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Synthesis of a star-shaped polymer by coordination of 2.2'-bipyridyl-terminated poly(propylene glycol) with ruthenium ion

Gen-ichi Konishi, Yoshiki Chujo*

Department of Polymer Chemistry, Graduate School of Engineering,
Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan

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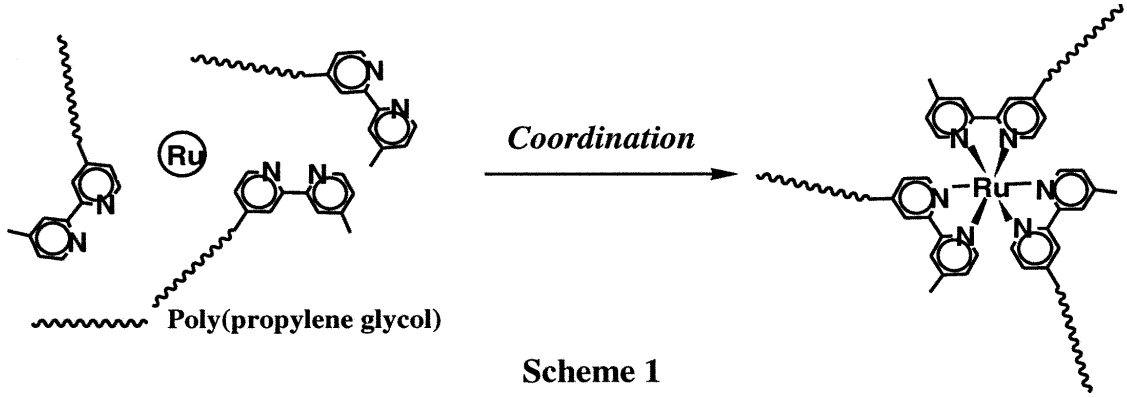
Summary
The Ru(II)-centered star-shaped polymer was prepared by coordination of 2,2'-bipyridyl-terminated poly(propylene glycol) with ruthenium ion. The structure was confirmed by GPC analysis and UV/Vis spectrum. The resulting polymer complex was well-soluble in various organic solvents and water.

Introduction

Metallo-polymers or gels containing transition metal complexes have been extensively investigated from synthetic viewpoints [1-6]. In particular, the construction of polymer structure *via* coordination between transition metal ions and ligands is simple and fruitful synthetic method [2, 4, 6].

Previously, we reported the preparation of metal-centered star-shaped polymers by coordination of 2,2'-bipyridyl-terminated poly(oxyethylene) with ruthenium ion [4]. This type of star polymer is one of homogeneous organic-inorganic composites on molecular level. Metal-centered star-shaped polymers can be constructed by infinite combinations of both organic polymers and transition metal complexes and have considerable potentials such as electronic, magnetic, photochemical properties and polymer blend. It is very important to extend their scope toward other organic polymers. Poly(propylene glycol) is a common organic polymer and shows excellent solubility in various organic solvents or processability distinct from poly(oxyethylene).



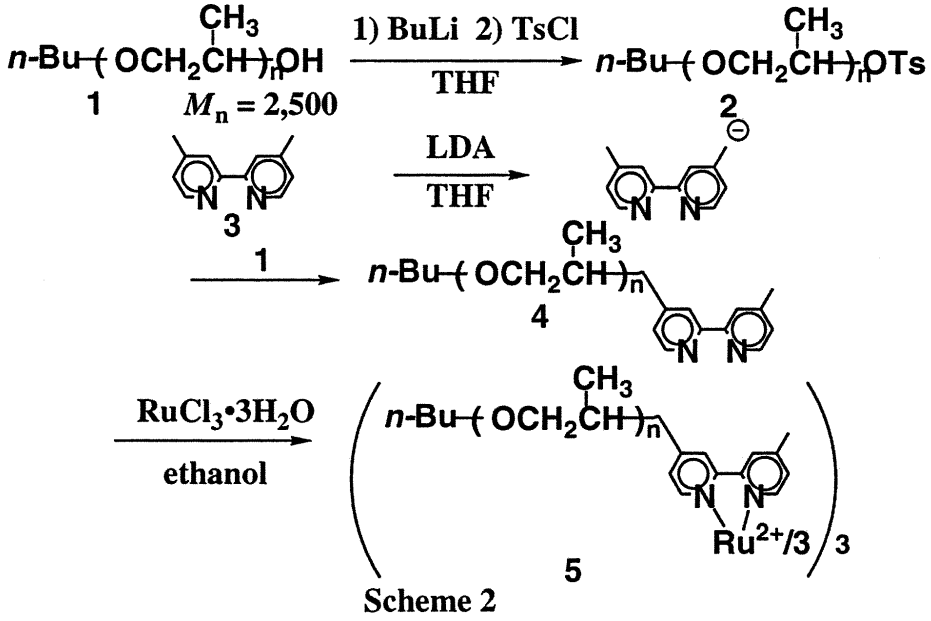
Scheme 1

* Corresponding author

In this paper, we report the preparation of a novel Ru(II)-centered star-shaped polymer by coordination of a 2,2'-bipyridyl-termhiated poly(propylene glycol) with ruthenium ion. (**Scheme 1**)

Results and discussion

2,2'-Bipyridyl-terminated poly(propylene glycol) (**bpy-PPG**) (**4**) was prepared from commercially available poly(propylene glycol) monobutyl ether (M_n = 2,500) as a starting material according to **Scheme 2**. **4** was obtained by the reaction of tosylate of poly(propylene glycol) monobutyl ether (**2**) with a mono-anion of 4,4'-dimethyl-2,2'-bipyridyl (**3**) in 10% yield. Purification of **4** was carried out by a strong acidic ion-exchange resin (Amberlist 15E). It is noted that using the ion-exchange resin the pure ligand was obtained although the end-functionalization was not completely achieved. A star-shaped polymer (**5**) was prepared by coordination of **4** with ruthenium ion. A water-ethanol solution containing 3 equiv. of **4** and 1 equiv. of $RuCl_3 \cdot 3H_20$



Scheme 2

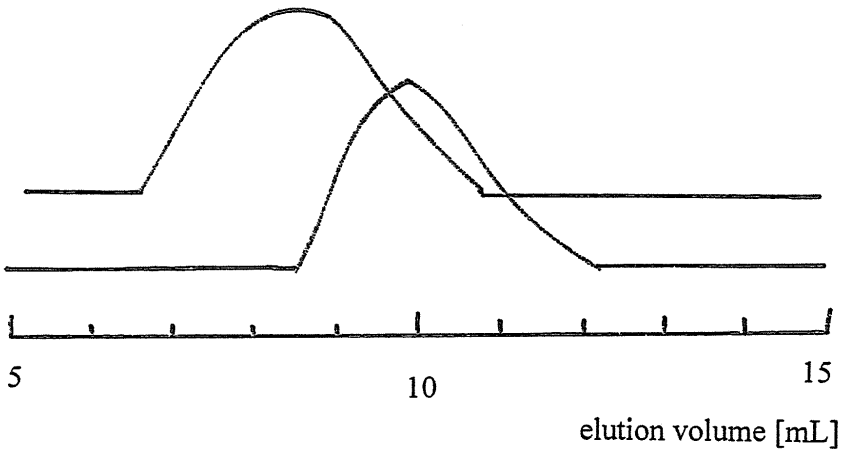
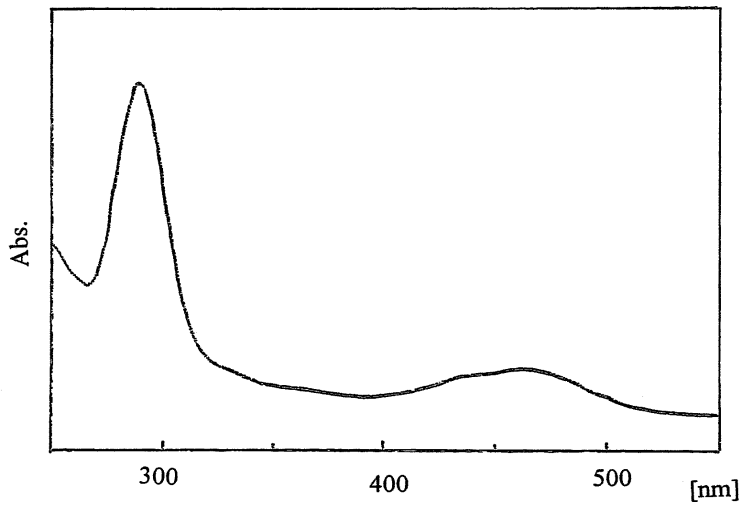


Fig. 1 GPC traces of **4** and **5**

was refluxed under nitrogen atmosphere for 4 days. After purification by gel-filtration, **5** was obtained in 96 % yield as an orange-red solid. (**Scheme 2**)

The GPC analysis of **4** is demonstrated in **Fig 1**. The peak of 5 was unimodal and was found to be shifted to a higher molecular weight region than that of **4**.



The UV/Vis spectrum of **5** is shown in **Fig. 2**. The spectrum was very similar to that of the model complex [Ru(4,4'-dimethyl-2,2'-bipyridyl)$_3^{2+}$] [7]. The characteristic absorption around 400 - 500 nm (λ_{max} = 462) assigned to the metal-to-ligand charge transfer (MLCT) absorption.

From these results, it is confirmed that a desirable star-shaped polymer (**5**) was obtained. **5** was well-soluble in chloroform, benzene, methanol, THF, and water. The solubility of **5** was similar to that of the corresponding poly(propyleneglycol). **4** is a liquid but **5** is a solid. The present star-shaped polymer showed a film-forming property, and is expected as a novel photochemical device. As a further investigation, we will design mixed-armed metal-centered star-shaped polymers as a new class of star polymers or block copolymers by using several types of 2,2'-bipyridyl-terminated organic polymer.

Experimental section

Materials and instruments

Unless otherwise noted, all materials were obtained from commercial suppliers and used without purification. Poly(propylene glycol) monobutyl ether (M_n = 2,500) (**1**) was obtained from Aldrich and stored under high vacuum at 50 °C for 12 h before use. THF was distilled from sodium benzophenone ketyl. Chromatographic separations were carried out by Sephadex LH-60 (Pharmacia) by using chloroform as an eluent. ^{1}H-NMR spectrum was recorded at 270 MHz on a JEOL EX-270 in $CDCl_3$ solution with TMS as an internal standard. GPC analysis was carried out on a Shodex K803 by using chloroform as an eluent. UV/Vis spectra were recorded by a JASCO V-530 spectrometer.

Tosylate of poly(propylene glycol) monobutyl ether (2)

To a solution made from 150 mL of THF and 1 (25 g, 10 mmol), was added *n*-BuLi (1.5 N in *n*-hexane solution) (7.4 mL, 11 mmol) at 0°C for 10 min. After stirring for 15

min at the same temperature, 20 mL of THF solution of *p*-toluenesulfonyl chloride (1.9 g, 10 mmol) was added to the resulting solution. The reaction mixture was stirred overnight at room temperature. The resulting solution was filtered and concentrated *in vacuo* and used without further purification. The crude product (**2**, 27 g) was obtained.

2,2'-Bipyridyl-terminated poly(propylene glycol) (bpy-PPG) (4)

Preparation of **4** was carried out according to Meyer's method [8]. In a 200 mL round bottom flask were introduced, under nitrogen atmosphere, 4,4'-dimethyl-2,2'-bipyridyl (**3**) (1.84 g, 10 mmol) and 120 mL of THF. The resulting solution was cooled to - 10°C and 2.0 M lithium diisopropylamide (LDA) (5 ml, 10 mmol) was added for 15 min by a syringe. After 15 min, the flask was cooled to - 78°C and stored for 2 h. Then 80 mL of THF solution of **2** (27 g, 10 mmol) was added to the dark brown solution for 30 min via cannula and stored for overnight. The reaction was quenched by a small portion of methanol. The resulting solution was concentrated under reduced pressure. The terminal 2,2'-bipyridyl group of the crude polymer was absorbed to 20 g of Amberlyst 15E (a strong acidic ion-exchange resin) in 200 mL of methanol. The ion-exchange resin was washed with methanol and then treated with 300 mL of a basic solution ($MeOH/Et_3N$ = 1 : 1). The resulting solution was concentrated under reduced pressure. The residue was purified by gel-filtration four times to give **bpy-PPG** (**4**) (2.72 g, 10%). ^{1}H-NMR ($CDCl_3$): δ = 0.90-1.30 (PPG), 2.43) (5H, Ar-CH3 & Ar-CH2), 3.20-3.70 (PPG), 7.12 (2H, bpy), 8.22 (2H, bpy), 8.52 (2H, bpy) ; UV/Vis (CH3OH): 282 [bpy] (nm).

Preparation of the star-shaped polymer (5)

A mixture of **4** (165 mg, 60 µmol), $RuCl_3 \cdot 3H_20$ (5.22 mg, 20 µmol) and 5 ml of ethanol was refluxed under nitrogen atmosphere for 4 days. The reaction mixture was cooled at room temperature and concentrated under reduced pressure. The residue was dissolved in chloroform and filtered. After purification by gel-filtration, the star-shaped polymer (**5**) was obtained (161 mg, 96%) as an orange-red solid. UV/Vis (CH_30H): 289, 462 [MLCT] (nm).

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