Supporting Information

Autonomous Viscosity Oscillation by Reversible Complex Formation of Terpyridine-Terminated Poly(ethylene glycol) in the BZ Reaction

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1. Materials and characterization

Materials obtained from commercial suppliers were used without further purification. The materials were synthesized according to procedures described in the literatures [1,2], and the products were checked with UV/VIS, MALDI-TOFMS, and GPC.

1.1 Preparation of tetra hydroxyl-polyethylene glycol

Tetrahydroxyl-terminated-poly(ethylene glycol) was synthesized by successive anionic polymerization reaction of ethylene oxide from potassium alkoxide of pentaerythritol [3]. The molecular weight was estimated from ^{1}H NMR. The ^{1}H NMR spectra were obtained on JEOL JNM-AL (300 MHz) spectrometer with Tetramethylsilane (TMS) as the internal standard and $CDCl_3$ as the solvent. The determined molecular weight was 16,200. The polydispersity were estimated from a gel permeation chromatography (TOSOH HLC-8220) system equipped with two TSK gel columns (G4000HHR and G3000HHR). The columns were eluted with DMF containing lithium chloride (10 mM) with a flow rate of 0.8 mL/min at 40°C. The molecular weights were calibrated with poly(ethylene glycol) standards (Polymer Laboratories, Ltd., UK). The determined polydispersity was 1.03.

1.2 Preparation of α, ω-bis(2,2':6',2"-terpyrid-4'-yl)-poly(ethylene glycol) (1)

7.0 g poly(ethylene glycol) (Wako ; polyethylene glycol 6,000 : average molecular weight 7,500) and 0.5g KOH were added into 75ml anhydrous dimethyl sulfoxide. After stirring for 1h at 60 °C and cooling at room temperature, 0.5g 4'-chloro-2,2':6',2"-terpyridine (Aldrich) was added. The synthesis was conducted for 48h at 60 °C with stirring. Then, the mixture was poured into 800 ml cold water. The insoluble white precipitate was filtered, the solution was extracted with chloroform (3×150ml) and the water included in combined organic layers was removed with Na_2SO_4. The solvent was volatilized in vacuum, the residue was dissolved in tetrahydrofuran and the solution was added by drops into diethyl ether. Finally, the white precipitate was yield (6.0g, 80%).

The UV/VIS spectrum and MALDI-TOFMS spectrum of obtained product were described in SI Figure 1 and SI Figure 3, respectively.

1.3 Preparation of tetra(2,2':6',2"-terpyrid-4'-yl)-poly(ethylene glycol) (4)

The procedure for synthesis was same as section 1.2. The 1.4 g (70%) tetra(2,2':6',2'-terpyrid-4'-yl)-poly(ethylene glycol) was obtained from 2.0 g tetra hydroxyl-poly(ethylene glycol) prepared in section 1.1 and 0.15g 4'-chloro-2,2',6',2"-terpyridine. The UV/VIS spectrum of the product was described in SI Figure 2.

1.4 Preparation of α,ω-bis(2,2':6',2"-terpyrid-4'-yl-ruthenium(III)chloride)-poly(ethylene glycol) (2) and tetra (2,2':6',2"-terpyrid-4'-yl-ruthenium(III)chloride)-poly(ethylene glycol) (5)

A solution of α,ω-bis(2,2':6',2"-terpyrid-4'-yl)-poly(ethylene glycol) or tetra (2,2':6',2"-terpyrid-4'-yl)-poly(ethylene glycol) and equimolar amount of $RuCl_3 \cdot nH_2O$ (Wako) was added in ethanol and it was stirred at 60 °C for 8h. The mixture was cooled to -78 °C. The precipitate was collected by filtration and purified by means of dialysis in ethanol for three days. The solvent was removed in vacuum and then the product was obtained.

The UV/VIS spectra of these compounds were shown in SI Figure 1 and 2, respectively.

1.5 Preparation of poly (bis(2,2':6',2"-terpyrid-4'-yl)-poly(ethylene glycol) ruthenium(II)) (3)

α,ω-bis(2,2':6',2"-terpyrid-4'-yl)-poly(ethylene glycol) and α, ω-bis(2,2':6',2"-terpyrid-4'-yl-ruthenium(III)chloride)-poly(ethylene glycol) were added into ethanol and then a small amount of *N*-ethylmolpholine as a catalyst was added. After the mixture was heated at 60 °C for overnight, excess ammonium hexafluorophosphate was added in order to exchange counter ion and stirred for a day. The solution was purified by means of dialysis in water for 3 days and the coordination polymer was obtained by using freeze dry method.

The UV/VIS spectrometer was shown in SI Figure 1. The GPC profiles were described Figure 4.

1.6 Preparation of poly(tetra(2,2':6',2"-terpyrid-4'-yl)-poly(ethylene glycol) ruthenium(II)) gel (6)

Tetra(2,2':6',2"-terpyrid-4'-yl)-poly(ethylene glycol) and tetra(2,2':6',2"-terpyrid-4'-yl-ruthenium(III) chloride)-poly(ethylene glycol) were added into ethanol and then a small amount of *N*-ethylmolpholine as a catalyst was added. A gelation was confirmed in several minutes but the mixture was heated at 60 °C for overnight to complete the reaction. The gel was taken out in ethanol and excess ammonium hexafluorophosphate was added in order to exchange the counter ion and stirred for a day. The gel was purified in water for 3 days and the dried gel was obtained by using freeze dry method. The photograph of the obtained gel was shown in SI Figure 4(b).

2. Experimental

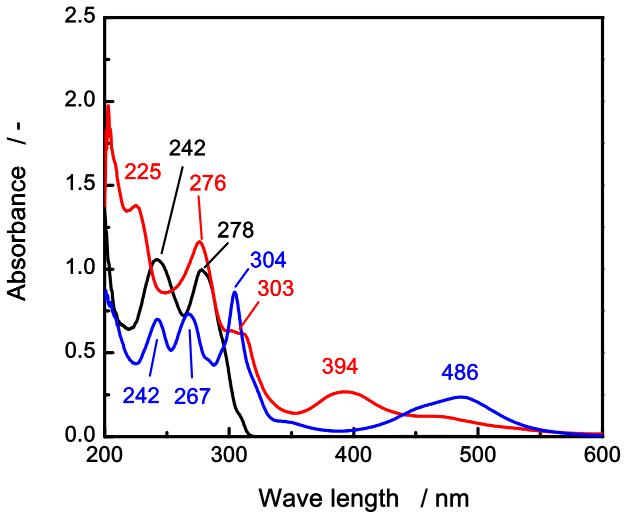
UV/VIS spectra for the polymer solution was measured using a (UV-2500PC, Shimadzu) spectrophotometer. And also, the absorbance change during the oscillating reaction was measured under constant temperature and stirring conditions. The 485 nm wavelength was selected to detect the absorbance changes. The volume of the solution was 2ml.

The viscosity measurements of the polymer solution were performed with a conical disk type rotational rheometer (Physica, MCR-301) equipped with a measuring cone (CP50-1) and a plate (P-PTD200). The volume of solution for the measurement was 0.6 ml. All the measurements were done at a constant shear rate of 50 s^{-1}. Under a constant temperature at 25 °C, viscosity changes of the polymer solution were monitored as a function of time.

[1] Schubert, U. S.; Hien, O.; Eschbaumer, C. *Macromol Rapid Comm* **2000**, *21*, 1156.

[2] Lohmeijer, B. G. G.; Schubert, U. S. *Angew Chem Int Edit* **2002**, *41*, 3825.

[3] Sakai, T.; Matsunaga, T.; Yamamoto, Y.; Ito, C.; Yoshida, R.; Suzuki, S.; Sasaki, N.; Shibayama, M.; Chung, U. I. *Macromolecules* **2008**, *41*, 5379.



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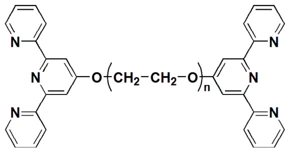

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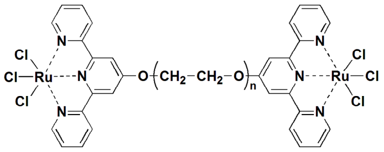

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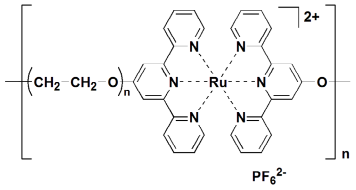
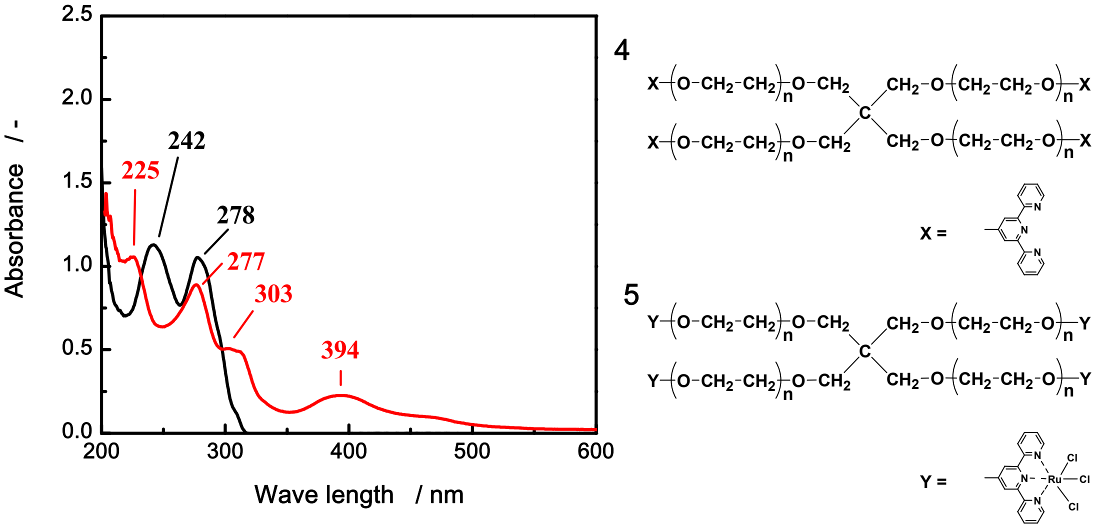
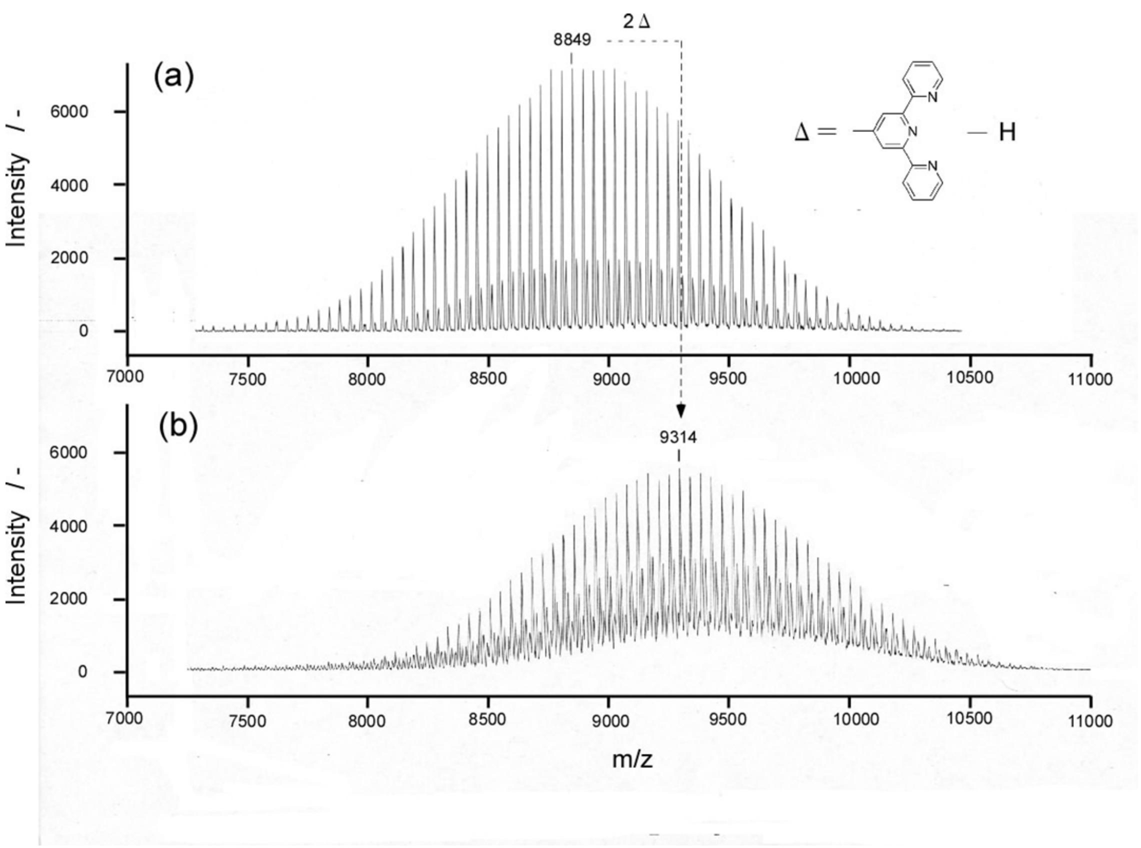


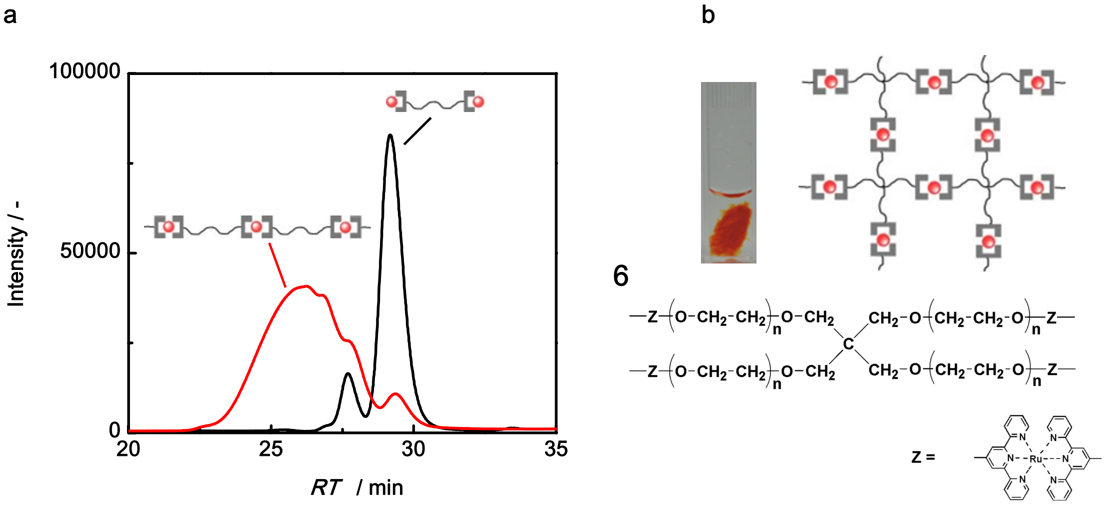
SI Figure 1 UV/VIS spectra of **1** (▬ : 0.2 mg/ml in acetonitrile), **2** (▬ : 0.2 mg/ml in methanol) and **3** (▬ : 0.18 mg/ml in acetonitrile).



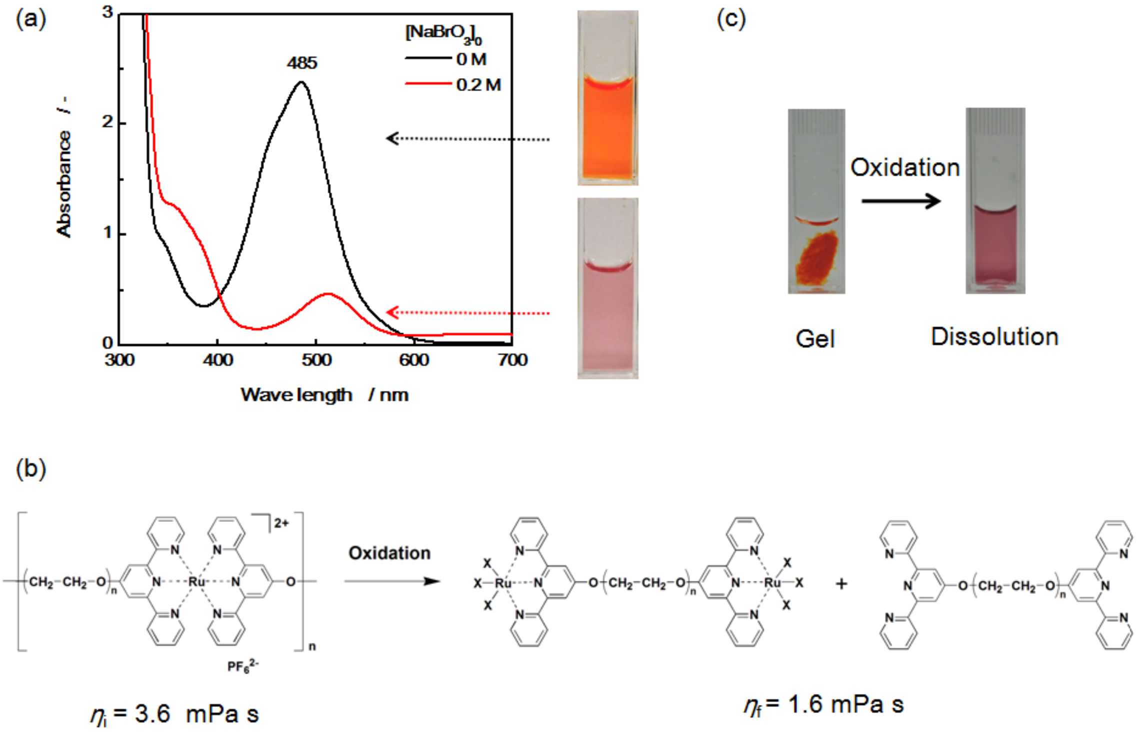
SI Figure2 UV/VIS spectra of **4** (— : 0.24 mg/ml in acetonitrile), **5** (— : 0.19 mg/ml in methanol).



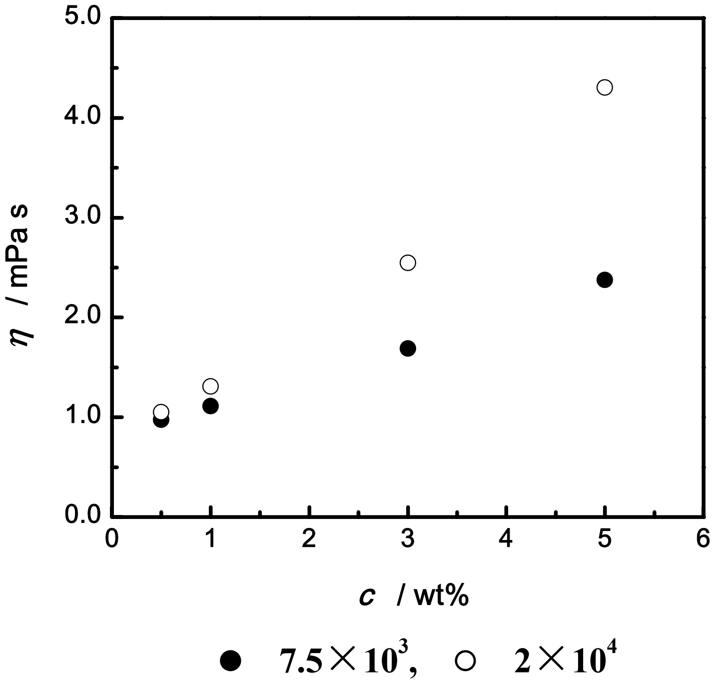
SI Figure 3 Mass spectra obtained by MALDI-TOF/MS. α-Cyano-4-hydroxycinnamic acid (in acetone) was used as a matrix. (a) poly(ethylene glycol) and (b) α, ω-bis(2,2':6',2"-terpyrid-4'-yl)-poly(ethylene glycol). The mass numbers shifted to higher mass numbers only the molecular weights of terpyridine.



SI Figure 4 The checks of binding between polymers via Ru(terpy)$_2$. (a) Gel permeation chromatographs of (━━: α,ω-bis(2,2':6',2"-terpyrid-4'-yl-ruthenium(III)chloride)-poly(ethylene glycol) **2**), and (━━ : Poly (bis(2,2':6',2"-terpyrid-4'-yl)-poly(ethylene glycol) ruthenium(II)) **3**) in DMF containing LiBr. The molecular weight is higher as the retention time (*RT*) is shorter. The molecular weight of **3** was higher than that of **2**. (b) Photographs of poly(tetra(2,2':6',2"-terpyrid-4' -yl)-poly(ethylene glycol) ruthenium(II)) gel **6**.



SI Figure 5 UV/VIS spectrum, viscosity and formation changes by adding of NaBrO$_3$. (a) UV/VIS spectrum,— : in aqueous solution containing **3** (0.5 wt%) and HNO$_3$ (0.3M) and — : in aqueous solution containing **3** (0.5 wt%), HNO$_3$ (0.3M) and NaBrO$_3$ (0.2M). By adding of NaBrO$_3$, Ru(terpy)$_2$ was oxidized and the absorbance of Ru(terpy)$_2$ at 485 nm from MLCT disappeared. (b) The viscosity of the initial state after adding NaBrO$_3$ (η_i), and the viscosity of final state after the reaction (η_f) in the aqueous solution containing **3** (3 wt %), HNO$_3$ (0.3 M), and NaBrO$_3$ (0.4 M). The viscosity decreased from 0.0036 to 0.0016 Pa s. (c) Poly(tetra(2,2':6',2"-terpyrid-4'-yl)-poly-(ethylene glycol) ruthenium(II)) gel was oxidized by in aqueous solution containing HNO$_3$ (0.3 M) and NaBrO$_3$ (0.4M). The gel was solved into the solution.



SI Figure 6 Concentration and molecular weight dependence of the viscosity of poly(ethylene glycol) aqueous solution.