### **Electronic Supplementary Information (ESI)**

## Autonomous unimer-vesicle oscillation by totally synthetic diblock copolymers: Effect of block length and polymer concentration on spatio-temporal structures

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#### A brief explanation of the BZ reaction

Although the overall reaction of the BZ reaction is the oxidation of an organic acid by an oxidant catalyzed by a metal, it includes a lot of elementary processes. However, according to the Field-Körös-Noyes (FKN) mechanism,<sup>S1</sup> it can be summarized into three processes:

Process A (consumption of Br<sup>-</sup>):

 $BrO_3^- + 2Br^- + 3H^+ \rightarrow 3HOBr$ 

Process B (autocatalytic formation of HBrO<sub>2</sub> with oxidation of a metal catalyst):

 $BrO_3^- + HBrO_2 + 2M_{red} + 3H^+ \rightarrow 2HBrO_2 + 2M_{ox} + H_2O$ 

Process C (formation of Br<sup>-</sup> with reduction of a metal catalyst):

 $2M_{ox} + CH_2(COOH)_2 + BrCH(COOH)_2 \rightarrow fBr^- + 2M_{red} + other products$ 

 $M_{red}$  and  $M_{ox}$  represent the reduced and the oxidized states of a metal catalyst, and f is the stoichiometric factor. During the BZ reaction, these processes cyclically occur, resulting in the oscillatory reduction and oxidization of the metal catalyst.

#### Consideration of unimer diffusion and collision during the BZ reaction

For three dimensional Brownian motion, the mean-square displacement  $\langle r^{2} \rangle$ can be expressed as  $\langle r^{2} \rangle = 6Dt$ , where *D* is the diffusion coefficient and *t* is the diffusion time. For example, ENR-3 had the diffusion coefficient  $D_{h} = 4.1 \times 10^{-11}$  $(m^{2}/s)$  and  $R_{h} = 5.2$  (nm) at its unimer state (20 °C) that were obtained by the DLS measurement with the cumulant analysis. As the oscillating period of the BZ reaction in this study is several tens of seconds, if we substitute t = 10 (s), we can estimate that the average diffusion distance is calculated as  $\sqrt{\langle r^{2} \rangle} = 50$  (µm). On the other hand, from the polymer concentration (0.5 mg/cm<sup>3</sup>) and the average molecular weight (89 kg/mol for ENR-3), the number density of unimers is  $3.4 \times 10^{15}$  (/cm<sup>3</sup>). Therefore, the average distance of each unimer can be estimated as  $(3.4 \times 10^{15})^{-1/3} = 67$  (nm). Consequently, this indicates that the timescale of the BZ reaction was long enough for

each unimer to diffuse and encounter other unimers.

# Scheme S1. Synthesis of the PEO-*b*-P(NIPAAm-*r*-NAPMAm-*r*-NAPMAmRu(bpy)<sub>3</sub>) diblock copolymer.



PEO-b-P(NIPAAm-r-NAPMAm-r-NAPMAmRu(bpy)<sub>3</sub>)



**Fig. S1.** Temperature dependence of the  $R_h$  for 0.05 wt% self-oscillating diblock copolymers with an *f*<sub>PEO</sub> of 34.1 wt% ( $N_{PEO} = 114$  and  $N_{PNIPAAm} = 85$ ) in the reduced state.



**Fig. S2.** Arrhenius plots of oscillation frequencies for each diblock copolymer solution. Oscillation frequencies were considered as the reciprocal of oscillating periods.



**Fig. S3.** Plot of oscillating period versus the Ru(bpy)<sub>3</sub>Cl<sub>2</sub> concentration. The concentrations of the BZ reaction substrates are as follows: 0.3 M HNO<sub>3</sub>, 0.4 M NaBrO<sub>3</sub>, and 0.025 M CH<sub>2</sub>(COOH)<sub>2</sub>. Temperature was 28 °C.



**Fig. S4.** Representative autocorrelation functions for the (a) reduced and (b) oxidized states, respectively, during the self-oscillatory behaviors in Fig. 6a, 29 °C. The broad  $\mu_2/\Gamma^2$  value and the fairly larger  $R_h$  value than that of a single polymer chain in the oxidized state indicates that the break-up of vesicles does not completely proceed.

#### **Supporting Reference**

(S1) R. J. Field, E. Körös, and R. M. Noyes, J. Am. Chem. Soc., 1972, 94, 8649-8664.