## Supporting Information of Manuscript Entitled with

## Pathway-Dependent Re-assembly of Dual-Responsive ABC Terpolymer in Water

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Table S1 Summary of copolymer molecular weights and compositions.

Sample	[M] <sub>0</sub> /[macro-CTA] <sub>0</sub>	<sup>a</sup> Conv. (%)	DP	PDI	<i>M</i> <sub>n</sub> (GPC)/kDa	<i>M</i> <sub>n</sub> (NMR)/kDa
EB	30	93	28	1.09	5.6	6.2
EBD	35	92	32	1.14	12.6	11.2

a) Calculated by <sup>1</sup>H NMR in CDCl<sub>3</sub>.



**Figure S1**. DLS results (left) and TEM images (right) of aggregates formed from 0.1 wt%  $PEG_{45}$ -*b*- $PnBMA_{28}$  diblock aqueous solution at RT and pH=7 with an angle of 90°.



**Figure S2.** CryoTEM images of aggregates formed from 0.1 wt% EBD terpolymer aqueous solution: (**a**) pH=4, (**b**) pH=6, (**c**) pH=10, and (**d**) pH=12 in RT.



**Figure S3.** Angular dependent DLS (solid) and SLS (open) measurements performed on EDB aqueous solution (0.1-wt %) at (**a**) pH=8 and (**b**) pH=10 at RT.



**Figure S4**. Apparent size distributions of aggregates formed from 0.1-wt% EBD terpolymer aqueous solution upon pH variations in RT at an angle of 90°.



**Figure S5**. TEM images of aggregates formed from 0.1-wt% EBD trerpolymer aqueous solution after adjusting solution from (a) pH = 8 to pH=2, and (b) from pH=10 to pH 2 at RT.



**Figure S6.** Transmittance of 0.1-wt% EBD terpolymer aqueous solution at (a) pH=8 and (b) pH=10 in a heating/cooling cycle with a heating rate of 1 °C /min.



**Figure S7**. TEM image of of EBD terpolymer aggregates with pH 8 after heating at 55 °C for (a) 0 hour, (b) 1 hour and EBD terpolymer aggregates with pH 10 after heating at 35 °C for (c) 0 hour, (d) 1 hour (stained with uranyl acetate).



**Figure S8.** Angular dependent DLS (solid) and SLS (open) measurements performed on EDB solution (0.1 wt %) in RT after heating at (**a**) 55 °C with pH=8 and (**b**) 35 °C with pH=10.



Figure S9. CryoTEM images of toroids and vesicles after 2 months' storage in RT.



**Figure S10**. TEM images of assemblies formed EBD solutions after first round of thermal annealing: (a) the solution pH was changed from 2 to 8 followed by annealing at 55  $^{\circ}$  for one hour, EBD micelle repeated the morphology transition from sphere to cylinder and then to toroid. (b) the solution pH was changed from 2 to 10 followed by annealing at 35  $^{\circ}$  for one hour, EBD micelle repeated the morphology transition from sphere to cylinder and then to toroid. (b) the solution pH was changed from 2 to 10 followed by annealing at 35  $^{\circ}$  for one hour, EBD micelle repeated the morphology transition from sphere to cylinder and then to vesicles. (stained with uranyl acetate).



**Figure S11**. <sup>1</sup>H-NMR spectra of 0.1 wt% EBD terpolymer in (a)  $CDCl_3$ ,  $D_2O$  with pD 2, pD 8 in RT, pD 8 after heating at 55 °C, (b) pD 10 in RT and after heating at 35 °C.



Figure S12. GPC traces of EBD after a transition cycle.



**Figure S13**.GPC traces of mPEG-CTA ( $M_n$ =3500, PDI=1.05), EB diblock ( $M_n$ =13800, PDI=1.08), and EBD triblock ( $M_n$ =35400, PDI=1.13) copolymers in THF.

(GPC was performed by a set of a Waters 515 HPLC pump and a Waters 2414 refractive index detector. THF was used as an eluent at a flow rate of 1.0 mL/min at 35 °C. Polystyrene standards were used for the calibration.)