

Preparation of Osmium(II)-Centered Star-Shaped Polymer by the Coordination of 2,2'-Bipyridyl-Terminated Poly(oxyethylene) with Osmium Ion

Gen-ichi Konishi and Yoshiki Chujo*

Department of Polymer Chemistry, Graduate School of Engineering,
Kyoto University, Kyoto 615-8510, Japan

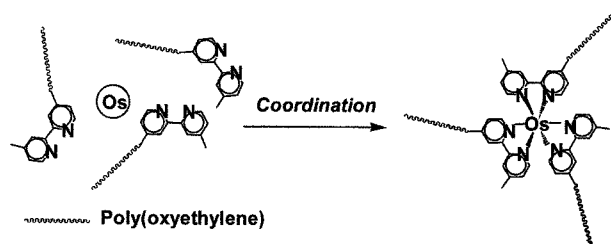
Received June 29, 2007; Revised October 19, 2007

Introduction

Metallo-polymers containing transition metal complexes have been extensively investigated from the synthetic viewpoint.^{1,2} In particular, the construction of a polymer structure *via* the coordination between transition metal ions and ligands appears promising as a simple and productive synthetic method. Previously, we reported the preparation of Ru(II)-centered star-shaped polymers by the coordination of 2,2'-bipyridyl-terminated poly(oxyethylene)³ or poly(propylene glycol)⁴ with the ruthenium ion. This type of star polymer is a homogeneous organic-inorganic composite on the molecular level. Metal-centered star-shaped polymers can be constructed by infinite combinations of both organic polymers and transition metal complexes and have considerable potential as electronic, magnetic and photochemical materials. It is thus very important to extend this methodology using the ruthenium complex to other transition metal complexes.

Osmium(II)-polypyridine complexes⁵⁻⁷ have a strong metal-to-ligand charge transfer (MLCT) absorption in the visible region and show a characteristic emission in the near-infrared region. They are also interesting as visible light-response photochemical devices or as photocatalysts similarly to ruthenium(II)-polypyridine complexes.

On the other hand, star-shaped polymers⁸ have significant



Scheme I. Preparation of Os(II)-bipyridyl complex-centered star-shaped polymer.

*Corresponding Author. E-mail: chujo@chujo.synchem.kyoto-u.ac.jp

material potential. Compared to a linear polymer, the characteristic properties of these polymers derived from their unique shape were observed in solution or in bulk from various viewpoints. For example, a high-ordered structure was constructed from asymmetric star polymer.^{8(b)}

In this paper, we report the preparation of a novel Os(II)-centered star-shaped polymer by the coordination of 2,2'-bipyridyl-terminated poly(oxyethylene) with the osmium ion (Scheme I).

Experimental

Materials and Instruments. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Poly(ethylene glycol) monomethyl ether ($M_n = 2,000$) (**1**) was obtained from Aldrich. THF and benzene were distilled from sodium benzophenone ketyl. Chromatographic separations were carried out by Sephadex LH-60 (Pharmacia) by using methanol as an eluent. ¹H-NMR spectrum was recorded at 270 MHz on a JEOL EX-270 in CDCl₃ 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(ethylene glycol) Monomethyl Ether (2). To a solution made from 150 mL of benzene and poly(ethylene glycol) monomethyl ether ($M_n = 2,000$) (**1**) (20 g, 10 mmol), was added *n*-BuLi (1.5 N in hexane solution) (7.4 mL, 11 mmol) at 5 °C for 10 min. After stirring for 15 min at the same temperature, 20 mL of a benzene 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 under reduced pressure. The obtained solid was freeze-dried with benzene and used without further purification. The crude product (**2**, 22 g) was obtained.

2,2'-Bipyridyl-terminated Poly(oxyethylene) (bpy-POE) (4). Preparation of **4** was carried out according to Meyer's method.⁹ 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 100 mL of THF-benzene (THF : benzene = 1 : 1) solution of **2** (20 g, 9 mmol) was added to the dark brown solution for 45 min via a cannula and stored 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

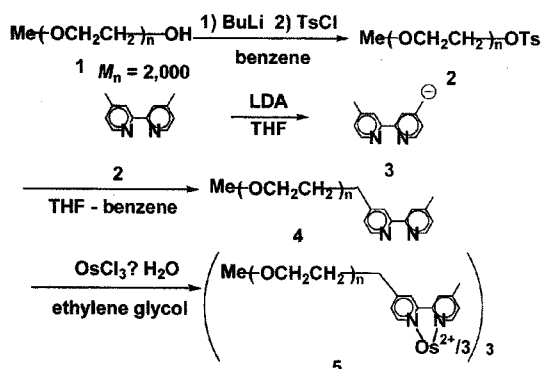
resin was washed with methanol and then treated with 300 mL of a basic solution (MeOH/Et₃N = 1 : 1). The resulting solution was concentrated under reduced pressure. The residue was dissolved in dichloromethane and then reprecipitated in diethyl ether. After purification by gel-filtration, bpy-POE (**4**) (6.1 g, 30%) was obtained as a pale pink solid. ¹H-NMR (CDCl₃): δ 2.30 (s, 3H, Ar-CH₃), 2.44 (t, 2H, Ar-CH₂), 3.30-3.70 (m, POE), 7.12 (m, 2H, bpy), 8.22 (m, 2H, bpy), 8.52 (m, 2H, bpy); UV/Vis (CH₃OH): 282 [bpy] (nm).

Preparation of the Star-Shaped Polymer (5). The star-shaped polymer (**5**) was prepared according to Bard's method.⁶ A mixture of **4** (264 mg, 120 μmol), OsCl₃·3H₂O (7.0 mg, 20 μmol) and 5 mL of ethylene glycol was refluxed under argon atmosphere for 3 days. The reaction mixture was cooled to room temperature and concentrated *in vacuo*. The residue was dissolved in chloroform and filtered. After purification by gel-filtration four times, the star-shaped polymer (**5**) was obtained (82.7 mg, 60%) as a dark green solid. The results of GPC measurement and UV/Vis spectrum are shown in the text.

Results and Discussion

Preparation of Star-Shaped Polymer. 2,2'-Bipyridyl-terminated poly(oxyethylene) (bpy-POE) (**4**) was prepared from commercially available poly(ethylene glycol) monomethyl ether (*M_n* = 2,000) as starting material, representing an improvement to our previous method.³ **4** was obtained by the reaction of tosylate of poly(ethylene glycol) monomethyl ether (**2**) with a mono-anion of 4,4'-dimethyl-2,2'-bipyridyl (**3**) in 30% yield. **4** was purified using a strong acidic ion-exchange resin (Amberlist 15E) and reprecipitation. It should be noted that the pure ligand was isolated using ion-exchange resin, but that end-functionalization was not completely achieved.

The star-shaped polymer (**5**) was prepared by coordination of bpy-POE (**4**) with the osmium(III) ion according to Bard's method.⁶ An ethylene glycol solution containing 6 equiv. of **5** and 1 equiv. of OsCl₃·3H₂O was refluxed under argon atmosphere for 4 days. After purification by gel-filtration four



Scheme II. Preparation of star-shaped polymer.

times, **5** was obtained in 60% yield as a dark green solid. (Scheme II).

Characterization. The GPC trace of **5** is demonstrated in Figure 1. The peak of **5** (*M_n* = 11,800; polystyrene standards) was unimodal and was found to be shifted to a higher molecular weight region than that of **4** (*M_n* = 5,200). In the case of branched polymers such as star polymer and graft polymer, a molecular weight (*M_n*) based on GPC analysis may be observed smaller than that of an accurate one. Therefore, this result may indicate the association of **4** to form **5**.

The UV/Vis spectrum of **5** is shown in Figure 2. This spectrum was very similar to that of the model complex [Os(4,4'-dimethyl-2,2'-bipyridyl)₃²⁺ = Os(bpy-DM)₃²⁺]^{5(a)} (Table I). The characteristic absorption above 350 nm was attributed to the MLCT absorption. **5** had a visible - near-infrared absorption.

The results of the present study indicate that the desired star-shaped polymer (**5**) was obtained. **5** was well-soluble in chloroform, benzene, methanol, DMF and water but insoluble in hexane and diethyl ether. It should be noted that

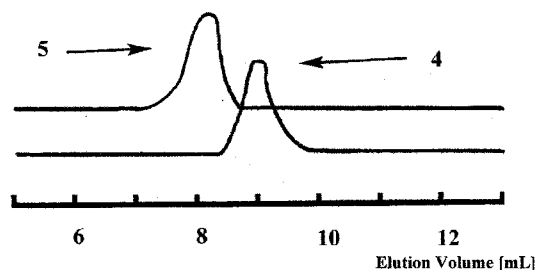


Figure 1. GPC traces of **4** and **5**.

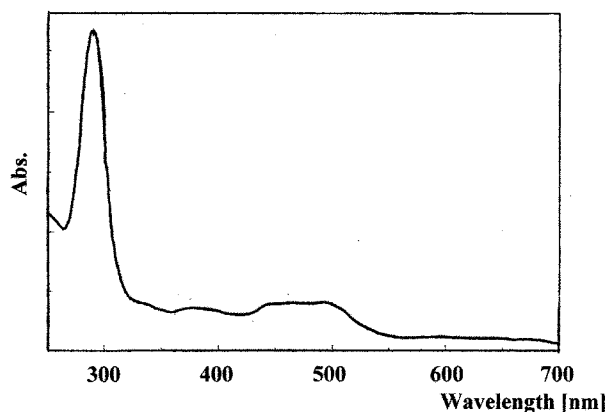


Figure 2. UV/vis spectrum of **5**.

Table I. Spectral Data of Os(II) Complexes in Water

Os(4,4'-dm-bpy) ₃ ²⁺ ^a	Abs. ^b	600	488	455	372	335	288
	ε ^c	0.34	1.2	1.2	1.1	1.1	15.6
Os(bpy-POE) ₃ ²⁺ ^a	Abs. ^b	588	491	460	375	335	291
	ε ^c	0.28	1.8	1.8	1.5	1.5	15.0

^aRef. (10). ^bλ: Absorption (nm). ^c10⁻⁴ M⁻¹ cm⁻¹.

osmium(II) complexes with no polymer chains can be dissolved in limited organic solvents only in low concentration. The present star-shaped polymer has a film-forming property. From these results, the solubility and processability of **5** were similar to that of the corresponding poly(oxyethylene) ($M_n = 2,000$). It is noted that we can design functional star-shaped polymers with desirable properties by an appropriate combination of metal ion and polymer ligand. The stability to heating and ligand exchange reactions of the osmium star-polymer was identical to that of ruthenium(II) complex-centered star-shaped polymers.^{3,4} This type metal-centered star-shaped polymer can thus be considered as a novel photochemical device with photo- and electrochemical properties that differ from those of the ruthenium(II) polymer complex.

Conclusions

Os(II)-Centered star-shaped polymer was prepared by the coordination of 2,2'-bipyridyl-terminated poly(oxyethylene) (bpy-POE) with osmium ion. The complexation of polymer ligand with metal ion proceeded as efficiently as that of the low molecular weight ligand. This methodology can easily be extended to various combinations of transition metal ion and polymer ligand. For example, we plan to design a star-shaped polymer with a polynuclear Ru(II)-Os(II) bimetallic complex¹⁰ at the center core, thus creating a new class of photofunctional materials.

References

- (1) (a) I. Manners, *Angew. Chem. Int. Ed. Engl.*, **35**, 1602 (1996). (b) U. S. Schubert and C. Eschbaumer, *Angew. Chem. Int. Ed.*, **41**, 2892 (2002). (c) E. Holder, B. M. W. Langeveld, and U. S. Schubert, *Adv. Mater.*, **17**, 1109 (2005). (d) G. Konishi and Y. Chujo, *Mol. Cryst. Liq. Cryst.*, **342**, 87 (2000).
- (2) (a) G. Konishi, K. Naka, and Y. Chujo, *J. Inorg. Organomet. Polym.*, **9**, 179 (1999). (b) K. Naka, G. Konishi, K. Kotera, and Y. Chujo, *Polym. Bull.*, **41**, 263 (1998). (c) S. Abraham, C. S. Ha, and I. Kim, *Macromol. Rapid Commun.*, **27**, 1386 (2006). (d) S. J. Choi and K. E. Geckeler, *Polymer*, **48**, 1445 (2007).
- (3) Y. Chujo, A. Naka, M. Krämer, K. Sada, and T. Saegusa, *J. Macromol. Sci. Pure Appl. Chem.*, **A32**, 1213 (1995).
- (4) G. Konishi and Y. Chujo, *Polym. Bull.*, **9**, 43 (1999).
- (5) (a) C. Creutz, M. C. Thomas, L. Netzel, M. Okumura, and N. Sutin, *J. Am. Chem. Soc.*, **102**, 1309 (1980). (b) E. M. Kober, B. P. Sullivan, W. J. Dressick, J. V. Caspar, and T. J. Meyer, *J. Am. Chem. Soc.*, **102**, 7385 (1980).
- (6) J. G. Gaudiello, P. G. Bradley, K. A. Norton, W. H. Woodruff, and A. J. Bard, *Inorg. Chem.*, **23**, 3 (1984).
- (7) V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroi, and M. Venturi, *Acc. Chem. Res.*, **31**, 26 (1998).
- (8) (a) A. Hirao, M. Hayashi, S. Loykulnant, and K. Sugiyama, *Prog. Polym. Sci.*, **30**, 111 (2005). (b) N. Hadjichristidis, M. Pitsikalis, S. Pispas, and H. Iatrou, *Chem. Rev.*, **101**, 3747 (2001). (c) A. Hirao, Y. Tsunoda, A. Matsuo, K. Sugiyama, and T. Watanabe, *Macromol. Res.*, **14**, 272 (2006). (d) T. Higashihara, K. Inoue, M. Nagura, and A. Hirao, *Macromol. Res.*, **14**, 287 (2006). (e) J. Huh, S. H. Kim, and W. H. Jo, *Macromol. Res.*, **10**, 18 (2002). (f) K. Nagahama, Y. Ohya, and T. Ouchi, *Polym. J.*, **38**, 852 (2006). (g) H. Kudo, H. Inoue, T. Nishikubo, and T. Anada, *Polym. J.*, **38**, 289 (2006). (h) H. J. Lee, K. Lee, and S. N. Lee, *J. Polym. Sci. Polym. Chem. Ed.*, **44**, 2679 (2006).
- (9) L. D. Ciana, I. Hamachi, and T. J. Meyer, *J. Org. Chem.*, **54**, 1731 (1989).
- (10) A. Juris, V. Balzani, S. Campagna, G. Denti, S. Serroni, G. Frei, and H. U. Gudel, *Inorg. Chem.*, **33**, 1491 (1994).