The Importance of Macroligand Molecular Weight and Solvent Polarity in Modulating Metal Core Reactivity in Heteroleptic Polymeric Ruthenium Tris(bipyridine) Complex Synthesis

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ABSTRACT: By using metal ions as templates for polymer synthesis, functional materials with a wide range of molecular architectures may be readily generated. Polystyrene macroligands, bpyPS and bpyPS$_2$, with bipyridine (bpy) donors at the end and center of the chain, respectively, were generated by copper-catalyzed atom transfer radical polymerization (ATRP). Heteroleptic polymeric Ru(II) tris(α-diimine) complexes were prepared by combining nonpolymeric ligands and polymeric bpyPS$_n$ ligands of different molecular weights. The reaction of bpyPS$_2$ with Ru(DMSO)$_4$Cl$_2$ in CHCl$_3$ solution to form a putative [Ru(bpyPS$_2$)(DMSO)$_m$Cl$_2$]$^{2+}$ intermediate, followed by dehalogenation with AgPF$_6$ in the presence of excess 2,2′-bipyridine, led to linear polymeric complexes, [Ru(bpyPS$_2$)(bpy)$_2$]$^{2+}$. More versatile were sequences involving chelation of 2 equiv of a bpyPS$_n$, followed by association of another polymeric or nonpolymeric ligand with the Ru(II) center. Ruthenium-centered linear polymers, [Ru(bpyPS)$_2$(L)]$^{2+}$ (L = bpy or 4,4′-bis(hydroxymethyl)-2,2′-bipyridine), and analogous four-arm stars, [Ru(bpyPS$_2$)$_2$(L)]$^{2+}$ (L = bpy, 1,10-phenathroline, 4,4′-bis(hydroxymethyl)-2,2′-bipyridine, and 4,4′-bis(tricosanyl)-2,2′-bipyridine) were prepared in this fashion. Reactions forming [Ru(bpyPS$_n$)$_2$Cl$_2$] and [Ru(bpyPS$_n$)$_2$(solvent)$_m$]$^{2+}$ intermediates showed a marked molecular weight dependence. In certain cases, reactivity at the Ru center could be modulated by changing the polarity of the reaction media (DME vs DME/MeOH). Differences in the conformation of polystyrene chains in different solvents were exploited as a "protecting group" strategy in polymeric metal complex synthesis. By using two different kinds of bpyPS$_n$ macroligands, homo-block copolymer Ru-centered stars, [Ru(bpyPS)$_2$(bpyPS$_2$)]$^{2+}$ and [Ru(bpyPS$_2$)$_2$(bpyPS)]$^{2+}$, were generated. GPC and UV/vis spectroscopy confirm that the Ru(II) chromophores are associated with eluting polymer fractions and allow for comparison of relative chelation efficiencies.

Introduction

The ability of metal ions to serve as templates has been exploited in many different areas of synthetic chemistry. For example, metals are often used to promote otherwise difficult macrocyclization reactions.[1] In catalysis, metal centers serve as the locus for the controlled assembly and activation of substrates for conversion to products.[2] Metals serve as functional cross-links in elaborate molecular scaffolding in supramolecular chemistry.[3] Also, dendrimers with metals at the centers or other sites in the branched structures are an interesting example from polymer chemistry.[4,5] Recently, we have begun using metals as templates for the controlled assembly of linear polymers as an avenue to functional materials.[6] Polymers with tailored binding sites and narrow molecular weight distributions are generated using living polymerizations. These macroligands are then chelated to metal ions or complexes using standard inorganic procedures that are modified to ensure compatibility of metal and polymeric reagents. Polymeric metal complexes resemble metalloproteins in that metal ions are in discrete locations in well-defined macromolecular environments. Moreover, natural metal-containing polymers suggest possible uses for these and related systems as electron donors or acceptors, as magnetic materials, chromophores, and receptors, and as sites where smaller molecules might bind and be activated in catalytic transformations.

The idea of using polymeric ligands in inorganic reactions is both simple and far-reaching. As compared with most common initiator[7] and terminator[8] approaches to polymers, metal template-assisted synthesis is highly modular. Macromolecular architecture may be varied in a systematic and convenient manner. Some representative structures are illustrated in Figure 1. The preparation of ruthenium tris(bipyridine) functionalized linear polymers (Figure 1, **A** and **B**) and homoleptic three- and six-arm star-shaped polystyrenes (Figure 1, **D** and **H**) was discussed in a previous paper.[6] Alternative metalloinitiator[9] and coupling[10] routes to Ru-centered polystyrenes have also been described. In this account the synthesis of heteroleptic polymeric complexes is outlined (Figure 1, **C** and **E**−**G**, and an alternative route to **A** and **B**). These more elaborate mixed ligand targets typically possess two or more polymeric ligands and require additional steps for their synthesis. Related block copolymer synthesis by chelation has also been communicated recently.[11]

In addition to architectural diversity, polymeric metal complexes also present considerable versatility in terms of sites where functionality might be introduced. In this study, both macroligands and nonpolymeric ligands were varied. This provides means of tuning the optical properties of the materials and of rendering them capable of further derivatization. Depending on the particular application and the number of functionalities that are required, groups may also be introduced at chain termini or on polymer side chains. The metal plays both a structural and functional role in these materials. With the appropriate choice of metal and ligand set, heat, light, pH, reagents, or other stimuli may trigger the release of polymeric or nonpolymeric ligands from the metal center.[12,13] These changes in metal geometry and/or polymer architecture may be

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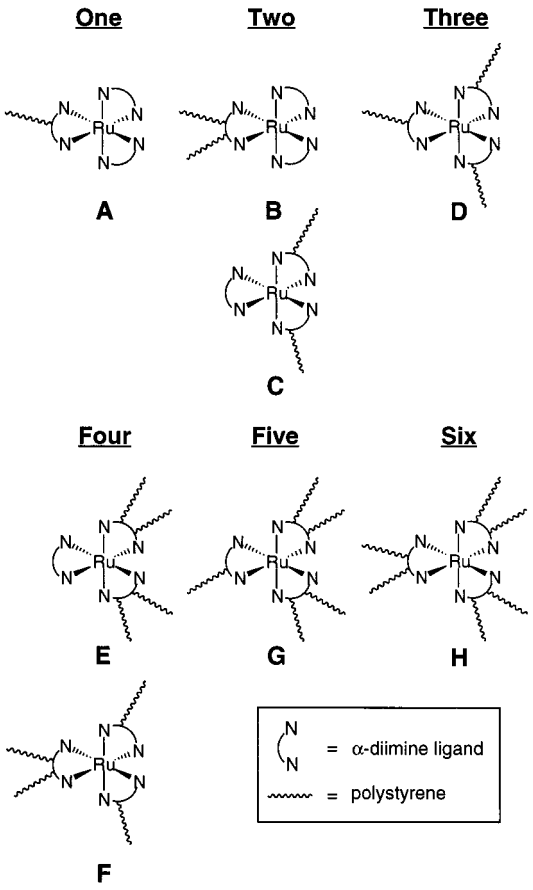

Figure 1. Representative architectures for Ru(II) polymeric complexes with bipyridine-functionalized polystyrene macroligands classified according to the number of polymer chains emanating from the dicationic Ru(II) center.

coupled to switching the optical, magnetic, or other properties of the material or to varying accessibility of recognition elements on polymer side chains or ligands at the core.

To determine the practicality of this route to functional polymers, this study further explores the scope and limitations of the macroligand chelation approach. Previous studies utilizing polymeric ligands in substitution reactions have often focused on low molecular weight materials.[14−17] Because they are the most straightforward extensions of the small molecule analogues on which they are based, oligomeric metal complexes are generally easiest to prepare by standard procedures. For higher molecular weight polymeric metal complexes, however, additional considerations come into play.[4,6] As is true for nonpolymeric metal complex synthesis, the reaction medium must be capable of solubilizing both the metal complex precursor and the ligand undergoing substitution. Likewise, the solvent may facilitate ligand substitution by better solvating leaving groups and rendering metal centers more labile through the formation of solvento intermediates. However, a new factor is present in polymeric metal complex synthesis for which there is no parallel in small molecule synthesis. For reactions with macroligands, polymer chain conformation and aggregation in different media must be taken into consideration.[18] This account further documents our efforts to better understand the factors that influence substitution reactions with polymeric ligands of different molecular weights.

Experimental Section

A. Materials and Methods. Reagents and solvents were obtained and purified as previously described.[6] Macroligands bpyPS, **1**, and $bpyPS_2$, **2**, were generated from 4-chloromethyl-2,2′-bipyridine[19] and 4,4′-bis(chloromethyl)-2,2′-bipyridine[20] by reported ATRP methods (see Table 1).[6] The polymers were characterized by GPC ($CHCl_3$, ∼25 °C; flow rate, 1.0 mL/min) using a Hewlett-Packard 1100 system equipped with a vacuum degasser, diode array detector, Polymer Labs 5 μm "mixed c" guard column and two GPC columns, Wyatt Technology Corporation DAWN multiangle laser light scattering (5 mW polarized He−Ne laser, $\lambda = 633$ nm) and Optilab refractive index detectors and accompanying Astra software. The d*n*/d*c* for polystyrene, 0.145 mL/g ($CHCl_3$, 35 °C, $\lambda = 633$ nm), was obtained from Wyatt Technologies and was used in all calculations. ^{1}H NMR spectra were recorded on a GE QE 300 spectrometer in the solvents specified. UV/vis spectra were recorded for 30 μM $CHCl_3$ solutions using a Hewlett-Packard 8452A diode array spectrophotometer with absorbances reported at this concentration unless otherwise specified. IR spectra were recorded for samples as Nujol mulls with a Nicolet Impact 400 D spectrophotometer. Reaction temperatures indicated refer to oil bath settings.

B. Synthesis of Polymeric Ru Complexes with One Macroligand. $[Ru(bpyPS_2)(DMSO)_2Cl_2]$, 3, Determination of Optimal Reaction Time. The macroligand $bpyPS_2$, **2b**, (54.6 mg, 6.87 μmol) and $Ru(DMSO)_4Cl_2$ (6.66 mg, 13.7 μmol) were dissolved in $CHCl_3$ (10 mL) and heated at reflux under N_2. Aliquots (1 mL) of the red solution were removed over the course of 6 d and were concentrated in vacuo. The resulting yellow solids were dissolved in $CHCl_3$ to prepare 30 μM solutions for analysis by UV/vis spectroscopy. For reaction times of 2 d, λ_{max} (MLCT) = 403 nm, $A = 0.216$; for 3 d, λ_{max} (MLCT) = 402 nm, $A = 0.221$; for 4 d, λ_{max} (MLCT) = 402 nm, $A = 0.229$; for 5 d, λ_{max} (MLCT) = 402 nm, $A = 0.235$; for 6 d, λ_{max} (MLCT) = 402 nm, $A = 0.235$, and GPC ($CHCl_3$) M_n = 6900, M_w = 7300, PDI = 1.07.

$[Ru(bpyPS_2)(bpy)_2]^{2+}$, 4. The solvento complex, **3**, was prepared as described above using the same reagents, loadings, and reaction conditions with a reaction time of 5 d. Bpy (6.56 mg, 41.2 μmol) was added to the red solution of intermediate **3**, and the reaction mixture was heated at reflux under N_2 for 2 d. The deep-purple solution was concentrated in vacuo and redissolved in DME (10 mL), and then $AgPF_6$ (21.8 mg, 86.2 μmol) was added. The reddish mixture was heated at reflux under N_2 for 2 d. The product was cannula filtered to remove Ag^+ salts, and the red-orange filtrate was concentrated in vacuo. The residue was triturated with refluxing EtOH, then was dissolved in THF (15 mL) for filtration through a neutral alumina plug (∼5 mm × 6 cm). After filtration, CH_2Cl_2 (35 mL) was added to the THF solution, and the organic layer was washed with H_2O (75 mL). After standing for ∼12 h, the resulting emulsion clarified, and the organic layer was concentrated in vacuo to produce an orange product, **4**. Yield: 32.8 mg, 60%.[21,22] GPC: M_n = 10 600, M_w = 10 800, PDI = 1.02. UV/vis: λ_{max} = 457 nm, $A = 0.283$.

C. Synthesis of Polymeric Ru Complexes with Two Macroligands. $[Ru(bpyPS)_2Cl_2]$, 5. Polymeric complexes, **5**, were prepared as described below for **6**. For **1a**, the following results were obtained (reaction time of 6 d). GPC: M_n = 12 300, M_w = 13 300, PDI = 1.08. UV/vis: λ_{max} = 562 nm, $A = 0.240$. Subsequent use of intermediates **5** (prepared from macroligands **1**, of the specified molecular weights) in the synthesis of other Ru complexes, **7**, **9** **10**, and **15**, is outlined below.

$[Ru(bpyPS_2)_2Cl_2]$, 6. A representative preparation of $[Ru(bpyPS_2)_2Cl_2]$ is described below for low molecular weight $bpyPS_2$, **2a**. A $CHCl_3$ solution (10 mL) of $Ru(DMSO)_4Cl_2$ (26.9 mg, 55.5 μmol) was prepared, then a portion of it (0.892 mL, 4.95 μmol) was delivered to a 25 mL round-bottom flask containing a DME solution (10 mL) of $bpyPS_2$, **2a** (47.7 mg, 9.90 μmol). The pale yellow-green solution was heated under N_2 at 120 °C.

(a) Determination of Optimal Reaction Time. Aliquots (1 mL) were removed every day for ∼1 wk. Fractions were

concentrated in vacuo and dissolved in $CHCl_3$ for analysis by GPC and UV/vis spectroscopy. Molecular weight and absorbance data corresponding to different reaction times are provided in Table 2. (Note: Reaction times increase with macroligand molecular weight.)

(b) Preparative Reactions. After 6 d, an aliquot was removed and analyzed by GPC with in-line UV/vis spectroscopy. GPC ($CHCl_3$): $M_n = 7000$, $M_w = 7600$, PDI = 1.08. UV/vis (in-line diode array) $\lambda_{max} = 571$ nm. Use of intermediates **6** thus formed in the preparation of polymeric metal complexes, **8** **11**−**14**, and **16**, is described below.

$[Ru(bpyPS)_2(S)_n]^{2+}$, 7. Intermediates **7** were prepared as described below for **8** with simultaneous addition of $AgPF_6$ and MeOH (method A).

$[Ru(bpyPS_2)_2(S)_n]^{2+}$, 8 (S = Solvent. For S = MeOH, *n* = 2; S = DME, *n* = 1). (a) Preparation. Method A. A $Ru(bpyPS_2)_2Cl_2$ intermediate, **6**, was prepared from $bpyPS_2$, **2f**, as described above with the following exceptions. A shorter reaction time (2 d) and the following reagent loadings were employed: $Ru(DMSO)_4Cl_2$ (0.90 mL, 1.77 μmol of a 1.96 mM stock $CHCl_3$ solution), **2f** (86.1 mg, 3.55 μmol), and DME (10 mL). After 2 d, MeOH (4 mL) and then $AgPF_6$ (22.8 mg, 90 μmol) were added to the deep purple DME solution. The resulting red mixture was heated at 90 °C for 18 h and cannula filtered to remove a brown solid precipitate. The red filtrate was concentrated in vacuo, and a small aliquot was removed for GPC analysis prior to use in subsequent chelation reactions. GPC: $M_n = 43\,800$, $M_w = 47\,900$, PDI = 1.10. (No bands were evident in the 420−600 nm range by in-line diode array UV/vis analysis.)

Method B. For synthesis of **8** from $bpyPS_2$ with M_n > 20,000, the following alternative procedure (illustrated for **2f**) can also be employed: After 2 d, $AgPF_6$ (22.8 mg, 90 μmol) was added to the purple solution containing $[Ru(bpyPS_2)Cl_2]$. The resulting red solution was heated at 90 °C for 18 h. Methanol (4 mL) was added to the cloudy pale purple suspension, and the mixture was refluxed for 2 h. During this time, a pale yellow precipitate formed in the red solution. The reaction mixture was cannula filtered and was analyzed by GPC prior to use in subsequent chelation reactions. GPC: $M_n = 45\,200$, $M_w = 51\,500$, PDI = 1.15. (No bands were evident in the 420−600 nm range by in-line diode array UV/vis analysis.)

(b) Effect of MeOH/DME Ratio on Product Outcome in $[Ru(bpyPS_2)_2Cl_2]^{2+}$ Dehalogenation Reactions. *Solubility Test.* Into five separate round-bottom flasks were weighed macroligand, $bpyPS_2$, **2c** (49.8 mg, 3.98 mmol), and $Ru(DMSO)_4Cl_2$ (0.966 mg, 1.99 mmol). DME/MeOH solvent mixtures, 10/4, 9/5, 8/6, 7/7, and 6/8 mL, respectively (total volume = 14 mL), were added and the five reactions were heated at 90 °C for 3 h. A significant portion of the macroligand remained insoluble when the polarity of the DME/MeOH solvent mixture was increased to a 7/7 mL ratio.

Influence of Solvent Polarity on Product Outcome. $[Ru(bpyPS_2)_2Cl_2]^{2+}$ was prepared as described above for **6** using $bpyPS_2$, **2c** ($M_n = 12\,500$, $M_w = 13\,600$, PDI = 1.09) with the following exceptions: A 6.96 mM $CHCl_3$ solution of $Ru(DMSO)_4Cl_2$ (33.7 mg, 69.6 μmol) was prepared and then a portion of it (0.571 mL, 3.97 μmol) was delivered to a 25 mL round-bottom flask containing $bpyPS_2$, **2c** (99.3 mg, 7.94 μmol), in DME (10 mL). The pale yellow-green solution was heated at 120 °C under N_2. After 3 d, the deep purple reaction mixture was evenly distributed into three 25 mL round-bottom flasks, and the solvents were removed in vacuo. To each of the three flasks were added $AgPF_6$ (23.2 mg, 91.8 μmol) and DME/MeOH in ratios of 10/4, 9/5, and 8/6 mL, respectively. The resulting reddish solutions were heated at 90 °C for 18 h under N_2. After cooling, the red reaction mixtures were filtered through paper. Solvents were removed on a rotary evaporator. The resulting residues were redissolved in $CHCl_3$, insoluble salts were removed by filtration through paper, and the resulting yellow filtrates were dried under high vacuum overnight before analysis by GPC and UV/vis spectroscopy. For DME/MeOH ratios as given the following data were obtained. 10/4 mL: GPC $M_n = 19\,200$, $M_w = 20\,700$, PDI = 1.08; UV/vis (460 nm) $A = 0.099$. 9/5 mL: GPC $M_n = 18\,900$, $M_w = 20\,700$, PDI = 1.07; UV/vis (460 nm) $A = 0.094$. 8/6 mL: GPC (multimodal peak) $M_n = 28\,100$, $M_w = 31\,900$, PDI = 1.14; UV/vis (460 nm) $A = 0.103$.

$[Ru(bpyPS)_2(bpy)]^{2+}$, 9. Polymeric Ru complexes **9** were prepared by reaction of the bpyPS intermediates **7** with 2,2′-bipyridine by a procedure analogous to that described below for $[Ru(bpyPS_2)_2(bpy)]^{2+}$, **11**. Yield: 49.2 mg, 96%.[21−23]

$[Ru(bpyPS)_2\{bpy(CH_2OH)_2\}]^{2+}$, 10. Polymeric Ru complexes **10** were prepared by reaction of bpyPS intermediates **7** with $bpy(CH_2OH)_2$ by a procedure analogous to that described below for $[Ru(bpyPS_2)_2(bpy)]^{2+}$, **11**. Yield: 68.1 mg, 93%.[21−23] IR (O−H): $\nu = 3452$ cm^{-1}.

$[Ru(bpyPS_2)_2(bpy)]^{2+}$, 11. The dehalogenated intermediate, $[Ru(bpyPS_2)_2(S)_n]^{2+}$, **8** ($bpyPS_2$, **2f**), was prepared as described above using the reagent loadings indicated. The yellow product, **8**, was dissolved in DME (10 mL) for transfer to a 50 mL round-bottom flask containing 2,2′-bipyridine (0.282 mg, 1.77 μmol) dissolved in $CHCl_3$ (∼0.5 mL). The reaction mixture was heated at 120 °C under N_2 for 2 d, was cooled and cannula filtered, and then the resulting orange filtrate was concentrated on the rotary evaporator. The crude product was triturated for ∼1 h with refluxing EtOH (2 × 100 mL), collected by filtration, and washed with additional EtOH. The resulting solid was redissolved in $CHCl_3$ (∼25 mL), washed with H_2O (3 × 50 mL), then the orange organic layer was concentrated in vacuo to give the product as an orange solid. Yield: 38.4 mg, 94%.[21,22,24] (Note: Reactions employing excess 2,2′-bipyridine were performed in an analogous manner using the stoichiometry indicated and were obtained in comparable yield.)

$[Ru(bpyPS_2)_2(phen)]^{2+}$, 12. The Ru phen complex **12** was prepared as described above for **11** using 1,10-phenathroline in place of 2,2′-bipyridine. Yield: 59.4 mg, 64%.[21,22,24]

$[Ru(bpyPS_2)_2\{bpy(CH_2OH)_2\}]^{2+}$, 13. The alcohol complex **13** was prepared as described above for **11** with the following exceptions: The ancillary ligand, 4,4′-(hydroxymethyl)-2,2′-bipyridine, $bpy(CH_2OH)_2$[25] (used in place of 2,2′-bipyridine) was dissolved in MeOH (∼1 mL) instead of $CHCl_3$. Yield: 57.9 mg, 84%.[21,22,24] IR (O−H): $\nu = 3440$ cm^{-1}.

$[Ru(bpyPS_2)_2\{bpy(C_{23}H_{47})_2\}]^{2+}$, 14. The Ru complex **14** was prepared by the procedure described above for **11** using 4,4′-bis(tricosanyl)-2,2′-bipyridine[26] in place of 2,2′-bipyridine, and the crude product was purified by trituration and washing with hexanes instead of EtOH. Yield: 65.5 mg, 95%.[22,24] ^{1}H NMR: 7.2−6.9 (br m, $-C_6H_5$), 6.7−6.3 (br m, $-C_6H_5$), 2.1−1.2 (br m, $-CH$PhCH_2-). (A peak corresponding to the $-CH_2-$ groups on the $C_{23}H_{47}$ side chains is evident at 1.25 ppm.)

D. Synthesis of Polymeric Ru Complexes with Three Macroligands. $[Ru(bpyPS)_2(bpyPS_2)]^{2+}$, 15. The four-arm star **15** was prepared as described below for **16** with the following reagent loadings and reaction conditions: $Ru(DMSO)_4Cl_2$ (0.578 mL, 3.17 μmol of a 5.49 mM $CHCl_3$ stock solution), bpyPS **1a** (43.3 mg, 6.34 μmol), DME (10 mL), 120 °C, 6 d; then $AgPF_6$ (26.8 mg, 106 μmol), $bpyPS_2$, **2b** (16.1 mg, 2.03 μmol). Yield: 38.9 mg, 82%.[22] Note: $BpyPS_2$ loading was scaled according to $[Ru(bpyPS)_2(solvent)_m]^{2+}$ remaining after aliquot removal.

$[Ru(bpyPS_2)_2(bpyPS)]^{2+}$, 16. The solvento intermediate, $[Ru(bpyPS_2)_2(S)_n]^{2+}$, **8**, was prepared as described above using the following reagent loadings and reaction conditions. Formation of **6**: $Ru(DMSO)_4Cl_2$ (0.64 mL, 2.45 μmol of a 3.84 mM $CHCl_3$ stock solution), $bpyPS_2$, **2d** (79.9 mg, 4.90 μmol); DME (10 mL); 120 °C; 2 d. Formation of **8**: $AgPF_6$ (30.5 mg, 0.121 mmol), MeOH (4 mL), 18 h, 90 °C. After cannula filtration through paper and analysis of the dehalogenated intermediate $[Ru(bpyPS_2)_2(S)_n]^{2+}$, **8**, by GPC, the reddish filtrate was concentrated on a rotary evaporator and redissolved in $CHCl_3$ to produce a yellow solution. The insoluble salts were removed by filtration through paper, and the yellow filtrate was concentrated in vacuo. Crude yield: 61.6 mg. Macroligand, bpyPS, **1a** (12.9 mg, 1.89 μmol) (1:1 **1a**:$[Ru(bpyPS_2)_2(S)_n]^{2+}$, **8**), and the Ru intermediate, **8**, were dissolved in DME (10 mL). Additional $AgPF_6$ (24.2 mg, 95.7 μmol) was added, and the resulting red reaction mixture was refluxed under N_2. After 2 d, the brown suspension was filtered through Celite and

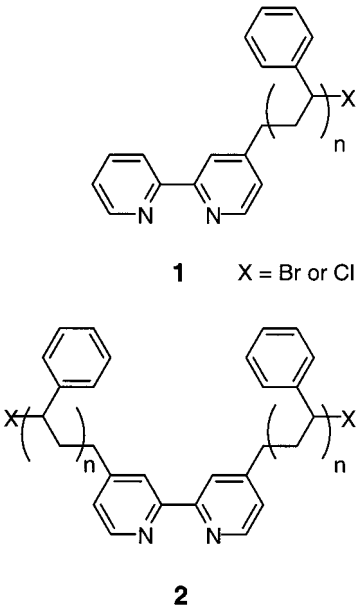

Figure 2. Bipyridine-functionalized polystyrene macroligands, bpyPS, **1**, and $bpyPS_2$, **2**.

Table 1. Molecular Weight Data for Macroligands bpyPS, 1, and $bpyPS_2$, 2[a,b]

$bpyPS_n$	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	PDI
1a	6.8	7.2	1.06
1b	18.3	21.3	1.16
1c	22.4	25.4	1.13
1d	34.1	39.0	1.15
2a	4.8	5.1	1.06
2b	7.9	8.2	1.03
2c	12.5	13.6	1.09
2d	16.3	17.2	1.05
2e	20.8	21.8	1.04
2f	24.2	25.1	1.03
2g	34.3	35.0	1.02

[a] Determined by GPC at 25 °C with RI and MALLS detection. [b] Macroligands were prepared as previously described.[6]

concentrated in vacuo. The orange residue was dissolved in $CHCl_3$ and was washed with H_2O, and then the organic layer was concentrated in vacuo to yield an orange solid. Yield: 67.9 mg, 91%.[21,22] GPC: $M_n = 34\,200$, $M_w = 38\,100$, PDI = 1.11. UV/vis: $\lambda_{max} = 460$ nm, $A = 0.323$.

Results and Discussion

Polystyrene macroligands used in chelation reactions with ruthenium precursor complexes were prepared using 4,4′-dichloromethyl-2,2′-bipyridine and 4-chloromethyl-2,2′-bipyridine initiators via copper-catalyzed atom transfer radical polymerization (ATRP)[27−29] as previously described (Figure 2).[6] Molecular weight data for polystyrene macroligands, bpyPS and $bpyPS_2$, employed in this study are presented in Table 1. Two general approaches to heteroleptic polymeric ruthenium complexes of the form $[Ru(L)(L')_2]^{2+}$, with linear and star-shaped architectures, were explored wherein L and L′ represent either polymeric or nonpolymeric bipyridine ligand derivatives. One equivalent of ligand L may be first chelated to a ruthenium source, [Ru], to generate an intermediate, $[Ru(L)(X)_n]$ (X = ancillary ligands). In a second step, 2 equiv of L′ are coordinated to form the $[Ru(L)(L')_2]^{2+}$ product (eq 1). Alternatively, $[Ru(L')_2X_m]$ intermediates are formed first and subsequently combined with a second type of ligand, L, to generate the desired mixed ligand polymeric metal complex targets $[Ru(L')_2(L)]^{2+}$ (eq 2). (In this account, polymeric complexes are named with bipyridine (or phen) ligands listed according to their order of addition to the Ru center.)

$$[Ru] + L \rightarrow [Ru(L)(X)_n] + 2L' \rightarrow [Ru(L)(L')_2]^{2+} \quad (1)$$

$$[Ru] + 2L' \rightarrow [Ru(L')_2(X)_m] + L \rightarrow [Ru(L')_2(L)]^{2+} \quad (2)$$

There are advantages to preparing batches of metal precursor complexes bearing a single α-diimine ligand, L, for subsequent combination with macroligands of different types and molecular weights (eq 1, L = nonpolymeric ligand). However, attempts to use standard approaches that have been developed for nonpolymeric precursor complexes were largely unsuccessful. For example, neither reaction of [(4,4′-dimethyl-2,2′-bipyridine)$RuCl_2(DMSO)_2$][30] with $bpyPS_2$, **2b**, nor modified procedures incorporating a dehalogenation step or $CHCl_3$ as the solvent produced the targeted tris(bipyridine) products. Similar difficulties were encountered in $MeOH/H_2O$ when the oligomeric precursor complex, $[Ru(4,4'\text{-dimethyl-}2,2'\text{-bipyridine})Cl_3]_x$ was utilized as the Ru source.[31] Consequently, other avenues were explored for the synthesis of $[Ru(L)(bpyPS_n)_2]^{2+}$ complexes.

Reactions employing polymeric rather than small molecule ligands in $[Ru(L)(X)_n]$ intermediates (eq 1) were more successful. For example, reaction of $Ru(DMSO)_4Cl_2$ with $bpyPS_2$ in $CHCl_3$ resulted in the chelation of 1 equiv of macroligand to Ru as determined by GPC. On the basis of comparison of spectral data for related nonpolymeric analogues, this yellow complex is assumed to be $[Ru(bpyPS_2)(DMSO)_2Cl_2]$, **3**. (For **3**, UV/vis ($CHCl_3$): $\lambda_{max} = 402$ nm. Compare to [(4,4′-dimethyl-2,2′-bipyridine)$Ru(DMSO)_2Cl_2$]: $\lambda_{max} = 400$ nm.) Subsequent addition of a second ligand, L′ = bpy, to the $[Ru(bpyPS_2)(DMSO)_2Cl_2]$ intermediate, **3**, heating for 2 days, and then dehalogenating with $AgPF_6$ resulted in the formation of the targeted heteroleptic product, $[Ru(bpyPS_2)(bpy)_2]^{2+}$, **4** (UV/vis ($CHCl_3$) λ_{max} (MLCT) = 457 nm). To drive the desired reactions to completion in this sequence (eq 1), excess $Ru(DMSO)_4Cl_2$ was employed in the first step whereas excess bpy was utilized in the second step. Excess Ru reagent was carried through the synthesis, because it and other nonpolymeric reagents are readily separated from the targeted polymeric products by trituration with refluxing EtOH and filtration through alumina. This represents an alternative route[6] to polymeric complexes of type A and B shown in Figure 1. Attempts to prepare the hydroxyl derivative, $[Ru(bpyPS_2)\{(bpy(CH_2OH)_2\}_2]^{2+}$ (or the nonpolymeric analogue, $[Ru(bpy)\{(bpy(CH_2OH)_2\}_2]^{2+}$) by this method were unsuccessful. Broad GPC traces indicative of oligomeric byproducts were observed after the dehalogenation step.

Polymeric complexes with two macroligands include Ru-centered linear polymers with two bpyPS ligands (Figure 1, **C**) as well as four-arm stars generated from two $bpyPS_2$ ligands (Figure 1, **E**). The remaining binding site allows for the introduction of a variety of ancillary ligands. A number of different avenues were explored for the generation of heteroleptic systems by the route involving the chelation of 2 equiv of ligand, L′ followed by 1 equiv of L (eq 2). Previously, complexes of the form $[Ru(\alpha\text{-diimine})_2Cl_2]$ have been generated by a variety of methods.[32,33] Those deemed most promising

Table 2. GPC Molecular Weight[a] and UV/Vis Absorbance[b] Data for Polymer Samples Monitored as a Function of Time for the Preparation of $[Ru(bpyPS_2)_2Cl_2]$ from $bpyPS_2$, 2a (M_n = 4800), in Refluxing DME

time (d)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	PDI	λ_{max} (nm)	*A*
2	7.7	8.2	1.07	567	0.123
3	7.7	8.0	1.05	569	0.135
5	8.5	9.2	1.09	572	0.145
6	7.8	8.1	1.05	570	0.190
7	7.7	7.9	1.04	571	0.189

[a] Determined by GPC at 25 °C with RI and MALLS detection. Calculated M_n = 9800. [b] Determined for 30 μM $CHCl_3$ solutions.

for testing were ones utilizing $Ru(DMSO)_4Cl_2$ as the starting material,[34,35] because reactions are typically run in nonprotic solvents such as chloroform, which is also capable of dissolving $bpyPS_n$ macroligands. Attempts to prepare $[Ru(bpyPS_2)_2Cl_2]$ intermediates by reaction of $Ru(DMSO)_4Cl_2$ with 2 equiv of $bpyPS_2$ in $CHCl_3$ solution revealed that rates of reactions with macroligands are considerably slower than those with analogous nonpolymeric ones. For example, a mono $bpyPS_2$ intermediate, presumably $[Ru(bpyPS_2)Cl_2(S)_n]$, formed over the course of 5 days. Only after refluxing for 1 week did trace amounts of the targeted $[Ru(bpyPS_2)_2Cl_2]$ species become evident, as determined by the presence of an absorption band at λ_{max} = 560 nm in the UV/vis spectrum. This constitutes a striking difference between polymeric and nonpolymeric metal complex synthesis; nonpolymeric Ru bis(bpy) complexes are routinely prepared by this method with much shorter reaction times (~3−6 h).

Because higher reaction temperatures may be obtained with DME (bp = 85 °C), this solvent was used in combination with chloroform in an attempt to increase the rates of ligand substitution. Though DME is not a good solvent for polystyrene,[36] it is capable of solubilizing $bpyPS_n$ macroligands, and it is compatible with the Ru reagents. Improved chelation efficiencies were observed in DME, yet reaction times were still considerably longer than what is typical for nonpolymeric ligands. For example, when the low molecular weight $bpyPS_2$ macroligand **2a** was employed, reaction times of 6 days were required to drive the formation of $[Ru(bpyPS_2)_2Cl_2]$ to completion. Molecular weight and UV/vis absorbance data for $[Ru(bpyPS_2)_2Cl_2]$ formation as a function of time are provided in Table 2. For higher molecular weight $bpyPS_n$ ligands, rates of substitution only decrease. Reaction rates are typically faster for bpyPS macroligands with more accessible chain end donors as compared to $bpyPS_2$ ones with bidentate chelates at the center of the polystyrene chain. Reactions with bpyPS, **1a**, turned red after ~30 min, signaling the formation of a $[Ru(bpyPS)(solvent)_2Cl_2]$ intermediate, and became purple in color over the course of 1−2 days. Similar color changes were observed for reactions with $bpyPS_2$ ligands; however, they occurred at a slower rate than those run with bpyPS ligands of comparable molecular weight (red, ~3−4 h; purple, ~2 days). As was seen for $[Ru(bpyPS_n)_3]^{2+}$ synthesis,[6] there also exists an upper molecular weight threshold for $[Ru(bpyPS_n)_2Cl_2]$ targets, above which chelation is no longer efficient. For preparations of $[Ru(bpyPS_n)_2Cl_2]$ employing bpyPS **1d**, $bpyPS_2$ **2g**, or those of higher molecular weight, it was not possible to obtain the desired Ru bis(bpy) intermediates. Reactions did not become purple but instead retained a red-violet color, indicative of

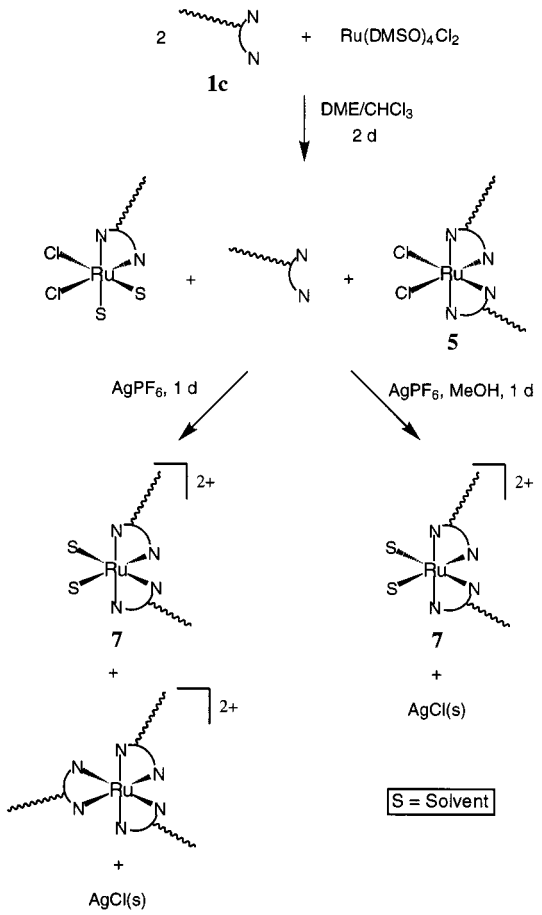

Figure 3. Schematic representation of solvent effects on product outcome in the synthesis of the dehalogenated intermediate, $[Ru(bpyPS)_2(S)_n]^{2+}$, **7** (*S* = solvent = DME or MeOH) prepared from bpyPS **1c** (M_n = 22 400). (Note: For lower molecular weight macroligands, the Ru tris(bipyridine) impurity forms even when MeOH is present.)

significant quantities of $[Ru(bpyPS_n)(S)_mCl_2]$ intermediates.

Because efficient $[Ru(bpyPS_n)_2Cl_2]$ formation requires long reaction times even for the smallest macroligands **1a** and **2a**, with times only increasing for higher molecular weight $bpyPS_n$ ligands, alternative procedures for generating $[Ru(bpyPS_n)_2(S)_m]$ intermediates were explored. Although reactions to form $[Ru(bpyPS_n)_2Cl_2]$ did not proceed to completion after 2 days, considerable amounts of Ru bis(bpy) dichloride products, **5** and **6**, had formed after this time. For example, GPC analysis after 2 days of a reaction run with **2f** reveals, for the major peak, a molecular weight close to the targeted value (M_n = 43 800); however, a low molecular weight shoulder is also evident. Addition of $AgPF_6$ to the reaction mixture at this stage not only dehalogenates the targeted Ru bis(bpy) product to form a labile $[Ru(bpyPS_n)(S)_m]^{2+}$ solvento intermediate, but any Ru intermediates with a single macroligand bound may be dehalogenated and activated for reaction with free macroligand that remains as well (Figure 3). Moreover, a marked dependence of reaction outcome on macroligand molecular weight was noted. These studies also allowed for the fortuitous discovery that, within a certain molecular weight range, reactivity at the Ru center can be controlled by solvent polarity.

The solvent dependence in dehalogenation reactions of Ru intermediates prepared from **1c**, a bpyPS macro-

ligand of moderate molecular weight, is illustrated in Figure 3. Addition of $AgPF_6$ to a DME/$CHCl_3$ reaction mixture (presumed to consist of $[Ru(bpyPS)_2Cl_2]$, $[Ru(bpyPS)(S)_nCl_2]$, and bpyPS) followed by heating at reflux for 18 h, and subsequent addition of MeOH to break up the AgCl emulsion that formed, yielded an orange product rather than anticipated red solvento one, $[Ru(bpyPS)_2(S)_2]^{2+}$. GPC and UV/vis analysis of this reaction mixture revealed that a Ru tris bipyridine complex had formed as the major product (GPC M_n = 56 800, M_w = 66 200, PDI = 1.17; UV/vis λ_{max} = 460 nm) and that a trace amount of unreacted macroligand remained. This suggests that the mono and bis Ru intermediates react with comparable facility in DME/$CHCl_3$. The tris complex may predominate due to its greater stability as compared with bis(solvento) intermediates.

In contrast, when $AgPF_6$ and MeOH were added together for dehalogenation of the intermediate formed from **1c**, thus increasing the polarity of the reaction medium, only the desired $[Ru(bpyPS)_2(S)_n]^{2+}$ species, **7** was formed (M_n = 40 000, M_w = 45 500, PDI = 1.14). Neither Ru tris(bpy) nor unreacted macroligand was observed in the GPC and UV/vis traces in this case. Under these more polar reaction conditions, unreacted macroligand preferentially chelated to the less sterically hindered Ru center bearing a single macroligand. Even intentional addition of an extra equivalent of bpyPS to this solvento intermediate and refluxing for several days did not produce orange solutions of $[Ru(bpyPS)_3]^{2+}$ (Figure 4). Thus, the addition of methanol along with $AgPF_6$ seemed to inhibit macroligand chelation to the bis(bpy) solvento intermediate prepared from **1c**.

Interestingly, quite different results were obtained in reactions of $bpyPS_2$, **2e**, a macroligand of similar molecular weight, as solvent polarity was varied. For example, treatment of the purple DME reaction mixture (containing $Ru(bpyPS_2)_2Cl_2$, and unreacted macroligand, **2e**) with excess $AgPF_6$, followed by heating at 90 °C for 18 h, and subsequent addition of MeOH, yielded a red, not orange, solution. GPC analysis of the red solvento intermediate, $[Ru(bpyPS_2)_2(S)_n]^{2+}$, **8**, revealed a single polymer fraction of narrow PDI with a molecular weight close to the anticipated value (M_n = 45 200, M_w = 51 500, PDI = 1.15). The absence of a UV/vis band at ~560 nm corresponding to $[Ru(bpyPS_2)_2Cl_2]$ confirmed that dehalogenation with $AgPF_6$ was efficient. Moreover, even though dehalogenation was effected in a nonpolar medium, there was no evidence of a Ru tris(bpy) impurity. Comparable molecular weight data were obtained when $AgPF_6$ and MeOH were added together: M_n = 43 900, M_w = 50 900, PDI = 1.16. In summary, while product outcome was influenced by solvent polarity for reactions forming linear polymeric intermediates **7** from bpyPS (M_n = 22 400), no similar dependence was observed for reactions generating Ru-centered four-arm star intermediates **8** from bpy-centered polystyrene (M_n = 24 200) in an identical reaction medium. The increased steric demand of two difunctional $bpyPS_2$ macroligands as compared with two mono-arm bpyPS chelates in the coordination sphere of the corresponding $[Ru(bpyPS_n)_2(S)_m]^{2+}$ solvento intermediates may account for the differences that are observed. That is, with the bulkier $bpyPS_2$ ligands, the Ru center in $[Ru(bpyPS_2)_2(S)_n]^{2+}$ intermediates may be sufficiently blocked to macroligand chelation even in less polar reaction media where the chains are better solvated and more extended.

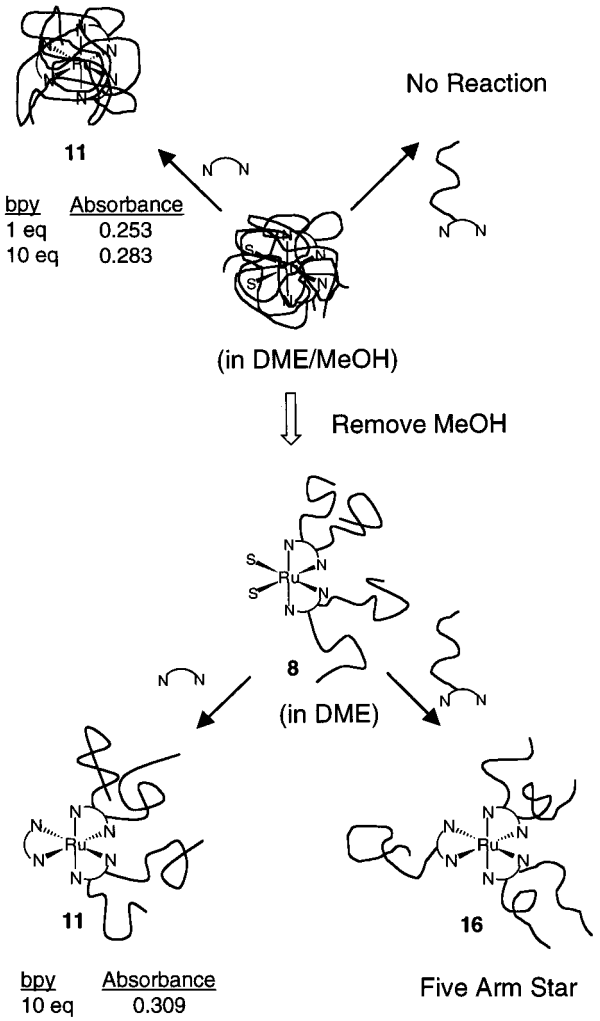

Figure 4. Schematic representation of the effect of solvent polarity and reagent loading on the reactions of $[Ru(bpyPS_2)_2(S)_n]^{2+}$, **8** (prepared from **2d**; S = solvent = DME or MeOH) with the nonpolymeric ligand, 2,2′-bipyridine and the polymeric ligand, bpyPS **1a**. (For $[Ru(bpyPS_2)_2(bpy)]^{2+}$ products, absorbances at λ_{max} = ~460 nm for 30 μM solutions are provided for comparison.)

Solvent polarity also plays little role in preparations of $[Ru(bpyPS_n)_2(S)_2]^{2+}$ from low molecular weight $bpyPS_n$ macroligands. Tris impurities were observed regardless of DME/MeOH composition in reactions with bpyPS, **1a**, and $bpyPS_2$, **2c**, and those of lower molecular weight. In an attempt to quantify whether amounts of Ru tris(bpy) impurity observed in preparations of $[Ru(bpyPS_2)_2(S)_n]^{2+}$ vary with percent MeOH in the reaction medium, a $[Ru(bpyPS_2)_2Cl_2]$ precursor mixture made from **2c**, M_n = 12 500 was split into three portions for dehalogenation in the presence of DME/MeOH loadings of 10/4, 9/5, and 8/6 mL. (Solubility studies revealed that DME/MeOH ratios of 7/7 mL did not fully dissolve the $bpyPS_2$ macroligand even at elevated reaction temperatures.) Interestingly, no significant differences were observed in the amounts of Ru tris(bpy) impurities as determined by UV/vis spectroscopy.

In addition to driving certain $[Ru(bpyPS_n)_2(S)_2]^{2+}$ syntheses to completion, dehalogenation of $[Ru(bpyPS_n)_2Cl_2]$ intermediates with $AgPF_6$ was also necessary for chelating a third α-diimine ligand at polymeric Ru complex centers. Even refluxing $[Ru(bpyPS_n)_2Cl_2]$ intermediates, **5** (n = 1) and **6** (n = 2), with bpy analogues

Table 3. Molecular Weight[a] and UV/Vis[b] Data for $[Ru(bpyPS)_2L]^{2+}$ Polymeric Complexes[c] in $CHCl_3$

	macroligand			ruthenium polymeric complex					
entry no.	bpyPS	$M_n \times 10^{-3}$	ancillary ligand, L	calcd M_n[d] $\times 10^{-3}$	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	PDI	λ_{max} (nm)	*A*
1	**1b**	18.3	bpy	37.2	40.1	45.8	1.14	460	0.284
2	**1c**	22.4	$bpy(CH_2OH)_2$	45.5	41.4	49.4	1.19	459	0.194
3[e]	**1c**		$bpy(CH_2OH)_2$	45.5	42.0	50.6	1.20	462	0.229
4[e,f]	**1c**		$bpy(CH_2OH)_2$	45.5	41.8	50.2	1.20	460	0.350
5	**1d**	34.1	$bpy(CH_2OH)_2$	68.7	51.5	57.7	1.12	460	0.222

[a] Determined by GPC in $CHCl_3$ at 25 °C with RI and MALLS detection. [b] *A* = absorbance, λ_{max} (nm) determined for 30 μM solutions. Calculated M_n values were used to determine concentration. [c] $Ru(DMSO)_4Cl_2$:L = 1:1; $AgPF_6$ and MeOH were added together for dehalogenation unless otherwise indicated. [d] Determined using bpyPS M_n values obtained by GPC with RI and MALLS detection. [e] $Ru(DMSO)_4Cl_2$:L = 1:10. [f] After addition of L to $[Ru(bpyPS)_2(S)_n]^{2+}$, MeOH was removed in vacuo prior to heating for 2 d.

Table 4. Molecular Weight[a] and UV/Vis[b] Data for $[Ru(bpyPS_2)_2L]^{2+}$ Polymeric Ruthenium Complexes[c] in $CHCl_3$

	macroligand			ruthenium polymeric complex					
entry	$bpyPS_2$	M_n[a] $\times 10^{-3}$	ancillary ligand, L	calcd $M_n \times 10^{-3}$	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	PDI	λ_{max} (nm)	*A*
1	**2d**	16.3	bpy	33.2	32.4	34.6	1.07	464	0.253
2[d]	**2d**		bpy		32.2	34.2	1.06	462	0.283
3[d,e]	**2d**		bpy		32.3	34.5	1.07	460	0.309
4[f]	**2f**	24.2	bpy	49.1	46.6	52.9	1.14	458	0.332
5[f]	**2f**		phen		50.6	56.7	1.12	460	0.219
6[f]	**2f**		$bpy(CH_2OH)_2$		47.2	52.2	1.11	464	0.185
7	**2f**		$bpy(C_{23}H_{47})_2$	49.7	43.9	48.5	1.11	466	0.251

[a] Determined by GPC in $CHCl_3$ at 25 °C with RI and MALLS detection. [b] *A* = absorbance, λ_{max} (nm) determined for 30 μM solutions. Calculated M_n values (column 5) were used to determine concentration. Note: Concentrations determined using calculated M_n overestimate *A* if M_n, M_w < calculated M_n and underestimate *A* if M_n, M_w > calculated M_n. [c] $Ru(DMSO)_4Cl_2$:L = 1:1, and $AgPF_6$ and MeOH were added together unless otherwise indicated. [d] $Ru(DMSO)_4Cl_2$:L = 1:10. [e] After addition of L to the dehalogenated intermediate, MeOH was removed in vacuo prior to heating for 2 days. [f] MeOH added ~18 h after $AgPF_6$ addition.

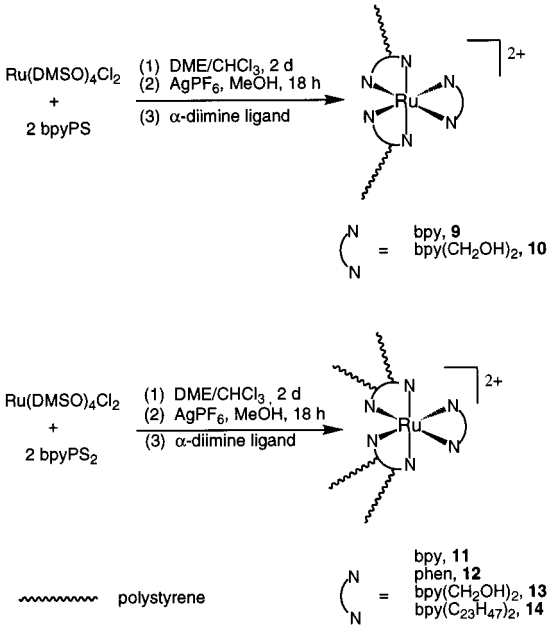

Figure 5. Synthesis of Ru polymeric complexes containing two $bpyPS_n$ macroligands, $[Ru(bpyPS)_2(L)]^{2+}$ (L = bpy, **9**; $bpy(CH_2OH)_2$,**10**), and $[Ru(bpyPS_2)_2(L)]^{2+}$ (L = bpy, **11**; phen, **12**; $bpy(CH_2OH)_2$, **13**; $bpy(C_{23}H_{47})_2$, **14**).

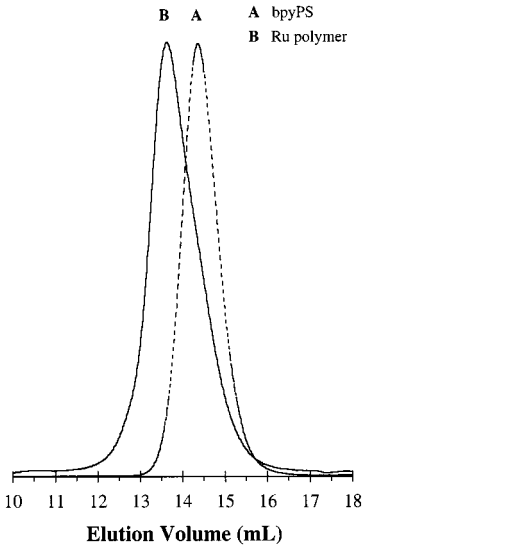

Figure 6. Overlay of the GPC traces ($CHCl_3$): (A) the bpyPS macroligand **1c** (M_n = 22 400, M_w = 25 400, PDI = 1.13); (B) $[Ru(bpyPS)_2\{bpy(CH_2OH)_2\}]^{2+}$, **10** ($M_n$ = 41 400, M_w = 49 400, PDI = 1.19).

in DME solution for extended periods of time (~1 week) did not yield significant quantities of the targeted $[Ru(bpyPS_n)_2(bpy)]$ products. Instead, different types of Ru tris(bipyridine) products were formed by adding non-polymeric ancillary ligands, bpy, phen, $bpy(CH_2OH)_2$,[25] and $bpy(C_{23}H_{47})_2$,[26] to $[Ru(bpyPS)_2(S)_m]$ and $[Ru(bpyPS_2)_2(S)_m]$ intermediates (Figure 5). Molecular weight and UV/vis absorbance data for $[Ru(bpyPS)_2(L')]^{2+}$ polymeric complexes are provided in Table 3 and those for $[Ru(bpyPS_2)_2(L')]^{2+}$ complexes are given in Table 4. A GPC overlay of **10** and the bpyPS macroligand **1c**, from which it was prepared is provided in Figure 6, thus confirming the efficiency of bpy end functionalization of polystyrene (i.e., of initiation during macroligand synthesis) and $[Ru(bpyPS)_2\{bpy(CH_2OH)_2\}]^{2+}$ formation. GPC with in-line UV/vis analysis (Figure 7) confirmed formation of the bis complex, its dehalogenation, and the presence of the associated Ru tris bipyridine chromophore in $[Ru(bpyPS_2)_2(bpy)]^{2+}$, **11**. The presence of hydroxy groups in **13** was evidenced by IR spectroscopy. These alcohol substituents provide opportunities for further derivatization. The presence of the alkyl chains in the hetero-arm block copolymer, $[Ru\{bpy(C_{23}H_{47})_2\}(bpyPS_2)_2]^{2+}$, **14**, with oligoethylene and polystyrene segments, was indicated by ^1H NMR spectroscopy.

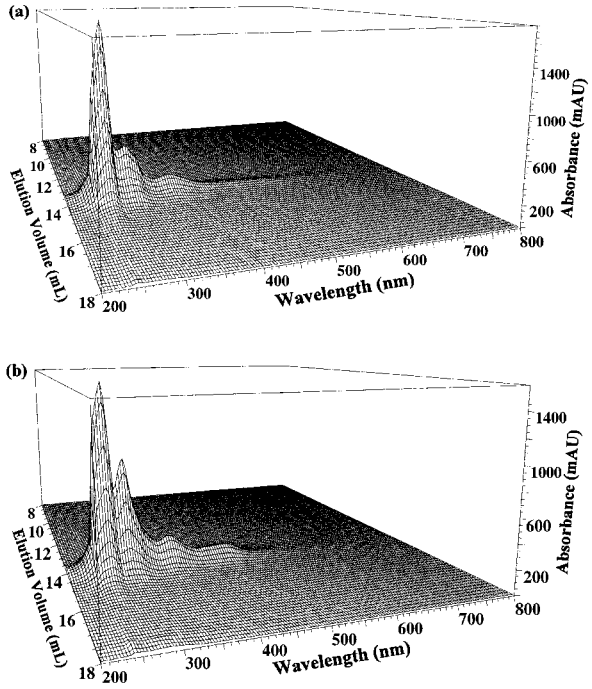

Figure 7. 3D correlation of the GPC elution volume and in-line diode array UV/vis spectra in $CHCl_3$: (a) the dehalogenated intermediate $[Ru(bpyPS_2)_2(S)_n]^{2+}$, **8** ($M_n$ = 28 200, M_w = 29 900, PDI = 1.06), made from $bpyPS_2$, **2d** (M_n = 16 300, M_w = 17 200, PDI = 1.05); (b) the corresponding $[Ru(bpyPS_2)(bpy)]^{2+}$ polymeric complex **11** (M_n = 32 200, M_w = 32 400, PDI = 1.06). MLCT: λ_{max} = 462 nm.

To optimize the efficiency of chelation of the third α-diimine ligands to the $[Ru(bpyPS_n)_2(S)_m]^{2+}$ intermediates, different reaction conditions were explored. In a previous study,[6] polymer molecular weight played a role in chelation efficiency; absorbances at 460 nm (MLCT) were generally lower for complexes made from higher molecular weight $bpyPS_n$ ligands.[6] To determine whether a similar phenomenon exists in these heteroleptic polymeric metal complex syntheses, initially 1 equiv of the selected third, nonpolymeric ligand was added to the DME/MeOH mixtures of the dehalogenated intermediate (e.g., preparation of $[Ru(bpyPS_2)_2(bpy)]^{2+}$ using 1:1 $[Ru(bpyPS_2)_2(S)_n]^{2+}$:bpy). Comparison of absorbances listed in Tables 3 and 4 indicate that there is no obvious correlation between chelation efficiency and polymer molecular weight for targets with the same inner coordination spheres within the molecular weight range investigated. (Compare Table 3, entries 2 and 5; Table 4 entries 1 and 4.) Because nonpolymeric α-diimine ligands may be readily removed from polymer products by precipitation or, in some cases, by washing with dilute aqueous acid, certain reactions were also run at higher ligand loading. Comparison of absorbances measured for equimolar solutions of $[Ru(bpyPS)_2(bpy)]^{2+}$ (Table 3, entries 2 and 3) and $[Ru(bpyPS_2)_2(bpy)]^{2+}$ (Table 4, entries 1 and 2) prepared under these different conditions reveals that efficiencies are improved when larger amounts of bpy are employed (Figure 4). Finally, the solvents in which third ligand coordination is performed could also play a role. Different solvent conditions correlate with different solvento intermediates, and perhaps even more importantly, they affect polymer conformation. Slight increases in absorbances were observed when chelation was performed in DME (Table 3 entry 4; Table 4 entry 3) as compared with reactions run in DME/MeOH. In summary, optimal

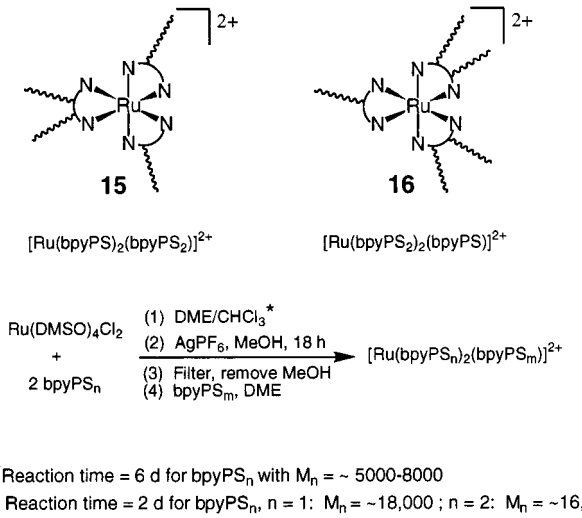

Figure 8. Synthesis of homo-block copolymer Ru complexes with three macroligands, $[Ru(bpyPS)_2(bpyPS_2)]^{2+}$, **15**, and $[Ru(bpyPS_2)_2(bpyPS)]^{2+}$, **16**.

conditions for the formation of heteroleptic metal complexes of the form $[Ru(bpyPS_n)_2L]^{2+}$ (L = nonpolymeric ligand) involve the use of excess ligand, L, and performing the final ligand chelation reaction in DME in which the polymer is better solvated, and thus, the metal center is more accessible for reaction (Figure 4).

Though differences in solvent polarity interfere to only a small extent with substitution by nonpolymeric bpy derivatives (Table 3, entries 3 and 4), if the third ligand, L, is a high molecular weight macroligand, this effect is far more pronounced. Changes in polymer conformation that polar solvents bring about serve to protect the metal center in the precursor complex from macroligand coordination (Figure 4). Likewise, the macroligand undergoing substitution is expected to be more compact and aggregation could occur. In these cases, it was necessary to remove the MeOH for the targeted heteroleptic product with three macroligands to be formed. Preparations of star-shaped polymers of the form $[Ru(bpyPS)_2(bpyPS_2)]^{2+}$, **15**, and $[Ru(bpyPS_2)_2(bpyPS)]^{2+}$, **16**, require chelation of two macroligands of one type, followed by attachment of another (Figure 8). The successful synthesis of **15** and **16** adds a new type of four-arm star (compare **E** and **F** in Figure 1), as well as a five-arm star-shaped analogue (Figure 1, **G**) to the Ru-centered polymer series. Because it is not possible to access the four-arm polymeric complex intermediate, $[Ru(bpyPS_2)_2(S)_n]^{2+}$ efficiently using high molecular weight $bpyPS_2$, macroligands of intermediate molecular weights, namely $bpyPS_2$, **2d** (M_n = 16 300) and **2f** (M_n = 24 200), and low molecular weight **2a** (M_n = 4800) were chosen for investigation. For **2d** and **2f**, $AgPF_6$ and MeOH were added together to remove the chloro ligands from the inner sphere of $[Ru(bpyPS_2)_2Cl_2]^{2+}$, both to drive the reaction forming Ru bis(bpy) polymeric complexes to completion, and to inhibit tris(bpy) formation at this intermediate stage. For low molecular weight five-arm star products (Figure 1, **G**) made from **2a**, and four-arm stars (Figure 1, **F**) made from **1a**, long reaction times (~6 days) were employed for the formation of $[Ru(bpyPS_n)_2Cl_2]$ intermediates prior to dehalogenation. (Recall that this is necessary because $[Ru(bpyPS_n)_3]^{2+}$ impurities form regardless of solvent polarity if the dehalogenation is performed after 2 days for these low molecular weight macroligands.) After the formation of

Table 5. Molecular Weight[a] and UV/Vis Absorbance[b] Data for Polymeric Complexes with Two Types of bpyPS$_n$ Macroligands, [Ru(bpyPS)$_2$(bpyPS$_2$)]$^{2+}$, 15, and [Ru(bpyPS$_2$)$_2$(bpyPS)]$^{2+}$, 16

entry	bpyPS$_n$[c]	bpyPS$_m$[c]	calcd $M_n \times 10^{-3}$	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	PDI	λ_{max} (nm)	A
1	**1a**	**2b**	22.0	16.9	18.9	1.12	462	0.299
2	**2a**	**1a**	16.8	13.0	14.7	1.13	463	0.497
3	**2d**	**1a**	39.9	34.2	38.1	1.11	466	0.323
4	**2f**	**1c**	55.5	39.7	47.4	1.19	460	0.533

[a] Determined by GPC in $CHCl_3$ at 25 °C with RI and MALLS detection. [b] A = absorbance, λ_{max} (nm) determined for 30 μM solutions. Calculated M_n values (column 4) were used to determine concentration. Note: Concentrations determined using calculated M_n overestimate A if M_n, M_w < calculated M_n and underestimate A if M_n, M_w > calculated M_n. [c] bpyPS$_n$ = macroligand added first (1:2 Ru:bpyPS$_n$). bpyPS$_m$ = macroligand added second (1:1 Ru:bpyPS$_m$).

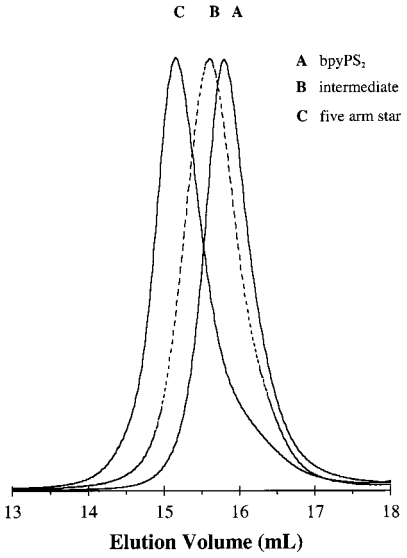

Figure 9. Overlay of the GPC traces ($CHCl_3$): (A) the bpyPS$_2$ macroligand, **2a** (M_n = 4800, M_w = 5100, PDI = 1.06); (B) the dehalogenated intermediate, [Ru(bpyPS$_2$)$_2$(solvent)$_n$]$^{2+}$, **8** (M_n = 7700, M_w = 8300, PDI = 1.09); (C) the five-arm star [Ru(bpyPS$_2$)$_2$(bpyPS)]$^{2+}$, **16** (M_n = 13 000, M_w = 14 700, PDI = 1.13), formed with **1a**.

the [Ru(bpyPS$_n$)$_2$(S)$_m$]$^{2+}$ intermediates was confirmed by GPC and the second type of macroligand (bpyPS for five-arm stars, bpyPS$_2$ for four-arm stars) was added, the MeOH was removed in vacuo to facilitate chelation, thus forming the desired tris(bpy) products. As these reaction sequences illustrate, changes in solvent polarity may be used to advantage, to shut down or to promote tris(bpy) formation as the various steps in polymeric complex synthesis demand.

Selected molecular weight and absorbance data for selected star-shaped polymeric complexes **15** and **16**, bearing three macroligands, are provided in Table 5. Figure 9 illustrates that this reaction sequence is quite efficient when macroligands of the appropriate sizes are selected (e.g., **2a** and **1a**). It was also possible to prepare five-arm stars with higher molecular weight macroligands (**2d** and **1c**). However, a more prominent low molecular weight shoulder corresponding to unreacted macroligand or dehalogenated intermediate indicated diminished efficiency. As was demonstrated for nonpolymeric ligands, it may be possible to drive these reactions to completion by the addition of excess macroligand. Although product purification could be more complicated in this case, since excess ligand is also polymeric. Attempts to form star complexes with macroligands of higher combined weights (**2f** and **1c**) were unsuccessful; neither the molecular weight nor the spectral properties of these polymers correlated with what was expected for the targeted five-arm star (calculated M_n: 71 400. GPC: M_n = 40 500, λ_{max} = 404 nm).

Conclusion

This account described the roles that macroligand molecular weight, the position of the bpy donor in the polystyrene chain, and solvent polarity play in polymeric metal complex synthesis. In summary, the macroligand chelation route is useful for preparing Ru polystyrene complexes in the low to moderate molecular weight ranges (< ~50 000). This nicely complements a metalloinitiator approach, for which lower molecular weights are sometimes difficult to achieve with control, and those > 50 000 are generally easily attainable. With the chelation approach, upper molecular weight thresholds are dependent upon a variety of different reaction parameters. Polymer conformation and steric crowding around the metal center play a significant role. If there is sufficient steric bulk surrounding the Ru center in [Ru(bpyPS$_n$)(S)$_m$]$^{2+}$, the metal is protected from further reaction with additional bpyPS$_n$ macroligand. The reaction efficiency with small molecule ligands such as bpy is also slightly diminished. Ruthenium solvento intermediates prepared from higher molecular weight macroligands offer greater protection to the metal center than do those generated from lower molecular weight ones. And bpyPS$_2$ macroligands crowd the metal center more than do end-functionalized bpyPS.

For polymeric metal complexes of sufficiently high molecular weight, solvent polarity offers another way of modulating reactivity at the metal core. The polystyrene chains are more collapsed around the metal center in polymeric complexes and in free macroligands in poor solvents (i.e when MeOH is present); whereas, in better ones, the chains adopt more extended conformations. Specifically, DME is a better solvent for polystyrene than is the more polar DME/MeOH mixture. Aggregation of polymers in poorer solvents could also restrict access of bpy donor groups to metal centers. To our knowledge, the use of solvent polarity to alter ligand conformation and thus, to control reactivity at metal centers in this manner has no direct parallel in small molecule metal complex synthesis. This new "protecting group" strategy offers a way of turning reactions on and off. Moreover, controlling access to functionalities attached to nonpolymeric ancillary ligands at the metal core in this way is also a compelling one for selective attachment and recognition applications. Extension of these synthetic methodologies to more elaborate targets and tailoring polymeric metal complex materials for specific applications will serve as topics of future reports.

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