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Synthesis of Star-Shaped Polymers via Coordination of Bipyridyl-Terminated Polyoxyethylene with Metal Ions

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SYNTHESIS OF STAR-SHAPED POLYMERS VIA COORDINATION OF BIPYRIDYL-TERMINATED POLYOXYETHYLENE WITH METAL IONS

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ABSTRACT

This paper describes the synthesis of various star-shaped polymers by means of complexation of bipyridyl-terminated polyoxyethylene with Ru(II) ion. Three kinds of bipyridyl-terminated polyoxyethylenes of different molecular weights were prepared from the corresponding polyoxyethylene monomethyl ethers with narrow molecular weight distributions. Bipyridyl was found to be introduced quantitatively at the end of the polymers based on the results of UV spectra. The formation of a star-shaped polymer was carried out by the reaction of $RuCl_3$ with three equivalents of bipyridyl-terminated polyoxyethylene. The UV spectrum of the star-shaped polymer obtained supported the formation of a typical Ru(II) tris(bipyridyl) complex. From the results of GPC, the star-shaped polymer obtained had a higher molecular weight than the prepolymer and showed a narrow molecular weight distribution. In the case

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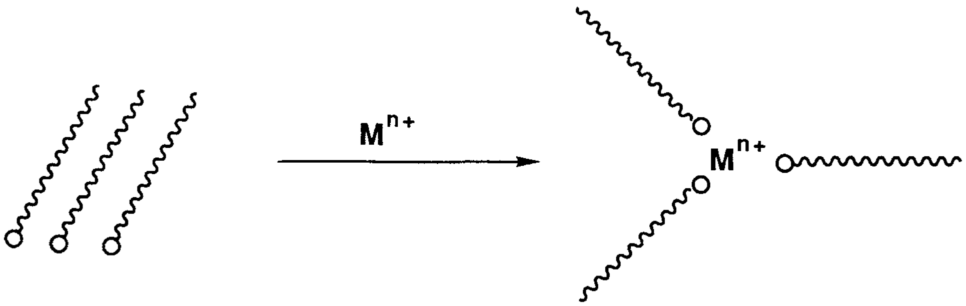
of a Ni(II) or a Co(II) complex, however, the star-shaped polymer was found to be dissociated into three linear prepolymers under the conditions of GPC measurement.

INTRODUCTION

Polymer architecture has gained increasing interest because of recent developments in living polymerization techniques. Examples are graft and block copolymers, starburst dendrimers, and hyperbranched polymers. Star-shaped polymers with well-defined structures are also of interest. A star-shaped polymer can be defined as a kind of branched polymer having more than three linear polymeric arms attached to the center core. This unique shape leads to characteristic properties in solution and in bulk that are usually different from those of linear polymers. A wide variety of star-shaped polymers has been prepared by various methods using divinyl compounds [1], coupling reagents such as multifunctional chlorosilanes [2], polyfunctional initiators [3], and so on [4].

We recently reported the preparation of polymer networks via coordination of 2,2′-bipyridyl-modified poly(*N*-acetylethylenimine) with metal ions [5]. These polymer networks show the characteristic nature of thermally or redox-reversible hydrogels corresponding to the properties of metal complexes [6]. 2,2′-Bipyridyl is a well-known bidentate ligand and tends to coordination with such transition metal ions as Fe(II), Ni(II), Cu(II), and Ru(II) to form stable complexes [7]. Ru(II) tris(bipyridyl) complex has been widely used, especially as a photosensitizer for splitting water [8]. As an approach to artificial photosynthesis, many kinds of polymeric 2,2′-bipyridyl ligands have also been prepared [9].

This paper describes the synthesis of three-armed star-shaped polymers by coordination of bipyridyl-terminated polyoxyethylene with metal ion as illustrated in Scheme 1. A star-shaped polymer with well-defined structure can be expected as a model polymer for the elucidation of characteristic properties of branched structure. These polymers also have the potential to respond to such external conditions as temperature, photoirradiation, and redox conditions due to the nature of the centered metal complexes. In other words, the interconversion between a star-shaped polymer and its dissociated form (original linear polymers) should be ob-



SCHEME 1.

served by changing the conditions. Thus, star-shaped polymers having metal complexes as cores might be interesting environmental response polymers.

EXPERIMENTAL

Instruments and Materials

UV spectra were measured in methanol on a Hitachi 200 UV-VIS spectrometer. ^{1}H-NMR spectra were obtained on a Hitachi R-600 (60 MHz) or on a JEOL JNM-JX-400 (400 MHz) spectrometer. All ^{1}H-NMR spectra were recorded in $CDCl_3$ solutions with tetramethylsilane as the internal standard. GPC analysis was carried out on a Shodex PAK K-802 or AC-803 by using chloroform as an eluent after calibration with standard polystyrene samples. In the cases of Ni(II) and Co(II) complexes, GPC measurements were carried out on a TSK-Gel GMH6X2 by using chloroform/pyridine (99/1) as an eluent. Fast atom bombardment mass spectra (FAB-MS) were obtained on a JMS-DX 300 using *m*-nitrobenzyl alcohol as a matrix.

All solvents and reagents were used as supplied except the following materials. Tosylates of polyoxyethylene monomethyl ethers (**2a**-**2c**) were prepared by the reaction of lithium alcoholates of polyoxyethylene monomethyl ethers with tosyl chloride as reported earlier [11]. Tetrahydrofuran and benzene were dried over sodium and distilled before use. Tosyl chloride was recrystallized from a mixture of chloroform and *n*-hexane. Triethylene glycol monoethyl ether (**1d**) was distilled before use.

Tosylate of Triethylene Glycol Monoethyl Ether (2d)

To a 100-mL benzene solution of triethylene glycol monoethyl ether (**1d**) (4.14 g, 23.2 mmol), 1.41 N *n*-hexane solution of *n*-butyllithium (18.1 mL, 25.5 mmol) was added at 5°C under nitrogen. After stirring for 15 minutes at the same temperature, a benzene solution of tosyl chloride (5.10 g, 26.6 mmol) was added to the resulting solution. The reaction mixture was stirred overnight at room temperature under nitrogen atmosphere. The solvent was evaporated in vacuo, leading to **2d** (7.66 g, 100%), which was used for the following reaction without further purification. ^{1}H-NMR ($CDCl_3$): δ 1.08 (t, 3H), 2.04 (s, 3H), 3.20–3.70 (m, 12H), 4.03 (t, 2H), 7.28 (d, 2H), 7.65 (d, 2H).

Bipyridyl-Terminated Polyoxyethylene (4)

As a typical procedure, in the case of bipyridyl-terminated polyoxyethylene (**4b**, M_n = 2000) a 1.66 N *n*-hexane solution of *n*-butyllithium (4.6 mL, 7.6 mmol) was added to an 8-mL THF solution of diisopropylamine (0.80 g, 7.8 mmol) at −78°C under nitrogen. The mixture was stirred for 15 minutes, and a 40-mL THF solution of 4,4′-dimethyl-2,2′-bipyridyl (**3**) (1.41 g, 7.64 mmol) was siphoned dropwise through a Teflon cannula for 30 minutes [12]. The resulting dark brown solution was stirred for 2 hours at −78°C. To the lithiated bipyridyl solution was added a 20-mL THF solution of tosylate of polyoxyethylene monomethyl ether (**2b**, 18.1 g, 8.40 mmol) by using a syringe. The mixture was allowed to warm to room temperature and stirred overnight. After the insoluble part was filtered off, the orange solution was concentrated under reduced pressure. The residue was extracted with dichloromethane and reprecipitated into *n*-hexane repeatedly. The terminal bipyridyl group of the crude polymer obtained was absorbed to a strong acidic ion-exchange resin (Amberlist E-15) in methanol. The ion-exchange resin was washed by methanol and then treated with basic solution (triethylamine/methanol = 1/1). After purification by gel filtration, the bipyridyl-terminated polyoxyethylene (**4b**) was obtained as a slightly pink solid (4.17 g, 28%). The results of GPC measurement and UV spectrum are shown in the Results and Discussion Section.

A model compound, triethylene glycol bipyridyl ethyl ether (**4d**), was prepared by using a method similar to that described above. **4d**: ^{1}H-NMR ($CDCl_3$): δ 1.19 (t, 3H), 1.96 (q, 2H), 2.44 (s, 3H), 2.30 (t, 2H), 3.30–3.70 (m, 12H), 7.14 (m, 2H), 8.23 (m, 2H), 8.52 (m, 2H).

Star Polymers (5) via Coordination with Ru(II) Ion

A typical experimental procedure is as follows. Bipyridyl-terminated polyoxyethylene (**4b**) (89.6 mg, 45.4 μmol/bpy) and $RuCl_3 \cdot xH_2O$ (14.9 μmol) were dissolved in 1.5 mL ethanol and refluxed for 3 days under nitrogen. The orange solution was evaporated in vacuo, and purification by gel filtration (Sephadex LH-20, eluent: methanol) led to the star polymer (**5b**, 83.3 mg).

The model complex (**5d**) was similarly prepared from **4d**. **5d**: ^{1}H-NMR ($CDCl_3$): δ 1.13 (t, 9H), 1.60–2.36 (6H), 2.06–2.42 (9H), 2.75–3.23 (6H), 3.23–3.89 (36H), 7.11–7.91 (12H), 8.45–8.95 (6H); FAB-MS 1134 (M^+-2Cl), 790 (M^+-2Cl-**4d**).

Star Polymer via Coordination with Ni(II) Ion

An aqueous 1 N solution of $NiCl_2 \cdot 6H_2O$ was added to three equivalents of **4a** and refluxed for 30 minutes. The resulting solution was dried in vacuo to yield the star polymer quantitatively.

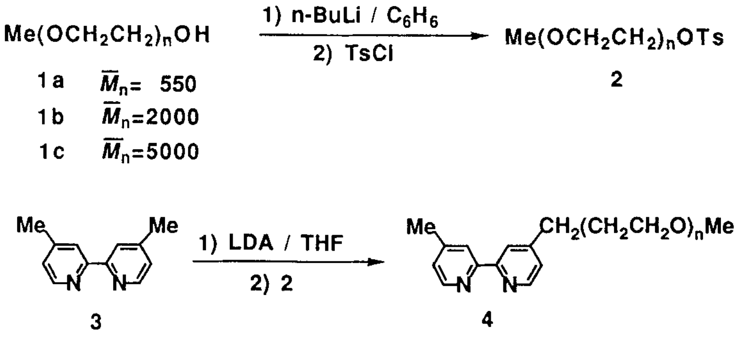
Star Polymer via Coordination with Co(II) Ion

The procedure was similar to that for Ni(II) ion except that ethanol was used as a solvent. In the case of Co(II) ion, the reaction was carried out under nitrogen atmosphere to avoid oxidation during the reaction.

RESULTS AND DISCUSSION

Preparation of Bipyridyl-Terminated Polyoxyethylene

Starting from commercially available polyoxyethylene monomethyl ethers (**1a**, M_n = 550; **1b**, M_n = 2000; **1c**, M_n = 5000), three kinds of bipyridyl-terminated polyoxyethylenes (**4a**–**4c**) with different molecular weights were prepared according to Scheme 2. The starting samples (**1a**–**1c**) have very narrow molecular weight distributions ($M_w/M_n < 1.1$). The terminal hydroxyl group in **1** was first converted



SCHEME 2.

to the tosyl group. The tosylate of **2** was then reacted with lithiated 4,4′-dimethyl-2,2′-bipyridyl, which was formed by the reaction of **3** with lithium diisopropylamide (LDA) to produce bipyridyl-terminated polyoxyethylene (**4a**–**4c**). Polymers containing no bipyridyl groups were removed by treatment with an ion-exchange resin. **4a**–**4c** were further purified by gel filtration.

As a typical example, the UV spectrum of **4b** in methanol is represented in Fig. 1. The absorption maximum of the bipyridyl group in **4b** is at 288 nm. The starting bipyridyl (**3**) has similar absorption, $\lambda = 288$ nm ($\epsilon = 12{,}780$). From the result of Fig. 1, the molecular weight of **4b** could be estimated on the basis of the molecular absorptivity (ϵ) for the starting compound (**3**). Table 1 summarizes the results of characterization of **4a**–**4c**. The molecular weight of bipyridyl-terminated polyoxyethylene was also calculated by the ^{1}H-NMR method. This value (805) was found to be close to that from UV (710), especially for the case of **4a**.

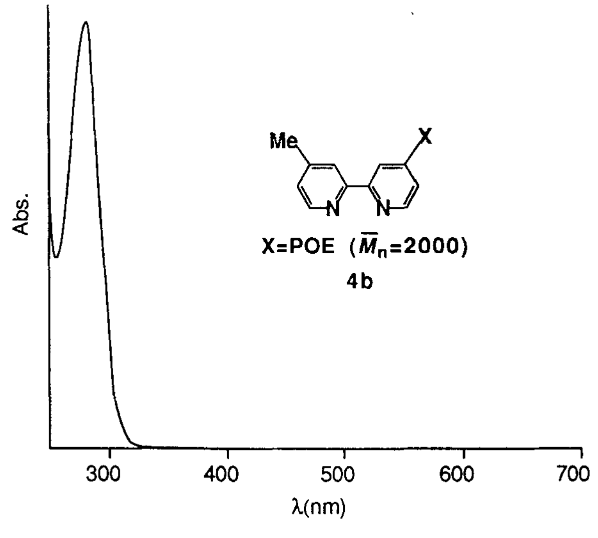


FIG. 1. UV spectrum of bipyridyl-terminated polyoxyethylene (**4b**).

TABLE 1. Preparation of Bipyridyl-Terminated Polyoxyethylene (**4**)

Run	**1**, $\overline{M}_n$	**4**, $\overline{M}_n$/bpy[a]	**4**, functionality[c]
1	550	710 (805)[b]	0.95
2	2000	1980	0.95
3	5000	5090	1.08

[a] Calculated from the results of UV spectra.
[b] Calculated from the results of ^{1}H-NMR.
[c] Theoretical $\overline{M}_n$/observed $\overline{M}_n$ of bpyPOE.

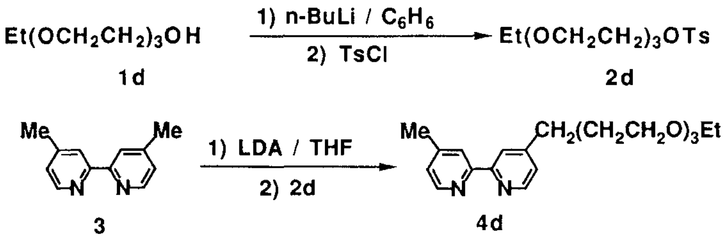
These results indicate that the bipyridyl group was effectively introduced at one end of polyoxyethylene. The functionality of the bipyridyl group in each polyoxyethylene is listed in Table 1.

A Model Reaction

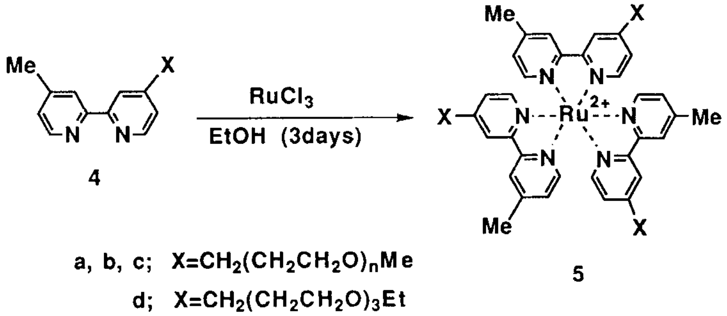
As a model compound, triethylene glycol bipyridyl ethyl ether (**4d**) was similarly prepared starting from triethylene glycol monoethyl ether (**1d**) as shown in Scheme 3. Ruthenium ion was used for the complexation with bipyridyl group because Ru(II) tris(bipyridyl) complexes are known to be thermally stable and kinetically inert [5]. Thus, three equimolar amounts of **4d** were reacted with $RuCl_3$ as shown in Scheme 4. After purification by gel filtration, the product complex (**5d**) was isolated and characterized by FAB-MS and ^{1}H-NMR spectra. These data support the formation of the tris(bipyridyl) complex in **5d**. As shown in Fig. 2(b), the absorption maximum in the UV spectrum of **5d** was observed at 459 nm, which is reasonable for the tris(bipyridyl) complex. The peak of **5d** in GPC was shifted to a higher molecular weight region in comparison with the starting **4d**, as illustrated in Fig. 3(b).

Star-Shaped Polymers via Coordination with Ru(II) Ion

Similarly to the model compound (**4d**), the bipyridyl-terminated polyoxyethylenes (**4a**-**4c**) were subjected to complexation with $RuCl_3$ (Scheme 4). The color of the solution changed from brown to orange during the reaction. The product poly-



SCHEME 3.



SCHEME 4.

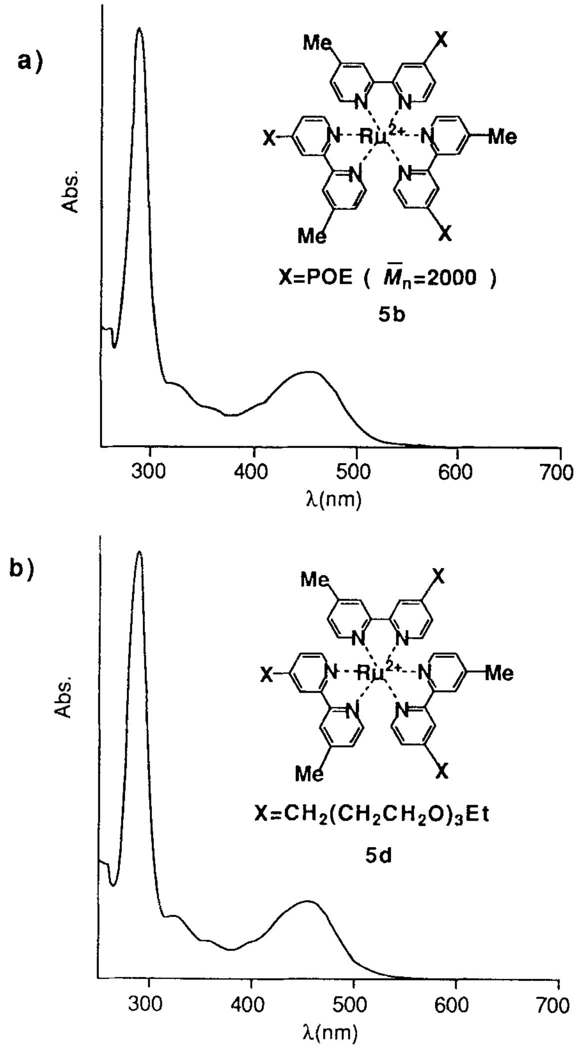


FIG. 2. UV spectra of (a) star-shaped polymer complex (**5b**) and (b) model tris(bipyridyl) complex (**5d**).

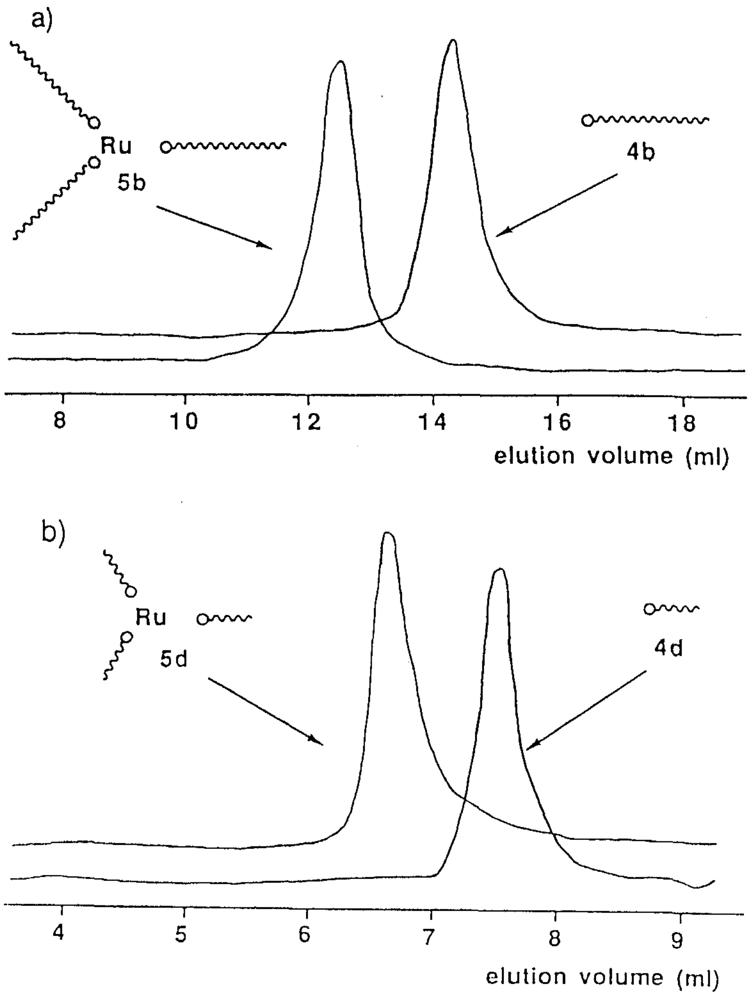


FIG. 3. GPC traces of (a) **4b** and **5b** (AC-803 column) and (b) **4d** and **5d** (K-802 column).

mer was isolated after gel filtration. Figures 2(a) and 3(a) show the results of absorption spectrum and GPC measurement of **5b**, respectively. The UV absorption of **5b** was very similar to that of a model complex (**5d**) which had an absorption maximum at 459 nm. As represented in Fig. 3(a), the peak of **5b** in GPC was found to be shifted to a higher molecular weight region than that of the starting prepolymer (**4b**). These results strongly support the formation of the tris(bipyridyl) complex in **5b**. Accordingly, it can be concluded that a star-shaped polymer having three polyoxyethylene arms was obtained via coordination of Ru(II) ion with the terminal bipyridyl group of polyoxyethylene.

Ru(II) bipyridyl complexes (**5a**–**5d**) should be a mixture of isomers (*facial* and *meridinal* forms). The exact composition of these isomers has not been clarified in the present study. However, the effect of these isomeric structures on such characteristic properties as stability, solubility, and the micelle-forming property of star-shaped polymers might be interesting, which is one of our next targets.

Coordination with Other Metal Ions

Star-shaped polymers from complexation of bipyridyl-terminated polyoxyethylene (**4a**) with Ni(II) or Co(II) ion were similarly prepared. The UV spectra of the obtained polymers are shown in Fig. 4. The absorption maxima are located at

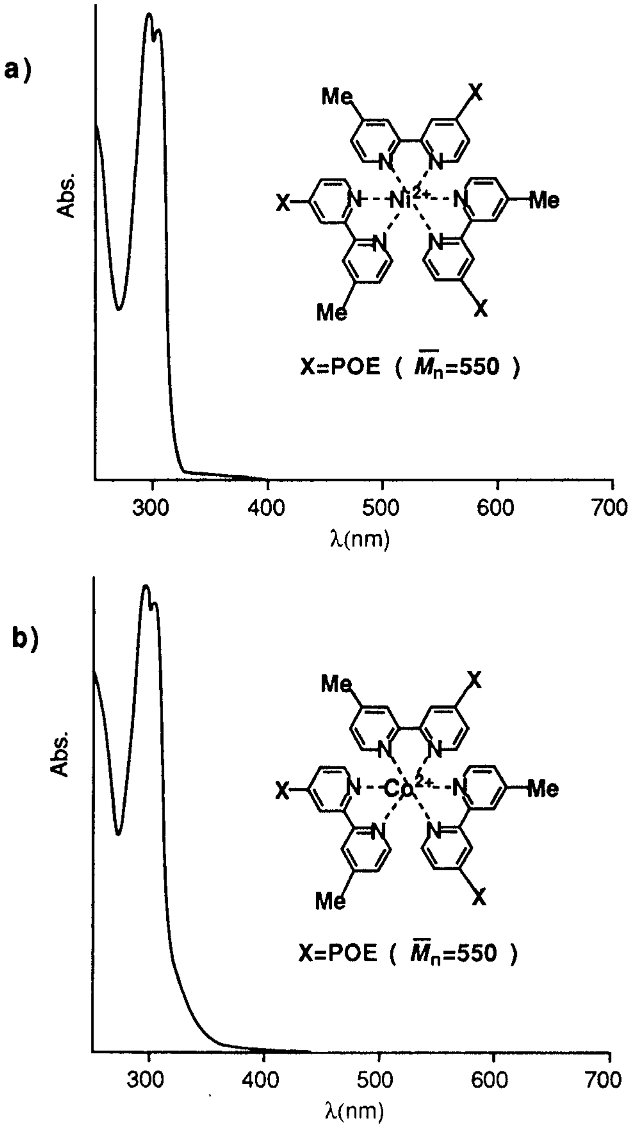


FIG. 4. UV spectra of (a) star-shaped polymer Ni(II) complex and (b) star-shaped polymer Co(II) complex.

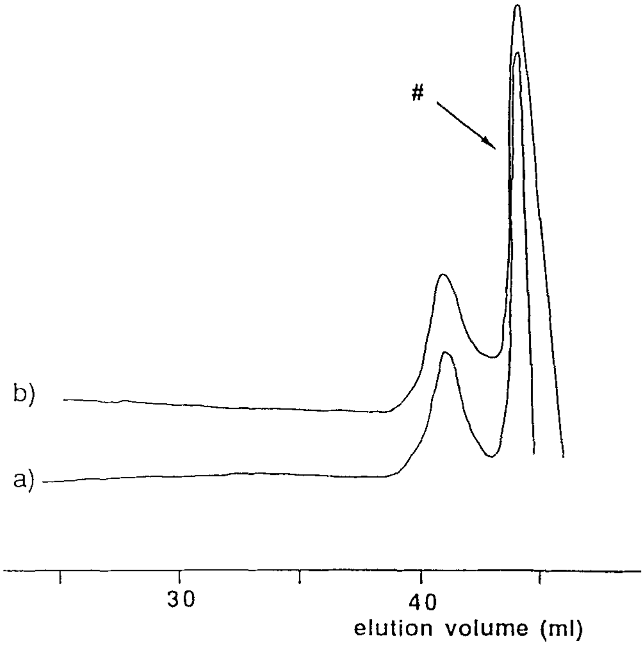


FIG. 5. GPC traces of (a) star-shaped polymer Ni(II) complex and (b) star-shaped polymer Co(II) complex (TSK Gel, GMH6X2). The mark # denotes the peak for solvent.

294 and 305 nm [for the Ni(II) complex] and at 295 and 303 nm [for the Co(II) complex]. These results support the formation of metal bipyridyl complexes. However, the results of GPC measurements (Fig. 5) showed that the peaks for these star-shaped polymers were located in the same region as the peak of the starting **4a**. The rate of dissociation of the tris(bipyridyl) complexes of these metal ions was investigated by Basolo et al. [10]. From their results, the rate of ligand exchange decreases in the order Co(II) > Ni(II) > > Ru(II). It is thus suggested that, under the conditions of GPC measurement, the Ni(II) and Co(II) complexes were dissociated into three linear polymers because of their kinetic labilities [5]. It should be pointed out that the labilities of these metal complexes might be used as characteristic functions. In other words, these star-shaped polymers with their Ni(II) or Co(II) cores can be expected to show various structures (star-shaped polymers or dissociated linear polymers) depending upon the external conditions.

Conclusion

Star-shaped polymers with metal-bipyridyl complexes as cores were effectively prepared by complexation of bipyridyl-terminated polyoxyethylene prepolymers with metal ions. The stability of these star-shaped polymers was found to depend on the nature of the core metal ions. Ru(II) bipyridyl complex formed stable star-shaped polymers, while Ni(II) or Co(II) cores were labile complexes.

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