Synthesis and Characterization of Bis(2,2′:6′,2″-terpyridine)ruthenium(II)-Connected Diblock Polymers via RAFT Polymerization

Guangchang Zhou and Issifu I. Harruna*

Department of Chemistry, Clark Atlanta University, 223 James P. Brawley Drive SW, Atlanta, Georgia 30314

Received October 4, 2004; Revised Manuscript Received March 7, 2005

ABSTRACT: We report the synthesis and uses of a novel terpyridine-functionalized chain transfer agent (CTA) that produces well-controlled macromolecular architectures with terpyridine functionalities at one chain end via reversible addition−fragmentation chain transfer (RAFT) polymerization. The terpyridine-terminated macromolecules with well-defined structures were further used for preparation of supramolecular diblock metallomacromolecules by bis(2,2′:6′,2″-terpyridine)ruthenium(II) complex connectivity. The successful connectivity between two macromolecular blocks via the metallocomplex was confirmed by UV−vis, size exclusion chromatography (SEC), and differential scanning calorimetry (DSC) as well as atomic force microscopy (AFM) techniques.

Introduction

Metal-containing polymers are attracting significant interest as these materials may combine the processability and mechanical properties of polymers with the unique optoelectronic properties of metal complexes.[1,2] The development of metal-containing polymers with unique property profiles has been propelled by their (potential) use in diverse areas such as solar energy conversion,[3] luminescent sensing,[4] electroluminescence display,[5] biotechnology,[6] molecular machines,[7] and molecular electronics.[8] Thus, a number of metal-containing polymers, whose metal moiety is in either the polymer backbone or the side chain, have been reported in the literature.[9−11] In particular, metal-containing polymers with well-defined architectures are currently under extensive investigation.[12−15] However, most synthetic approaches to date have involved the construction of systems with broad molecular weight distributions and lack of control over polymer architecture. To overcome these drawbacks, living and controlled polymerization techniques have been employed.[12−15] For example, Fraser et al.[14] synthesized a variety of metal-centered linear and star-shaped metallopolymers using metallosupramolecular or metal-free bipyridine-functionalized initiators by atom transfer radical polymerization (ATRP) and ring-opening polymerization (ROP); Schubert et al.[15] prepared terpyridine end-group-functionalized polystyrene polymers using a terpyridine-functionalized initiator via nitroxide-mediated polymerization (NMP). Another approach to well-defined metal-containing polymers involves the preparation of ligand-terminated monochelic or telechelic polymers or oligomers with well-defined structures by simple organic reactions, followed by their chelation to metal ions.[16−18] For example, Schubert et al.[16−18] prepared some bis(2,2′:6′,2″-terpyridine)ruthenium(II) ($Ru(tpy)_2(II)^{2+}$) complex-connected supramolecular block (co)polymers.

In addition to ATRP, ROP, and NMP, reversible addition−fragmentation chain transfer (RAFT) polymerization is accessible to control molecular weight and molecular weight distribution[19] as well as advanced architectures such as block,[20] comb,[21] and star[22] copolymers. In contrast, the RAFT process is distinguished by its versatility with respect to both monomer choice and polymerization conditions. The key to successful operation of RAFT polymerization lies on the use of a highly efficient chain transfer agent (CTA), which is typically a thiocarbonylthio compound.[23] In general, the vast majority of RAFT-prepared (co)polymer chains bear CTA fragment groups at both ends.[24] This point has been confirmed by NMR and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) techniques.[25,26] For utilizing the feature of RAFT technique, few bipyridine-functionalized RAFT agents have recently been synthesized and used to prepare metal-containing polymers.[27,28] For years, the 2,2′:6′,2″-terpyridine ligand has been of interest in the assembly of metallomacromolecules and metallosupramolecules because of its chelating effect for a wide range of transition metal ions.[29] In this paper, a new terpyridine-functionalized dithioester was first synthesized and further used as a RAFT agent in the polymerization of styrene and *N*-isopropylacrylamide (NIPAM) to generate terpyridine end-functionalized well-defined low-polydispersity polystyrene and poly(*N*-isopropylacrylamide) (PNIPAM) polymers. The RAFT-prepared terpyridine-terminated polymers were further used for preparation of supramolecular diblock metallopolymers by $Ru(tpy)_2(II)^{2+}$ complex connectivity. The prepared supramolecular metallopolymers were further characterized by UV−vis, size exclusion chromatography (SEC), and differential scanning calorimetry (DSC) as well as atomic force microscopy (AFM) techniques.

Experimental Section

Materials. Thiourea (99%, Aldrich), carboxymethyl dithiobenzoate (CMDB, 99%, Aldrich), ammonium hexafluorophosphate (NH_4PF_6, 99.99%, Aldrich), ruthenium(III) chloride hydrate ($RuCl_3{\cdot}xH_2O$, 35−40% Ru, ACROS), *N*-ethylmorpholine (99%, ACROS), and 1,4-dioxane (99+%, spectrophotometric grade, Aldrich) were used as received. 2,2′-Azobis(isobutyronitrile) (AIBN, 97%, Aldrich) was purified by recrystal-

---

* Author to whom correspondence should be addressed. E-mail: iharruna@cau.edu. Telephone: 404-880-6883. Fax: 404-880-6890.

10.1021/ma047955c CCC: $30.25

Table 1. Experimental Conditions and Characterization Data for RAFT Polymerization of Styrene and *N*-isopropylacrylamide (NIPAM) with the Terpyridine-Functionalized Dithioester 1 as a CTA

sample	monomer (concn in 1,4-dioxane, °C)	CTA **1** ($M \times 10^{-2}$)	initiator ($M \times 10^{-2}$)	time (hr)	conv (%)	M_n[c] (theory)	M_n[d] (NMR)	M_n[e] (SEC)	PDI[e] (SEC)
PS-L1-1	styrene (bulk, 100)	4.00	thermal[a]	4	12.5	3330	3440	4500	1.06
PS-L1-2				6	23.4	5740	5880	7010	1.04
PS-L1-3				11	33.7	8180	8370	9460	1.06
PS-L1-4				13	40.1	9630	9840	10 300	1.18
PS-L1-5				20	54.7	12 930	13 180	13 900	1.13
PNIPAM-L1-1	NIPAM (4.00 M, 75)	2.02	AIBN[b](1.22)	1.5	18.9	4700	4770	1910	1.06
PNIPAM-L1-2				2.5	34.3	8150	8270	2300	1.08
PNIPAM-L1-3				3.3	43.2	10 140	10 330	2600	1.08
PNIPAM-L1-4				4.0	52.4	12 270	12 450	2860	1.11

[a] No added initiator. [b] Abbreviations: AIBN, 2,2′-azobis(isobutyronitrile). [c] The theoretical molecular weight was calculated from the expression: $M_{n(\text{theory})} = ([M]_i/[CTA]_i)CM_0 + M_{CTA}$, where $[M]_i$ and $[CTA]_i$ are the initial concentrations of the monomer and the chain transfer agent **1** respectively, C is the fractional conversion, and M_0, M_{CTA} are the molecular weights of the monomer and the used RAFT agent **1**. [d] Determined by ^1H NMR spectroscopy, according to two equations: For polystyrene series, $M_{n,NMR(PS)} = [(I_{1.0-2.5} \div 3)/(I_{8.35-8.70} \div 6)] \times 104.15 + 475.63$; for PNIPAM series, $M_{n,NMR(PNIPAM)} = [(I_{4.00}/(I_{8.82} \div 6)] \times 113.16 + 475.63$, where $I_{1.0-2.5}$, $I_{4.00}$, $I_{8.35-8.70}$, and $I_{8.82}$ are integral values of the peaks at $\delta = 1.0-2.5$, 4.00, 8.35−8.70, and 8.82, 104.15, 113.16, and 475.63 are the molecular weights of styrene, NIPAM, and **1**, respectively (cf. Figure 4A and B). [e] Determined by SEC using THF as eluent, and molecular weights were reported as polystyrene equivalents; PDI = M_w/M_n.

lization from methanol and stored in a freezer. 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. *N*-Isopropylacrylamide (NIPAM, 97%, Aldrich) was purified by recrystallization from a mixture (60:40, v/v) of toluene and hexane. 4′-(4-Bromomethylphenyl)-2,2′:6′,2″-terpyridine (**1a**) was synthesized according to literature procedures.[30] All other reagents and solvents were used as received unless indicated otherwise.

Characterization. ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX400 spectrometer at 400 and 100 MHz, respectively. UV−vis spectra were recorded using a Beckman DU640 spectrophotometer. High-resolution mass spectrometry (HRMS) was performed on a VG Instruments 70SE using electron impact (EI) ionization. Melting points were measured with a Thomas-Hoover capillary melting point apparatus without calibration. SEC was carried out on a Viscotek SEC assembly consisting of a model P1000 pump, a model T60 refractive index-viscometer dual detector, a model LR40 laser refractometer, and three mixed bed columns (bead size: 10 μm, the molecular weight range for those columns is 1000−5 000 000) from American Polymer Standards Corporation 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 ($M_n = 9870$, $M_w = 10\,300$, $M_p = 10\,300$, $M_w/M_n = 1.04$). 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, at a heating rate of 10 °C/min. The glass transition temperature, T_g, was defined as the midpoint of the change in heat capacity. AFM was performed using a Thermomicroscope CP Research AFM instrument in tapping mode with a silicon tip. The AFM image was obtained at room temperature in air.

Synthesis of 4-[2,2′:6′,2″]Terpyridin-4′-yl-benzyl Dithiobenzoate (1). A solution of 4′-(4-bromomethylphenyl)-2,2′:6′,2″-terpyridine (**1a**) (1.609 g, 4.00 mmol) and 0.381 g (5.01 mmol) of thiourea in 130 mL of ethanol-acetone mixture solvents (1:1, v/v) was heated at reflux for 22.5 h. After cooling, the precipitate was filtered, washed with acetone, and dried to give 1.739 g (91%) of **1b**. A mixture of **1b** (1.739 g, 3.64 mmol) and NaOH (0.160 g, 4.00 mmol) in 40 mL of water was heated at 70 °C for 4.5 h. After cooling, the precipitate was filtered and washed with water, and then dried under vacuum at room temperature overnight to give 4′-(4-mercaptomethylphenyl)-2,2′:6′,2″-terpyridine (**1c**) (1.324 g). Carboxymethyl dithiobenzoate (**CMDB**) (0.795 g, 3.74 mmol) and NaOH (0.315 g, 7.88 mmol) were dissolved in 95 mL of water to give a clear solution, then 4′-(4-mercaptomethylphenyl)-2,2′:6′,2″-terpyridine (**1c**) (1.324 g, 3.73 mmol) was added to the solution. The resulting mixture was stirred at 60 °C for 18 h. The red precipitate was filtered, washed with water, dried under vacuum, and further extracted with toluene to give crude product **1** (1.325 g, 75%). The crude product was further purified by column chromatography on aluminum oxide using hexanes-ethyl acetate (2:1, v/v) as an eluent to afford pure **1**: mp 166−167 °C. ^1H NMR ($CDCl_3$): $\delta = 8.75-8.67$ (m, 4H, tpy$H_{3',5'}$ and tpy$H_{6,6''}$), 8.64 (d, 2H, $J = 8.00$ Hz, tpy$H_{3,3''}$), 8.01 (dd, 2H, $J = 7.2$, 1.2 Hz, S═C−Ph$H_{2,6}$), 7.90−7.78 (m, 4H, tpy$H_{4,4''}$ and tpy-Ph$H_{2,6}$), 7.54−7.47 (m, 3H, tpy-Ph$H_{3,5}$ and S═C−PhH_4), 7.40−7.28 (m, 4H, tpy$H_{5,5''}$ and S═C−Ph$H_{3,5}$), 4.64 ppm (s, 2H, CH_2S). ^{13}C NMR ($CDCl_3$): $\delta = 227.3$ (C═S), 156.1 (tpy$C_{2',6'}$), 155.9 (tpy$C_{2,2''}$), 149.5 (tpy$C_{4'}$), 149.1 (tpy$C_{6,6''}$), 144.7 (S═C−PhC_1), 137.9 (tpy-PhC_4), 136.9 (tpy$C_{4,4''}$), 136.0 (tpy-PhC_1), 132.4 (S═C−PhC_4), 129.8 (tpy-Ph$C_{3,5}$), 128.4 (S═C−Ph$C_{3,5}$), 127.8 (tpy-Ph$C_{2,6}$), 126.9 (S═C−Ph$C_{2,6}$), 123.9 (tpy$C_{5,5''}$), 121.3 (tpy$C_{3,3''}$), 118.7 (tpy$C_{3',5'}$), 41.9 ppm (CH_2S). HRMS (EI): calcd for $C_{29}H_{21}N_3S_2$ $m/z = 475.1177$, found $m/z = 475.1128$.

Polymerization Procedure and Kinetics. Two series of parallel polymerizations were performed under argon. Polymerization mixtures were prepared according to the recipes shown in Table 1.

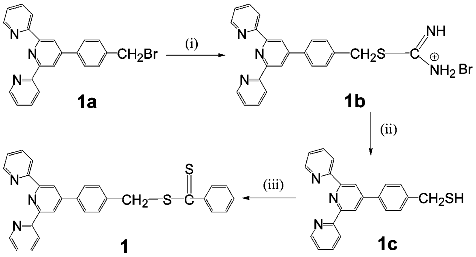
A typical procedure for bulk polymerization of styrene was as follows. RAFT agent **1** (28.0 mg, 5.89×10^{-2} mmol) and styrene (1.334 g, 12.8 mmol) were added into a 10 mL Schlenk flask. The polymer mixture was degassed through four freeze−evacuate−thaw cycles, sealed under argon, and heated at 100 °C for 4 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 0.195 g of a pink polymer, **PS-L1−1**. The conversion of the monomer, styrene, was gravimetrically determined to be 12.5%. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.84-8.50$ (br, m, tpy), 7.94−7.54 (br, m, Ph-C═S and tpy), 7.50−6.10 (br, m, Ph), 2.50−1.05 ppm (br, m, CH_2CH). SEC: $M_n = 4500$, $M_w = 4780$, $M_w/M_n = 1.06$.

The following is a typical procedure for RAFT polymerization of *N*-isopropylacrylamide: NIPAM (1.132 g, 10.0 mmol), **1** (24.0 mg, 5.0×10^{-2} mmol), AIBN (5.0 mg, 3.0×10^{-2} mmol), and 2.5 mL of 1,4-dioxane were charged into a Schlenk flask equipped with a magnetic stirrer. The mixture was degassed by five freeze−evacuate−thaw cycles and then heated at 75 °C under argon in a thermostated oil bath for 1.5 h. The polymer mixture was precipitated in a large excess of diethyl ether, isolated by filtration and dried at 50 °C under vacuum to give 0.238 g of PNIPAM polymer, **PNIPAM-L1-1**. The conversions of the monomer NIPAM were determined to be 18.9% by gravimetrical method. ^1H NMR ($CDCl_3$): $\delta = 9.12-8.57$ (br, m, tpy), 8.38−7.75 (br, m, Ph-C═S, and tpy), 7.70−7.15 (br, m, tpy and Ph-C═S), 7.15−5.75 (br, s, NH), 3.99 (br, s, N−CH), 2.50−1.25 (br, m, CH_2CH), 1.13 ppm (br, s, $C(CH_3)_2$). SEC: $M_n = 1910$, $M_w = 2030$, $M_w/M_n = 1.06$.

Preparation of Bis(terpyridine)ruthenium(II) Complex-Centered Polystyrene. Terpyridine-terminated polystyrene, **PS-L1-5**, (200.0 mg, 1.55×10^{-2} mmol based on M_n, theory = 12930 g/mol) and $RuCl_3{\cdot}xH_2O$ (61.0 mg, 24.4×10^{-2} mmol) were charged into a 50-ml Schlenk flask with 10 mL of EtOH and 10 mL of THF. The mixture was deoxygenated by purging argon for half hour and then heated at 85 °C under argon for 25 h. The precipitate was filtered and washed with water, followed by diethyl ether, and finally dried under reduced pressure to give Ru^{III}(terpyridine)Cl_3-terminated polystyrene, **PS-L1-5-RuCl$_3$**. The Ru^{III}(terpyridine)Cl_3-terminated polystyrene, **PS-L1-5-RuCl$_3$**, and terpyridine-terminated polystyrene, **PS-L1-5**, (250.0 mg) were charged into a 50-ml Schlenk flask with 20 mL of THF and 10 mL of EtOH. The mixture was heated at 85 °C under argon for 24 h, followed by the addition of *N*-ethylmorpholine (0.10 mL), and then continued stirring at the same temperature under argon for an additional 24 h. After the mixture was cooled to room temperature, an excess of NH_4PF_6 (45 mg, 0.27 mmol) was added. Stirring was continued for 1 h, and subsequently, the solvents were removed in vacuo. The crude product was obtained by the addition of methanol to the residue, washed with water, and dried under vacuum. The crude complex was stirred in diethyl ether at room temperature for 2 days, then filtered and dried to give target complex. The complex was further dissolved in THF (20 mL) and filtered to give a clear solution, and then hexane (60 mL) was added dropwise into the clear polymer solution. As a result, the complex was precipitated out, whereas the trace uncomplexed polystyrene was left in solution. The pure supramolecular dimeric polystyrene ruthenium complex, **PS-Ru(tpy)$_2$-PS**, was obtained after the removal of the clear solution by pipet and dried in an oven under reduced pressure. Yield was 365.0 mg (91%). ^1H NMR ($CDCl_3$): $\delta = 7.50-6.12$ (br, m, Ph), 2.39−1.07 ppm (br, m, CH_2CH). UV−vis (CH_2Cl_2): λ_{max}-MLCT(ϵ) = 491 nm (23 069 M^{-1} cm^{-1}). $M_{n,theory}{}^{31} = 26\,240$, $M_{n,UV-vis}{}^{32} = 28\,210$.

Preparation of Thermosensitive Bis(terpyridine)ruthenium(II) Complex-Connected Diblock Copolymers. Terpyridine-terminated polystyrene, **PS-L1-3**, (100.0 mg, 1.22×10^{-2} mmol based on M_n, theory = 8180 g/mol) and $RuCl_3{\cdot}xH_2O$ (40.0 mg, 13.9×10^{-2} mmol) were charged into a 25-ml Schlenk flask with 15 mL of EtOH-THF (2:1, v/v) mixture solvents. The mixture was heated at 85 °C under argon for 25 h. The solvents were removed under reduced pressure, and then methanol was added to precipitate the polymeric monocomplex. The monocomplex was filtered and washed with water, followed by diethyl ether, and finally dried under reduced pressure to give Ru^{III}(terpyridine)Cl_3-terminated polystyrene, **PS-L1-3-RuCl$_3$**, (104.0 mg). Ru^{III}(terpyridine)Cl_3-terminated polystyrene, **PS-L1-3-RuCl$_3$**, (104.0 mg) and terpyridine-terminated PNIPAM polymer, **PNIPAM-L1-3**, (250.0 mg, 2.5×10^{-2} mmol based on M_n, theory = 10 140 g/mol) were charged into a 25-ml Schlenk flask with 10 mL of THF and 7.5 mL of EtOH. The mixture was heated at 85 °C under argon for 1 h 10 min, followed by the addition of *N*-ethylmorpholine (0.10 mL), and then stirring continued at the same temperature under argon for an additional 21.5 h. After the mixture was cooled to room temperature, an excess of NH_4PF_6 (40.0 mg, 24.5×10^{-2} mmol) was added. Stirring was continued for 1 h, and subsequently, the solvents were removed in vacuo. Methanol was added, and trace precipitate was filtered off. The methanolic filtrate was evaporated to almost dryness under vacuum, and then diethyl ether was added and stirred at room temperature for 2 days. The precipitate was filtered and water added. The aqueous mixture was stirred at room temperature for 2 days. The aqueous mixture was separated by centrifugation and further purified by repetitive centrifugation and redispersion with water and methanol in turn. The pure complex, **PS-Ru(tpy)$_2$-PNIPAM**, was recovered by the addition of diethyl ether and dried under vacuum to give 148.0 mg of product (67%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.42-5.59$ (br, m, Ph and NH), 4.01 (br, s, CH−N), 2.69−1.25 (br, m, CH_2CH), 1.14 ppm (br, s, $C(CH_3)_2$). UV−vis (CH_2Cl_2): λ_{max}-MLCT(ϵ) = 491 nm (22 371 M^{-1} cm^{-1}). $M_{n,theory}{}^{33} = 18\,170$, $M_{n,UV-Vis}{}^{32} = 20\,140$.

Scheme 1. Synthetic Route of the Terpyridine-functionalized CTA



Reagents and Conditions: (i) Thiourea, Ethanol-acetone (1: 1, v/v), Reflux, 22.5 H, 91%; (ii) NaOH, H_2O, 70 °C, 4.5 h; (iii) Ph-C(=S)-S−CH_2COOH, NaOH, H_2O, 60 °C, 18 H, 75%.

Results and Discussion

Synthesis of Terpyridine-Functionalized CTA. A CTA, which is typically a thiocarbonylthio compound, Z−C(=S)-S−R, plays a key role in RAFT polymerization and its molecular structural design needs to consider two important factors.[27] First, Z should not only activate the C=S double bond toward radical addition to form the intermediate radical, but also favor the fragmentation of the intermediate radical to free the reinitiating radical ($R^{\bullet}$). Second, R should be a good leaving group that efficiently reinitiates polymerization. In producing a CTA to efficiently control polymerization, both the activating substituent Z and the R leaving group should be properly chosen. To date, numerous CTAs have been designed and synthesized through different synthetic approaches for different monomer systems.[27] Among these synthetic routes, the ester exchange reaction between dithiocarboxylic acid and thiol is quite simple and has been used to synthesize some dithioesters.[27,34] We used the ester exchange approach to synthesize a novel terpyridine-functionalized CTA from the only commercially available carboxymethyl dithiobenzoate according to the synthetic route shown in Scheme 1.

During the preparative course of the terpyridine-functionalized CTA, a key terpyridine-functionalized thiol intermediate, **1c**, was formed by careful alkaline hydrolysis of the isothiourea hydrobromide salt, **1b**, produced through the reaction of 4′-(4-bromomethylphenyl)-2,2′:6′,2″-terpyridine (**1a)** with thiourea at reflux using an ethanol-acetone mixture as a reaction media. The formation of the thiol, **1c**, was confirmed by its accurate mass analysis (HRMS (EI): calcd for $C_{22}H_{17}N_3S$ *m/z* = 355.1143, found *m/z* = 355.1104, HRMS spectrum is shown in Figure S1 in the Supporting Information). The thiol, **1c**, was in situ reacted with carboxymethyl dithiobenzoate (**CMDB**) to produce terpyridine-functionalized CTA, **1**. The crude CTA, **1**, was purified by column chromatography on alumium oxide using hexanes-ethyl acetate (2:1, v/v) as an eluent to afford pure CTA, **1**, in moderate yield. The observed exact mass of the CTA, **1**, (*m/z* = 475.1128) is in excellent agreement with the calculated value (*m/z* = 475.1177) for $C_{29}H_{21}N_3S_2$ (HRMS spectrum in Figure S2). Both ^1H NMR and ^{13}C NMR spectra also elucidate the structure of the CTA **1** (Figure 1).

RAFT Polymerization of Styrene. To test the effectiveness of the terpyridine-functionalized dithioester, **1**, as a RAFT agent, styrene was polymerized thermally in the presence of the CTA **1** at 100 °C (Scheme 2). The molar ratio between styrene and the CTA, **1**, was kept

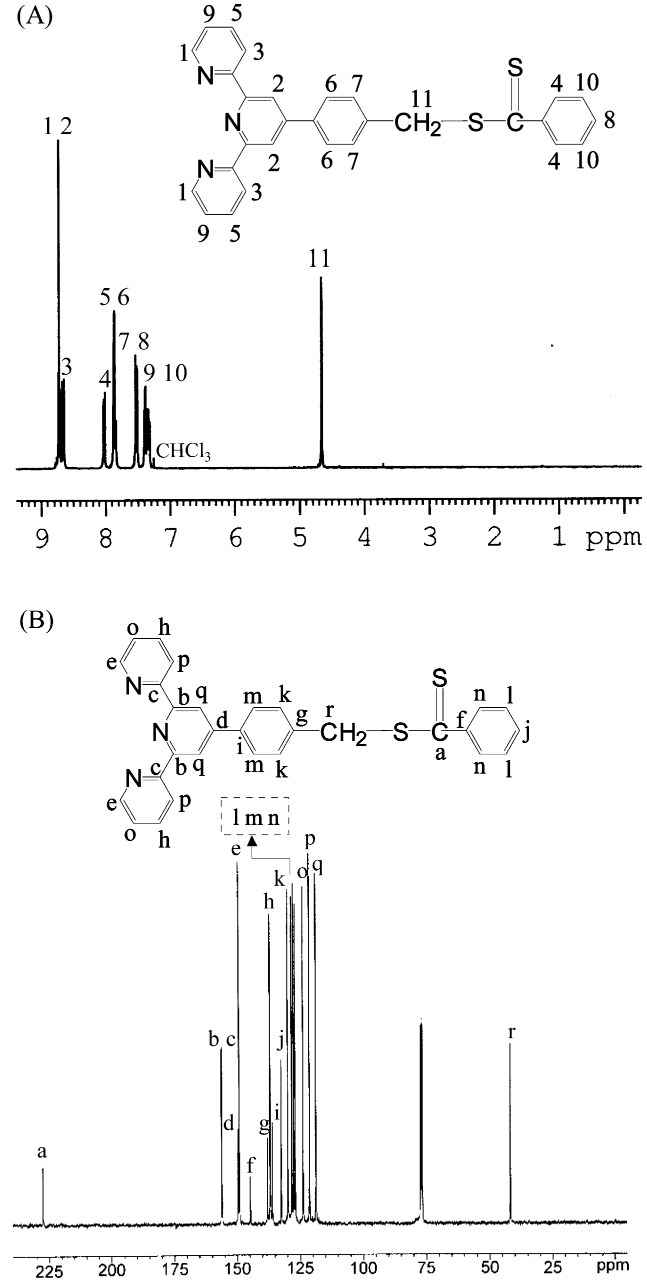
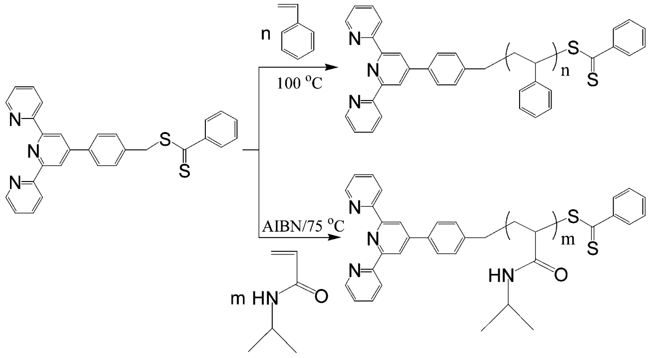


Figure 1. ^{1}H NMR (A) and ^{13}C NMR (B) spectra (CDCl$_3$) of the terpyridine-functionalized CTA **1**.

Scheme 2



constant at 216 in all of the polymerizations. The conversion and the molar mass evolution were studied as a function of time. The molar mass characteristics of the polymers were determined by SEC.

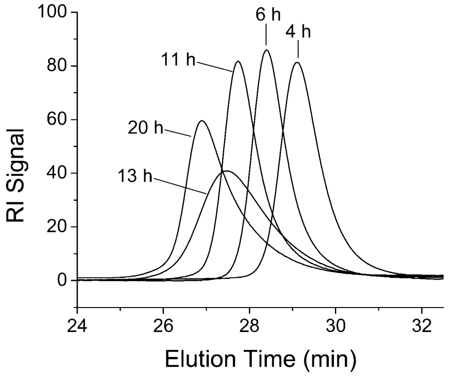


Figure 2. SEC chromatograms (RI traces) of polystyrenes prepared by bulk RAFT polymerization of styrene using the terpyridine-functionalized dithioesters **1** as a CTA at 100 °C via thermal auto-initiation for different polymerization times (Sample **PS-L1-1** to **PS-L1-5** in Table 1). [Styrene] = 8.70 M, [**1**] = 0.04 M, [Styrene]/[**1**] = 216/1.

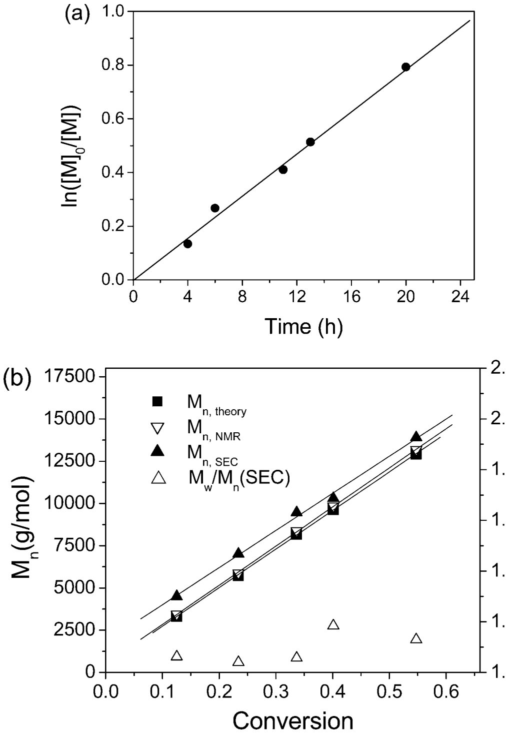


Figure 3. (a) First-order kinetic plot of ln([M]$_0$/[M]) vs polymerization time and (b) number average molecular weight and polydispersity as a function of conversion for bulk polymerization of styrene by RAFT using **1** as a transfer agent at 100 °C via thermal auto-initiation (Sample **PS-L1-1** to **PS-L1-5** in Table 1). [Styrene] = 8.70 M, [**1**] = 0.04 M, [Styrene]/[**1**] =216/1.

Figure 2 shows the SEC curves of the polystyrene samples prepared at different polymerization times. A continuous shift of the curves toward shorter elution times is observed, indicating continuously increasing molar masses. Furthermore, first-order kinetics with respect to monomer concentration showed a linear relationship throughout the studied region (12–55% conversion) (Figure 3a). Also, the molecular weights determined by SEC and NMR increased linearly with conversion as shown in Figure 3b. However, there are deviations between SEC-determined and theoretical molecular weights (Table 1 and Figure 3b). The possible cause for this discrepancy is the effect of the chain end-group–terpyridinyl. As the measured molecular weight

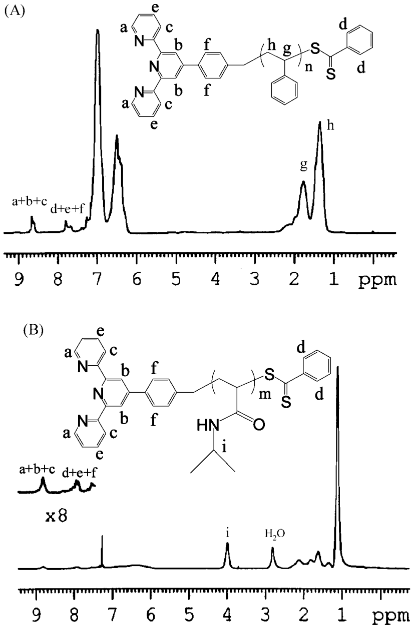


Figure 4. ^{1}H NMR ($CDCl_3$) spectra of the representative RAFT-prepared polystyrene sample **PS-L1-2** (A) and poly(*N*-isopropylacrylamide) sample **PNIPAM-L1-1** (B).

is lowered, the effect of the terpyridine chain end group becomes more obvious, and consequently results in a relatively large deviation (Table 1). Additionally, the NMR-determined molecular weights are quite close to the theoretical molecular weight (Figure 3b and Table 1). The resulting polydispersities are generally low, ranging from 1.04 to 1.18 at all polymerization times. The linear increase in molecular weight and low polydispersity demonstrates that the new terpyridine-functionalized dithioester **1**-mediated bulk polymerization of styrene is a living radical polymerization.

On the basis of the RAFT polymerization mechanism, RAFT polymerization provides a means of introducing specifically placed functional moieties into polymer chains using appropriately functionalized RAFT agents.[24] Therefore, the terpyridine-functionalized RAFT agent **1**-mediated styrene polymerization can produce terpyridine-terminated polystyrene polymers. To confirm this point, NMR end group analysis was performed. Figure 4A shows the ^{1}H NMR spectrum of a representative sample, **PS-L1-2**. The characteristic peak of the terpyridine-functional end groups derived from the RAFT agent **1** was observed at 8.70 ppm, and was used to calculate the molecular weight, assuming that each polystyrene chain end bears a terpyridyl group derived from the RAFT agent **1**. The close agreement between the NMR-determined and theoretical molecular weight confirms that most of polystyrene chains are terminated by the terpyridine-functional group derived from the used RAFT agent **1** for polymerization, as expected in a reversible addition−fragmentation chain transfer mechanism. However, a small percentage of nonterpyridine end-fuctionalized polymer chains are inevitably formed by the thermal autoinitiation-produced radicals.

RAFT Polymerization of *N*-Isopropylacrylamide. PNIPAM is one of the most widely studied temperature-responsive polymers that undergoes a reversible, inverse phase transition at a temperature known as the lower critical solution temperature (LCST) of about 32 °C in pure water.[35] Below the LCST, the polymer chain is hydrated and adopts an extended coil conformation, while above the LCST, the polymer is dehydrated and adopts a globular conformation and the globular polymer chains form intermolecular aggregates. This interesting property has been applied in various ways in organic chemistry, biotechnology, and materials sciences.[36] Recently, the RAFT polymerization of NIPAM has received much attention.[26,37] Few chain transfer agents such as benzyl dithiobenzoate and 2-dodecylsulfanylthiocarbonyl-sulfanyl-2-methyl propionic acid have been used and confirmed to be efficient RAFT agents for polymerization of NIPAM.[26,37]

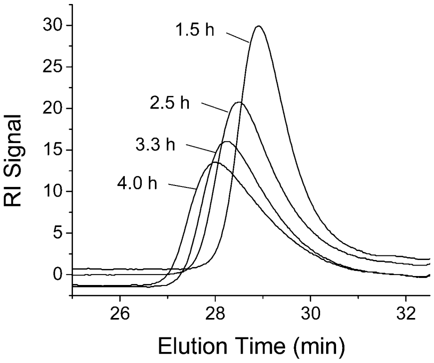


Figure 5. SEC chromatograms (RI traces) of poly(*N*-isopropylacrylamide)s prepared by RAFT polymerization of NIPAM at 75 °C using 1,4-dioxane as reaction media, **1** as a transfer agent, AIBN as an initiator. [NIPAM] = 4.00 M, [NIPAM]/[**1**]/[AIBN] =328/1.66/1 (Sample **PNIPAM-L1-1** to **PNIPAM-L1-4** in Table 1).

Although the novel terpyridine-functionalized dithioester, **1**, is an efficient RAFT agent for polymerization of styrene, it is not certain whether it is efficient for polymerization of NIPAM. To examine this point, a series of parallel polymerizations of NIPAM were performed at 75 °C using 1,4-dioxane as solvent and AIBN as an initiator in the presence of the CTA **1** for different reaction times. The polymerization conditions and characterization data are summarized in Table 1.

Figure 5 shows an overlay of the RI traces from the polymerization of NIPAM at different times. The traces clearly shift to lower elution times with increasing conversion, one indicator of a controlled polymerization. However, these SEC traces show unobvious shoulders on the low molecular weight side, which were caused by progressive decomposition of the initiator AIBN during the polymerization. Figure 6 shows the first-order rate plot of $\ln([M]_0/[M])$ vs polymerization time. There is an induction period of approximately 30 min, after which the polymerization exhibits pseudo-first-order kinetics, consistent with a controlled polymerization. An induction period is often observed in RAFT polymerization.[38] The induction period was attributed to the slow initiation by the more stable 4-[2,2′:6′,2″]-terpyridin-4′-yl-benzyl radical generated from the CTA **1**. As observed from Figure 6b, the molecular weights determined by NMR and SEC increased linearly with conversion (the range 18−53%). Moreover, the NMR-determined molecular weight agrees well with the theoretical molecular weight calculated according to the monomer conversion (Figure 6b and Table 1). However, there is marked deviation between the SEC-determined and theoretical molecular weights. The main cause for this discrepancy is that a polystyrene standard (M_n = 9870 g/mol) was used for calibration. Also evident from Table 1, and plotted in Figure 6b, are the low polydispersity indexes (PDI) observed for the PNIPAM poly-

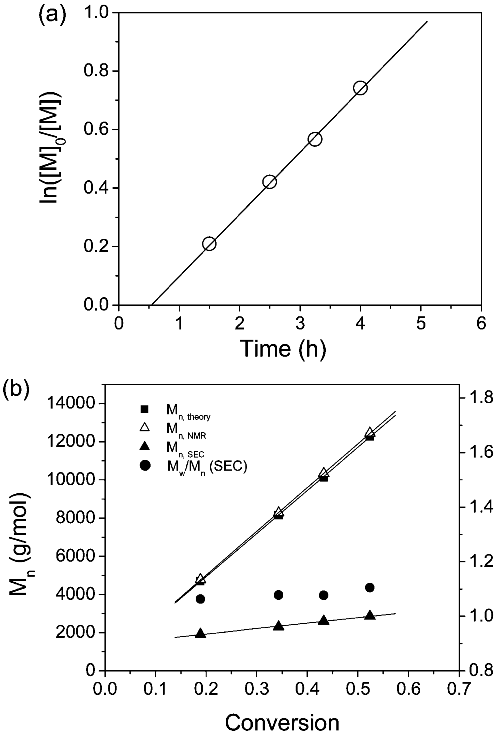


Figure 6. (a) Pseudo-first-order kinetic plot of ln([M]$_0$/[M]) vs polymerization time and (b) number average molecular weights and polydispersity as a function of conversion for RAFT polymerization of NIPAM at 75 °C using 1,4-dioxane as reaction media, **1** as a transfer agent, AIBN as an initiator. [NIPAM] = 4.00 M, [NIPAM]/[**1**]/[AIBN] = 328/1.66/1 (Sample **PNIPAM-L1-1** to **PNIPAM-L1-4** in Table 1).

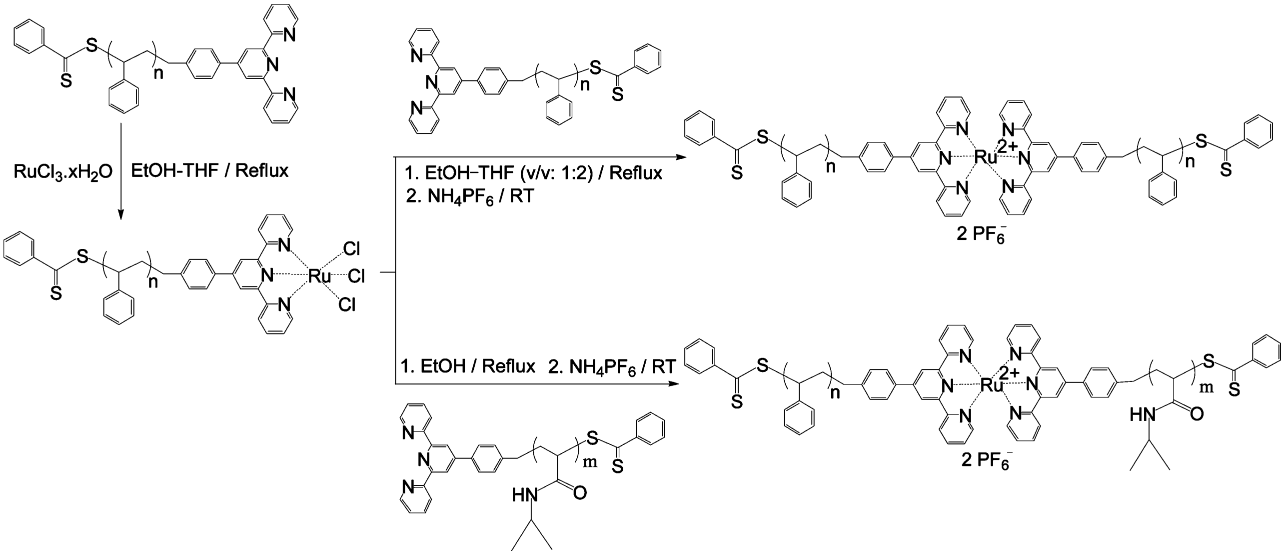
mers synthesized using the terpyridine-functionalized dithioester **1** as a RAFT agent. In all instances, the PDIs are $\leq$ 1.18. All the polymerization characteristics indicate that the terpyridine-functionalized dithioester **1** is a quite efficient RAFT agent for the polymerization of NIPAM.

Like the styrene polymerization, the polymerization of NIPAM in the presence of the CTA, **1**, produces terpyridine-terminated thermosensitive PNIPAM polymers. Figure 4B shows the ^{1}H NMR spectrum of the representative sample, **PNIPAM-L1-3**, prepared by RAFT polymerization of NIPAM using **1** as a CTA. The characteristic peak of terpyridine functional groups is clearly observed at 8.82 ppm. The integral areas of the characteristic peaks at 8.82 and 4.00 ppm corresponding to the terpyridine and isopropyl groups, respectively, were used to determine the molecular weight of the RAFT-prepared PNIPAM polymers. The calculated values are given in Tale 1. The good agreement between the NMR-determined and theoretical molecular weights indicates that most of polymer chains bear terpyridine-functional end groups originating from the CTA, **1**. Undoubtedly, a few polymer chains do not bear a terpyridine functional group at one end because AIBN-decomposed radicals also participate in initiating polymerization. The content of the polymers without terpyridine functional end groups depends mainly on the amount of the efficient radicals formed from initiators.

Bis(terpyridine)ruthenium Complex-Connected Diblock Copolymers. The purpose of synthesizing the novel terpyridine-functionalized RAFT agent is to prepare a variety of terpyridine-terminated polymers by mediated RAFT polymerization. Terpyridine-terminated polystyrene and PNIPAM polymers with controlled, narrow molecular weight were successfully synthesized by the RAFT process using **1** as a CTA. Terpyridine ligands form mono- and biscomplexes with a wide variety of transition metal ions.[17] The stability constants and the kinetics of formation of the different complexes strongly depend on the nature of the metal ions used.[17] In this respect, Ru^{III} forms a very stable monocomplex with one terpyridine ligand, while Ru^{II} only forms a stable biscomplex with terpyridine ligands.[17] Therefore, Ru(tpy)$_2$(II)$^{2+}$ complex-connected diblock polymers were synthesized using RAFT-prepared terpyridine-terminated polymers.

To form ruthenium complexes, the representative terpyridyl-terminated polystyrene, **PS-L1-5**, was treated with an excess of Ru^{III}Cl$_3$·xH$_2$O to give an intermediate monocomplex, **PS-L1-5-Ru^{III}Cl$_3$**. The monocomplex was then further treated with a slight excess of terpyridyl-terminated polystyrene, **PS-L1-5** (Scheme 3). In this approach, ethanol was utilized as the reducing agent and *N*-ethylmorpholine as the catalyst to reduce the Ru^{III} ions to Ru^{II} ions. Subsequently, a biscomplex was formed between the ruthenium-filled terpyridine unit

Scheme 3



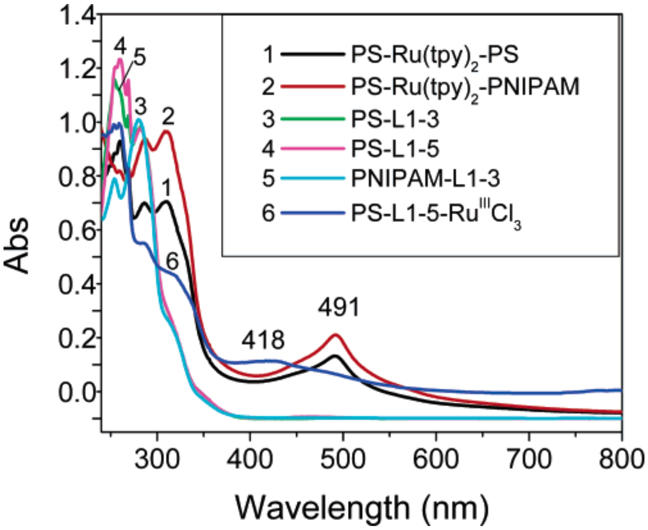


Figure 7. UV−vis spectra (CH_2Cl_2) of the prepared supramolecular dimeric polystyrene ruthenium complex, **PS-Ru(tpy)$_2$-PS**, and bis(terpyridine)ruthenium complex-connected polystyrene and poly(*N*-idopropylacrylamide) diblock copolymer, **PS-Ru(tpy)$_2$-PNIPAM**, as well as their corresponding terpyridine-terminated precursor polymers, **PS-L1-5** for **PS-Ru(tpy)$_2$-PS**, and both **PS-L1-3** and **PNIPAM-L1-3** for **PS-Ru(tpy)$_2$-PNIPAM**. For comparison, a representative intermediate monocomplex, **PS-L1-5-Ru^{III}Cl$_3$** was also added.

and the uncomplexed terpyridine unit, which resulted in symmetrical dimers. After exchange of the counterions by the addition of an excess of NH_4PF_6, the supramolecular dimeric polystyrene ruthenium complex, **PS-Ru(tpy)$_2$-PS**, was isolated by precipitation. The uncomplexed polystyrene **PS-L1-5**, which is soluble in diethyl ether, and trace inorganic salts were removed using diethyl ether and THF, respectively. As a result, the pure supramolecular dimeric polystyrene ruthenium complex, **PS-Ru(tpy)$_2$-PS**, was obtained.

The purified bis(terpyridine) ruthenium polystyrenic complex **PS-Ru(tpy)$_2$-PS** was analyzed by SEC. However, there is a remarkable difference between the SEC curves of the complex and its precursor polystyrene (Figure S4). Particularly, there is no RI signal corresponding to the complex. The main cause is that the bis(terpyridine)ruthenium(II) complex in the center of dimeric polystyrene chain seem to adsorb more strongly to the stationary phase than the precursor polystyrene **PS-L1-5**. This further proved that the purification procedure was quite successful.

As a powerful proof for the formation of biscomplex, the UV−vis spectrum (Figure 7) of the polystyrene ruthenium complex revealed clearly the typical metal−ligand charge-transfer (MLCT) band of the Ru(tpy)$_2$(II)$^{2+}$ complex at λ = 491 nm as well as the $\pi-\pi^*$ transitions of the terpyridine ligand at λ = 310 nm.[18,39] Meanwhile, the characteristic peak at λ = 418 nm, attributed to the intermediate monocomplex **PS-L1-5-Ru^{III}Cl$_3$**, disappeared. To further elucidate and support the content, the Ru(II) metal complex in the polystyrene dimer, the UV−vis absorbance at λ = 491 nm in CH_2Cl_2 was accurately measured and used to calculate the molar absorptivity (ϵ). On the basis of the theoretical molecular weight of **PS-Ru(tpy)$_2$-PS** (M_n = 26 240 g/mol),[31] ϵ = 20369 M^{-1} cm^{-1}, which is close to the literature value ϵ = 24 800 M^{-1} cm^{-1} for the standard complex bis[4′-(4-tolyl)-2,2′:6′,2″-terpyridine]ruthenium hexafluophosphate ([Ru(tpy-Ph-CH_3)$_2$](II)[PF_6]$_2$$^{2-}$) [40] (the schematic structure in Figure S3). This indicates that the degree of metallation is quite high.

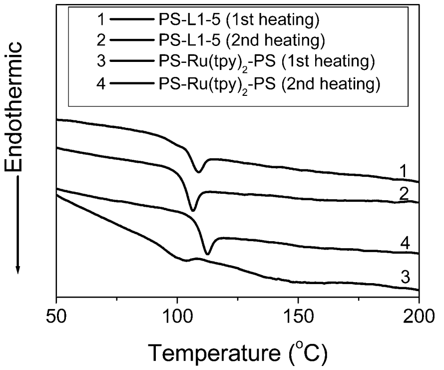


Figure 8. DSC curves of the prepared supramolecular dimeric polystyrene ruthenium complex, **PS-Ru(tpy)$_2$-PS**, and its corresponding terpyridine-terminated precursor polymers, **PS-L1-5**, after two time heating runs.

The biscomplex, **PS-Ru(tpy)$_2$-PS**, was further characterized by DSC. Figure 8 shows the DSC curves of the biscomplex and its corresponding precursor **PS-L1-5** with two heating runs. During the first heating run, the glass transition of the biscomplex, **PS-Ru(tpy)$_2$-PS**, is not obvious because of the existence of polar solvents in the complex. However, the glass transition of the biscomplex becomes obvious during the second heating run. The glass transition temperatures (T_gs) of the biscomplex, **PS-Ru(tpy)$_2$-PS**, and its corresponding polystyrene precursor, **PS-L1-5**, are 108 and 102 °C, respectively. The increase in T_g for the biscomplex arise from the actual formation of Ru(tpy)$_2$(II)$^{2+}$ complexes between two terpridine-terminated polystyrene macromolecules. All analysis data further indicate the successful formation of the supramolecular dimeric polystyrene ruthenium complex, **PS-Ru(tpy)$_2$-PS**.

As in the preparation of the supramolecular dimeric polystyrene ruthenium complex, **PS-Ru(tpy)$_2$-PS**, the RAFT-prepared terpyridine-terminated polystyrene, **PS-L1-3**, was reacted with an excess of $RuCl_3 \cdot xH_2O$ in THF-EtOH (2:1, v/v) mixture solvents at 85 °C for 25 h to give a monocomplex, **PS-L1-3-Ru^{III}Cl$_3$** (Scheme 3). The excess of $RuCl_3 \cdot xH_2O$ was removed by washing with MeOH. The monocomplex, **PS-L1-3-Ru^{III}Cl$_3$**, was further complexed with slightly excess terpyridine-terminated **PNIPAM-L1-3** in EtOH at 85 °C under catalysis of *N*-ethylmorpholine for 22 h, and then an excess amount of ammonium hexafluorophosphate (NH_4PF_6) was added into the cooled mixture. As a result, a Ru(tpy)$_2$(II)$^{2+}$ complex-connected polystyrene and PNIPAM diblock metallopolymer, **PS-Ru(tpy)$_2$-PNIPAM**, was formed (Scheme 3) and further purified by removing the uncomplexed precursors, **PS-L1-3** and **PNIPAM-L1-3**, with diethyl ether and water, respectively.

The purified biscomplex, **PS-Ru(tpy)$_2$-PNIPAM**, was characterized by UV−vis technique. Figure 7 shows the UV−vis spectra of the biscomplex and its corresponding precursor polymers, **PS-L1-3** and **PNIPAM-L1-3**. As observed from Figure 7, a new absorption band at λ = 491 nm attributed to the metal−ligand charge-transfer (MLCT) band of the Ru(tpy)$_2$(II)$^{2+}$ complex appeared through the comparison with the two precursor polymers. Similarly, on the basis of the theoretical molecular weight of the complex, **PS-Ru(tpy)$_2$-PNIPAM** (M_n = 18 718 g/mol),[33] the molar absorptivity (ϵ) was determined by UV−vis technique to be 22 371 M^{-1} cm^{-1} at λ

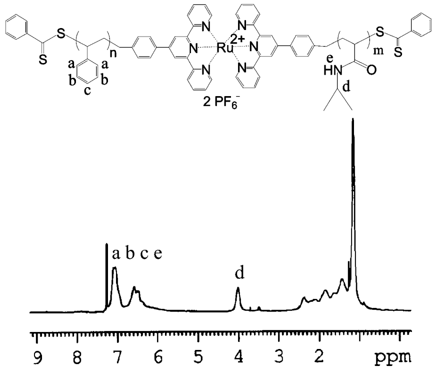


Figure 9. ^{1}H NMR spectrum ($CDCl_3$) of the bis(terpyridine)ruthenium complex-connected polystyrene and poly(*N*-isopropylacrylamide) diblock metallopolymer, **PS-Ru(tpy)$_2$-PNIPAM**.

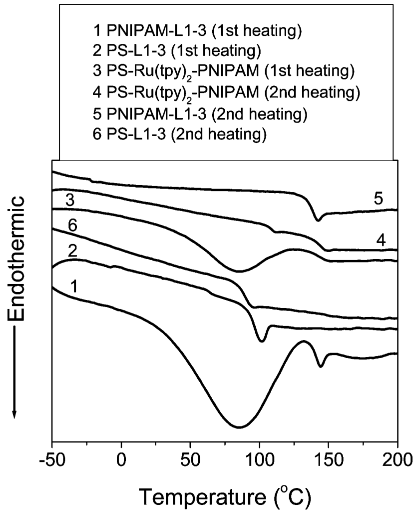


Figure 10. DSC curves of the supramolecular ruthenium complex, **PS-Ru(tpy)$_2$-PNIPAM**, and its corresponding two terpyridine-terminated precursor polymers, **PS-L1-3** and **PNIPAM-L1-3**, during two heating runs.

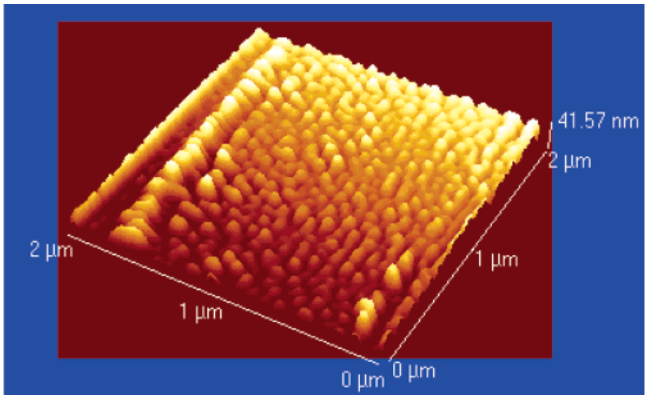


Figure 11. AFM image of the bis(terpyridine)ruthenium complex-connected polystyrene(PS) and poly(*N*-isopropylacrylamide) (PNIPAM) diblock metallopolymer, **PS-Ru(tpy)$_2$-PNIPAM** ($M_{n,theory}$ = 18 170 g/mol, PS mol % (theory) = 46.7%). AFM image size: 2 μm × 2 μm. Data scale: Height 41.57 nm.

= 491 nm in CH_2Cl_2, which is close to the literature value ϵ = 24 800 M^{-1} cm^{-1} for the standard complex $[Ru(tpy\text{-}Ph\text{-}CH_3)_2](II)[PF_6]_2^{2-}$ and the measured value for the biscomplex, **PS-Ru(tpy)$_2$-PS**. This indicates that the degree of metallation is larger than 90%. To further exclude the remaining two precursors, **PS-L1-3** and **PNIPAM-L1-3**, in the biscomplex, the purified complex **PS-Ru(tpy)$_2$-PNIPAM** was characterized by SEC.

The SEC curve (Figure S5) of the purified biscomplex is different from its corresponding two precursor polymers. The main cause for the absence of RI signal corresponding to the purified complex is that the Ru(tpy)$_2$(II)$^{2+}$ complex in the connection of polystyrene and PNIPAM chains interact strongly with the stationary phase, leading to serious adsorption compared with the two precursor polymers, **PS-L1-3** and **PNIPAM-L1-3**. This further shows that the purification procedure is efficient. Figure 9 shows the ^{1}H NMR spectrum ($CDCl_3$) of the Ru(tpy)$_2$(II)$^{2+}$ complex-connected polystyrene and PNIPAM diblock metallopolymer, **PS-Ru(tpy)$_2$-PNIPAM**. The characteristic peaks at 6.00−7.40 and 4.00 ppm corresponding to the polystyrene and PNIPAM segments, respectively, were observed. This further confirmed that the polystyrene and PNIPAM were connected by the Ru(tpy)$_2$(II)$^{2+}$ complex. To further show the existence of polystyrene and PNIPAM segments in the supramolecular complex, **PS-Ru(tpy)$_2$-PNIPAM**, thermal characterization was performed by DSC. Figure 10 shows the DSC curves of the biscomplex and its corresponding two precursors, **PS-L1-3** and **PNIPAM-L1-3**, during two heating runs. During the first heating run, the glass transition of the biscomplex, **PS-Ru(tpy)$_2$-PNIPAM**, is not clear for the polystyrene segment because of hydrogen bonding in the PNIPAM segment in the biscomplex. However, two glass transitions corresponding to polystyrene and PNIPAM segments were clearly observed for the biscomplex, **PS-Ru(tpy)$_2$-PNIPAM**, during the second heating run.

The two glass transition temperatures (T_gs) of the biscomplex and its corresponding two precursors, **PS-L1-3** and **PNIPAM-L1-3**, were determined to be 106, 142, 92, and 136 °C, respectively. The increase in T_g for both polystyrene and PNIPAM segments of the biscomplex arise from the formation of Ru(tpy)$_2$(II)$^{2+}$ complexes between terpridine-terminated polystyrene and PNIPAM macromolecular chains. All analysis data further indicate the successful formation of the supramolecular ruthenium complex, **PS-Ru(tpy)$_2$-PNIPAM**. Interestingly, the transition corresponding to the phase transition temperature, namely, LCST of the PNIPAM segment of the biscomplex and the precursor **PNIPAM-L1-3** disappeared during the second heating run. Hydrogen bonding from PNIPAM was destroyed before the second heating run. On the basis of the DSC results, it can be deduced that the LCST phenomena of PNIPAM actually originates from the hydrogen bonds existing in the PNIPAM chains.

The diblock metallopolymer, **PS-Ru(tpy)$_2$-PNIPAM**, has a strong tendency to form micelles because of its structural amphiphilic property. AFM was used on solid substrates to observe the surface morphology. Figure 11 shows the AFM image of the diblock metallopolymer, **PS-Ru(tpy)$_2$-PNIPAM**. Spherical particles from micelle aggregation were observed, some formed self-assembled arrays. This further demonstrates the formation of amphiphilic diblock metallopolymer via the connectivity of Ru(tpy)$_2$(II)$^{2+}$ complex.

Conclusions

A novel terpyridine-functionalized dithioester was synthesized by a simple thioester exchange reaction and further used as a RAFT agent in the RAFT polymerizations of styrene and NIPAM. For each monomer, the pseudo-first-order kinetic plot of ln([M]$_0$/[M]) vs polymerization time is linear; moreover, the molecular weights determined by SEC and NMR increased linearly with conversion. The polydispersities of these RAFT-prepared polymers are generally low ($M_w/M_n \leq 1.20$). The results indicate that the new terpyridine-functionalized RAFT agent is quite efficient for the preparation of polystyrene and PNIPAM polymers with low polydispersity and controlled molecular weight. The ^{1}H NMR spectra of the RAFT-prepared polymers indicate that they were functionalized by terpyridine groups at one end. The good agreement of the NMR-determined number average molecular weight with theoretical values indicates that most of polymer chains were functionalized at one chain end by terpyridine group derived from the RAFT agents used for polymerization.

The terpyridine end-functionalized polystyrene polymer was treated with an excess of $Ru^{III}Cl_3 \cdot xH_2O$ to produce an intermediate, monocomplex$-Ru^{III}$(terpyridine)Cl_3-terminated polystyrene. The monocomplex was then further treated with a slight excess of terpyridine end-functionalized polystyrene and PNIPAM polymers to form supramolecular dimeric polystyrene ruthenium complex and amphiphilic diblock metallopolymer, respectively. The purified metallopolymers were characterized by UV−vis and DSC. Their UV−vis spectra clearly revealed the typical metal−ligand charge-transfer (MLCT) band of the $Ru(tpy)_2(II)^{2+}$ complex at $\lambda = 491$ nm as well as the $\pi-\pi^*$ transitions of the terpyridine ligand at $\lambda = 310$ nm. Similarly, the glass transition temperatures of the metallopolymers are higher than that of their corresponding precursor polymers. The results indicate the formation of bis(terpyridine)ruthenium complex at the conjunction of two blocks. In addition, surface observation by AFM shows amphiphilic diblock metallopolymers are able to form spherical particles.

Acknowledgment. The financial support for this research work from the Office of Naval Research (ONR Grant No. N00014-01-1-1042) is gratefully acknowledged. We thank Dr. Airan Perez of the Office of Naval Research, Arlington, VA for helpful discussions. Also, we thank Dr. David Bostwick, Georgia Institute of Technology, for HRMS analysis.

Supporting Information Available: The HRMS spectra of the thiol intermediate **1c** and the new terpyridine-functionalized CTA **1**, the schematic structure of the standard complex bis[4′-(4-tolyl)-2,2′:6′,2″-terpyridine]ruthenium hexafluophosphate, and SEC curves of the bis(terpyridine)ruthenium complex-connected diblock metallopolymers **PS-Ru(tpy)$_2$-PS** and **PS-Ru(tpy)$_2$-PNIPAM**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Wöhrle, D.; Pomogailo, A. D., Eds. *Metal Complexes and Metals in Macromolecules*; Wiley-VCH: Weinheim, **2003**.

(2) (a) Schubert, U. S.; Eschbaumer, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 2892−2926. (b) Andres, P. R.; Schubert, U. S. *Adv. Mater.* **2004**, *16*, 1043−1068.

(3) (a) Schultze, X.; Serin, J.; Adronov, A.; Fréchet, J. M. J. *Chem. Commun.* **2001**, 1160−1161. (b) Serin J.; Schultze, X.; Adronov, A.; Fréchet, J. M. J. *Macromolecules* **2002**, *35*, 5396−5404. (c) Fleming, C. N.; Maxwell, K. A.; DeSimone, J. M.; Meyer, T. J.; Papanikolas, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 10336−10347. (d) Hara, K.; Sugihara, H.; Tachibana, Y.; Islam, A.; Yanagida, M.; Sayama, K.; Arakawa, H. *Langmuir* **2001**, *17*, 5992−5999.

(4) (a) De Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515−1566. (b) Beer, P. D. *Acc. Chem. Res.* **1998**, *31*, 71−80. (c) Kimura, M.; Horai, T.; Hanabusa, K.; Shirai, H. *Adv. Mater.* **1998**, *10*, 459−462. (d) Pei, J.; Ding, A.-L.; Yu, W.-L.; Lai, Y.-H. *Macromol. Rapid Commun.* **2002**, *23,* 21−25. (e) Zhang, Y.; Murphy, C. B.; Jones, W. E., Jr. *Macromolecules* **2002**, *35*, 630−636.

(5) (a) Yu, S.-C.; Kwok, C.-C.; Chan, W.-K.; Che, C.-M. *Adv. Mater.* **2003**, *15*, 1643−1647. (b) Wu, A.; Yoo, D.; Lee, J.-K.; Rubner, M. F. *J. Am. Chem. Soc.* **1999**, *121*, 4883−4891. (c) Lee, J.-K.; Yoo, D.; Rubner, M. F. *Chem. Mater.* **1997**, *9*, 1710−1712. (d) Barron, J. A.; Bernhard, S.; Houston, P. L.; Abruna, H. D.; Ruglovsky, J. L.; Malliaras, G. G. *J. Phys. Chem. A* **2003**, *107*, 8130−8133. (e) Ng, W. Y.; Gong, X.; Chan, W. K. *Chem. Mater.* **1999**, *11*, 1165−1170. (f) Bloom, C. J.; Elliott, C. M.; Schroeder, P. G.; France, C. B.; Parkinson, B. A. *J. Am. Chem. Soc.* **2001**, *123*, 9436−9442. (g) Wong, C. T.; Chan, W. K. *Adv. Mater.* **1999**, 455−459.

(6) (a) Suh, J.; Lee, J. Y.; Hong, S. H. *Bioorg. Med. Chem. Lett.* **1997**, *7*, 2383−2386. (b) Suh, J.; Hong, S. H. *J. Am. Chem. Soc.* **1998**, *120*, 12545−12552. (b) Zhou, M.; Roovers, J.; Robertson, G. P.; Grover, C. P. *Anal. Chem.* **2003**, *75*, 6708−6717. (c) Weizman, H.; Tor, Y. *J. Am. Chem. Soc.* **2001**, *123*, 3375−3376.

(7) (a) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348−3391. (b) Sauvage, J.-P. *Acc. Chem. Res.* **1998**, *31*, 611−619.

(8) (a) Tyson, D. S.; Bignozzi, C. A.; Castellano, F. N. *J. Am. Chem. Soc.* **2002**, *124*, 4562−4563. (b) Raymo, F. M. *Adv. Mater.* **2002**, *14*, 401−407.

(9) (a) Peng, Z.; Yu, L. *J. Am. Chem. Soc.* **1996**, *118*, 3777−3778. (b) Yu, S. C.; Hou, S.; Chan, W. K. *Macromolecules* **2000**, *33*, 3259−3273. (c) Wang, Q.; Yu, L. *J. Am. Chem. Soc.* **2000**, *122*, 11806−11811. (d) Ng, P. K.; Gong, X.; Chan, S. H.; Lam, L. S. M.; Chan, W. K. *Chem.−Eur. J.* **2001**, 4358−4367. (e) Trouillet, L.; Nicola, A. D.; Guillerez, S. *Chem. Mater.* **2000**, *12*, 1611−1621.

(10) (a) Beck, J. B.; Rowan, S. J. *J. Am. Chem. Soc.* **2003**, *125*, 13922−13923. (b) Schmatloch, S.; van den Berg, A. M. J.; Alexeev, A. S.; Hofmeier, H.; Schubert, U. S. *Macromolecules* **2003**, *36*, 9943−9949. (c) Knapp, R.; Schott, A.; Rehahn, M. *Macromolecules* **1996**, *29*, 478−480. (d) Kelch, S.; Rehahn, M. *Macromolecules* **1997**, *30*, 6185−6193. (e) Hofmeier, H.; El-Ghayoury, A.; Schenning, A. P. H. J.; Schubert, U. S. *Chem. Commun.* **2004**, 318−319. (f) Dobrawa, R.; Wurthner, F. *Chem. Commun.* **2002**, 1878−1879. (g) Schmatloch, S.; Fernandez González, M.; Schubert, U. S. *Macromol. Rapid Commun.* **2002**, *23*, 957−961.

(11) (a) Zhou, G.; Harruna, I. I. *Tetrahedron Lett.* **2003**, *44*, 4617−4619. (b) Holder, E.; Meier, M. A. R.; Marin, V.; Schubert, U. S. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3954−3964. (c) Marin, V.; Holder, E.; Schubert, U. S. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 374−385. (d) El-Ghayoury, A.; Hofmeier, H.; de Ruiter, B.; Schubert, U. S. *Macromolecules* **2003**, *36*, 3955−3959. (e) Schubert, U. S.; Hofmeier, H. *Macromol. Rapid Commun.* **2002**, *23,* 561−566. (f) Calzia, K. J.; Tew, G. N. *Macromolecules* **2002**, *35*, 6090−6093. (g) Potts, K. T.; Usifer, D. A. *Macromolecules* **1988**, *21,* 1985−1991. (h) Ito, Y.; Nogawa, M.; Yoshida, R. *Langmuir* **2003**, *19*, 9577−9579.

(12) (a) Chen, B.; Sleiman, H. F. *Macromolecules* **2004**, *37*, 5866−5872. (b) Peter, K.; Thelakkat, M. *Macromolecules* **2003**, *36*, 1779−1785. (c) Aamer, K. A.; Tew, G. N. *Macromolecules* **2004**, *37*, 1990−1993. (d) Hoogenboom. R.; Wouters, D.; Schubert, U. S. *Macromolecules* **2003**, *36*, 4743−4749. (e) Hochwimmer, G.; Nuyken, O.; Schubert, U. S. *Macromol. Rapid Commun.* **1998**, *19,* 309−313. (f) Viau, L.; Even, M.; Maury, O.; Haddleton, D. M.; Bozec, H. L. *Macromol. Rapid Commun.* **2003**, *24*, 630−635. (g) Cho, Y.-S.; Ihn, C.-S.; Lee, H.-K.; Lee, J.-S. *Macromol. Rapid Commun.* **2001**, *22*, 1249−1253.

(13) (a) Marin, V.; Holder, E.; Hoogenboom, R.; Schubert, U. S. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4153−4160. (b) Schubert U. S.; Heller, M. *Chem.−Eur. J.* **2001**, *7*, 5252−5259. (c) Heller, M.; Schubert, U. S. *Macromol. Rapid Commun.* **2001**, *22*, 1358−1363.

(14) (a) Smith, A. P.; Fraser, C. L. *Macromolecules* **2003**, *36*, 2654−2660. (b) Smith, A. P.; Fraser, C. L. *Macromolecules* **2002**, *35*, 594−596. (c) Wu, X.; Fraser, C. L. *Macromolecules* **2000**, *33*, 7776−7785. (d) Smith, A. P.; Fraser, C. L. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 4250−4255. (e) Fraser, C. L.; Smith, A. P.; Wu, X.; *J. Am. Chem. Soc.* **2000**, *122*, 9026−9027. (f) Collins, J. E.; Fraser, C. L. *Macromolecules* **1998**, *31*, 6715−6717. (g) Johnson, R. M.; Corbin, P. S.; Ng, C.; Fraser, C. L. *Macromolecules* **2000**, *33*, 7404−7412. (h) Lamba, J. J. S.; Fraser, C. L. *J. Am. Chem. Soc.* **1997**, *119*,

1801−1802. (i) Wu, X.; Fraser, C. L. *Macromolecules* **2000**, *33*, 4053−4060. (j) Smith, A. P.; Fraser, C. L. *Macromolecules* **2003**, *36*, 5520−5525. (k) Corbin, P. S.; Webb, M. P.; McAlvin, J. E.; Fraser, C. L. *Biomacromolecules* **2001**, *2*, 223−232. (l) Johnson, R. M.; Fraser, C. L. *Macromolecules* **2004**, *37*, 2718−2727. (m) Wu, X.; Collins, J. E.; McAlvin, J. E.; Cutts, R. W.; Fraser, C. L. *Macromolecules* **2001**, *34*, 2812−2821. (n) McAlvin, J. E.; Fraser, C. L. *Macromolecules* **1999**, *32*, 6925−6932. (o) McAlvin, J. E.; Scott, S. B.; Fraser, C. L. *Macromolecules* **2000**, *33*, 6953−6954. (p) Johnson, R. M.; Fraser, C. L. *Biomacromolecules* **2004**, *5*, 580−588.

(15) Lohmeijer, B. G. G.; Schubert, U. S. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4016−4027.

(16) (a) Gohy, J.-F.; Lohmeijer, B. G. G.; Varshney, S. K.; Décamps, B.; Leroy, E.; Boileau, S.; Schubert, U. S. *Macromolecules* **2002**, *35*, 9748−9755. (b) Lohmeijer, B. G. G.; Schubert, U. S. *Macromol. Chem. Phys.* **2003**, *204*, 1072−1078. (c) Gohy, J.-F.; Lohmeijer, B. G. G.; Schubert, U. S. *Macromol. Rapid Commun.* **2002**, *23,* 555−560. (d) Lohmeijer, B. G. G.; Schubert, U. S. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 1413−1427. (e) Schubert, U. S.; Eschbaumer, C. *Macromol. Symp.* **2001**, *163*, 177−187. (f) Gohy, J.-F.; Lohmeijer, B. G. G.; Schubert, U. S. *Macromolecules* **2002**, *35*, 4560−4563. (g) Gohy, J.-F.; Lohmeijer, B. G. G.; Varshney, S. K.; Schubert, U. S. *Macromolecules* **2002**, *35*, 7427−7435. (h) Hofmeier, H.; Schmatloch, S.; Wouters, D.; Schubert, U. S. *Macromol. Chem. Phys.* **2003**, *204*, 2197−2203. (i) Hofmeier, H. H.; Andres, P. R.; Hoogenboom, R.; Herdtweck, E.; Schubert, U. S. *Aust. J. Chem.* **2004**, *57*, 419−426.

(17) Gohy, J.-F.; Lohmeijer, B. G. G., Schubert, U. S. *Chem.−Eur. J.* **2003**, *9*, 3472−3479.

(18) Lohmeijer, B. G. G.; Schubert, U. S. *Angew. Chem., Int. Ed.* **2002**, *41*, 3825−3829.

(19) (a) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, G.; Moad, C. L.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559−5562. (b) Quinn, J. F.; Rizzardo, E.; Davis, T. P. *Chem. Commun.* **2001**, 1044−1045. (c) Lutz, J.-F.; Neugebauer, D.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2003**, *125*, 6986−6993.

(20) (a) Mayadunne, R. T.; Rizzardo, E.; Chiefari, J.; Krstina, J.; Moad, G.; Postma, A.; Thang, S. H. *Macromolecules* **2000**, *33*, 243−245. (b) Chong, (Bill) Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 2071−2074. (c) Moad, G.; Mayadunne, R. T. A.; Rizzardo, E.; Skidmore, M.; Thang, S. H. *Macromol. Symp.* **2003**, *192*, 1−12. (d) Tang, C.; Kowalewski, T., Matyjaszewski, K. *Macromolecules* **2003**, *36*, 8587−8589. (e) Sumerlin, B. S.; Lowe, A. B.; Thomas, D. B.; McCormick, C. L. *Macromolecules* **2003**, *36*, 5982−5987 (f) Mitsukami, Y.; Donovan, M. S.; Lowe, A. B.; McCormick, C. L. *Macromolecules* **2001**, *34*, 2248−2256. (g) Shi, L.; Chapman, T. M.; Beckman, E. J. *Macromolecules* **2003**, *36*, 2563−2567. (h) Albertin, L.; Stenzel, M.; Barner-Kowollik, C. B.; Foster, L. J. R.; Davis, T. P. *Macromolecules* **2004**, 37, 7530−7537. (i)Yusa, S.-I.; Shimada, Y.; Mitsukami, Y.; Mitsukami, Y.; Yamanoto, T.; Morishima, Y. *Macromolecules* **2003**, *36*, 4208−4215. (j) Krasia, T.; Soula, R.; Börner, H. G.; Schlaad, H. *Chem. Commun.* **2003**, 538−539. (k) He, T.; Zheng, G.-H.; Pan, C.-Y. *Macromolecules* **2003**, *36*, 5960−5966. (l) Schilli, C. M.; Zhang, M.; Rizzardo, E.; Thang, S. H.; Chong, (Bill) Y. K.; Edwards, K.; Karlsson, G.; Müller, A. H. E. *Macromolecules*, **2004**, *37*, 7861−7866.

(21) (a) Quinn, J. F.; Chaplin, R. P.; Davis, T. P. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2956−2966. (b) Vosloo, J.; Tonge, M. P.; Fellows, C. M.; D'Agosto, F.; Sanderson, R. D.; Gilbert, R. G. *Macromolecules* **2004**, *37*, 2371−2382.

(22) (a) Mayadunne, R. T. A.; Jeffery, J.; Moad, G.; Rizzardo, E. *Macromolecules* **2003**, *36*, 1505−1513. (b) Feng, X.-S.; Pan, C.-Y. *Macromolecules* **2002**, *35*, 4888−4893. (c) Duréault, A.; Taton, D.; Destarac, M.; Leising, F.; Gnanou, Y. *Macromolecules* **2004**, *37*, 5513−5519. (d) Stenzel, M. H.; Davis, T. P.; Barner-Kowollik, C. *Chem. Commun.* **2004**, 1546−1547.

(23) (a) Chong, Y. K.; Krstina, J.; Le, T. P. T.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2003**, *36*, 2256−2272. (b) Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Skidmore, M. A.; Thang, S. H. *Macromolecules* **2003**, *36*, 2273−2283. (c) Moad, G.; Mayadunne, R. T. A.; Rizzardo, E.; Skidmore, M.; Thang, S. H. ACS Symposium Series 854; American Chemical Society: Washington, DC, 2003; pp 520−535.

(24) Chen, M.; Ghiggino, K. P.; Mau, A. W. H.; Rizzardo, E.; Sasse, W. H.; Thang, S. H.; Wilson, G. J. *Macromolecules* **2004**, *37*, 5479−5481.

(25) (a) Favier, A.; Ladavière, C.; Charreyre, M.-T.; Pichot, C. *Macromolecules* **2004**, 37, 2026−2034. (b) D'Agosto, F.; Hughes, R.; Charreyre, M.-T.; Pichot, C.; Gilbert, R. G. *Macromolecules* **2003**, *36*, 621−629 (c) Vana, P.; Albertin, L.; Barner, L.; Davis, T. P.; Barner-Kowollik, C. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 4032−4037. (d) Ladavière, C.; Dorr, N.; Claverie J. P. *Macromolecules* **2001**, *34*, 5370−5372.

(26) (a) Ganachaud, F.; Monteiro, M. J.; Gilbert, R. G.; Dourges, M.-A.; Thang, S. H.; Rizzardo, E. *Macromolecules* **2000**, *33*, 6738−6745. (b) Schilli, C.; Lanzendorfer, M. G.; Müller, A. H. E. *Macromolecules* **2002**, *35*, 6819−6827.

(27) Zhou, G.; Harruna, I. I. *Macromolecules* **2004**, *37*, 7132−7139.

(28) Chen, M.; Ghiggino, K. P.; Launikonis, A.; Mau, A. W. H.; Rizzardo, E.; Sasse, W. H. F.; Thang, S. H.; Wilson, G. J. *J. Mater. Chem.* **2003**, *13*, 2696−2700.

(29) (a) Hofmeier, H.; Schubert, U. S. *Chem. Soc. Rev.* **2004**, *33,* 373−399. (b) Newkome, G. R.; Kim, H. J.; Choi, K. H.; Moorefield, C. N. *Macromolecules* **2004**, 37, 6268−6274. (c) Newkome, G. R.; Yoo, K. S.; Kim, H. J.; Moorefield, C. N. *Chem.−Eur. J.* **2003**, *9*, 3367−3374. (d) Newkome, G. R.; Cho, T. J.; Moorefield, C. N.; Mohapatra, P. P.; Godinez, L. A. *Chem.−Eur. J.* **2004**, *10*, 1493−1500. (e) Newkome, G. R.; Yoo, K. S.; Hwang, S.-H.; Moorefield, C. N. *Tetrahedron* **2003**, *59*, 3955−3964.

(30) (a) Spahni, W.; Calzaferri, G. *Helv. Chim. Acta* **1984**, *67*, 450−454. (b) Collin, J.-P.; Guillerez, S.; Sauvage, J.-P.; Barigelletti, F.; Cola, L. D.; Flamigni, L.; Balzani, V. *Inorg. Chem.* **1991**, *30*, 4230−4238.

(31) The theoretical molecular weight of **PS-Ru(tpy)$_2$-PS** was calculated according to the equation: $M_{\mathrm{n,theory(PS-Ru(tpy)_2-PS)}} = 2M_{\mathrm{n,theory(PS-L1-5)}} + M_{\mathrm{Ru(PF_6)_2}}$.

(32) The number average molecular weight of Ru(tpy)$_2^{2+}$-connected diblock metallopolymers was determined through the analysis of the characteristics absorption band at $\lambda_{\max} = 491$ nm of Ru(tpy)$_2^{2+}$ functional group in the polymer chain by UV−vis technique with the use of the literature-reported molar absorptivity value of the standard complex bis[4′-(4-tolyl)-2, 2′:6′, 2″-terpyridine]ruthenium hexafluophosphate (its structural scheme shown in Figure S3).

(33) The theoretical molecular weight of **PS-Ru(tpy)$_2$-PNIPAM** was calculated according to the equation: $M_{\mathrm{n,theory(PS-Ru(tpy)_2-PNIPAM)}} = M_{\mathrm{n,theory(PS-L1-3)}} + M_{\mathrm{n,theory(PNIPAM-L1-3)}} + M_{\mathrm{Ru(PF_6)_2}}$.

(34) (a) Favier, A.; Charreyre, M.-T.; Chaumont, P.; Pichot, C. *Macromolecules* **2002**, *35*, 8271−8280. (b) Donovan, M. S.; Lowe, A. B.; Sumerlin, B. S.; McCormick, C. L. *Macromolecules* **2002**, *35*, 4123−4132.

(35) Schild, H. G. *Prog. Polym. Sci.* **1992**, *17*, 163−249 and references therein.

(36) Kobayashi, M.; Matsumoto, Y.; Uchiyama, M.; Ohwada, T. *Macromolecules* **2004**, *37*, 4339−4341.

(37) Convertine, A. J.; Ayres, N.; Scales, C. W.; Lowe, A. B.; McCormick, C. L. *Biomacromolecules* **2004**, *5*, 1177−1180. (b) Ray, B.; Isobe, Y.; Matsumoto, K.; Habaue, S.; Okamoto, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2004**, *37*, 1702−1710. (c) Zhu, M.-Q.; Wang, L.-Q.; Exarhos, G. J.; Li, A. D. Q. *J. Am. Chem. Soc.* **2004**, *126*, 2656−2657. (d) Arotçaréna, M.; Heise, B.; Ishaya, S.; Laschewsky, A. *J. Am. Chem. Soc.* **2002**, *124*, 3787−3793. (e) Shan, J.; Nuopponen, M.; Jiang, H.; Kauppinen, E.; Tenhu, H. *Macromolecules* **2003**, *36*, 4526−4533.

(38) (a) Covertine, A. J.; Sumerlin, B. S.; Thomas, D. B.; Lowe, A. B.; McCormick, C. L. *Macromolecules* **2003**, *36*, 4679−4681. (b) Sumerlin, B. S.; Donovan, M. S.; Mitsukami, Y.; Lowe, A. B.; McCormick, C. L. *Macromolecules* **2001**, *34*, 6561−6564.

(39) Heller, M.; Schubert, U. S. *Macromol. Rapid Commun.* **2002**, *23,* 411−415.

(40) Newkome, G. R.; Cho, T. J.; Moorefield, C. N.; Cush, R.; Russo, P. S.; Godinez, L. A.; Saunders: M. J.; Mohapatra, P. *Chem.−Eur. J.* **2002**, *8*, 2946−2954.

MA047955C