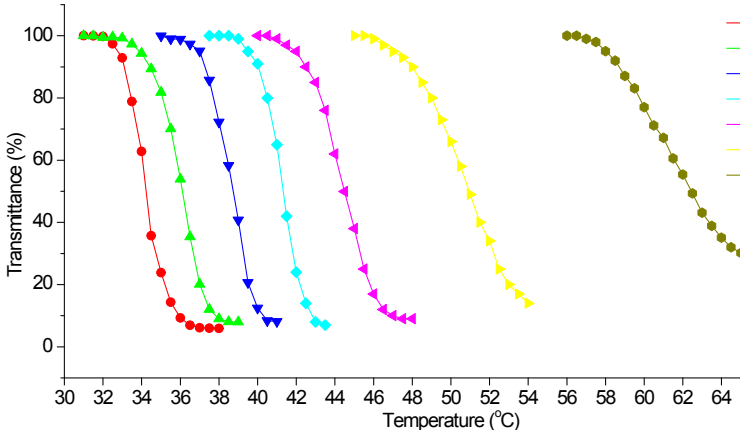


Fig. S6 Transmittance versus temperature for ***hb*-PTA-OEG** (0.2 wt%) with different Ag^+ ion concentrations (1×10^{-5}, 2×10^{-5}, 3×10^{-5}, 4×10^{-5}, 5×10^{-5}, 1×10^{-4}, and 2×10^{-4} mmol/mL).

Table S1. Solubility of hyperbranched polymers

	Et_2O	DCM	$CHCl_3$	$(CH_3)_2CO$	CH_3OH	DMF	THF	MeCN	H_2O
***hb*-PTA**	□□	□□	□□	□□	□□	□□	□□	□□	□□
***hb*-PTA-OEG**	□□	□□	□□	□□	□□	□□	□□	□□	□□