Electronic Supplementary Material (ESI) for Polymer Chemistry.

A pH-responsive Amphiphilic Supramolecular Graft Copolymer Constructed by Crown Ether Based Molecular Recognition†

Kecheng Jie, Yujuan Zhou and Xiaofan Ji*

Department of Chemistry, Zhejiang University, Hangzhou, Zhejiang 310027, P. R. China; Fax and Tel: +86-571-8795-3189; Email address: xiaofanji@zju.edu.cn.

Supporting Information (7 pages)

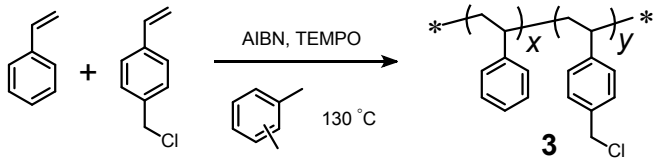
1.	*Materials and methods*	*S2*
2.	*Synthesis of polymers **3**, **1** and **2***	*S3*
3.	*Comparison of the ^{1}H NMR spectra of **3** and **1***	*S6*
4.	*Characterization of the grafting process*	*S6*
	References	*S7*

1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Side chain polymer **2**[S1] was prepared according to the published procedure. Polymer **3** was also prepared according to the published procedure.[S2] NMR spectra were recorded with a Bruker Avance DMX 400 spectrophotometer using the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) with a Waters 1515 pump and Waters 1515 differential refractive index detector (set at 30 ºC). It used a series of three linear Styragel columns (HT2, HT4, and HT5) at an oven temperature of 45 ºC. The eluent was THF at a flow rate of 1.0 mL/min. A series of low polydispersity polystyrene standards was employed for the GPC calibration. Dynamic light scattering (DLS) was carried out on a Malvern Nanosizer S instrument at room temperature. SEM investigations were carried out on a JEOL 6390LV instrument. Transmission electron microscopy investigations were carried out on a HITACHI HT-7700 instrument.

*2. Synthesis of polymers **3**, **1** and **2***

*2.1. Synthesis of polymer **3***



A mixture of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (832 mg, 5.33 mmol, 2.5 eq) and 2,2-azobisisobutyronitrile (AIBN, 350 mg, 2.13 mmol, 1.0 eq) was added to a 50 mL Schlenk flask equipped with a stirring bar. This flask was then deoxygenated by degassing and backfilling with nitrogen for two times and charged with deoxygenated styrene (10.2 mL, 107 mmol, 25 eq) and *p*-chloromethylstyrene (3.30 mL, 21.3 mmol, 5 eq) through syringes. After three freeze-pump-thaw cycles, the reaction mixture was heated by immersing into a 130 °C oil bath for 72 h. The polymerization was stopped through cooling with an ice bath. The reaction mixture was dissolved in 50 mL of toluene and quickly passed through neutral Al_2O_3 column, and then precipitated into cold methanol (500 mL). The precipitate was collected by filtration and dried overnight in a vacuum to give **3** as a white power (Solution polymerization in xylene: 5.70 g, 45 %; $M_{n,GPC}$ = 8.11 kDa, $M_{w,GPC}$ = 9.06 kDa, PDI = 1.11). The ^{1}H NMR spectrum of compound **3** is shown in Fig. S1. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 7.23–6.21 (m, 40H, *Ar*), 4.53 (m, 2H, Ar-CH_2-), 2.00–1.61 (m, mainchain, 4H), 1.53–1.18 (m, mainchain, 14H). The value of *x*/*y* is 7.2/1, *x* = 65, and *y* = 9.0 as measured by NMR and GPC.

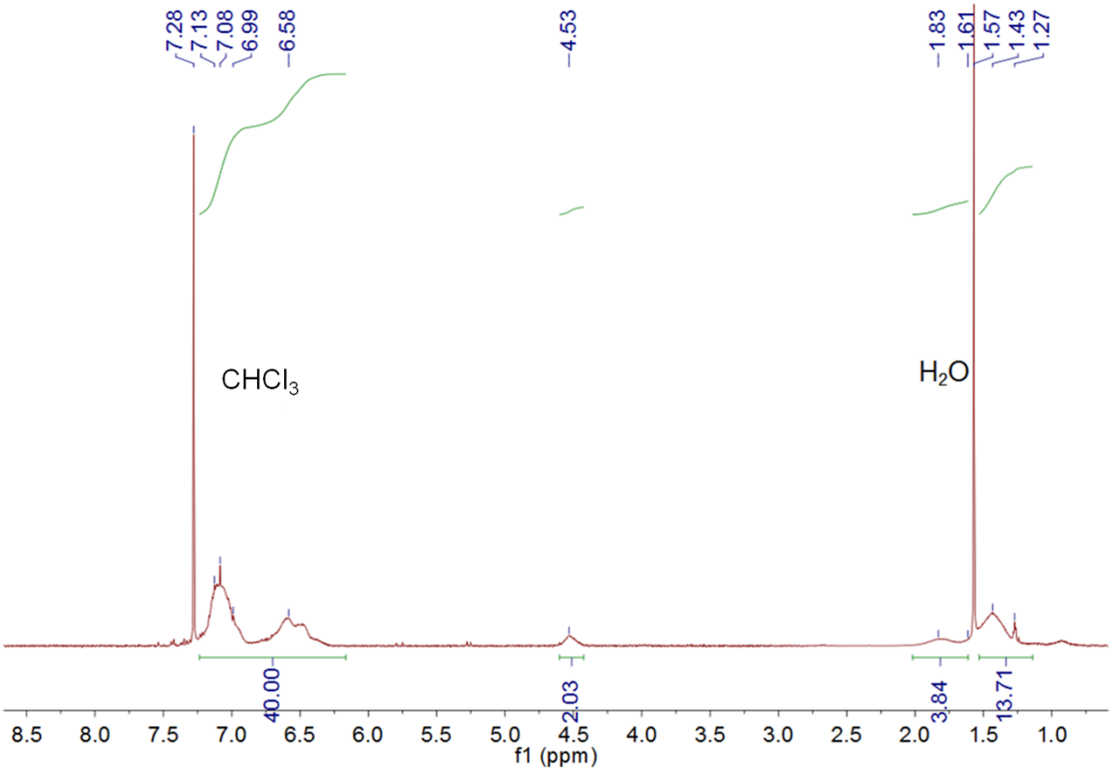
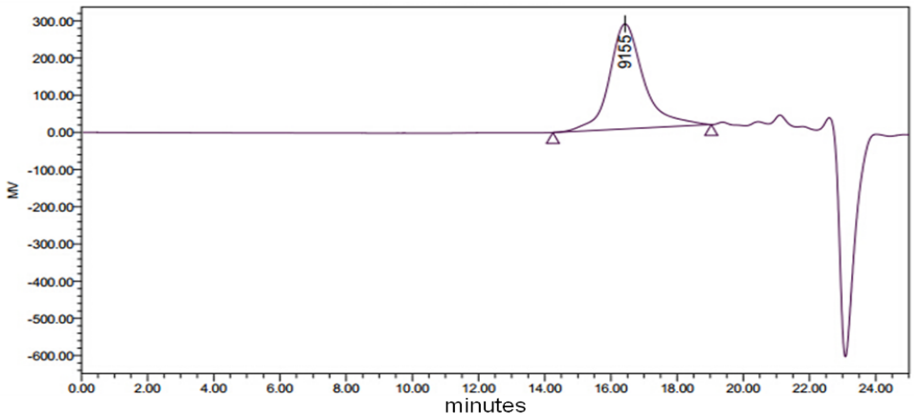


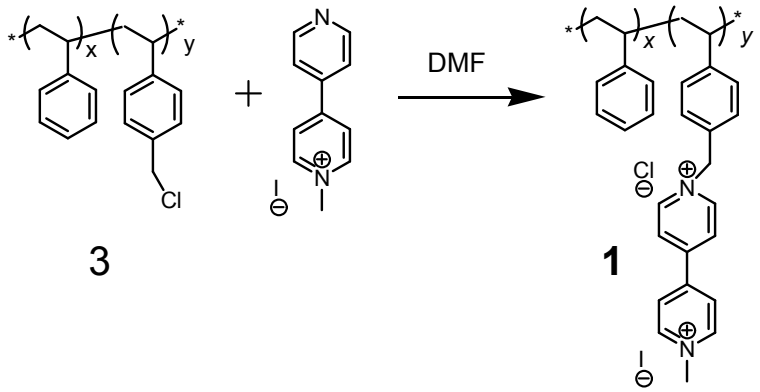
Fig. S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **3**.



	Mn	Mw	Mp	Mz	Mz + 1	dispersion	Mz/Mw	Mz + 1/Mw
3	8114	9062	9155	9984	10993	1.116836	1.101663	1.212992

Fig. S2. GPC data of **3**.

*2.2. Synthesis of polymer **1***



A mixture of compound **3** (5.00 g, 0.616 mmol) and 1-methyl-4,4'-bipyridine (18.4 g, 61.6 mmol) in DMF (50 mL) was stirred at 80 °C overnight. After reaction, the solvent was evaporated and the residue was dissloved in 2.00 mL chloroform. Then the solution was dropped into cold methanol (100 mL, twice) and the precipitate was collected by filtration. The solid was dried overnight in a vacuum to give a brown power (5.85 g, 88 %). The ^{1}H NMR spectrum of polymer **1** is shown in Fig. S2. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 9.32 (m, 4H, pyridine), 8.86 (m, 4H, pyridine), 7.02 (m, 29H, Ar), 6.52 (m, 18H, Ar), 4.54 (m, 5H, Ar-CH_2-pyridine and methyl), 1.71-1.19 (m, 20H, main chain).

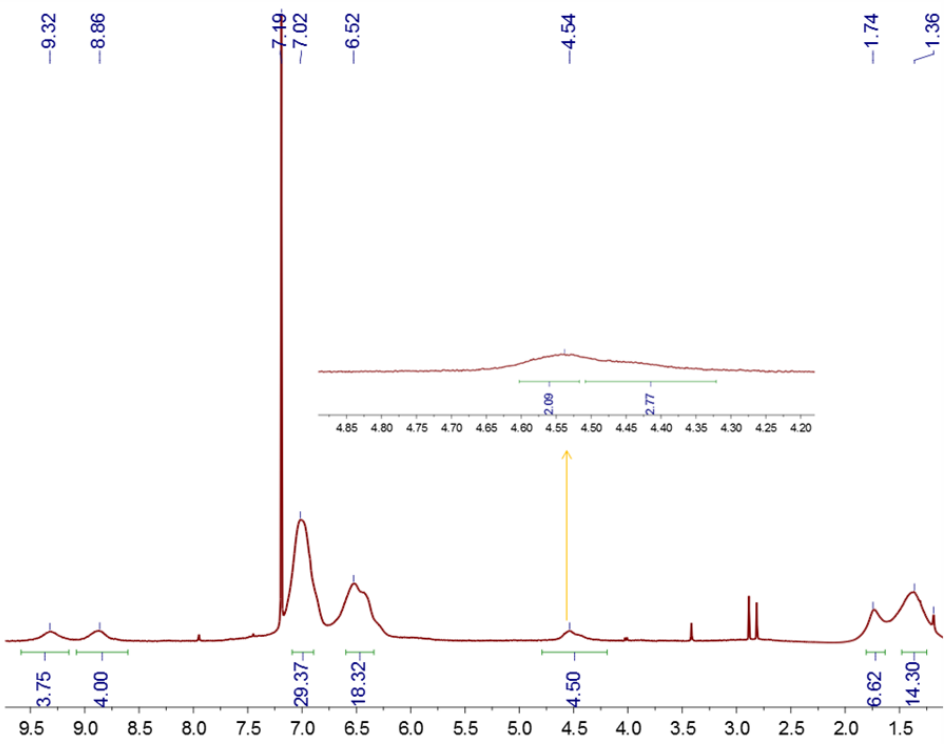


Fig. S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **1**.

*2.3. ^{1}H NMR spectrum of polymer **2***

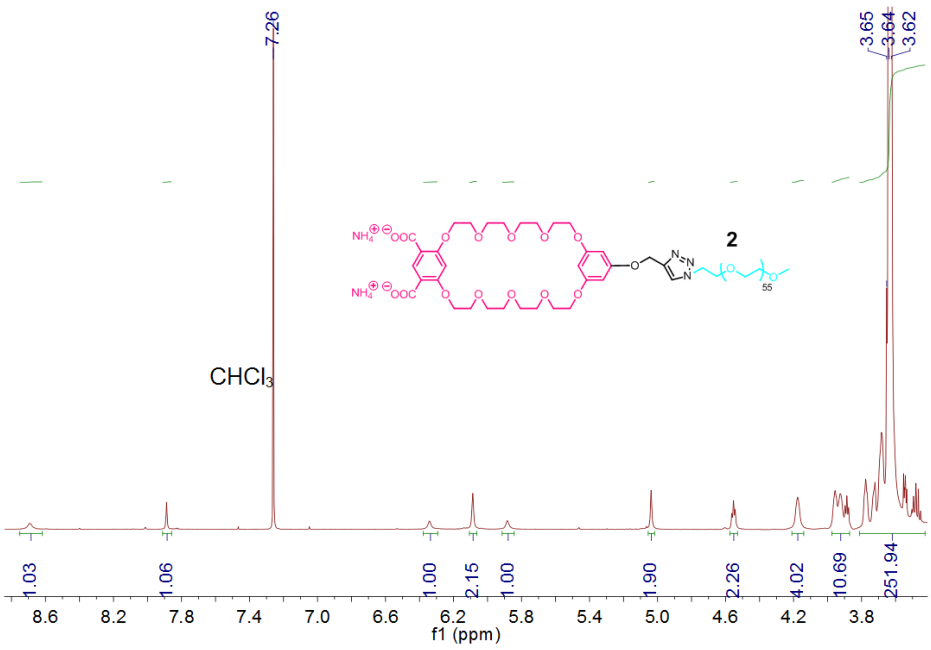


Fig. S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **2**.

*3. Comparison of the ^{1}H NMR spectra of **3** and **1***

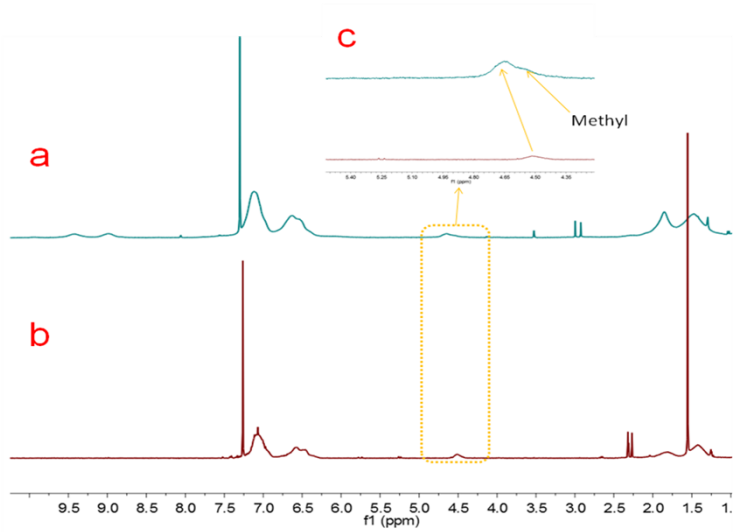


Fig. S5. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 293 K): (a) **1** (5.00 mM); (b) **3** (5.00 mM); (c) Enlarged picture of peaks at about 4.5 ppm.

4. Characterization of the grafting process

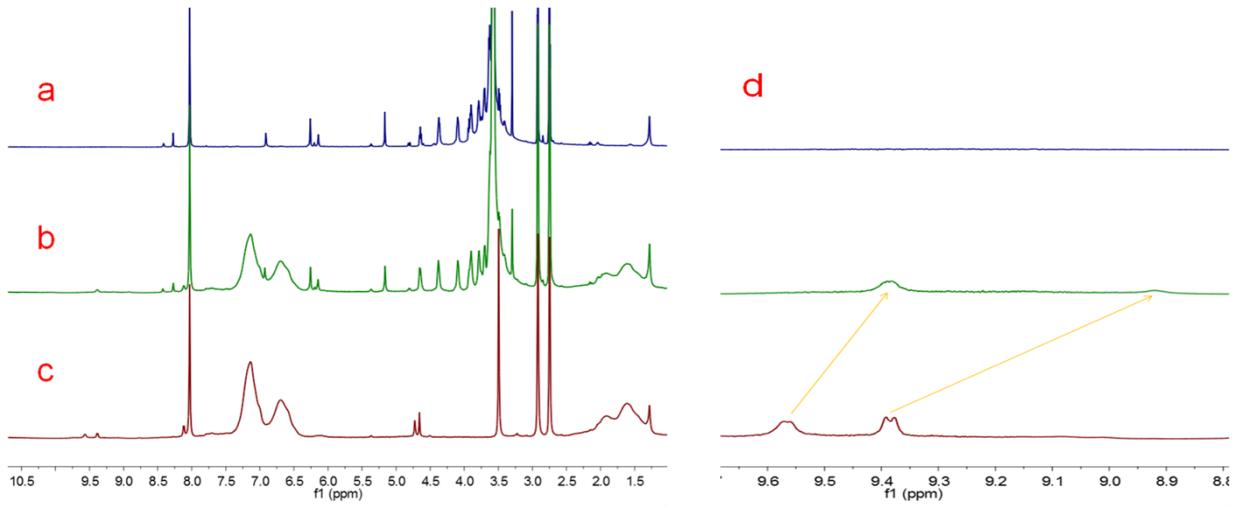


Fig. S6. Partial ^{1}H NMR spectra (400 MHz, DMF-d_7, 293 K): (a) **2** (9.00 mM); (b) **2** (9.00 mM) and **1** (1 mM); (c) **1** (1 mM); (d) Enlarged picture of peaks from 8.8 to 9.7 ppm. The two peaks refer to the protons on the paraquat moities.

Reference

S1. (a) X. Ji, K. Zhu, X. Yan, Y. Ma,; J. Li, B. Hu, Y. Yu, F. Huang, *Macromol. Rapid Commun.*, 2012, **33**, 1197; (b) X. Ji, J. Li, J. Chen, X. Chi, K. Zhu, X. Yan, M. Zhang and F. Huang, *Macromolecules*, 2012, **45**, 6457.

S2. X. Ji, J. Chen and M. Xue, *Macromol. Chem. Phys.*, 2014, **215**, 536.