[Supporting Information]

Influence of block sequence on the colloidal self-assembly of poly(norbornene)-block-

poly(ethylene oxide) amphiphilic block polymers using rapid injection processing

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Figure S1. ¹H NMR spectra of compound 1 in CDCl₃.



Figure S2. ¹H NMR spectra of mono-hydroxyl functionalized PEO in CDCl₃.



Figure S3. ¹H NMR spectra of mono-aldehyde functionalized PEO 2 in CDCl₃.



Figure S4. ¹H NMR spectra of di-aldehyde functionalized PEO 3 in CDCl₃.



Figure S5. ¹H NMR spectra of NO in CDCl₃.



Figure S6. ¹H NMR spectra of NON in CDCl₃.

Polymer	M _{n, total} ^a (kg/mol)	$M_{\rm n, \ total}^{\rm b}$ (kg/mol)
NO(3.6-1.4)	5.0	4.8
NO(5.8-1.4)	7.2	5.4
NO(7.7-1.4)	9.1	6.2
NON(1.8-4-1.8)	7.6	7.2
NON(3.2-4-3.2)	10.4	8.7

Table S1. Comparison of number-average molecular weights of the block copolymers using ¹H NMR spectroscopy and SEC.

^aNumber-average molecular weight determined from ¹H NMR spectroscopy. ^bNumber-average molecular weight determined from size exclusion chromatography (SEC). The dn/dc values of the block copolymers were calculated using block volume fraction obtained from ¹H NMR and homopolymer dn/dc values. The dn/dc value of PEO in THF (0.067 mL/g) was obtained from the website of Polymer Source. The dn/dc value of PNBE in THF is determined to be 0.17 mL/g using a BI-DNDC differential refractometer (Brookhaven Instruments Corporation). As shown, number-average molecular weights obtained from SEC are similar to the values obtained from ¹H NMR.



Figure S7. TEM images of (a) **IO** and (b) **IOI** self-assembled structures via rapid injection of 20 wt% polymer solutions in THF. The embedded pictures are aqueous polymer solutions in water after rapid injection.



Figure S8. Cryo-TEM image of microgel from rapid injection of a 30 wt% NON(3.2-4-3.2) THF solution into water. The cryo-TEM sample was prepared using

a FEI Vitrobot, stored and handled at frozen state in liquid nitrogen. The image was collected using low-dose mode.



Figure S9. Synthesis route for diblock copolymer IO and triblock copolymer IOI.