Synthesis and Characterization of

Tris(2,2'-bipyridine)ruthenium(II)-Centered Polystyrenes via Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization

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ABSTRACT: A novel bipyridine-functionalized dithioester, 5,5'-bis(thiobenzoylthiomethyl)-2,2'-bipyridine (**3**), was first synthesized through a simple ester exchange reaction with the commercially available dithioester, carboxymethyl dithiobenzoate (CMDB), and further used as a RAFT agent in bulk polymerization of styrene for the synthesis of well-defined bipyridine-centered polystyrene polymers. The molecular weight is well-controlled, and also the molecular weight distribution remains quite narrow. This shows that the novel bipyridine-functionalized dithioester **3** is an efficient RAFT agent. More importantly, the good agreement between theoretical and ¹H NMR-determined molecular weights indirectly indicates that almost all of the polymer chains are centered by the bipyridine functional groups derived from the new RAFT agent. Two of the bipyridine-centered polystyrene polymers were further complexed with ruthenium(II) ions to produce tris(bipyridine)ruthenium(II)-centered polystyrene metallopolymers. The metallopolymers were characterized by UV-vis, fluorescence, size exclusion chromatography (SEC), and differential scanning calorimetry (DSC) techniques. The center of polymer chains.

Introduction

In recent years, there has been increased interest in metal-containing macromolecules due to their unique photochemical and electrochemical properties.^{1–3} Such materials have found many practical applications as supported catalysts,⁴ sensors,⁵ luminescent films, and devices⁶ and for a wide range of other purposes. Therefore, a number of different synthetic approaches have been explored to prepare a variety of polymeric metal complexes. Specifically, these can be divided into four main types. First, conventional free radical polymeri*zation*, in which ligand^{7–11} or metal complex-functionalized^{12,13} monomers are copolymerized with other comonomers or homopolymerized. For example, employing this approach, Schubert has synthesized a series of vinyl polymers bearing bipyridine or terpyridine func-tional side chains.^{8,13} Also, Tew prepared random co-polymers containing terpyridine functional group by this means,¹¹ and Fréchet et al prepared copolymers containing tris(bipyridine)ruthenium(II) (Ru(bpy)₃(II)²⁺).⁹ More interestingly, thermosensitive hydrogels containing $Ru(bpy)_3(II)^{2+}$ have been prepared via conventional radical copolymerization.¹² Second, *condensation* polymerization/coupling reaction by which bipyridinebackboned polymers are generally produced.¹⁴ Third, end-group functionalization in which terpyridine or bipyridine mono- or difunctionalized oligomers first prepared by general chemical reactions and then further interacted with metal ions to form supramolecular metallopolymers.^{15–17} Fourth, *living or controlled* polymerization in which bipyridine- or terpyridinefunctionalized initiators with or without metal ions are used for atom transfer radical polymerization (ATRP)¹⁸⁻²⁰ or ring-opening polymerization (ROP).^{19,21} Living poly-

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Scheme 1. Mechanism of RAFT Polymerization

$$\begin{array}{c} P_{m}^{n} + S & S & P_{n} \longrightarrow P_{n} & S & S & P_{m} \longrightarrow P_{m} & S & S \\ M & Z & Z & M \end{array}$$
(1)
$$M + S & S & R & Initiator \\ Z & R & P_{\overline{x}} & S & C & S \\ Z & M = Monomer \end{array}$$
(2)

merizations allow for exquisite control over molecular weight and architecture in organic polymers. Moreover, the properties of the final metallopolymers depend mainly on several variable components: the metal complex, its ligand set, as well as molecular weight and architecture of the polymer itself. Thus, living polymerization is a powerful tool for synthesis of metalcontaining polymers with well-defined binding sites and architecture.

There has recently been a surge in interest in reversible addition-fragmentation chain transfer (RAFT) polymerization due to its applicability to a wide range of monomers under a broad range of experimental conditions as compared with ATRP and ROP techniques.^{22–27} Since its invention by the CSIRO group,²² numerous investigations have been performed to elucidate RAFT mechanism and kinetics. Rizzardo et al.²⁸ proposed the RAFT mechanism, in which a propagating radical P_m is added to a dormant species $\hat{S} = \hat{C}(Z) - S - \hat{C}(Z)$ P_n to form an adduct radical P_m -S-C·(Z)-S-P_n, which can be fragmented from either side into a dormant species $P_m - S - C(Z) = S$ and a propagating radical P_n . (where *m* and *n* are interchangeable and are equal to 0, 1, 2, ...) (eq 1 in Scheme 1). However, there has been an ongoing debate regarding the mechanism that causes the rate retardation phenomena observed in some RAFT polymerization systems.²⁹ Two opposing hypotheses have been proposed for the retardation. One is slow fragmentation in which the adduct radicals are suggested to be rather stable and have long lifetime,³⁰ and the other is cross-termination in which the adduct radicals terminate with themselves or with the propagating radicals.³¹ No matter how the RAFT mechanism actually operates, the overall process results in monomer units being inserted into the RAFT agent structure (eq 2 in Scheme 1). The presence of RAFT agent **1** fragments at chain ends of the resulting polymer **2** has been confirmed by several research groups using matrixassisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS).³²

The structure of RAFT agent **1** is crucial in controlling the radical polymerization, and its effectiveness strongly depends on the nature of the groups Z and R. The choice of the Z group should favor not only the formation but also fragmentation of adduct radicals and can avoid inducing severe rate retardation as well.²³ In light of the ongoing mechanism debate, it is best that the Z group is a nonstabilizing group such as benzyl.33 The selection of the R group is also important in RAFT polymerization. The R group should be a good homolytically leaving radical group that should also efficiently reinitiate polymerization. For this purpose, a variety of RAFT agents³⁴ including those that are water-soluble,³⁵ multiarmed,³⁶ and polymeric³⁷ have been reported in the literature for special systems. However, there are very few reports regarding the synthesis and utilization of ligand-functionalized RAFT agents.³⁸ In this paper, a novel bipyridine-functionalized dithioester was prepared and used as a RAFT agent in the polymerization of styrene to produce bipyridine-centered polystyrene polymers with different molecular weights and low polydispersities. The bipyridine-centered polymers were further complexed with ruthenium metal ions to form $Ru(bpy)_{3}$ -(II)²⁺-centered polystyrene metallopolymers. The metallopolymers were further characterized by UV-vis, fluorescence, size exclusion chromatography (SEC), and differential scanning calorimetry (DSC) techniques.

Experimental Section

Materials. Thiourea (99%), carboxymethyl dithiobenzoate (CMDB, 99%), 1,2-dimethoxyethane (DME, 99%), *cis*-bis(2,2'-bipyridine)dichlororuthenium(II) hydrate [Ru(bpy)₂Cl₂·xH₂O], and silver hexafluorophosphate (AgPF₆, 99.99%) were purchased from Aldrich Co. and used as received. Styrene (99%, Aldrich) was purified by washing with an aqueous solution of NaOH (5 wt %) to remove inhibitor, followed by distilled water until the washings were neutral to litmus and fractionally distilled under vacuum. 5,5'-Bis(bromomethyl)-2,2'-bipyridine (**3a**) was synthesized from 5,5'-dimethyl-2,2'-bipyridine as described by Vogtle et al.³⁹ All other reagents and solvents were used as received unless indicated otherwise.

Characterization. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ARX400 spectrometer at 400 Hz and 100 MHz, respectively. UV-vis spectra were recorded using a Beckman DU640 spectrophotometer. Fluorescence spectra were recorded on a Photon Technology International (PTI) spectrofluorimeter. High-resolution mass spectrometry (HRMS) was performed on a VG Instruments 70SE using electron impact (EI) ionization. Elemental analysis was performed by Atlantic Microlab, Inc., Norcross, GA. Melting points were measured with a Thomas-Hoover capillary melting point apparatus without calibration. Size exclusion chromatography (SEC) was carried out on a Viscotek SEC assembly consisting of a model P1000 pump, a model T60 dual detector, a model LR40 laser refractometer, and three mixed bed columns (pore size: 10 μ m; the molecular weight range for those columns is 1000-5 000 000) from America Polymer Standards Corp. using THF as an eluent with a flow rate of 1.0 mL min⁻¹ at ambient temperature. Polymer concentrations for SEC experiments were prepared in a concentration of about

3.0 mg/mL. The SEC system was calibrated using a narrow polystyrene standard ($M_n = 92\ 600$, $M_w = 95\ 050$, $M_p = 94\ 400$, $M_w/M_n = 1.03$). Differential scanning calorimetry (DSC) measurements were performed using a Seiko DSC 220C, which was calibrated for both temperature and enthalpy using an indium standard, under a nitrogen gas atmosphere with powder samples, heating from 30 to 250 °C at a heating rate of 10 °C/min. The glass transition temperature, $T_{\rm g}$, was defined as the midpoint of the change in heat capacity.

Synthesis of 5,5'-Bis(thiobenzoylthiomethyl)-2,2'-bipyridine (3). A solution of 1.539 g (4.50 mmol) of 5,5'-bis-(bromomethyl)-2,2'-bipyridine (**3a**) and 1.370 g (18.00 mmol) of thiourea in 100 mL of ethanol-acetone mixture solvents (1:1, v/v) was heated at reflux for 20 h. After cooling, the white precipitate was filtered, washed with acetone, and dried to give 2.084 g (94%) of **3b**; mp 239 °C (dec). ¹H NMR (DMSO-*d*₆): δ = 9.31 (s, 3H, NH), 9.07 (s, 3H, NH), 8.75 (s, 2H, bpy H^{6.6}), 8.39 (d, 2H, *J* = 8.00 Hz, bpy H^{3.3}), 8.01 (d, 2H, *J* = 8.4 Hz, bpy H^{4.4}), 4.63 (s, 4H, CH₂S). Anal. Calcd for C₁₄H₁₈N₆S₂Br₂: C, 34.02; H, 3.67; N, 17.00; S, 12.98; Br, 32.33. Found: C, 34.25; H, 3.78; N, 16.76; S, 12.77; Br, 32.26.

A mixture of 2.084 g (4.22 mmol) of **3b** and 1.350 g (33.75 mmol) of NaOH in 100 mL of water was heated at 70 °C for 1.0 h. After cooling, 2.060 g (9.70 mmol) of carboxymethyl dithiobenzoate (CMDB) was added. The mixture was stirred at room temperature for 21 h. The red precipitate was filtered and washed with water and dried under vacuum to give 1.857 g (90%) of 3. The crude product was further purified by extraction using toluene to afford pure 3; mp 183-184 °C. ¹H NMR (CDCl₃): $\delta = 8.70$ (s, 2H, bpy H^{6,6}), 8.35 (d, 2H, J =8.40 Hz, bpy H^{3,3'}), 8.00 (d, 4H, J = 8.40 Hz, aryl H^{2,2'} and $H^{6,6}$), 7.82 (d, 2H, J = 8.0 Hz, bpy $H^{4,4'}$), 7.53 (m, 2H, aryl $H^{4,4'}$), 7.38 (q, 4H, J = 7.6 Hz, aryl H^{3,3'} and H^{5,5}), 4.65 (s, 4H, CH₂S). ¹³C NMR (CDCl₃): $\delta = 226.7$ (C=S), 155.10 (bpy C^{2,2}), 149.8 (bpy C^{6,6}), 144.6 (aryl C^{1,1}), 137.6 (bpy C^{4,4}), 132.7 (aryl C^{4,4}), 131.6 (bpy C^{5,5}), 128.5 (aryl C^{2,2}), 127.0 (aryl C^{3,3}), 120.9 (bpy $C^{3,3}$), 38.7 (CH₂S). HRMS (EI): calcd for $C_{26}H_{20}N_2S_4$ m/z = 488.0509; found 488.0508.

Polymerization Procedure and Kinetics. A series of parallel polymerizations were performed under argon. Polymerization mixtures were prepared according to the recipes shown in Table 1. The conversions of the styrene monomer were determined by the gravimetric method. The following procedure is typical. RAFT agent **3** (58.0 mg, 11.9×10^{-2} mmol) and styrene (2.670 g, 25.6 mmol) were added into a 10 mL Schlenk flask. The polymer mixture was degassed through four freeze-thaw-evacuate cycles, sealed under argon, and heated at 100 °C for 6 h. The resulting polymerization mixture was poured into a large excess of methanol to precipitate the resulting polymer. The polymer was collected by filtration and dried under vacuum at 50 °C overnight to yield 0.711 g of a pink polymer **PS-L3-1**. The conversion of the monomer styrene was determined to be 24.5%. ¹H NMR (400 MHz, CDCl₃): $\delta =$ 8.40-8.10 (br, m, bpy), 8.00-7.75 (br, m, Ph-C=S), 7.50-6.20 (br, m, Ph), 2.40-1.10 (br, m, CH₂CH). SEC: $M_{\rm n} = 8490$, $M_{\rm w}$ $= 8560, M_{\rm w}/M_{\rm n} = 1.01.$

Synthesis of Ru(bpy)₃(II)²⁺-Centered Polystyrene.⁴⁰ Ru(bpy)₂Cl₂·xH₂O (55.0 mg, 108.6 µmol) was dissolved in methanol (15 mL), and then AgPF₆ (170.5 mg, 674.4 mmol) was added. The purple-red solution was heated at reflux under argon for 19 h. The resultant reddish methanol solution containing a white precipitate was filtered, and then the filtrate was transferred into a 25 mL Schlenk flask and evaporated to almost dryness. Bipyridine-centered polystyrene **PS-L3-1** (200.0 mg, 33.4 μ mol based on the molecular weight of $M_{\rm n,theory} = 5992$ g/mol, $M_{\rm w}/M_{\rm n,SEC} = 1.01$), DME (10 mL), and methanol (5 mL) were added into the flask. The reaction mixture was deoxygenated by purging with argon for half hour and then heated at reflux for 3 days. The reaction was cooled to room temperature and then evaporated to almost dryness, followed by the addition of methanol. The precipitated complex was filtered and washed with methanol to remove unreacted ruthenium complex to give 233.0 mg of a brown product. The crude complex was dissolved in THF (10 mL) to give a clear solution, and then hexane (35 mL) was added dropwise into

 Table 1. Experimental Conditions and Characterization Data for Bulk Polymerization of Styrene at 100 °C with the Bipyridine-Functionalized Dithioester 3 as a Chain Transfer Agent (CTA) via Thermal Autoinitiation

| | | | | | - | | | | |
|---------|-------------------|--|-------------|-----------------|-------------------|--------------------------------------|-------------------------------|---|----------------------|
| sample | styrene (mmol) | 3^{a} (mmol $	imes$ 10 ⁻²) | time (h) | convn (wt %) | M_{n}^{b} (SEC) | M _w ^b (SEC) | $M_{ m w}/M_{ m n}{}^b$ (SEC) | M _n ^c (theory) | $M_{ m n}{}^d$ (NMR) |
| PS-L3-1 | 25.6 | 11.9 | 6 | 24.5 | 8 490 | 8 560 | 1.01 | 5 992 | 6 157 |
| PS-L3-2 | 12.8 | 5.9 | 15 | 48.6 | 16 800 | 17 400 | 1.04 | 11 426 | 11 622 |
| PS-L3-3 | 12.9 | 6.0 | 10 | 35.7 | 12 300 | 14 800 | 1.20 | 8 532 | 8 657 |
| PS-L3-4 | 13.0 | 6.0 | 12 | 42.9 | 15 000 | 19 000 | 1.27 | 10 175 | 10 241 |
| PS-L3-5 | 12.9 | 6.0 | 7 | 27.4 | 9 2 2 0 | 9 390 | 1.02 | 6 653 | 6 807 |
| PS-L3-6 | 13.1 | 6.0 | 20 | 60.5 | 21 500 | 24 800 | 1.15 | 14 293 | 14 595 |
| | | | | | | | | | |

^{*a*} The molar amount of dithioester end group is 2 times the value of the CTA **3** shown in Table 1. ^{*b*} Determined by SEC using THF as eluent on the basis of a polystyrene calibration curve. ^{*c*} The theoretical molecular weight was calculated from the expression ([M]_{*i*}/[CTA]_{*i*})*CM*₀ + M_{CTA} , where [M]_{*i*} and [CTA]_{*i*} are the initial concentrations of the monomer styrene and the CTA **3**, respectively, *C* is the fractional conversion, and M_0 and M_{CTA} are the molecular weights of the styrene monomer and the used CTA **3**, respectively. ^{*d*} Determined by ¹H NMR spectroscopy according to the equation $M_{n,NMR} = [(I_{1.10-2.40} \div 3)/(I_{8.10-8.40} \div 4)] \times 104.15 + 488.71$, where $I_{1.10-2.40}$ and $I_{8.10-8.40}$ are integral values of the peaks at $\delta = 1.10-2.40$ and 8.10-8.40; 104.15 and 488.71 are the molecular weights of styrene and **3**, respectively (cf. Figure 4).

the clear polymer solution. As a result, the complex was precipitated out and the uncomplexed polystyrene was left in solution. After the removal of the clear solution by pipet, the precipitate was washed with diethyl ether twice and then stirred in methanol for 2 days. The pure supramolecular polystyrene–ruthenium complex **PS-L3-1-Ru** was obtained by filtration, washed in turn with methanol and water, and dried in an oven under vacuum. Yield: 179.2 mg, 80%. ¹H NMR (CDCl₃): $\delta = 8.64-8.09$ (br, m, bpy), 8.09–7.8 (br, m, bpy), 7.80–7.34(br, m, bpy and Ph–C=S) 7.31–6.25 (br, m, Ph), 2.45–1.15 (br, m, CH₂CH). UV–vis (CHCl₃): λ_{max} MLCT (ϵ) = 451 nm (15 286 M⁻¹ cm⁻¹). UV–vis (CH₂Cl₂): λ_{max} MLCT (ϵ) = 452 nm (14 640 M⁻¹ cm⁻¹).

PS-L3-2-Ru was similarly prepared as described above using the following reagent loadings and purification conditions. For formation of **PS-L3-2-Ru**: Ru(bpy)₂Cl₂·*x*H₂O (55.0 mg, 108.6 μmol), AgPF₆ (170.5 mg, 674.4 μmol), and **PS-L3-2** (300.0 mg, 26.3 μmol based on the molecular weight of $M_{n,theory} = 11\ 426\ g/mol$, $M_w/M_{n,SEC} = 1.04$). For purification of **PS-L3**. **2-Ru**: 12 mL of tetrahydrofuran (THF) vs 35 mL of hexane. Yield: 235.0 mg, 74%. ¹H NMR (CDCl₃): $\delta = 8.66-8.14$ (br, m, bpy), 8.14–7.82 (br, m, bpy) 7.82–7.33 (br, m, bpy and Ph–C=S), 7.31–6.25 (br, m, Ph), 2.45–1.10 (br, m, CH₂CH). UV–vis (CHCl₃): λ_{max} MLCT (ϵ) = 451 nm (14 963 M⁻¹ cm⁻¹). UV–vis (CH₂Cl₂): λ_{max} MLCT (ϵ) = 452 nm (14 547 M⁻¹ cm⁻¹).

Results and Discussion

Synthesis of Bipyridine-Functionalized RAFT Agent. The key to successful RAFT polymerization is the presence of a suitable chain transfer agent (CTA), which is typically a dithioester. These CTAs, with the exception of carboxymethyl dithiobenzoate (CMDB), are not commercially available. Using CMDB, ester exchange reactions between dithiocarboxylic acid and thiols have been applied to the synthesis of dithioesters such as tert-butyl dithiobenzoate.41 This synthetic route is quite simple, sometimes consisting of one-step procedure. Therefore, the ester exchange approach was used to synthesize a novel bipyridine-functionalized RAFT agent. Scheme 2 shows a synthetic route for the synthesis of bipyridine-functionalized RAFT agents. First, the bromomethyl groups of 3a were reacted with thiourea under reflux using ethanol/acetone (1:1 v/v) as a reaction media to give the corresponding isothiourea hydrobromide salts 3b. The isothiourea hydrobromide salts of **3b** were hydrolyzed into the corresponding thiols in the presence of a base catalyst at 70 °C, and then the dithiol 3c was reacted in situ with CMDB to afford the desired RAFT agent 3. The crude RAFT agent 3 was further purified by extraction with toluene to produce pure **3** in good yield.

Figure 1 shows the ¹H and ¹³C NMR spectra, recorded in CDCl₃, of the purified RAFT agent **3**. In the ¹H NMR

Scheme 2. Synthetic Route for Bipyridine-Functionalized RAFT Agent



spectrum, the resonances labeled 1, 2, and 4 (chemical shift $\delta \sim 8.70$, 8.35, and 7.83 ppm, respectively) represent the aromatic protons of the bipyridine functional group, those labeled 3, 5, and 6 ($\delta \sim 8.00$, 7.52, and 7.38 ppm, respectively) represent aromatic protons of the phenyl group from the starting reactant CMDB, and those labeled 7 represent the methylene protons in the junction of the bipyridine group. Similarly, the peaks are assigned and labeled in the ¹³C NMR spectrum. Moreover, the exact mass of the RAFT agent **3** was determined to be 488.0508, which is in excellent agreement with the calculated value m/z = 488.0509 for C₂₆H₂₀N₂S₄. (The HRMS spectrum is given in Figure S1 in the Supporting Information.) These show that the synthesized compound is the target RAFT agent **3**.

RAFT Polymerization of Styrene. To examine the effectiveness of the novel dithioester **3** as a RAFT agent, a series of styrene polymerizations were carried out in bulk at 100 °C for different durations. All experiments were conducted with \sim 0.04 M RAFT agent **3**. The polymerization condition and results (loading amounts, molecular weights, polydispersities, and conversion) of these experiments are summarized in Table 1.

The evolution of molecular weight is clearly observed as peak shifts to shorter elution times, as determined by SEC (Figure 2). Furthermore, the pseudo-first-order rate plot (Figure 3A) is linear; the molecular weights determined by SEC and NMR respectively increased linearly with conversion as shown in Figure 3B. The



Figure 1. ¹H NMR (upper) and ¹³C NMR (lower) spectra in CDCl₃ of the bipyridine-functionalized RAFT agent **3**.



Figure 2. SEC chromatograms (RI traces) of polystyrenes prepared by bulk RAFT polymerization of styrene using the bipyridine-functionalized dithioesters **3** as a chain transfer agent at 100 °C via thermal autoinitiation for different reaction times (Table 1, samples **PS-L3-1** to **PS-L3-6**). [Styrene] = 8.70 M, [**3**] = 0.040 M, [styrene]/[**3**] = 218/1.

most notable observation from Figure 3B is the marked deviation of the SEC molecular weight from the theoretical molecular weight. However, the NMR-determined molecular weight is in good agreement with the theoretical molecular weight (Figure 3B and Table 1). This indicates that the molecular weights determined by SEC are not absolute molecular weights. The main cause for this discrepancy is that a polystyrene standard $(M_{\rm n} = 92\,600)$ of higher molecular weight than the measured one ($M_n < 15000$) was used for calibration. The polydispersities are generally low, ranging from 1.01 to 1.27 at all polymerization times. In all cases, the polydispersity index (PDI) remains well below the theoretical limit of 1.5 for conventional free radical polymerization. All these results indicate that the new RAFT agent 3 is quite efficient for the preparation of



Figure 3. (A) Pseudo-first-order kinetic plot of $\ln([M]_0/[M])$ vs polymerization time and (B) number-average molecular weight and polydispersity as a function of conversion for bulk polymerization of styrene by RAFT using **3** as a transfer agent at 100 °C via thermal autoinitiation (Table 1, sample **PS-L3-1** to **PS-L3-6**). [Styrene] = 8.70 M, [**3**] = 0.04 M, [styrene]/[**3**] = 218/1.

polystyrenes with low polydispersity and controlled molecular weight. In addition to styrene, RAFT polymerization of *N*-isopropylacrylamide was also controlled using the RAFT agent **3** to produce bipyridine-centered thermosensitive polymers.⁴²

The new transfer agent 3 mediated RAFT polymerization of styrene produces polystyrene with a structure in which the bipyridine functional group is located in the center of polystyrene chains (see Scheme 3). These results are similar to those obtained by using other difunctional transfer agents with analogous structure such as 1,4-bis(2-(thiobenzoylthio)prop-2-yl)benzene.⁴³ To confirm the existence of the bipyridine functional group derived from the transfer agent **3** in the polystyrene, the prepared polystyrene (**PS-L3-1** in Table 1) was analyzed by ¹H NMR. Its ¹H NMR spectrum is shown in Figure 4. Peaks a and b at 8.10-8.40 ppm were attributed to the central bipyridine group derived from the CTA **3**, and the peak *c* is assigned to the characteristic peak of the dithiobenzoate end group derived similarly from the CTA 3. The characteristic peaks a and b can be used to calculate the molecular weight of the RAFT-prepared polystyrene with the assumption that each polystyrene chain was centered by a bipyridine group derived from the RAFT agent 3. In addition, the theoretical molecular weight can be calculated by the conversion of styrene monomer. Both theoretical and ¹H NMR determined molecular weights of all prepared polystyrenes are given in Table 1. The good agreement between $M_{n,theory}$ and $M_{n,NMR}$ shows that almost all the polystyrene chains are centered by the bipyridine functional group derived from the RAFT agent 3 used for polymerization.



Figure 4. The 400 MHz ¹H NMR spectrum (CDCl₃) of the RAFT-prepared polystyrene **PS-L3-1** using **3** as a RAFT agent.

Scheme 3. Schematic Representation for Preparation of Tris(2,2'-bipyridine)ruthenium(II)-Centered Polystyrene Metallopolymers



Tris(bipyridine)ruthenium Complex Centered Polystyrenes. Ruthenium(II) tris(bipyridine) complexes, $[Ru(bpy)_3]^{2+}$, and related derivatives are ubiquitous in chemistry.⁴⁴ The stability and unique photophysical properties of these systems have been exploited for artificial photosynthesis, in sensor, in photorefractive materials, and in the study of electron transfer in proteins and DNA.⁴⁴ To form ruthenium complexes, the bipyridine-centered polystyrenes prepared by RAFT polymerization using the dithioester **3** as a RAFT agent were further complexed with Ru(II) metal ion to give $[Ru(bpy)_3]^{2+}$ -centered polystyrenes according to the procedure reported by Fraser and coworkers⁴⁰ (Scheme 3).

Excess starting complex $Ru(bpy)_2Cl_2 \cdot xH_2O$ was removed by washing using methanol. The uncomplexed polystyrene can be removed according to the following typical procedure. The specific weight ratio χ_w in the hexane–THF mixture at room temperature, under which the complex can be precipitated out, was first determined ($\chi_w = 2.50$ for **PS-L3-1-Ru** and 2.20 for **PS-L3-2-Ru**). Meanwhile, χ_w was also determined for



Figure 5. UV–vis spectra (CHCl₃) of the supramolecular polystyrene ruthenium complexes **PS-L3-1-Ru** and **PS-L3-2-Ru** and their corresponding bipyridine-centered precursor polymers **PS-L3-1** and **PS-L3-2** as well as the starting complex Ru(bpy)₂Cl₂·*x*H₂O.

precipitating its corresponding precursor polymer ($\chi_w = 3.74$ for **PS-L3-1** and 2.48 for **PS-L3-2**), then the crude polymer was dissolved in THF weighed in advance to give a clear solution, and then a suitable amount of hexane was added dropwise into the clear polymer solution. (The amount of hexane added can be calculated using χ_w and the amount of THF used.) As a result, the complex precipitated and the uncomplexed polystyrene was left in solution. The pure complex was obtained after the removal of the clear solution by pipet. The purification procedure was repeated to yield pure complexed polystyrene. The purified complex was dried in an oven under reduced pressure.

The purified complexes were characterized by both UV-vis spectroscopy and fluorescence techniques. Their UV-vis spectra (Figure 5) exhibited a new absorption band at 451 nm attributed to the characteristic MLCT (metal-to-ligand charge transfer) absorption band of the tris(bipyridine)Ru(II) unit as compared with their corresponding precursor polymers and the starting complex $Ru(bpy)_2Cl_2 \cdot xH_2O$. Moreover, the fluorescence spectra of the two complexes PS-L3-1-Ru and PS-L3-2-Ru are different from that of their corresponding precursor polymers PS-L3-1 and PS-L3-2 (Figure 6). The emission spectra of the complexes show only the well-known $[Ru(bpy)_3]^{2+}$ band with $\lambda_{max} = 625$ nm, which can be excited by multiband lights, $\lambda_{ex} = 300$ and 465 nm, as observed from their excitation spectra. However, the emission spectra of the precursor PS-L3-1 and PS-L3-2 show a band with $\lambda_{max} = 350$ nm. The optical properties of the two complexes are summarized in Table 2. They indicate the successful grafting of the ruthenium bis-(bipyridine) onto the center of the polymer.

To estimate the extent of the metal complex formation, Fraser introduced a concept "chelation efficiency" based on the findings that extinction coefficients for polymeric metal complexes are comparable to that of their corresponding nonpolymeric complex and vary little with polymer composition.45,46 Here, we adopted Fraser's chelation efficiency method to estimate the ruthenium content in the metallopolymers. Chelation efficiency was defined as the ratio of the extinction coefficiency determined from λ_{max} for the polymeric metal complex with that of $[Ru(bpy)_3](PF_6)_2$. Extinction coefficients (ϵ) of the polymeric metal complexes were measured by UV-vis analysis using theoretically calculated number-average molecular weights to determine polymer concentrations. The extinction coefficient (ϵ) for the standard complex $[Ru(bpy)_3](PF_6)_2$ is reported to be

 Table 2. Absorption, Emission, and Thermal Properties for Tris(bipyridine)ruthenium-Centered Polystyrene

 Metallopolymers and Their Corresponding Precursor Polymers

| | | MLCT | | | | |
|------------|-------------------------|-----------------------|---|--------------------------|--|--|
| sample | $M_{\rm n}{}^a$ (calcd) | λ_{\max} (nm) | $\epsilon \; (\mathrm{M}^{-1} \mathrm{cm}^{-1})^c$ | chelation efficiency d | emission ^{<i>e</i>} λ_{\max} (nm) | $T_{\mathbf{g}}{}^{f}(^{\circ}\mathbf{C})$ |
| PS-L3-1 | 5 992 | | | | 350 | 102.6 |
| PS-L3-2 | 11 426 | | | | 350 | 104.5 |
| PS-L3-1-Ru | 6 695 | 452 | 14 640 | 0.92 | 625 | 114.5 |
| PS-L3-2-Ru | 12 129 | 452 | 14 547 | 0.91 | 625 | 110.6 |

^{*a*} The calculated molecular weights of the precursor polymers are their theoretical molecular weights shown in Table 1. The molecular weights of the ruthenium metallopolymers are calculated according to the equation $M_{n,calcd} = M_{n,calcd(PS)} + M_{[Ru(bpy)_2][PF_{6}]_2}$, where $M_{n,calcd(PS)}$ is the calculated molecular weights of the corresponding precursor polymer and $M_{[Ru(bpy)_2][PF_{6}]_2}$ is the molecular weight of $[Ru(bpy)_2][PF_{6}]_2$ is the molecular weight of $[Ru(bpy)_2][PF_{6}]_2$ (bpy = bipyridine) grafted on the center of the precursor polymer. ^{*b*} Metal-to-ligand charge transfer (MLCT) absorption band of the metallopolymer recorded in CH₂Cl₂ solution. ^{*c*} Molar absorptivity of the MLCT band of the metallopolymer. ^{*d*} The estimated chelation efficiency: $\epsilon_{MLCT}[Ru(bpy)_2(bpyPS_2)]^{2+}[PF_{6}]_2^{2-/}\epsilon_{MLCT}[Ru(bpy)_3]^2+[PF_{6}]_2^{2-/}$ (bpyPS₂ = **PS-L3-1** for **PS-L3-1-Ru**; **PS-L3-2** for **PS-L3-2-Ru**). $\lambda_{max} [Ru(bpy)_3]^{2+}[PF_{6}]_2^{2-}$ and $K = 16\ 000\ M^{-1}\ cm^{-1}$. ^{*c*} THe glass transition temperature (defined as the midpoint of the change in heat capacity) measured by DSC under nitrogen.



Figure 6. Fluorescence emission spectra (THF) (excitation wavelength $\lambda_{ex} = 300$ and 465 nm, respectively) and excitation spectra (emission wavelength $\lambda_{em} = 625$ nm for complex, 350 nm for precursor polystyrene) of the supramolecular polystyrene–ruthenium complexes **PS-L3-1-Ru** (A) and **PS-L3-2-Ru** (B) as well as their corresponding bipyridine-centered polystyrene **PS-L3-1** (A) and **PS-L3-2** (B).

16 000 M⁻¹ cm⁻¹ in CH₂Cl₂ ($\lambda_{max} = 452$ nm).⁴⁷ The literature value was used to calculate the chelation efficiencies of the two polymeric complexes. These data are summarized in Table 2. For each polymeric complex, the extent of the metal complex formation reached above 90% but less than 100%. To further exclude the residue of the uncomplexed precursor polystyrene in the complexes, the purified complexes were further characterized using the SEC technique. Their SEC curves are different from those of the corresponding precursor polymers (Figure S2 in the Supporting Information). There are no signals corresponding to either the complex or the precursor polymer in their SEC curves, which were although recorded by three different detectors. On one hand, this indicates that there is no precursor polymer remaining in the purified complex, thus further



Figure 7. DSC curves of the supramolecular polystyrene ruthenium complexes **PS-L3-1-Ru** and **PS-L3-2-Ru** as well as their corresponding bipyridine-centered polystyrene **PS-L3-1** and **PS-L3-2**.

proving that the purification procedure for the polymeric complexes is quite efficient. On the other hand, this shows that standard size exclusion chromatography (SEC) is rather difficult to analyze bipyridine metal complex containing polymers because of strong interactions (caused by the nitrogen atoms and the charge of the metal ions) of the compounds with the SEC column materials (most polystyrene/divinylbenzene cross-linked beads). Such a SEC problem had been met by the other authors.^{20,48} Nevertheless, some examples of successful analysis are reported in the literature.^{45,49} However, the SEC conditions for successful analyses are different from that used here. Furthermore, the molecular weights of the prepared polymeric complexes are relatively low; thus, the interactions of the charged compounds with SEC columns are stronger. These are probable causes why no SEC signal is observed in the SEC analysis of the polymeric complexes. However, the difference between the SEC curves of the complex and its corresponding bipyridine-centered polymer indicated that the complex was formed.

Since the change of the microstructure of the polymer chains can affect the flexibility of the polymer chains, which is only one contributing factor to glass transition temperature, it is possible to observe the change in the chain structure through the measurement of the change of glass transition temperature. Therefore, thermal characterizations of the two polystyrenic complexes **PS-L3-1-Ru** and **PS-L3-2-Ru** as well as their corresponding precursor polymers **PS-L3-1** and **PS-L3-2** were performed by DSC. The DSC curves are displayed in Figure 7. In all cases, glass transitions were evident in the DSC curves at higher than 100 °C, corresponding to standard polystyrenes in the low molecular weight range. The glass transition temperature ($T_{\rm g}$ s) of these samples are listed in Table 2. As can be seen from Table 2, the glass transition temperatures of all polymer complexes are higher than their corresponding precursor polymers due to the effect of the hexacoordinated tris(bipyridine)ruthenium(II) complex incorporated into the center of the polymer chain. Similar findings have been previously reported.²⁰ The observed elevation of $T_{\rm g}$ due to metalation is larger for lower molecular weight systems.

In summary, UV–vis, fluorescence, SEC, and DSC techniques show that $[Ru(bpy)_3]^{2+}$ has been successfully incorporated into the center of the chains of the polymer.

Conclusions

A novel bipyridine-functionalized chain transfer agent **3** has synthesized by a convenient multistep approach, which includes the reaction with thiourea, hydrolysis, and thioester exchange, starting from a commercially available ligand. The structure of the new chain transfer agent 3 was confirmed by ¹H NMR, ¹³C NMR, and HRMS techniques. The new bipyridine-functionalized dithioester 3 was further used as a RAFT agent in the RAFT polymerization of styrene. Kinetics studies show that it is a very efficient RAFT agent for polymerization of styrene. Excellent control of the molecular weight and very narrow molecular weight distribution were attained. The ¹H NMR spectrum confirmed the RAFTprepared polymer is centered by bipyridine functional groups. The bipyridine-centered polystyrene polymers were further reacted with Ru(bpy)₂(II) ion to produce metallopolymers. Successful metalation was confirmed by UV-vis, fluorescence, SEC, and DSC techniques.

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Supporting Information Available: HRMS spectrum of the new bipyridine-functionalized RAFT agent **3** and SEC curves, recorded on three different detectors (refractive index (RI) detector, viscometer (DP) detector, and light scattering (LS) detector), of the supramolecular polystyrene-ruthenium complexes **PS-L3-1-Ru** and **PS-L3-2-Ru** as well as their corresponding bipyridine-centered polystyrene **PS-L3-1** and **PS-L3-2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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