Supporting Information

Experimental

Materials

N-isopropylacrylamide (NIPAAm, Wako Pure Chemical Industries, Co., Ltd, Osaka, Japan) was purified by recrystallization from its toluene solution with hexane. Ruthenium(4-vinyl-4-methyl-2,2′-bipyridine)bis(2,2′-bipyridine)bis(chloride) ($Ru(bpy)_3$ monomer) was synthesized according to previous work. Other reagents were used without further purification.

Preparation of poly(NIPAAm-co-Ru(bpy)$_3$) macromonomer

The poly(NIPAAm-*co*-$Ru(bpy)_3$) macromonomer was prepared as follows (see Fig. S1).[S1] First, a semitelechelic poly(NIPAAm-*co*-$Ru(bpy)_3$) with a terminal amino end group was synthesized by radical telomerization of the NIPAAm and $Ru(bpy)_3$ monomer using 2-aminoethanethiol (AESH) as a chain-transfer agent. NIPAAm (6.34 g), $Ru(bpy)_3$ monomer (2.66 g), AESH (0.16 g), and 2, 2'-azobisisobutyrnitrile (0.17 g) as an initiator were dissolved in *N,N*-dimethylformamide (DMF, 45 mL). The ampoule that contained the solution was degassed by freeze–thaw cycles and then polymerized at 75 ˚C for 48 h. After dialysis, a polymerizable end group was introduced into the amino semitelechelic poly(NIPAAm-*co*-$Ru(bpy)_3$) using an amide condensation reaction between amino groups in poly(NIPAAm-*co*-$Ru(bpy)_3$) and N-acryloxysuccinimide (molar ratio 1:10) in DMF at 4 °C for 48 h. The molecular weight of the macromonomer determined by gel permeation chromatography was ~7,000. The introduced $Ru(bpy)_3$ units were 2.7 mol%, which was calculated by the absorbance of the solution.

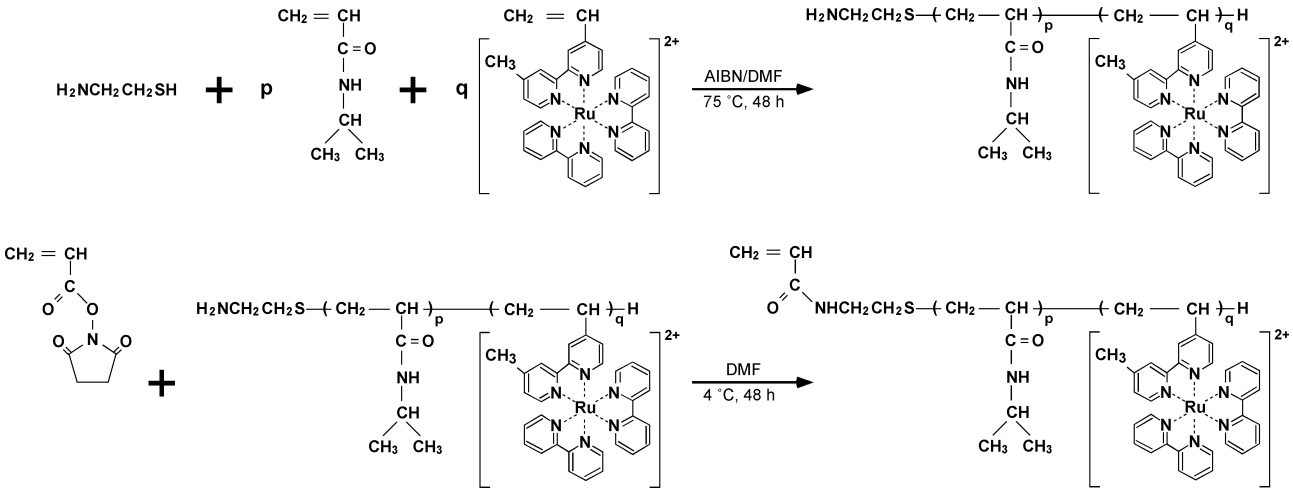

Figure S1 Preparation of poly(NIPAAm-*co*-$Ru(bpy)_3$) macromonomer using telomerization and amide condensation reactions.

Preparation of poly(NIPAAm-co-Ru(bpy)$_3$)-grafted poly(NIPAAm-co-Ru(bpy)$_3$) gel

PNR macromonomer (0 mg for MG and 61 mg for MSG), NIPAAm (50 mg), $Ru(bpy)_3$ monomer (4.5 mg for MG and 4.2 mg for MSG), *N,N'*-methylenebisacrylamide (1.3 mg), and tetramethylenediamine as an accelerator were dissolved in distilled water. The total amount of

solution was 1 mL. After the pre-gel solution was soaked in iced water under a nitrogen atmosphere for 20 min, ammonium persulfate as an initiator was added. Then glass capillaries with inner diameter 500 μm were put in the ampoule and radical copolymerization was conducted at 4 ˚C for 24 hours. After gelation, all of the cylindrical gel samples were taken out of the capillaries. They were thoroughly washed with distilled water to remove unreacted monomers for two days, changing the water every day. Then the gels were soaked in NH_4PF_6 solution for two days to exchange counter ions of Ru from Cl into PF_6. After that, the gels were preserved in distilled water to remove extra ions.

To estimate the effect of grafted side chains, the actual $Ru(bpy)_3$ concentration in MG should be the same as that in MSG. The $Ru(bpy)_3$ concentration in the gel was determined by measuring the absorbance of the gel sheet at 465 nm by using UV-Vis spectrophotometer. First, the relationship between $Ru(bpy)_3$ monomer concentration in the pre-gel solution and the actual $Ru(bpy)_3$ concentration in the MG gel was obtained as a calibration curve (Figure S2). Then the $Ru(bpy)_3$ concentration in the MSG was measured. From the calibration curve, the $Ru(bpy)_3$ monomer concentration in the pre-gel solution for MG which results in the same concentration as that in the MSG was obtained.

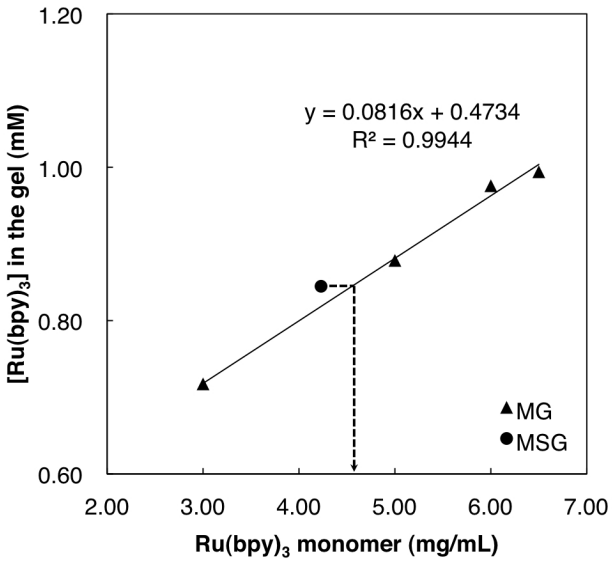

Figure S2 The relationship between $Ru(bpy)_3$ monomer concentration in the pre-gel solution and the actual $Ru(bpy)_3$ concentration in the gel at 20°C.

Measurements of equilibrium swelling ratio

The gel samples were equilibrated in the solutions: 5 mM $Ce(SO_4)_2$ and 894 mM HNO_3 for the oxidized Ru(III) state; 5 mM $Ce_2(SO_4)_3$ and 894 mM HNO_3 for the reduced Ru(II) state. The diameters of the cylindrical gel samples were measured by an optical microscope (Leica, MZ16). The swelling ratios were defined as the diameters of the gel normalized by the inner diameter of the glass capillary (d_0 = 500 μm) used in the gelation process.

Measurements of swelling and deswelling kinetics

The gels were stabilized in a solution (894 mM HNO_3 and 84 mM NaCl) at 20 °C. Swelling kinetics were measured by exchanging the external solution to the solution containing 894 mM

HNO_3 and 84 mM $NaBrO_3$. Deswelling kinetics were measured by exchanging the solution to the solution containing 894 mM HNO_3, 62.5 mM malonic acid and 84 mM NaCl. Swelling/deswelling kinetics of the gels were recorded by a digital videorecorder through a CCD camera (Toshiba Teli, CS5270B) attached to the optical microscope. A series of single-line images along the diameter of the gel were sampled every 1 s and the time series of the frames were pictured as a spatio-temporal pattern. The profiles of diameter variation were obtained from the spatio-temporal patterns.

Measurements of self-oscillation

MG and MSG were immersed in the catalyst-free BZ solution containing 894 mM HNO_3, 84 mM $NaBrO_3$ and 62.5 mM malonic acid at 20 ˚C. Oscillating behaviors of the gels were recorded by the same method of the kinetics measurements. The oscillation profiles were obtianed from the spatio-temporal patterns.

References

S1) K. Okeyoshi, R. Yoshida, *Adv. Funct. Mater.* **2010,** *20,* 708.

Supporting resluts

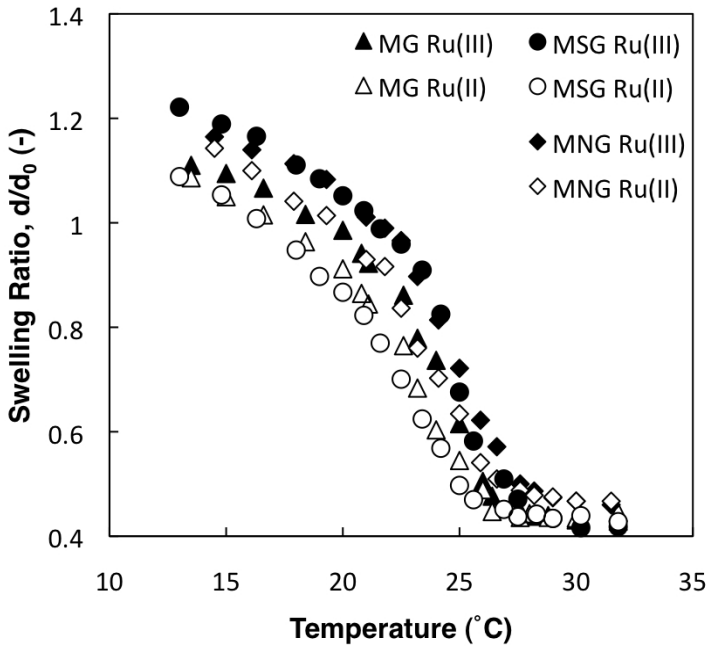

Figure S3 The equilibrium swelling ratio of MG, MSG, and the PNIPAAm-grafted poly(NIPAAm-*co*-Ru(bpy)$_3$) gel (MNG) in cerium sulfate solutions as a function of temperature. [Ce $(SO_4)_2$] = 5 mM for Ru(III), [$Ce_2(SO_4)_3$] = 5 mM for Ru (II), and [HNO_3] = 894 mM. The swelling ratio is defined as d/d_0 (d = the diameters of the gel, d_0 = the inner diameter of the glass capillary used in the gelation process, 500 μm). In preparation of MNG, the same weight of PNIPAAm macromonomer (M_w = 9,300) as that of poly(NIPAAm-*co*-Ru(bpy)$_3$) macromonomer contained in MSG was introduced.

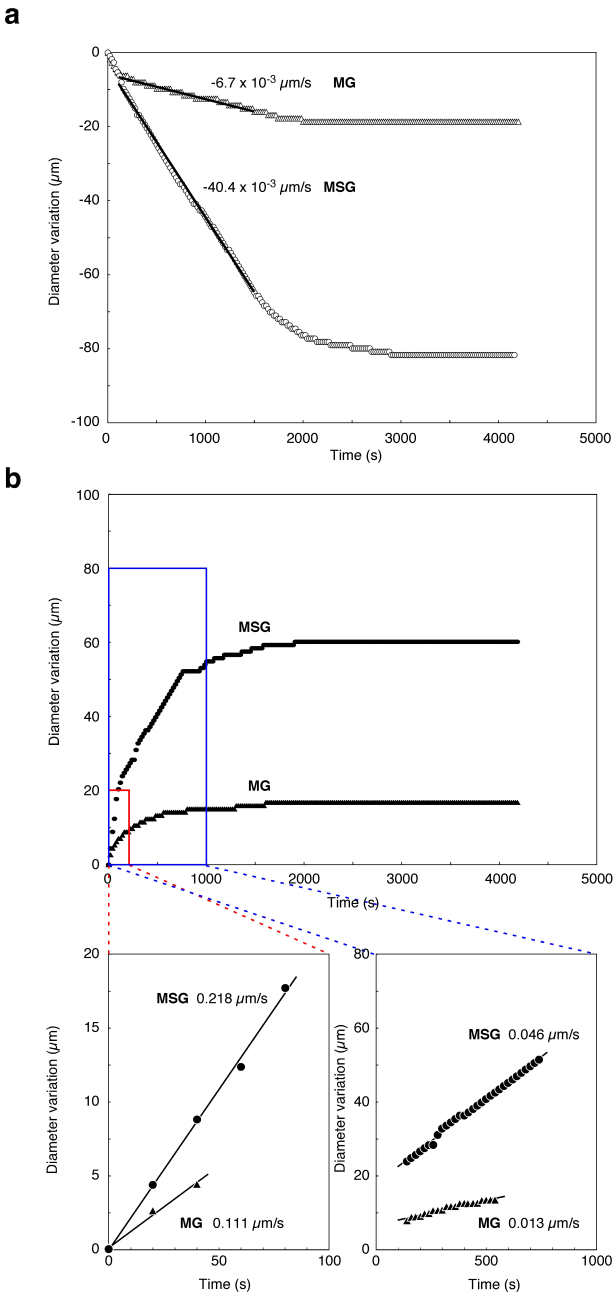

Figure S4 The initial rates of swelling and deswellng obtained from kinetics measurements for MG and MSG.

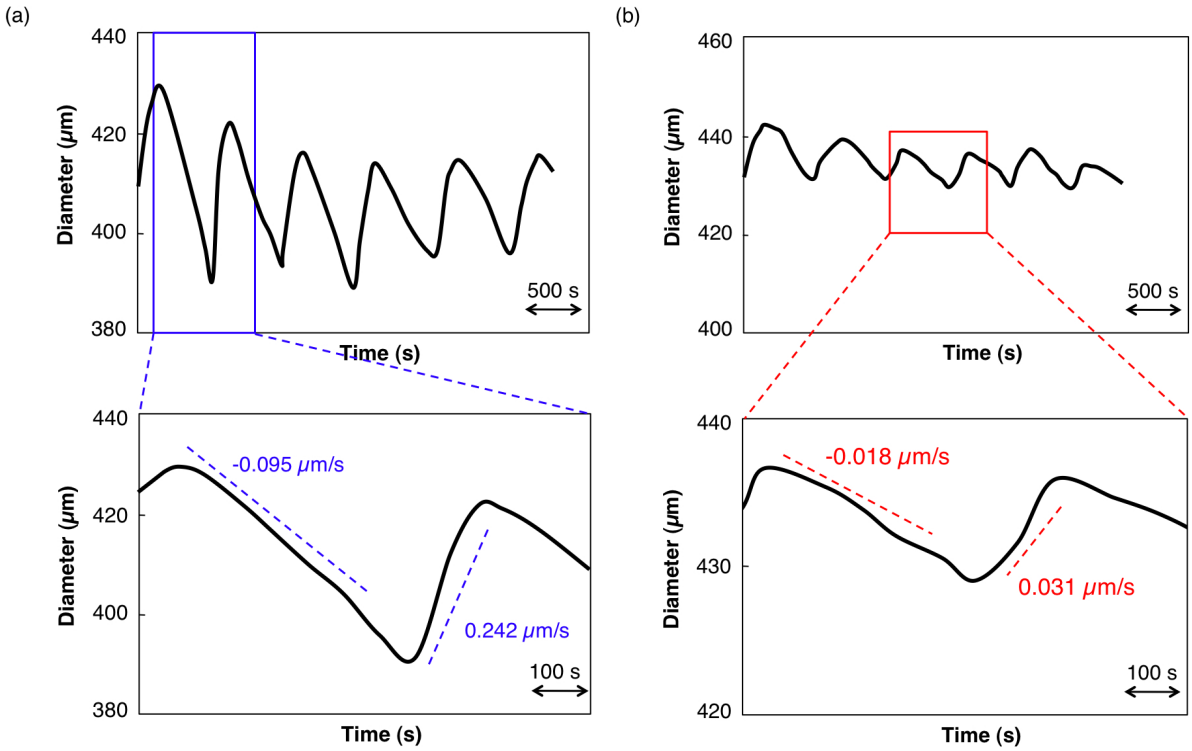

Figure S5 The swelling and deswelling rates during the oscillation for (a) MSG and (b) MG.