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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, it can be summarized into three processes:

**Process A (consumption of Br⁻):**

\[ \text{BrO}_3^- + 2\text{Br}^- + 3\text{H}^+ \rightarrow 3\text{HBr} \]

**Process B (autocatalytic formation of HBrO₂ with oxidation of a metal catalyst):**

\[ \text{BrO}_3^- + \text{HBrO}_2 + 2\text{M}_\text{red} + 3\text{H}^+ \rightarrow 2\text{HBrO}_2 + 2\text{M}_\text{ox} + \text{H}_2\text{O} \]

**Process C (formation of Br⁻ with reduction of a metal catalyst):**

\[ 2\text{M}_\text{ox} + \text{CH}_2(\text{COOH})_2 + \text{BrCH}(\text{COOH})_2 \rightarrow f\text{Br}^- + 2\text{M}_\text{red} + \text{other products} \]

\( \text{M}_\text{red} \) and \( \text{M}_\text{ox} \) 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 $<r^2>$ can be expressed as $<r^2> = 6Dt$, 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$^3$) and the average molecular weight (89 kg/mol for ENR-3), the number density of unimers is $3.4 \times 10^{15}$ (/cm$^3$). 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-\textit{b}-P(NIPAAm-\textit{r}-NAPMAm-\textit{r}-NAPMAmRu(bpy)\textsubscript{3}) diblock copolymer.
Fig. S1. Temperature dependence of the $R_h$ for 0.05 wt% self-oscillating diblock copolymers with an $f_{\text{PEO}}$ of 34.1 wt% ($N_{\text{PEO}} = 114$ and $N_{\text{PNIPAAm}} = 85$) 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)$_3$Cl$_2$ concentration. The concentrations of the BZ reaction substrates are as follows: 0.3 M HNO$_3$, 0.4 M NaBrO$_3$, and 0.025 M CH$_2$(COOH)$_2$. 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