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Yougen Chen,§a Nao Xiao,§b Toshifumi Satoh, a and Toyoji Kakuchi* a

This study describes the first convenient preparation of 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11-, and 12-armed star-shaped poly(styrene oxide) (PSO) Ru(II) complexes by a click-to-chelate approach. This approach involves the combination of the click reaction and stepwise chelating reactions of Ru(II)(DMSO)Cl2 with macroligands, 2-(1-PSO)n-1,2,3-triazol-4-ylpyridine (PSO-n-tapy) or 2-(1-PSO)n-1,2,3-triazol-4-yl)-6-(1-PSO)n-1,2,3-triazol-4-ylpyridine (PSO-n-bitapy-PSO)n (m, n = 1, 2, or 3). Click chemistry was used to prepare the PSO-tapy and PSO-n-bitapy-PSO n macroligands. More specifically, the PSO-tapy was prepared by reacting the azido-functionalized PSO0 (PSO0-N3) with excess 2-ethylnylpyridine. On the other hand, the PSO0-n-bitapy-PSO0 was obtained by the click reaction of excess PSO0-N3 with 2,6-diethynylpyridine to afford (PSO0)n-bitapy when m equals n, and by the stepwise click reactions of PSO0-N3 and PSO0-N3 with 2,6-diethynylpyridine to produce PSO0n-bitapy-PSO0 when m is not equal to n. In order to obtain these polymer-substituted macroligands, PSO0-N3 was initially synthesized by the living ring-opening polymerization (ROP) of styrene oxide (SO) using t-Bu-Pt as a catalyst and the azido-functionalized mono- or multi-hydroxyl compounds, e.g., 6-azido-1-hexanol, 2-((6-azidohexyloxy)methyl)-2-methylpropane-1,3-diol (I) and 2-((6-azidohexyloxy)methyl)-2-(hydroxymethyl)propane-1,3-diol (2), as the initiators.

Introduction

Non-covalent interactions, such as hydrogen bonding, guest-host inclusion, and electrostatic interaction, have been recognized to play an incredibly significant role in many natural phenomena and life processes. The most famous event in such fields can date back to the first discovery of the double-helix DNA, in which its two strands arrange in an anti-parallel way through a strong hydrogen bond between nucleotides. In general, such non-covalent interactions normally exhibit an interacting directionality and liability, and thus produce a very high accuracy in constructing molecular geometries. Among these non-covalent interactions, metal-ligand coordination undoubtedly plays a critical role and is a particularly attractive non-covalent interaction because of its diversity, specification, and directionality. For instance, metalloproteins and metalloenzymes have been found to serve as specific transporters of oxygen and other nutrients in living bodies. In the field of polymer chemistry, the metal-ligand coordination has been widely used to build macromolecular architectures, and the resulting metal-containing polymers, also referred to as polymer metal complexes or metallopolymers, are anticipated to have promising applications in catalysis,12 luminescent devices,4,5 and biological systems including sensing, imaging, surface modification, and drug delivery systems.6-10 A variety of metals, e.g., Zn(II), Fe(II), Cu(II), Ni(II), and Ru(II), can be used for building various molecular structures, and their chelating bonding strength significantly varies from labile to inert. This nature makes the structures of polymer metal complexes tunable and offers fascinating reversible or irreversible properties. For example, polymer metal complexes with labile metals, such as Zn(II) and Fe(II), are highly sensitive to external stimuli like heat and pH, for which they can be possibly utilized to design sensors. In comparison, those with inert metals, such as Ru(II) and Ir(II), are as stable as covalently bonded materials, which can be conveniently characterized. To date, a vast number of polymer metal complexes with various topologies, such as linear, star, dendric, and even two-dimensional motifs,11-13 have been synthesized by either a metalloinitiation (divergent) or a macroligand chelation (convergent) approach.14

In this study, the Ru(II)/ligand coordination as an extremely strong non-covalent interaction is used to prepare stable multi-arm star poly(styrene oxide) (PSOs) whose arms are held together by a luminescent Ru(II) core. In most cases, the synthesis of star polymers has been dominantly performed based on either an arm-first or a core-first procedure (covalent approach) so far, in which their arms are covalently bonded together by a core linker unit. The recent progress in the living/controlled polymerizations and click reactions has, in particular, afforded great versatility in preparing such star (co)polymers. However, this approach sometimes
encounters serious difficulty in precisely controlling the arm length and/or number due to various issues such as steric hindrance, side reactions between the living polymers, solubility problems, etc. In addition, the covalent approach also shows shortages in synthesizing mikto-arm copolymers due to the difficulty in controlling the stepwise introduction of different types of polymer arms. In contrast, for some cases, the non-covalent approach for star polymer synthesis is of great advantage. For instance, the synthesis of the star PSO with an arm number greater than four can hardly be achieved by the direct core-first ring-opening polymerization of styrene oxide (SO) due to the slight solubility of polystyrene and poly(tetrahydrofuran) (tHf) in THF. In comparison, its synthesis can be readily realized by the non-covalent method as reported in this study.

In general, the preparation of star polymer Ru(II) complexes can be implemented through two strategies (Scheme 1): (1) one-pot complexation using Ru(III)Cl₃, and (2) stepwise complexation using Ru(II)(DMSO)Cl₂ with ligands. It is notable that the utilization of Ru(III)Cl₃ initially involves the formation of a sensitive polymer Ru(III) mono-complex, which was then reduced to the Ru(II) mono-complex and further chelated with macroligands to form the polymer Ru(II) complex. Therefore, strategy (1) is very suitable for the one-pot synthesis of homopolymers. In contrast, the employment of Ru(II)(DMSO)Cl₂ can offer the opportunity to directly introduce Ru(II) species without any more reduction steps because Ru(II)(DMSO)Cl₂ can complex with a macroligand (macroligand A) at the ratio of 1:1 to form a stable Ru(II) mono-complex that can be easily isolated under common conditions. After isolation, the Ru(II) mono-complex can further chelate with another macroligand (macroligand B) to produce a polymer Ru(II) complex, which can be a homopolymer when A = B or a copolymer when A ≠ B. Strategy (2) is thus rather suitable for the stepwise synthesis of copolymers. The pioneering work involving the synthesis of star homoleptic and heteroleptic polystyrene Ru(II) complexes with arm numbers exactly controlled in the range from three to six was reported by Fraser et al.15-18 Harruna and coworkers then succeeded in the synthesis of thermo-responsive miktoarm Ru(II) complexes composed of a Ru(II) core and polystyrene and poly(N-isopropylacrylamide) arms.19-20 Thereafter, Schubert et al. reported the synthesis of homoleptic 3- and 4-arm star-shaped poly(ethylene oxide) (PEO) Ru(II) complexes.21 We also previously reported the one-pot synthesis of 3- and 4-arm star-branched polystyrene Ru(II) complexes and stepwise chelating synthesis of mikto-arm copolymers by the click-to-chelate approach.22-23 Based on the previously mentioned background, the click-to-chelate approach is now creatively utilized to synthesize 3- to 12-arm star PSOs, [Ru(PSO₂₂-tap)₃(SbF₅)₂], [Ru(PSO₂₂-tap)₂-bityp(DMSO)](SbF₅)₂, [Ru(PSO₂₂₂-bityp)(DMSO)](SbF₅)₂, and [Ru(PSO₂₂>bityp)(PSO₂₂₂-bityp)(DMSO)](SbF₅)₃ (n =1, 2 or 3).

**Experimental**

**Scheme 1.** Synthetic routes of polymer Ru(II) complexes by complexation using (1) Ru(III)Cl₃ and (2) Ru(II)(DMSO)Cl₂.

**Materials.** Toluene (> 99.5%; water content, < 0.001%) was purchased from Kanto Chemical Co., Inc., and distilled over sodium benzenophenone ketyl before use. Styrene oxide (SO; > 98.0%, Tokyo Chemical Industry Co., Ltd., TCI) was distilled over NaH prior to use. N,N-Dimethylformamide (DMF; > 99.5%) and N,N,N′,N″,N‴-pentamethyldiethylenetriamine (PMDETA; > 99.0%) from TCI, were used after distillation over CaH₂. 6-Azido-1-hexanol, 2-ethylhexylpyridine (98%), and silver hexafluoroantimonate (AgSbF₆, 98%) were commercially available from the Sigma-Aldrich Chemicals Co. and used as received. Sodium azide (NaN₃, > 97.0%) and benzoic acid (> 99.5%) were purchased from Kanto Chemical Co., Inc., and used as received. 6-Azido-1-hexanol, 2-[(6-azidohexyloxy)methyl]-2-methylpropane-1,3-diol (1), 2-[(6-azidohexyl)methyl]-2-(hydroxymethyl)propane-1,3-diol (2), and silver hexafluoroantimonate, were prepared according to the methods in the literatures.24-26

**Measurements.** The ¹H NMR spectra were recorded using a JEOL JNM-A0400 instrument in CDCl₃ as the solvent. The infrared (IR) spectra were recorded using a Perkin-Elmer Paragon 1000 FTIR instrument. The ring-opening polymerizations of styrene oxide (SO) using 6-azido-1-hexanol, 1, and 2 as initiators were carried out in an MBRAUN stainless steel glove-box equipped with a gas purification system (molecular sieves and copper catalyst) under a dry argon atmosphere (H₂O, O₂ < 1 ppm). The moisture and oxygen contents in the glove-box were monitored by an MB-MO-SE 1 and an MB-OX-SE 1, respectively. Preparative size exclusion chromatography (SEC) was performed using a JAI LC-9201 HPLC system equipped with a JAI RI-50s refractive index detector and a JAI JAI-GE-01H column (100 mm × 600 mm; exclusion limit, 7 × 10⁵) using CHCl₃. The SEC measurements in THF were performed using a Jasco GPC-900 system equipped with a Waters UltraTyrangal column (linear; 7.8 mm × 300 mm; exclusion limit, 1 × 10⁵) and two Shodex KF-804L columns (linear; 8 mm × 300 mm;
exclusion limit, 4 × 10^5) at the flow rate of 1.0 mL min^{-1} and 40 °C. The SEC measurements in CHCl₃ were performed using a Jasco GPC-900 system equipped with three Shodex K-805L columns (linear; 8 mm × 300 mm; exclusion limit, 4 × 10^5) with the flow rate of 0.8 mL min^{-1} at 40 °C. The number-average molecular weight (M_n(SEC)) and polydispersity (M_w/M_n) of the polymers were calculated on the basis of a polystyrene calibration. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) of the obtained polymers was performed using an Applied Biosystems Voyager-DE STR-H equipped with a 337-nm nitrogen laser (3-nm pulse width). Two hundred shots were accumulated for the spectra at a 25 kV acceleration voltage in the reflector mode and calibrated using the PS standard as a linear calibration. The MALDI-TOF MS measurement, the polymer (10 mg mL^{-1}) in THF, a matrix (dithranol, 20 mg mL^{-1}) in THF, and a cationizing agent (sodium trifluoroacetate, 10 mg mL^{-1}) in methanol were mixed in the ratio of the polymer/matrix/cationizing agent of 5 µL/25 µL/5 µL, and 1 µL, respectively, and the mixed solution was deposited on the sample holder.

Synthesis of azido-functionalized poly(styrene oxide) (PSO-N₃). t-Bu-PtCl₂ (221 µL, 1.0 M solution in n-hexane, 221 µmol) was added to a solution of 6-azido-1-hexanol (183.1 mg, 1.7 mmol) in toluene (1.5 mL). SO (2.52 mL, 2.26 g, 22.1 mmol) was then added to the solution. After stirring for 24 h, the polymerization was quenched by the addition of a small amount of benzoic acid (50 mg). The monomer conversion (Conv.) was directly determined by the 1H NMR measurement. Conv. = 93%. The polymerization mixture was purified by dialysis in methanol and dried in vacuo to give PSO-N₃ as a colorless glassy liquid (2.60 g, 90%). PSO-N₃: M_n(NMR), 2,200 g mol^{-1}; M_w(SEC), 2,200 g mol^{-1}; M_w/M_n, 1.06. Using the same polymerization procedure, the preparation of PSO-N₂ and PSO-N₃ was also achieved using 2 and 3 as initiators to give glassy solid products with yields of 90% (1.85 g) and 86% (1.72 g), respectively. PSO-N₂: Conv., 99%; M_n(NMR), 4,200 g mol^{-1}; M_w(SEC), 3,500 g mol^{-1}; M_w/M_n, 1.04. PSO-N₃: Conv., > 99%; M_n(NMR), 6,400 g mol^{-1}; M_w(SEC), 4,800 g mol^{-1}; M_w/M_n, 1.03.

Preparation of 2-[1-poly(styrene oxide)-1H-1,2,3-triazol-4-yl]pyrididine (PSO-tapy). PSO-N₃ (M_n(NMR), 2,200; 0.44 g, 0.2 mmol) and CuBr (22.9 mg, 1.6 mmol) were placed in a Schlenk tube. The tube was evacuated and backfilled with argon three times. A degassed mixture of 2-ethylpyrididine (60.6 µL, 0.6 mmol), PMDETA (41.8 µL, 0.2 mmol), and THF (10.0 mL) was then added. The reaction mixture was stirred at 90 °C for 24 h. After the removal of the solvent under reduced pressure, the residue was diluted in CH₂Cl₂, and washed with distilled water. The organic layer was dried over Na₂SO₄, CH₂Cl₂ was then evaporated under reduced pressure to give PSO-tapy as a light yellow viscous liquid (0.43 g, 93%). PSO-tapy: M_n(NMR), 2,300 g mol^{-1}; M_w(SEC), 2,000 g mol^{-1}; M_w/M_n, 1.06. Similarly, 2-[1-PSO-1H-1,2,3-triazol-4-yl]pyrididine (PSO-tapy) and 2-[1-PSO-1H-1,2,3-triazol-4-yl]pyridine (PSO-tapy) were prepared by click reactions with excess 2-ethylpyrididine to afford PSO-tapy (192.4 mg) and PSO-tapy (293.2 mg) with high yields of 90% and 90%, respectively. PSO-tapy: M_n(NMR), 4,500 g mol^{-1}; M_w(SEC), 3,600 g mol^{-1}; M_w/M_n, 1.04. PSO-tapy: M_n(NMR), 6,600 g mol^{-1}; M_w(SEC), 4,900 g mol^{-1}; M_w/M_n, 1.03.

Preparation of 2,6-bis[1-poly(styrene oxide)-1H-1,2,3-triazol-4-yl]pyrididine (PSO₂-tap). PSO-N₃ (M_n(NMR), 2,200; 1.1 g, 0.5 mmol) and Cu(I)Br (71.7 mg, 0.5 mmol) were placed in a Schlenk tube. The tube was evacuated and backfilled with argon three times. A degassed mixture of 2,6-diethynylpyridine (31.8 mg, 0.25 mmol), PMDETA (104.4 µL, 0.5 mmol), and THF (10.0 mL) was then added. The reaction mixture was stirred at 90 °C for 24 h. After the removal of the solvent under reduced pressure, the residue was diluted in CH₂Cl₂, and washed with distilled water. The organic layer was dried over Na₂SO₄, CH₂Cl₂ was then evaporated under reduced pressure to give (PSO₂)-tapy as a light yellow solid (0.93 g, 82%). PSO₂-tapy: M_n(NMR), 4,900 g mol^{-1}; M_w(SEC), 4,400 g mol^{-1}; M_w/M_n, 1.03. Similarly, 2,6-bis[1-PSO-1H-1,2,3-triazol-4-yl]pyridine ((PSO₂)-tapy) and 2,6-bis[1-PSO-1H-1,2,3-triazol-4-yl]pyridine (PSO₂-tapy) were prepared by click reactions with stoichiometric 2-ethylpyrididine to afford (PSO₂)-tapy (307.4 mg) and (PSO₂)-tapy (493.8 mg) with moderate yields of 72% and 76%, respectively. (PSO₂)-tapy: M_n(NMR), 9,000 g mol^{-1}; M_w(SEC), 6,600 g mol^{-1}; M_w/M_n, 1.03. (PSO₂)-tapy: M_n(NMR), 13,700 g mol^{-1}; M_w(SEC), 8,900 g mol^{-1}; M_w/M_n, 1.03.

Preparation of 2-ethyl-6-[1-PSO-1H-1,2,3-triazol-4-yl]pyrididine (PSO₂-tap). Cu(I)Br (7.2 mg, 0.05 mmol) was added to a single-neck 100-mL flask capped with a rubber plug under an argon atmosphere. A degassed mixture of PSO-N₃ (M_n(NMR), 4,200; 210 mg, 0.05 mmol), 2,6-diethynylpyridine (12.7 mg, 0.1 mmol), PMDETA (10.4 µL, 0.05 mmol), and THF (10.0 mL) was added to the 100-mL flask. After the reaction mixture was stirred at room temperature for 48 h, the reaction mixture was diluted with THF, then passed through a short SiO₂ column. The solvent was removed under reduced pressure. The residue was purified by dialysis in methanol and dried in vacuo to give PSO₂-tap as a light yellow solid (197.5 mg, 91%). PSO₂-tap: M_n(NMR), 4,600 g mol^{-1}; M_w(SEC), 3,600 g mol^{-1}; M_w/M_n, 1.04.

Preparation of 2-(1-PSO-1H-1,2,3-triazol-4-yl)6-[1-PSO-1H-1,2,3-triazol-4-yl]pyridine (PSO₂-bitap). Cu(I)Br (3.6 mg, 25 µmol) was added to a single-neck 100-mL flask capped with a rubber plug under an argon atmosphere. A degassed mixture of PSO₂-tap (M_n(NMR), 4,600; 115 mg, 0.5 mmol), PMDETA (10.4 µL, 0.5 mmol), and THF (10.0 mL) was added to the 100-mL flask. After stirring at room temperature for 48 h, the reaction mixture was diluted with THF, then passed through a short SiO₂ column. The residue was purified by preparative SEC using CHCl₃ as the eluent followed by dialysis in methanol to obtain (PSO₂)-bitap as a light yellow solid (193.9 mg, 71%). (PSO₂)-bitap: M_n(NMR), 11,300 g mol^{-1}; M_w(SEC), 8,100 g mol^{-1}; M_w/M_n, 1.04.

Preparation of Ru(PSO-tap)(DMSO)Cl₂. To a 10-mL needle flask containing CHCl₃ (1.0 mL), Ru(DMSO)Cl₂ (24.2 mg, 50 µmol) and PSO-tap (M_n(NMR), 2,300 g mol^{-1}; 57.5 mg, 25 µmol) were added. The mixture was degassed by three freeze-pump-thaw cycles. The yellow-green mixture was then heated at 65 °C for 24 h.
After cooling to room temperature, the solvent was removed. The crude product was further purified by preparative SEC using CHCl₃ as the eluent, followed by dialysis in methanol to give Ru(PSO-tapy)(DMSO)Cl₂ as a yellow solid (53.7 mg, 83%). Using the same method, the Ru(II) mono-complexes, Ru(PSO-tapy)(DMSO)Cl₂ (96.4 mg, 80%), Ru(PSO₂-tapy)(DMSO)Cl₂ (136.6 mg, 79%), Ru(PSO₂-bitapy)(DMSO)Cl₂ (213.5 mg, 82%), Ru(PSO₂₂-bitapy)(DMSO)Cl₂ (175.3 mg, 75%), and Ru(PSO₂₂-bitapy)(DMSO)Cl₂ (268.8 mg, 77%) were also prepared in moderate to high yields.

Preparation of [Ru(PSO-tapy)₃][SbF₆]₂. A mixture of Ru(PSO-tapy)(DMSO)Cl₂ (52 mg, 0.02 mmol) and AgSbF₆ (34.4 mg, 0.1 mmol) in acetone (2.0 mL) was heated in a 10-mL needle flask at 65 °C for 12 h. Followed by filtration of the precipitated AgCl, the solvent was removed to give Ru(PSO-tapy)(DMSO)[SbF₆]₂ as a yellow solid (109.5 mg, 78%). Using the same method, the Ru(II) complexes, Ru(PSO₂-tapy)(DMSO)[SbF₆]₂ (96.4 mg, 38%; Mₙ(SEC) 13,400 g mol⁻¹, 1-3 This journal is © The Royal Society of Chemistry 2012), Ru(PSO₂₂-tapy)(DMSO)[SbF₆]₂ (220.6 mg, 81%; Mₙ(SEC) 8,000 g mol⁻¹; Mₚ/Mₙ 1.12), [Ru(PSO₂₂-tapy)(DMSO)(COMe)₂][SbF₆]₂ (243.0 mg, 77%; Mₙ(SEC) 12,000 g mol⁻¹; Mₚ/Mₙ 1.14), [Ru(PSO₂₂₂-tapy)(DMSO)(COMe)₂][SbF₆]₂ (129.8 mg, 72%; Mₙ(SEC) 12,000 g mol⁻¹; Mₚ/Mₙ 1.14), and [Ru(PSO₂₂₂-tapy)(DMSO)(COMe)₂][SbF₆]₂ (235.6 mg, 59%; Mₙ(SEC) 13,400 g mol⁻¹; Mₚ/Mₙ 1.18), [Ru(PSO₂₂₂-tapy)(DMSO)(COMe)₂][SbF₆]₂ (97.1 mg, 43%; Mₙ(SEC) 14,500 g mol⁻¹; Mₚ/Mₙ 1.16), [Ru(PSO₂₂₂-tapy)(DMSO)(COMe)₂][SbF₆]₂ (96.4 mg, 38%; Mₙ(SEC) 15,600 g mol⁻¹; Mₚ/Mₙ 1.12), and [Ru(PSO₂₂₂-tapy)(DMSO)(COMe)₂][SbF₆]₂ (85.8 mg, 31%; Mₙ(SEC) 16,100 g mol⁻¹; Mₚ/Mₙ 1.19).

Results and discussion

Synthesis of azido-functionalized PSOₐ-N₃ (n = 1, 2, or 3). Azido-functionalized poly(styrene oxide)s (PSO-N₃, PSO₂-N₃, and PSO₂₂-N₃) were synthesized by the ring-opening polymerizations of styrene oxide (SO) in toluene using the phosphazene base of t-Bu-P₄ as the catalyst and 6-azido-1-hexanol, 1, and 2 as the initiators (Scheme 2), as described in our previous report.27 Table 1 summarizes the synthetic results of the PSOₐ-N₃s (n = 1, 2, or 3). The yields of the PSOₐ-N₃s were reasonable in the range of 86 - 90%. The number-average molecular weights (Mₙ(SEC)) of PSO-N₃, PSO₂-N₃, and PSO₂₂-N₃ estimated by the SEC measurements in CHCl₃ were 1,900, 3,800, and 5,800 g mol⁻¹, and were 2,000, 3,500, and 4,800 g mol⁻¹ in THF, respectively (Figure 1 (a)). The SEC traces measured in either CHCl₃ or THF showed unimodal and narrow molecular weight distributions (Mₚ/Mₙ ≤ 1.16). In order to maintain a uniform arm length in the homoleptic star PSOₐ-N₃s was well controlled. The calculated values of the repeating SO unit were 17.5 (nearly 17 × 1) for PSOₐ-N₃, 33.3 (nearly 17 × 2) for PSO₂-N₃, and 51.5 (nearly 17 × 3) for PSO₂₂-N₃, which indicated that each arm in the PSOₐ-N₃s had the same average length.

Scheme 2. Synthesis of tapy- and bitapy-functionalized polymers by click reactions of PSOₐ-N₃ (n = 1, 2, or 3) with 2-ethylpropylene or 2,6-diethylpropylene.
Figure 1. SEC traces of a) PSO$_{n}$N$_{3}$, b) PSO$_{n}$-tapy, and c) (PSO)$_{2}$-bitapy and PSO$_{n}$-bitapy-PSO$_{n}$, determined in THF at the flow rate of 1.0 mL min$^{-1}$, n = 1, 2, or 3.

Table 1. Synthesis of azido-functionalized PSO$_{n}$N$_{3}$ (n = 1, 2, or 3).

<table>
<thead>
<tr>
<th>run</th>
<th>Polymers</th>
<th>Conv. (%)$^{a}$</th>
<th>Yield (%)</th>
<th>$M_{n}$(NMR) (DP)$^{a}$</th>
<th>$M_{n}$(SEC)$^{b}$</th>
<th>$M_{w}/M_{n}$</th>
<th>$M_{n}$(SEC)$^{c}$</th>
<th>$M_{w}/M_{n}$</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>PSO$<em>{n}$N$</em>{3}$</td>
<td>93</td>
<td>90</td>
<td>2,200 (17.5)</td>
<td>1,900</td>
<td>1.14</td>
<td>2,000</td>
<td>1.06</td>
</tr>
<tr>
<td>2</td>
<td>PSO$<em>{2}$N$</em>{3}$</td>
<td>99</td>
<td>90</td>
<td>4,200 (33.3)</td>
<td>3,800</td>
<td>1.16</td>
<td>3,500</td>
<td>1.04$^{c}$</td>
</tr>
<tr>
<td>3</td>
<td>PSO$<em>{3}$N$</em>{3}$</td>
<td>&gt; 99</td>
<td>86</td>
<td>6,400 (51.5)</td>
<td>5,800</td>
<td>1.12</td>
<td>4,800</td>
<td>1.03$^{c}$</td>
</tr>
</tbody>
</table>

$^{a}$ Determined by $^{1}$H NMR in CDCl$_{3}$. $^{b}$ Determined by SEC in CHCl$_{3}$ using PS standards. $^{c}$ Determined by SEC in THF using PS standards.

The structural information of PSO$_{n}$N$_{3}$s was investigated by $^{1}$H NMR measurements. As a typical analysis for PSO-N$_{3}$ (Figure 2 (a)), the proton signals of “a” neighboring the azido group and of “b-e” due to the initiator residue were clearly observed around 3.21 ppm and in the range of 1.19-1.62 ppm, respectively. Similarly, the proton signals of “b-e” due to the residues of initiators 1 and 2 were also clearly observed in the range of 1.20-1.60 ppm for PSO$_{2}$-N$_{3}$ and 1.15-1.60 ppm for PSO$_{3}$-N$_{3}$ in Figures S1 (a) and S2 (a), respectively. In addition, the successful introduction of the azido group to PSO$_{n}$N$_{3}$ was verified by the FT-IR measurements. For instance, the characteristic stretching of azido group around 2100 cm$^{-1}$ in PSO-N$_{3}$ was clearly observed in Figure 3 (a). The same findings were also correspondingly observed for PSO$_{2}$-N$_{3}$ and PSO$_{3}$-N$_{3}$ as shown in Figures S4 (a) and S5 (a), respectively. These results, to an extent, suggested that the azido groups were introduced into PSO, PSO$_{2}$, and PSO$_{3}$ using the azido-functionalized initiators.

In order to provide a much deeper insight into the polymer structures of PSO$_{n}$N$_{3}$s, MALDI-TOF MS measurements were further carried out. As a typical example, the MALDI-TOF MS spectrum of PSO-N$_{3}$ showed a sub (●) and main series (○) of peaks in Figure 4 (a). The peak interval between the main/sub series was 120.1, which is identical to the molecular weight (M.W.) of SO. Additionally, a certain peak value of 1968.2 (m/z) agrees well with the theoretical isotopic M.W. of the sodium-cationized PSO (DP = 15) bearing an azido end group (C$_{126}$H$_{133}$O$_{16}$N$_{3}$Na: 1967.96). The main series with a stronger intensity were due to those of the denitrogenized products, which were generated during the ionization process. No other impurities were observed in the MALDI-TOF MS spectrum. These results lead to the conclusion that the azido group was quantitatively introduced to the PSO chain end. The same results were also obtained for PSO$_{2}$-N$_{3}$ and PSO$_{3}$-N$_{3}$, as supported by their MALDI-TOF MS measurements in Figures S6 (a) and S7 (a).

Figure 2. $^{1}$H NMR spectra of a) PSO-N$_{3}$, b) PSO-tapy, and c) (PSO)$_{2}$-bitapy determined in CDCl$_{3}$.

Figure 3. IR spectra of a) PSO-N$_{3}$, b) PSO-tapy, and c) (PSO)$_{2}$-bitapy.
Figure 4. MALDI-TOF MS spectra (reflector mode) of a) PSO-N$_3$, b) PSO-tapy, and c) (PSO)$_2$-bitapy.

Scheme 3. Synthesis of tapy- and bitapy-functionalized polymer ligands by click reactions of PSO$_n$N$_3$ (n = 1, 2, or 3) with 2-ethynylpyridine or 2,6-diethynylpyridine.

Table 2. Synthesis of polymer-substituted tapy and bitapy macroligands.

<table>
<thead>
<tr>
<th>run</th>
<th>Polymers</th>
<th>Yield (%)</th>
<th>$M_{n(NMR)}$ (DP)$^a$</th>
<th>$M_{n(SEC)}$ $^b$</th>
<th>$M_w/M_n$ $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>PSO-tapy</td>
<td>93</td>
<td>2,300 (17.7)</td>
<td>2,000</td>
<td>1.06</td>
</tr>
<tr>
<td>5</td>
<td>PSO$_2$-tapy</td>
<td>90</td>
<td>4,500 (35.5)</td>
<td>3,600</td>
<td>1.04</td>
</tr>
<tr>
<td>6</td>
<td>PSO$_2$-etapy</td>
<td>91</td>
<td>4,600 (35.7)</td>
<td>3,600</td>
<td>1.04</td>
</tr>
<tr>
<td>7</td>
<td>PSO$_2$-bitapy</td>
<td>82</td>
<td>4,900 (37.4)</td>
<td>4,400</td>
<td>1.03</td>
</tr>
<tr>
<td>8</td>
<td>PSO$_3$-tapy</td>
<td>90</td>
<td>6,600 (52.8)</td>
<td>4,900</td>
<td>1.03</td>
</tr>
<tr>
<td>9</td>
<td>(PSO)$_2$-bitapy</td>
<td>72</td>
<td>9,000 (70.3)</td>
<td>6,600</td>
<td>1.03</td>
</tr>
<tr>
<td>10</td>
<td>PSO$_2$-bitapy-PSO$_3$</td>
<td>71</td>
<td>11,300 (88.9)</td>
<td>8,100</td>
<td>1.04</td>
</tr>
<tr>
<td>11</td>
<td>(PSO)$_3$-bitapy</td>
<td>76</td>
<td>13,700 (108.6)</td>
<td>8,900</td>
<td>1.03</td>
</tr>
</tbody>
</table>

$^a$ Determined by $^1$H NMR in CDCl$_3$. $^b$ Determined by SEC in THF using PS standards.

Synthesis of polymer-substituted tapy and bitapy macroligands.

The polymer-functionalized tapy and bitapy macroligands were respectively synthesized by the click reactions of PSO$_n$N$_3$s with 2-ethynylpyridine or 2,6-diethynylpyridine, as illustrated in Scheme 3. Table 2 summarizes the synthetic results. For synthesizing the PSO$_n$-tapy, the PSO$_n$-N$_3$s were reacted with 2-ethynylpyridine to afford 2-[1-PSO-1,2,3-triazol-4-yl]pyridine (PSO$_n$-tapy), 2-[1-PSO$_2$-1,2,3-triazol-4-yl]pyridine (PSO$_2$-tapy), and 2-[1-PSO$_2$-1,2,3-triazol-4-yl]pyridine (PSO$_3$-tapy) in the good yields of 93, 90, and 90%, respectively. After the click reactions, the molecular weight measurements for PSO-tapy, PSO$_2$-tapy, and PSO$_3$-tapy were carried out by SEC measurements in THF, which, as expected, showed no obvious change when compared to those of their parent PSO$_n$-N$_3$s (Figure 1(b)). The $^1$H NMR spectra of the PSO$_n$-tapys (Figures 2(b), S2(b), and S3(b)), the novel proton signals due to the tapy group were observed in the range of 7.62-8.80 ppm along with those from the PSO chains. Additionally, the signals of the methylene protons neighboring the azido group in PSO$_n$-N$_3$ (3.14-3.24 ppm) completely disappeared after the click reaction. In the FT-IR measurements, it was observed that the characteristic stretching signal of the azido group around 2100 cm$^{-1}$ in the PSO$_n$-N$_3$s completely disappeared after the click reactions with 2-ethynylpyridine (see Figures 3(b), S4(b), and S5(b), respectively). The successful syntheses of PSO$_n$-tapys were further proven by their MALDI-TOF MS measurements. For instance, only one series of peaks with the peak interval of 120.1 (M.W. of SO) was observed for PSO-tapy in Figure 4(b). The peak at 20.71.6 (m/z) is identical to the theoretical isotopic M.W. of the sodium-cationized tapy end-functionalized PSO when its DP is 15 (C$_{13}$H$_{13}$O$_{4}$N$_{4}$Na: 2070.00). For the PSO$_2$-tapy and PSO$_3$-tapy, the MALDI-TOF MS measurements also afforded their perfect structural consistency as depicted in Figures S6(b) and S7(b). These investigations indicated that the tapy moiety was quantitatively introduced into PSO$_n$-s.

On the other hand, the synthesis of the structurally symmetrical 2,6-bis-[1-PSO$_2$-1,2,3-triazol-4-yl]pyridines, (PSO)$_2$-bitapy (n = 1, 2, or 3), was achieved by reacting the PSO$_n$-N$_3$s with 2,6-diethynylpyridine. The click reaction between PSO$_n$-N$_3$ and 2,6-diethynylpyridine proceeded with the initial molar ratio of [PSO$_n$-N$_3$]/[2,6-diethynylpyridine]$_0$ = 2.0, after which the SEC traces of the resulting (PSO)$_2$-bitapys shifted substantially to the higher molecular weight region in comparison to their precursors, PSO$_n$-N$_3$s, and maintained low $M_w/M_n$ of 1.03-1.04 (Figure 1(b)). Meanwhile, the $M_{n(NMR)}$s and DPs of the (PSO)$_2$-bitapys in Table 2 were almost twice those of their parent PSO$_n$-N$_3$s in Table 1. Namely, the $M_{n(NMR)}$s of (PSO)$_2$-bitapy, (PSO)$_2$-bitapy, and (PSO)$_3$-bitapy were 4,900, 9,000, and 13,700 g mol$^{-1}$, while those of PSO-N$_3$, PSO$_2$-N$_3$, and PSO$_3$-N$_3$ were 2,200, 4,200, and 6,400 g mol$^{-1}$, respectively. For the synthesis of the structurally asymmetrical 2-(1-PSO$_2$-1,2,3-triazol-4-yl)-6-[1-PSO$_2$-1,2,3-triazol-4-yl]pyridine (PSO$_2$-bitapy-PSO$_3$), the click reaction with 2,6-diethynylpyridine was carried out twice using two different...
azido-functionalized polymers, PSO$_2$-N$_3$ and PSO$_3$-N$_3$. The click reaction between an excess amount of 2,6-diethynylpyridine and PSO$_2$-N$_3$ was first carried out to afford the 2-ethynyl-6-(1-PSO$_2$-1,2,3-triazol-4-y)pyridine (PSO$_2$-etapy) in the yield of 91%, and PSO$_3$-N$_3$ was further reacted with PSO$_2$-etapy to produce PSO$_2$-etapy-PSO$_3$ with the yield of 71%. Similar to the PSO$_n$-tapy, all the characteristics concerning the structural consistency of the (PSO$_n$)$_2$-bitapys and PSO$_n$-bitapy-PSO$_3$ were followed by SEC, $^1$H NMR (Figures S1-S3), FT-IR (Figures S4-S5), and MALDI-TOF MS (Figures S6-S7) measurements.

**Scheme 3.** Synthesis of star PSO Ru(II) complexes by stepwise chelating of polymer-substituted tapy or bitapy ligands with Ru(DMSO)$_4$Cl$_2$.

**Synthesis of multi-arm star PSO Ru(II) complexes.** In this study, all the multi-arm star PSO Ru(II) complexes were synthesized by a stepwise chelating method as reported in our previous study (Scheme 4), i.e., a PSO-substituted tapy or bitapy ligand was first mono-chelated with excess Ru(II)(DMSO)$_4$Cl$_2$ to afford a stable Ru(II) mono-complex. Followed by purification, the Ru(II) mono-complex was further coordinated with another PSO-substituted tapy or bitapy ligand to produce the desired multi-arm star PSO Ru(II) complexes. After purifying by preparative SEC, the multi-arm star PSO Ru(II) complexes were obtained. During the stepwise chelating reactions, the PSO-substituted tapy/bitapy macroligands could be the same or different. When they were the same, we obtained the 3-, 4-, 6-, 8-, 9-, and 12-arm star-shaped PSO Ru(II) complexes. Otherwise, we obtained the 5-, 7-, 10-, and 11-arm star-shaped PSO Ru(II) complexes when the macroligands used in first and second chelating steps were different. In greater detail, a PSO$_n$-tapy/(PSO$_n$)$_2$-bitapy was first reacted with excess Ru(II)(DMSO)$_4$Cl$_2$ (first chelating step) in chloroform at 65°C to produce a stable Ru(II) mono-complex, Ru(PSO$_n$-tapy)(DMSO)$_2$Cl$_2$ or Ru((PSO$_n$)$_2$-bitapy)(DMSO)Cl$_2$, respectively. Thereafter, the isolated Ru(PSO$_n$-tapy)(DMSO)$_2$Cl$_2$ or Ru((PSO$_n$)$_2$-bitapy)(DMSO)Cl$_2$ was further chelated with a PSO$_n$-tapy or (PSO$_n$)$_2$-bitapy (second chelating step) to give the desired multi-arm star PSO Ru(II) complexes, i.e., 3-, 6-, and 9-arm star PSO Ru(II) complexes, [Ru(PSO$_n$-tapy)$_3$](SbF$_6$)$_2$, which were prepared from their precursors (Ru(PSO$_n$-tapy)(DMSO)$_2$Cl$_2$) with PSO$_n$-tapy, respectively. The 4-, 8-, and 12-arm star-branched PSO Ru(II) complexes, [Ru((PSO$_n$)$_2$-bitapy)$_2$](SbF$_6$)$_2$, were prepared from their precursors (Ru((PSO$_n$)$_2$-bitapy)(DMSO)Cl$_2$) with (PSO$_n$)$_2$-bitapy, respectively. Similarly, the 5-, 7-, 10-, and 11-arm star-branched PSO Ru(II) complexes, [Ru((PSO$_n$)$_2$-bitapy)(PSO$_n$-tapy)(DMSO)](SbF$_6$)$_2$, [Ru((PSO$_n$)$_2$-bitapy)(PSO$_n$-tapy)(DMSO)](SbF$_6$)$_2$, [Ru((PSO$_n$)$_2$-bitapy)((PSO$_n$)$_2$-bitapy)(PSO$_n$-tapy)(DMSO)](SbF$_6$)$_2$, and [Ru((PSO$_n$)$_2$-bitapy)((PSO$_n$)$_2$-bitapy-PSO$_n$-tapy)(DMSO)](SbF$_6$)$_2$, were obtained by the chelating reactions of Ru((PSO)$_2$-bitapy)(DMSO)Cl$_2$, Ru((PSO)$_2$-bitapy)(DMSO)Cl$_2$, Ru((PSO)$_2$-bitapy)(DMSO)Cl$_2$, and Ru((PSO)$_2$-bitapy)(DMSO)Cl$_2$ with PSO$_n$-tapy, PSO$_n$-tapy, (PSO$_n$)$_2$-bitapy,
and PSO₂-bitapy-PSO₃, respectively. After removing the unreacted macroligands by preparative SEC, the pure 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11-, and 12-armed star-shaped PSO Ru(II) complexes were obtained. Table 3 summarizes the synthetic results. The $M_{n,\text{SEC}}/M_b$ values of the 3- to 12-arm star-branched PSO Ru(II) complexes determined by SEC in CHCl₃ were in the range of 5,300–16,100 g mol⁻¹ and 1.12–1.19, respectively. The SEC traces of the multi-arm PSO Ru(II) complexes in Figure 5 exhibited a tailing effect in the high molecular weight range. We assign the emergence of this effect to the possible aggregation of the multi-arm PSO Ru(II) complexes in Figure 5 exhibited a tailing effect in the high molecular weight range. We assign the emergence of this effect to the possible aggregation of the multi-arm PSO Ru(II) complexes due to the hydrophilic interactions mostly caused by the cationic Ru(II) cores when low polarity CHCl₃ was used as the eluent solvent. It is rather clear that, with an increase in the arm numbers, the SEC trace obviously shifted to the higher M.W. region, which provided direct evidence that the multi-arm PSO Ru(II) complexes were successfully synthesized although we lacked the absolute molecular weight data from the SEC-MALS measurements.

**Figure 5.** SEC traces of 3- to 12-arm star-shaped PSO Ru(II) complexes determined in CHCl₃ at the flow rate of 0.8 mL min⁻¹.

**Table 3.** Synthesis of 3- to 12-arm star PSO Ru(II) complexes.

<table>
<thead>
<tr>
<th>run</th>
<th>star PSO Ru(II) complexes</th>
<th>Yield (%)</th>
<th>$M_{n,\text{theo.}}$ a</th>
<th>$M_{n,\text{SEC}}$ b</th>
<th>$M_b/M_n$ b</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td><a href="SbF%E2%82%86">Ru(PSO₃-tap)</a>₂</td>
<td>78</td>
<td>7,500</td>
<td>5,300</td>
<td>1.12</td>
</tr>
<tr>
<td>13</td>
<td><a href="SbF%E2%82%86">Ru(PSO₂-bitapy)</a>₂</td>
<td>81</td>
<td>10,400</td>
<td>7,700</td>
<td>1.14</td>
</tr>
<tr>
<td>14</td>
<td><a href="SbF%E2%82%86">Ru(PSO₂-bitapy)(PSO₃-tap)(DMSO)</a>₂</td>
<td>76</td>
<td>12,100</td>
<td>8,000</td>
<td>1.12</td>
</tr>
<tr>
<td>15</td>
<td><a href="SbF%E2%82%86">Ru(PSO₂-bitapy)</a>₂</td>
<td>81</td>
<td>14,100</td>
<td>10,000</td>
<td>1.14</td>
</tr>
<tr>
<td>16</td>
<td><a href="SbF%E2%82%86">Ru(PSO₂-bitapy)(PSO₂-bitapy)(DMSO)</a>₂</td>
<td>76</td>
<td>16,200</td>
<td>12,000</td>
<td>1.12</td>
</tr>
<tr>
<td>17</td>
<td><a href="SbF%E2%82%86">Ru(PSO₂-bitapy)</a>₂</td>
<td>72</td>
<td>18,600</td>
<td>12,800</td>
<td>1.14</td>
</tr>
<tr>
<td>18</td>
<td><a href="SbF%E2%82%86">Ru(PSO₂-bitapy)</a>₂</td>
<td>59</td>
<td>20,400</td>
<td>13,400</td>
<td>1.18</td>
</tr>
<tr>
<td>19</td>
<td><a href="SbF%E2%82%86">Ru(PSO₂-bitapy)(PSO₂-bitapy)</a>₂</td>
<td>43</td>
<td>23,300</td>
<td>14,500</td>
<td>1.16</td>
</tr>
<tr>
<td>20</td>
<td><a href="SbF%E2%82%86">Ru(PSO₂-bitapy-PSO₃)(PSO₂-bitapy)</a>₂</td>
<td>38</td>
<td>25,600</td>
<td>15,600</td>
<td>1.12</td>
</tr>
<tr>
<td>21</td>
<td><a href="SbF%E2%82%86">Ru(PSO₂-bitapy)</a>₂</td>
<td>31</td>
<td>28,000</td>
<td>16,100</td>
<td>1.14</td>
</tr>
</tbody>
</table>

* Calculated from (M.W. of macroligands) + (M.W. of Ru) + (2 × M.W. of SbF₆). b Determined by SEC in CHCl₃ using PS standards.

Conclusions

We succeeded in the precise synthesis of 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11-, and 12-armed star-shaped PSOs containing a chelating Ru(II) core by the click-to-chelate approach, whose synthesis can be only slightly realized by the direct living ring-opening polymerization of styrene oxide using multi-hydroxyl-functionalized initiators due to their slight solubility in solvent. The PSO₈, with a uniform arm length in the star-branched PSO Ru(II) complexes were non-covalently held by the central Ru(II)/tapy or Ru(II)/bitapy chelating interaction. In this study, the PSO₈-tapy and PSO₈-bitapy-PSO₈ complexes were more conveniently prepared by the simple click reactions of PSO₈-N₃ with ethynylpyridines than the previously reported polymer-substituted bipyridine and terpyridine ligands. In conclusion, the click-to-chelate approach provided a powerful tool for the preparation of the homoleptic multi-arm polymer Ru(II) complexes, which produced well-defined star polymers with precisely controlled architectures. More detailed investigations into other interesting polymer structures are now currently underway.

**Acknowledgements**

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**Notes and references**

a Faculty of Engineering, Hokkaido University, N13W8, Kitaku, Sapporo 060-8628, Japan. E-mail: kakuchi@poly-bm.eng.hokudai.ac.jp Division of Biotechnology and Macromolecular Chemistry, Faculty of Engineering, Hokkaido University, Sapporo, 060-8628, Japan. E-mail: kakuchi@poly-bm.eng.hokudai.ac.jp

b Present address: School of Chemical Biology and Pharmaceutical Sciences, Capital Medical University, No. 10, You’nan Men, Waixi Toutiao, Beijing, 100069, China

Y.-G. Chen and N. Xiao equally contributed to this work.

† Electronic Supplementary Information (ESI) available: ¹H NMR, IR, and MALDI-TOF MS data are available. See DOI: 10.1039/b000000x/


Yougen Chen,§,a Nao Xiao,§,b Toshifumi Satoh,a and Toyoji Kakuchi* a

The convenient preparation of multi-arm star-shaped poly(styrene oxide) Ru(II) complexes was achieved by a click-to-chelate approach which combines click reactions and stepwise chelating reactions.