Supporting Information

Control of swelling-deswelling behavior of self-oscillating gel by designing the chemical structure

*Tsukuru Masuda, Ayako Terasaki, Aya Mizutani Akimoto, Kenichi Nagase, Teruo Okano and Ryo Yoshida**

Experimental

Preparation of the calibration curve to determine the amount of Ru(bpy)$_3$ conjugated to the polymer

The calibration curve was independently made from aqueous solutions of $Ru(bpy)_3Cl_2$ with known concentrations. The absorbance spectra of the aqueous solutions of $Ru(bpy)_3Cl_2$ were measured by using a UV-vis measurement spectroscopy. Here, the absorbance at 700 nm (A_{700}) was defined as the baseline (i.e. $A_{700} = 0$), because there are no peak at 700 nm.

Measurements of swelling and deswelling kinetics

The kinetics of the ternary self-oscillating gel was measured as the following reference. The gel was immersed in the aqueous solution containing HNO_3 (810 mM) and NaCl (104 mM), and stabilized at 20 °C. Swelling kinetics were measured by exchanging the external solution to the aqueous solution containing HNO_3 (810 mM) and $NaBrO_3$ (104 mM). Deswelling kinetics were measured by exchanging the solution to the solution containing HNO_3 (810 mM), NaCl (104 mM), and MA (84 mM). Swelling or deswelling process of the gels were recorded by a digital video recorder through a CCD camera (Toshiba Teli, CS5270B) attached to a microscope (MZ16, Leica).

Reference:

[S1] R. Mitsunaga, K. Okeyoshi, R. Yoshida, *Chem. Commun.* 2013, **49**, 4935.

Supporting Results

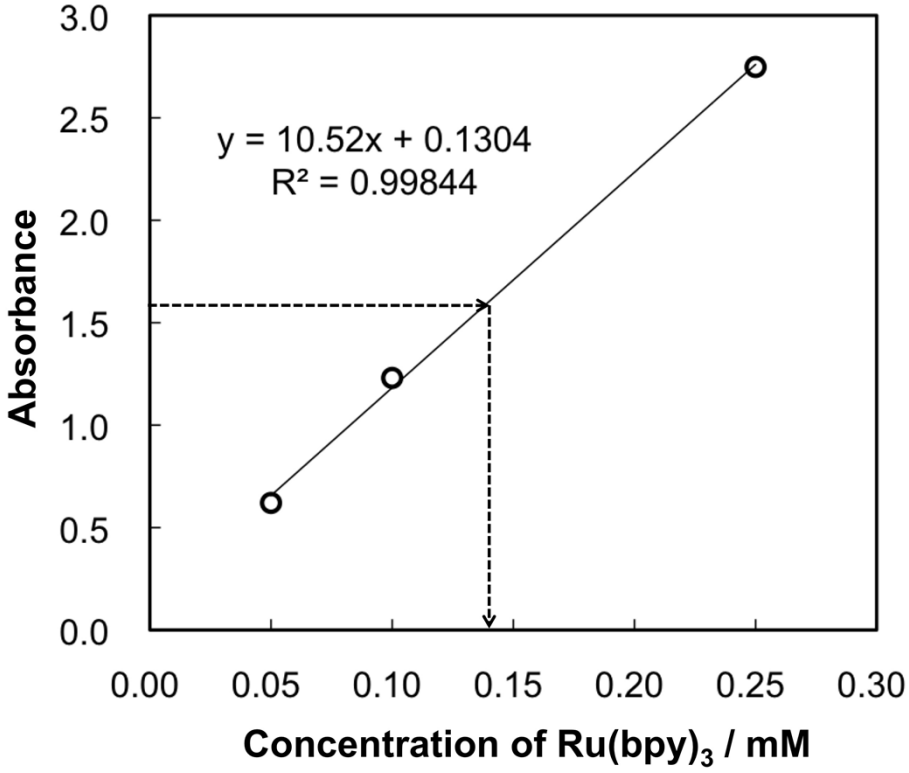

Fig. S1 Calibration curve to determine the amount of $Ru(bpy)_3$ conjugated to the polymer. The calibration curve was independently made from aqueous solutions of $Ru(bpy)_3Cl_2$ with known concentrations.

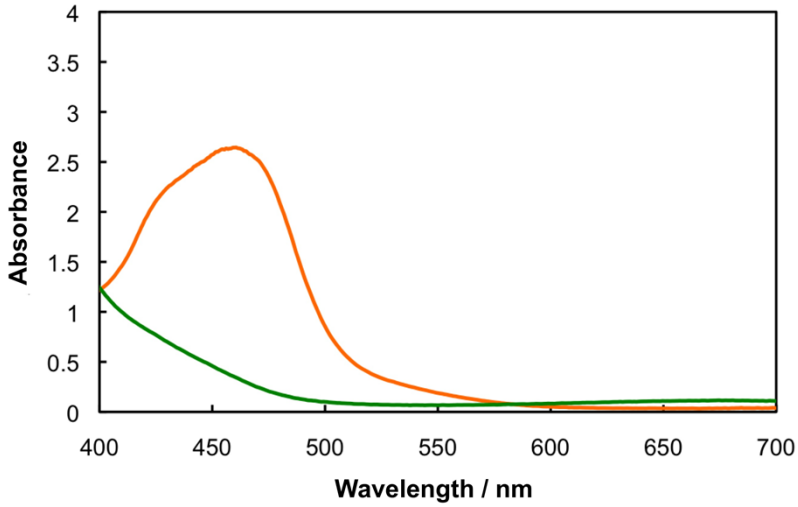

Fig. S2 Absorbance spectra for poly(NIPAAm-*co*-NAPMAm-*co*-$Ru(bpy)_3$NAPMAm) solutions (0.05 wt%) under the different conditions of the reduced Ru(II) state and oxidized Ru(III) state.

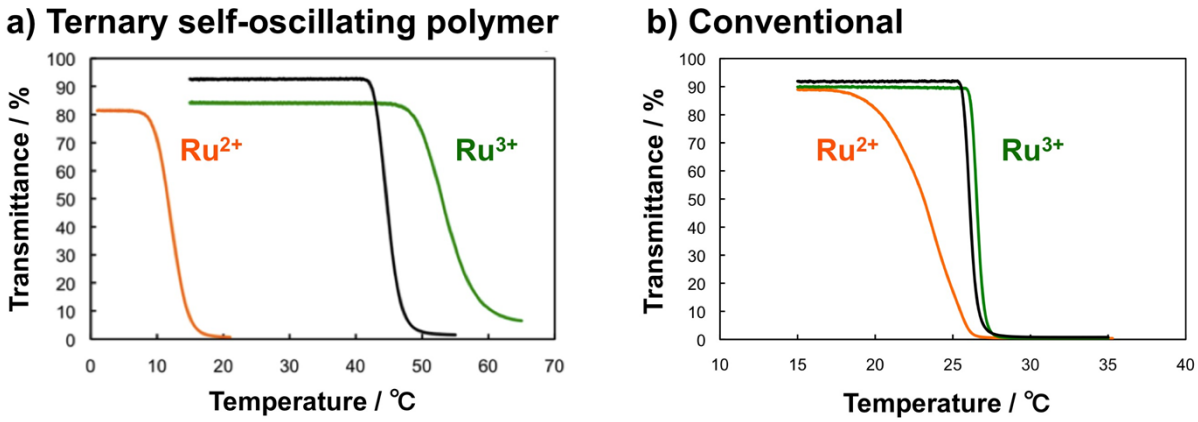

Fig. S3 Temperature dependence of optical transmittance for (a) the ternary self-oscillating polymer and poly(NIPAAm-*co*-NAPMAm) (black line), and (b) the conventional self-oscillating polymer (poly(NIPAAm-*co*-Ru(bpy)$_3$) and polyNIPAAm (black line) in aqueous solution containing 1 M HNO_3.

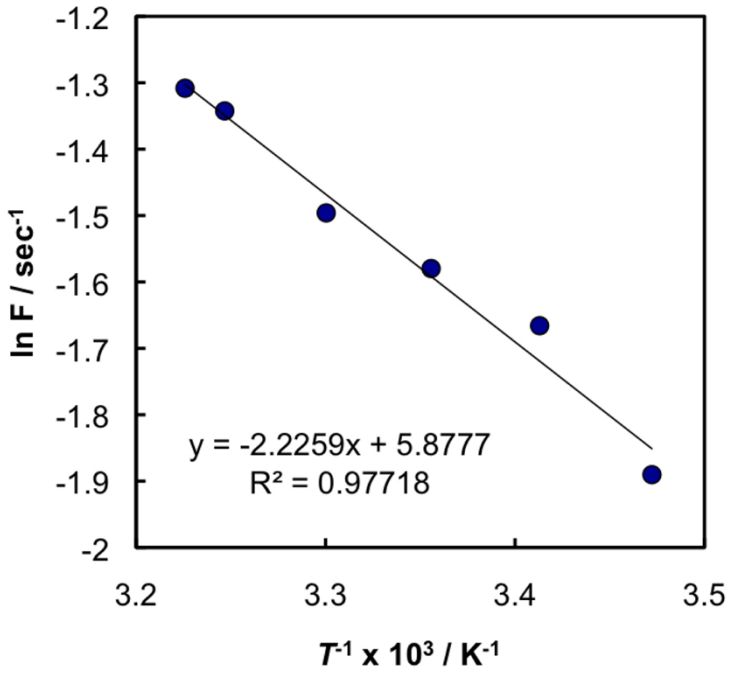

Fig. S4 Arrhenius plot of the self-oscillation of linear polymer.

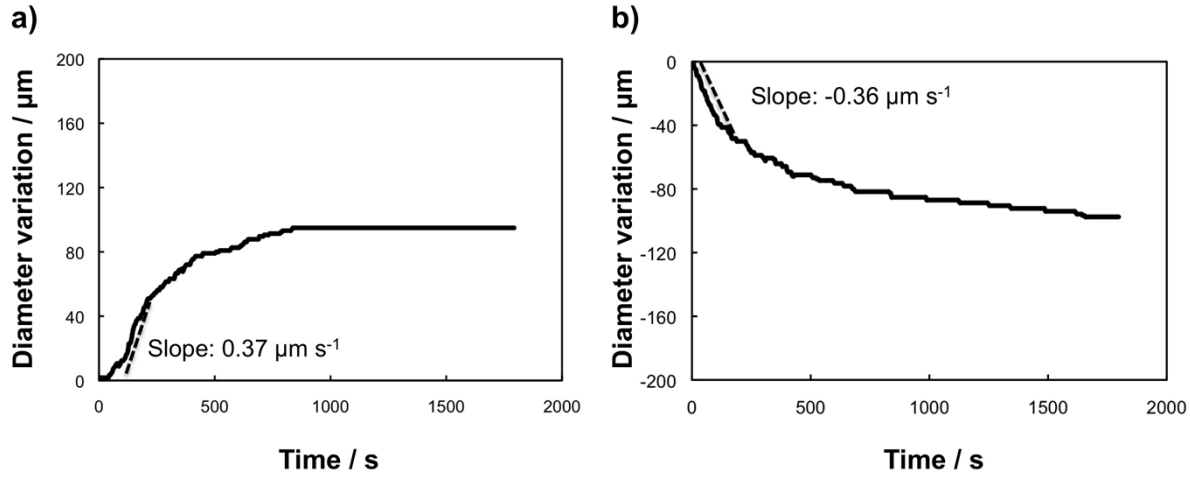

Fig. S5 The kinetics of PNNR-5-(100%) in (a) swelling process and (b) deswelling process. The initial rates were shown in the figure.

Table S1 Kinetics of ternaly self-oscillating gel (PNNR5-(100%)) and conventional gel.

Gel	Swelling process	Deswelling process
Ternaly self-oscillating gel (PNNR-5-(100%))	0.37 μm s^{-1}	0.36 μm s^{-1}
Conventional gel [S1]	0.11 μm s^{-1}	0.07 μm s^{-1}

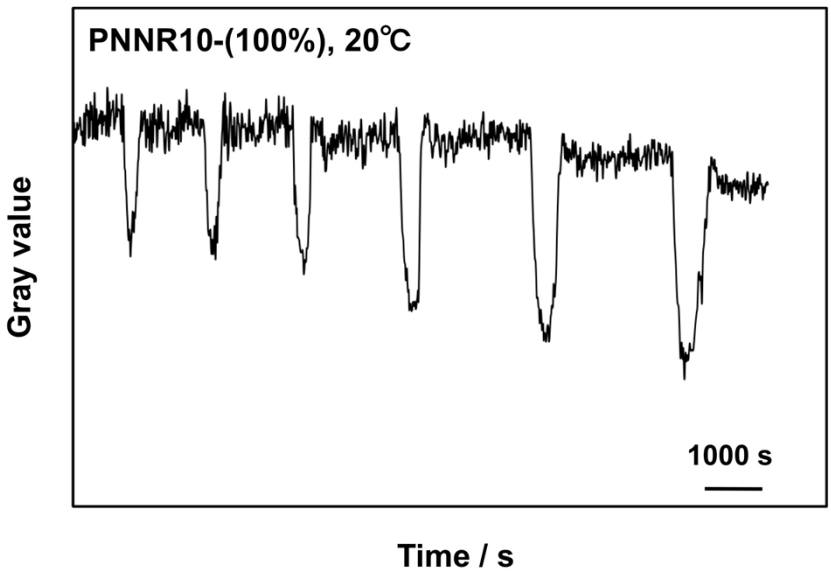

Fig. S6 Oscillating profile of the gray value of PNNR-10-(100%) at 20 °C.