Supporting Information

Synthesis and properties of pH-cleavable toothbrush-like copolymers comprising multi-reactive Y junctions and linear or cyclic backbone

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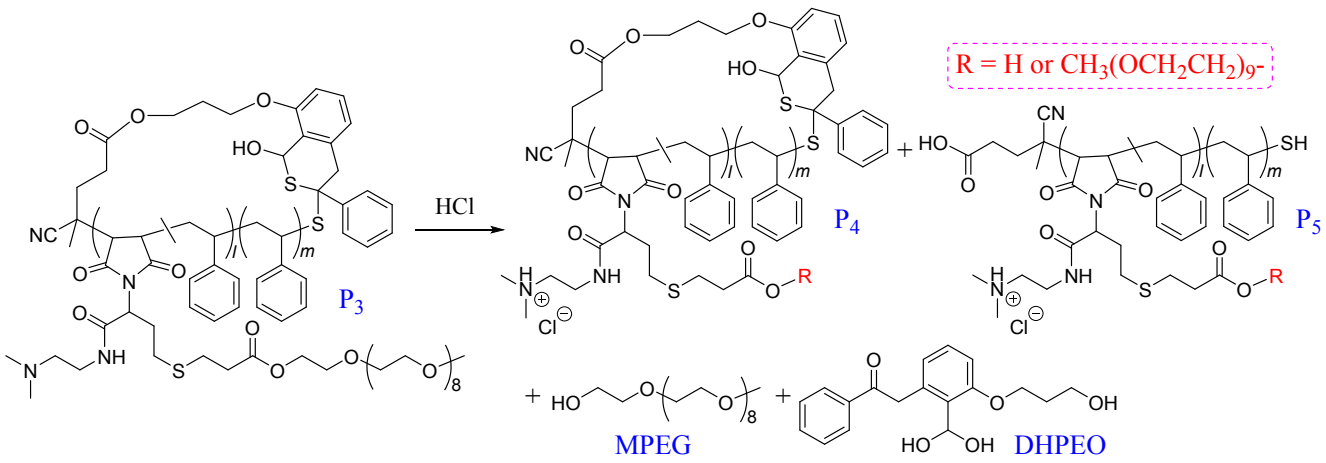

Scheme S1 Main products obtained by acid-triggered hydrolysis of P_3, in which P_4 with cyclic backbone and P_5 with linear backbone have the average number of PEG grafts in the range of 0 and 6.

Table S1 Results for synthesis of P(St-*co*-MTL) random copolymers and P(St-*co*-MTL)-*b*-PSt diblock copolymers via FBCP-mediated RAFT copolymerization of MTL with St[a]

run	t (h)	C_{MTL}[b]	C_{St}[b]	$M_{n,GPC}$ (Da)[c]	Đ[c]	m_{MTL}[d]	m_{St}[d]	$M_{n,NMR}$ (Da)[e]
1	0.5	0.30	0.012	820	1.08	1.8	2.4	1060
2	1	0.59	0.026	1500	1.09	3.5	5.2	1690
3	1.5	0.84	0.046	2230	1.09	5.0	9.2	2400
4	2	1	0.060	2750	1.10	6	12	2890
5	4	1	0.100	3640	1.10	6	20	3720
6	6	1	0.130	4300	1.09	6	26	4350
7	8	1	0.155	4720	1.09	6	31	4870
8	10	1	0.175	5150	1.09	6	35	5280
9	14	1	0.210	5960	1.07	6	42	6010
10	20	1	0.260	6970	1.08	6	52	7050

[a] Polymerization condition: $[St]_0:[MTL]_0:[FBCP]_0:[AIBN]_0$ = 200:6:1:0.1, $[St]_0 + [MTL]_0$ = 3.0 mol L^{-1}, in DMSO-d_6 at 70 °C. [b] Monomer conversion determined by ^1H NMR analysis. [c] Apparent molar mass ($M_{n,GPC}$) and dispersity (Đ) given by GPC analysis. [d] Number of monomer units determined by ^1H NMR analysis. [e] Molar mass determined by ^1H NMR analysis.

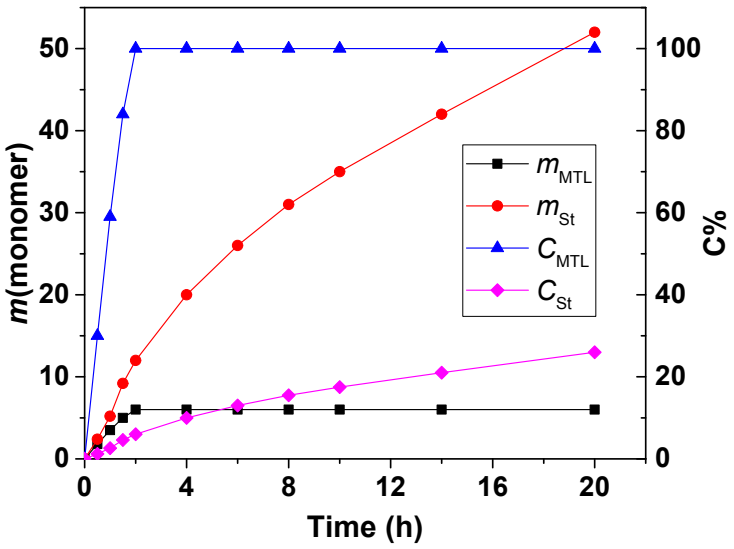

Fig. S1 Influence of polymerization time on number of monomer unit (m) and monomer conversion (C) during FBCP-mediated RAFT copolymerization of MTL with St. See Table S1 for polymerization conditions.

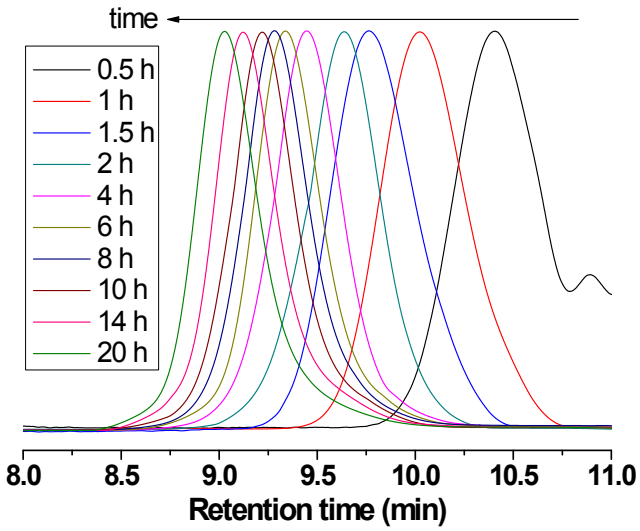

Fig. S2 GPC traces of linear random and diblock copolymers synthesized by FBCP-mediated RAFT copolymerization of MTL with St. See Table S1 for polymerization conditions.

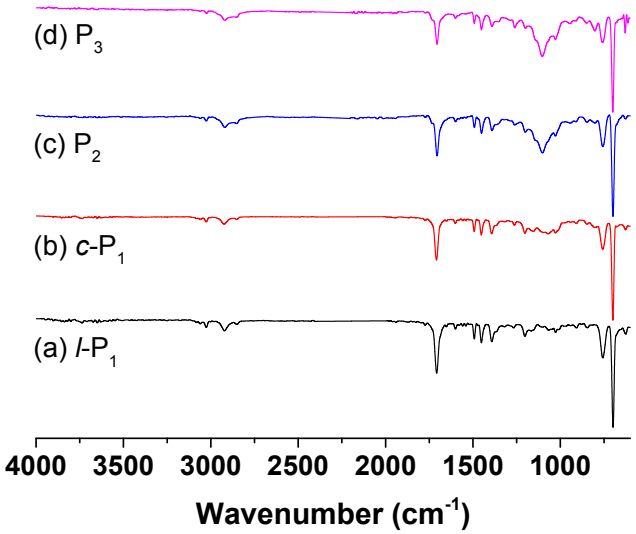

Fig. S3 FT-IR spectra of various copolymers.

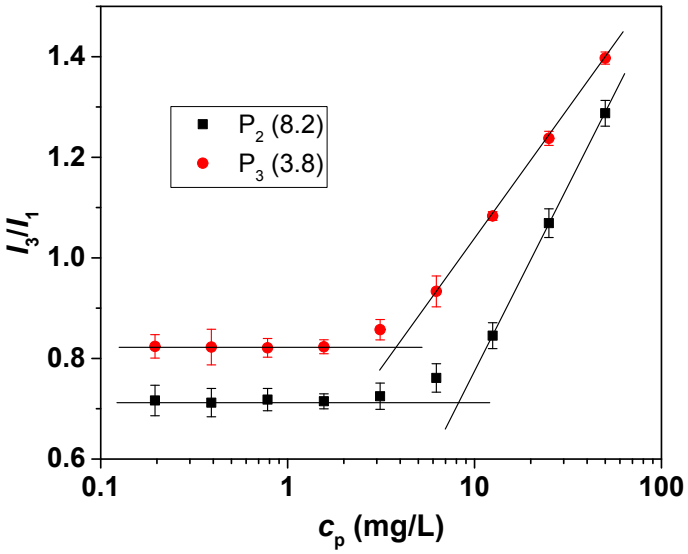

Fig. S4 Dependence of intensity ratios (I_3/I_1) on logarithm of copolymer concentrations in aqueous solution.

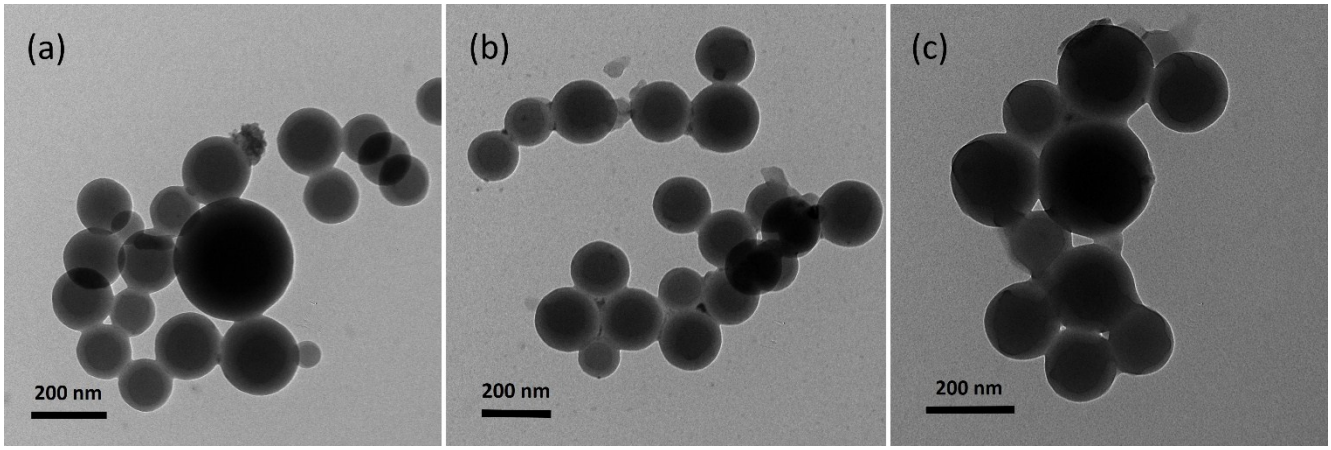

Fig. S5 Influence of heat (T = 60 °C, b) and sonication (T = 25 °C, c) for 60 min on TEM images of P_2 assemblies (c_p = 0.5 mg mL^{-1}, pH = 7.2), in which the original TEM image (a) was listed for comparison.

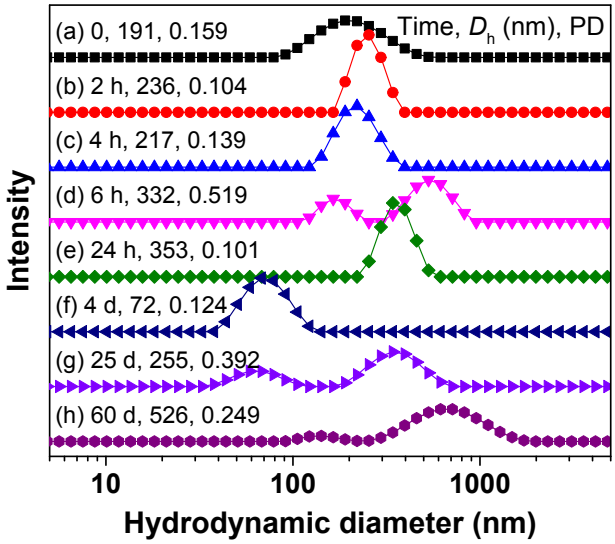

Fig. S6 Influence of time on DLS plots of P_2 assemblies (c_p = 0.5 mg mL^{-1}) formed in aqueous solution at pH 7.2 (a) and 3.0 (b-h).

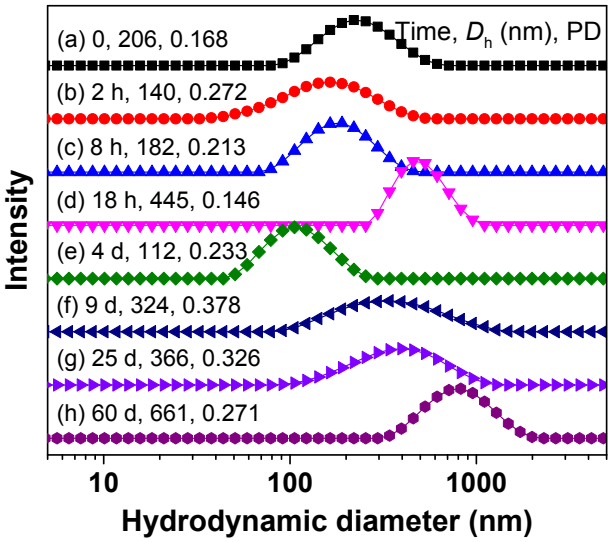

Fig. S7 Influence of time on DLS plots of P_3 assemblies (c_p = 0.5 mg mL^{-1}) formed in aqueous solution at pH 7.1 (a) and 3.0 (b-h).

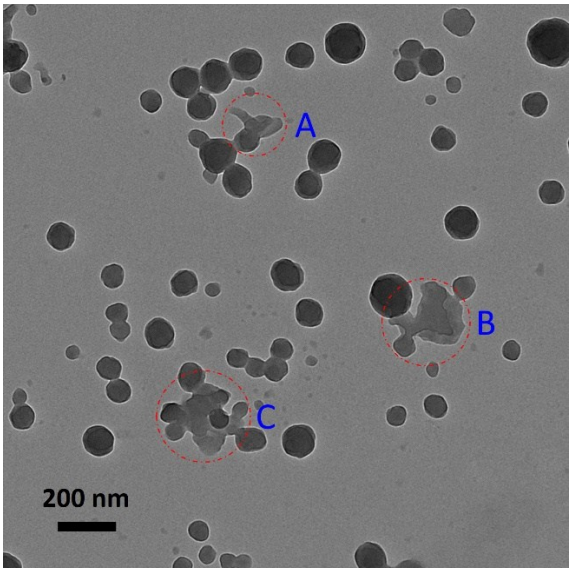

Fig. S8 TEM image of P_3 assemblies formed at pH 3.0 (c_p = 0.5 mg mL^{-1}, t = 2 h).

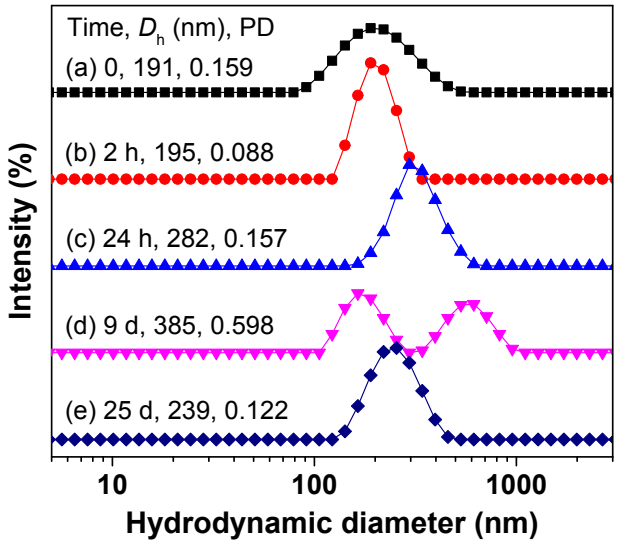

Fig. S9 Influence of time on DLS plots of P_2 assemblies (c_p = 0.5 mg mL^{-1}) formed in aqueous solution at pH 7.2 (a) and 10 (b-e).

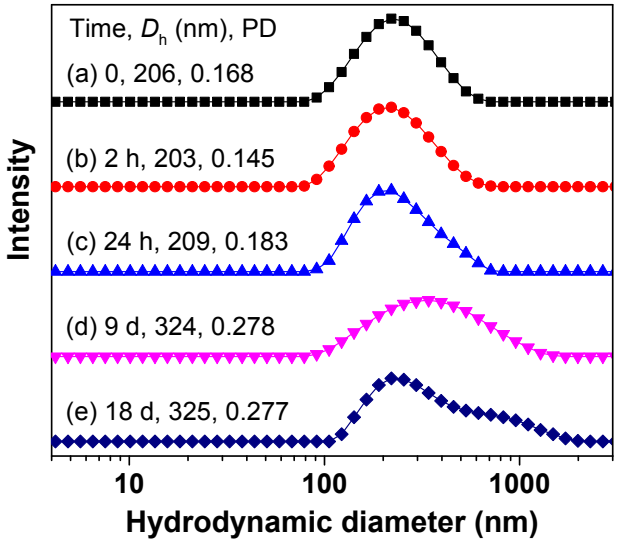

Fig. S10 Influence of time on DLS plots of P_3 assemblies (c_p = 0.5 mg mL^{-1}) formed in aqueous solution at pH 7.1 (a) and 10 (b-e).

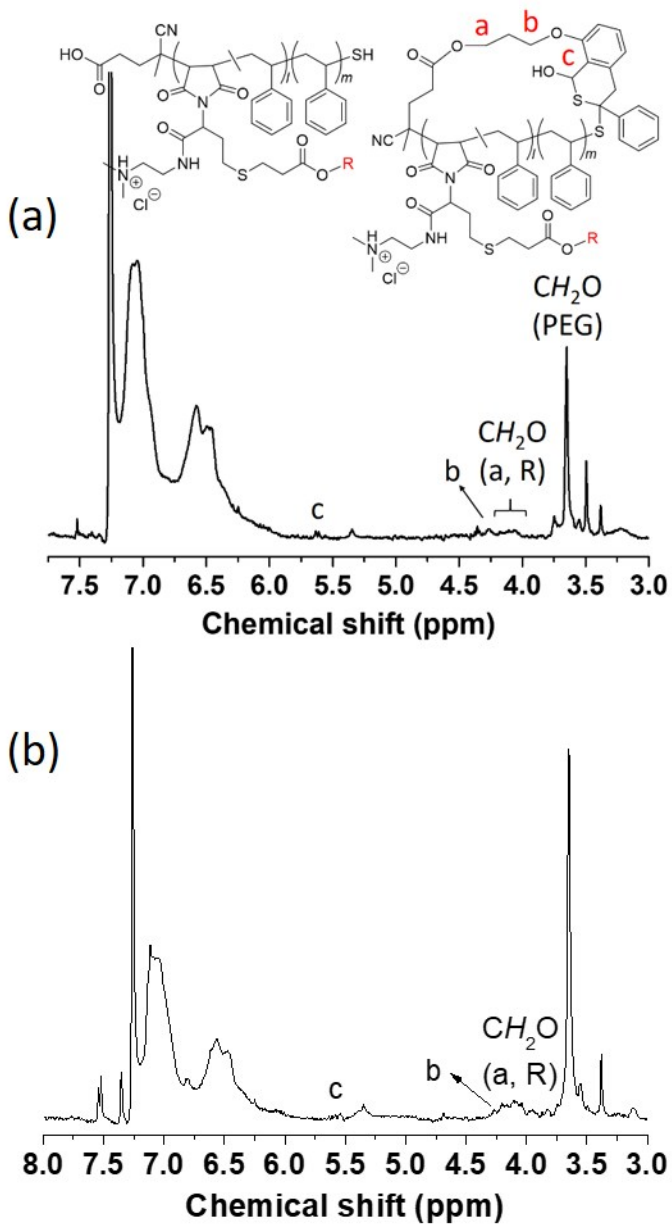

Fig. S11 ^{1}H NMR spectra of copolymer mixtures (R = H or $CH_3(OCH_2CH_2)_9$-) obtained by freeze-drying of P_3 assemblies upon acid (pH = 3.0, t = 60 days, a) and base (pH = 10, t = 18 days, b) treatments, followed by precipitation to remove cleaved MPEG.

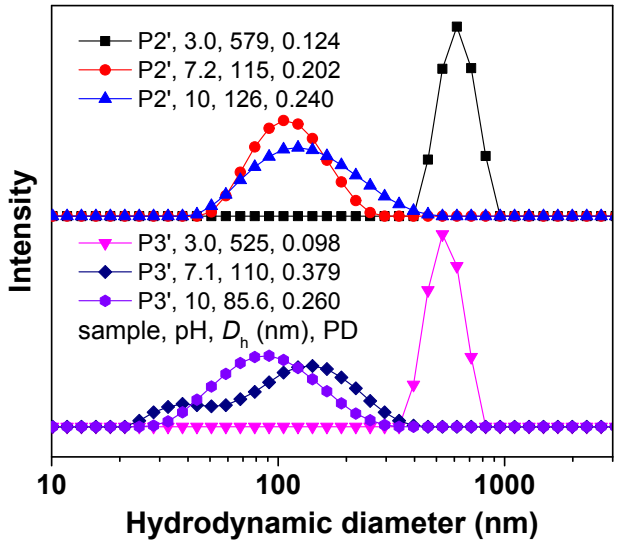

Fig. S12 DLS plots of copolymer assemblies (c_p = 0.5 mg mL^{-1}) formed from P_2 and P_3 in aqueous solution upon pH and oxidation stimuli, where the samples upon oxidation of P_2 and P_3 were abbreviated as P_2' and P_3'.

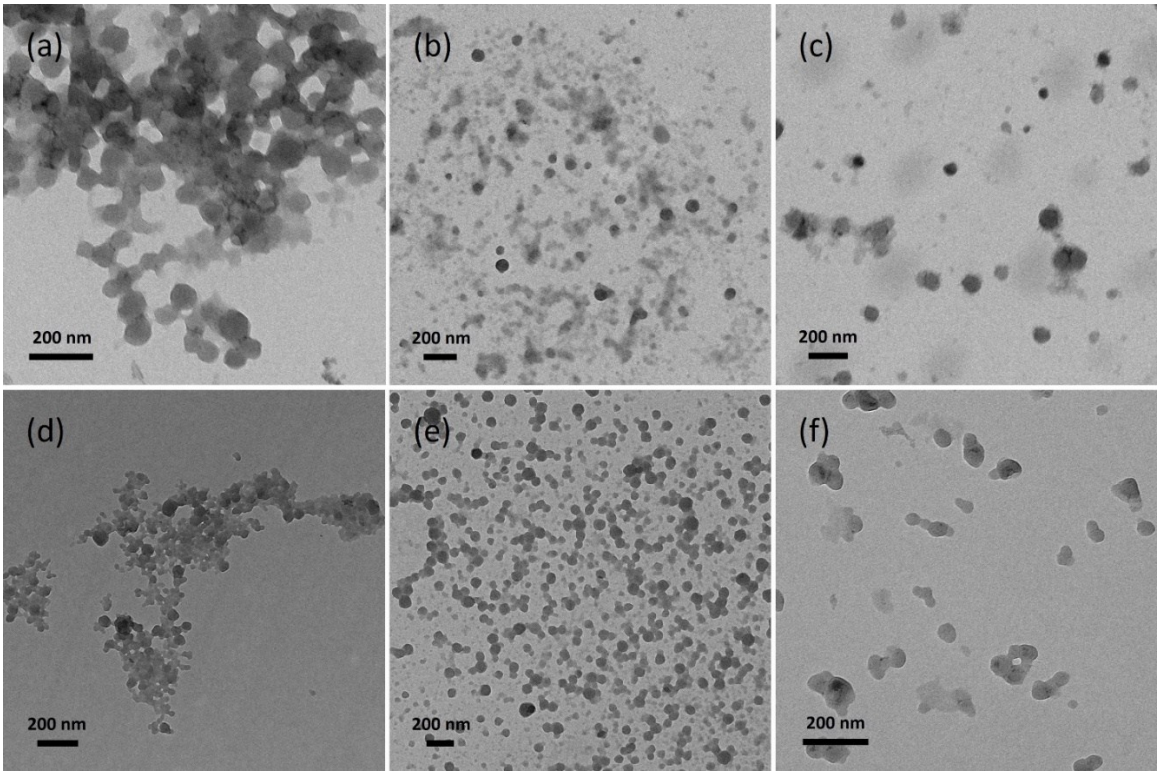

Fig. S13 TEM images of copolymer assemblies (c_p = 0.5 mg mL^{-1}) formed from P_2' and P_3' in aqueous solution at different pHs (pH ≈ 3 (a, d), 7 (b, e) and 10 (c, f)).

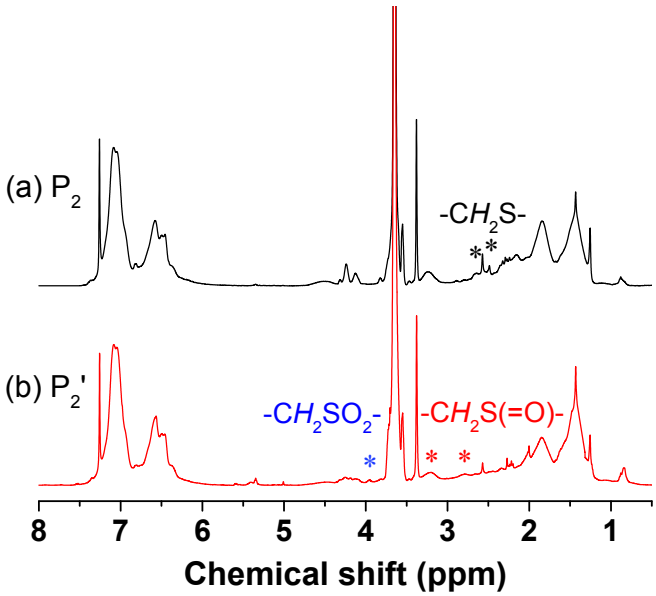

Fig. S14 ^{1}H NMR spectra of P_2 (a) and P_2' (b) recorded in $CDCl_3$, in which the star labeled the signals of CH_2S before and after oxidation, and the signal at 3.20 ppm of P_2' was overlapped with other signals.