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Architectural Diversity via Metal Template-Assisted Polymer Synthesis: A Macroligand Chelation Approach to Linear and Star-Shaped Polymeric Ruthenium Tris(bipyridine) Complexes

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ABSTRACT: Polymeric metal complexes are constructed by combining living polymerization techniques with coordination chemistry. These metal-centered linear and star-shaped materials combine the film-forming properties of polymers with optical and other features of metal complexes. A metal template approach described herein offers a versatile alternative to the metalloinitiator method previously employed to generate Ru tris(bipyridine)-centered polystyrenes. Specifically, 4,4′-bis(chloromethyl)-2,2′-bipyridine and 4-chloromethyl-2,2′-bipyridine were utilized as initiators for both the bulk and solution polymerization of styrene using atom transfer radical polymerization (ATRP). Narrow dispersity polystyrenes with bipyridine (bpy) binding sites at the end (bpyPS) or center ($bpyPS_2$) of the chains result. These $bpyPS_n$ macroligands were chelated to Ru precursor complexes, RuL_2Cl_2 (L = bpy, phen) or $Ru(DMSO)_4Cl_2$, to form complexes with one or three $bpyPS_n$ macroligands, respectively. Linear polymers, $[RuL_2(bpyPS_n)]^{2+}$, with Ru chromophores at the end or center of the chains, as well as Ru-centered star-shaped polymers, $[Ru(bpyPS_n)_3]^{2+}$, with three and six arms were produced. In all cases, dehalogenation with $AgPF_6$ was crucial for efficient macroligand chelation. The relative efficiency of these reactions was estimated by UV/vis spectroscopy. Molecular weight determination by GPC was coupled with in-line diode array UV/vis spectroscopy to confirm the presence of the Ru chromophores in the eluting polymer fractions. The convergent macroligand chelation approach to star-shaped polymeric metal complexes typically works best for polymers of low to moderate molecular weights (<∼65K), with higher molecular weights possible for systems with a single macroligand coordinated. Specific molecular weight thresholds encountered are determined by the number of macroligands, the position of the bpy on the polystyrene chain, and the total number of arms emanating from the metal core.

Introduction

Achieving unique and complex architectures via more convenient routes and introducing functionality with control are ongoing goals in macromolecular synthesis. Many applications benefit from the presence of metals in materials since they have a wide variety of reactivities, as well as optical, magnetic, and electrochemical properties.[1] For example, metal-containing macromolecules have been exploited as supported catalysts,[2] sensors,[3] luminescent films, and devices.[4] Polymer properties are determined by molecular weight and architecture, and the characteristics of metal complexes are influenced by their ligand sets. Recently, we and others[5−14] have been exploring the synthesis of metal complexes with macroligands, which couple the features of metal complexes and polymers. In their simplest form, these systems possess one metal per macromolecule, and considerable control over the metal binding site and the polymer local environment can be achieved. Because coordinate bonds range from labile to inert, and a wide variety of metal geometries are possible, metal ions serve as highly tunable structural motifs for the assembly of materials. Moreover, the metal-centered star-shaped polymer design offers some fascinating possibilities for responsive materials that operate by reversible or irreversible mechanisms. More fragile, labile metal-centered materials, such as those based on Fe, Zn, or Co tris(bipyridine), are difficult to characterize.[7] However, their greater sensitivity to reagents, heat, shear, and other types of stimuli could be desirable for certain applications. Moreover, the use of polymeric metal complexes in catalysis will likely require labile metals capable of ligand dissociation and substitution. Inert metals, on the other hand, provide structural integrity and durability. In Ru α-diimine systems, for example, this not only creates more options for the controlled synthesis of heteroleptic complexes with polymeric ligands, which is important for optical and electrochemical tuning, it also makes them amenable to standard chromatographic analysis.

Most of our efforts have been devoted to developing the metalloinitiator approach to metal complexes with macroligands (Figure 1). New syntheses of functionalized ligand[15,16] and metal complexes[17] as well as testing their viability as initiators for living polymerizations were required. We have synthesized a wide range of metal bipyridine-centered materials using metal complexes with initiator functionalities in their ligand periphery.[5−10] The metalloinitiator approach is not a new strategy for introducing metals into materials.[1] What is significant is the degree of molecular weight and architectural control that has been attained by extending this concept from conventional to controlled and living polymerizations. Narrow polydispersity linear and star polymers with different numbers of arms as well as metal-centered star block copolymers[9] are readily prepared using cationic[7−11] and radical mechanisms.[5,6] Purification is straightforward; polymer products are easily separated from unreacted monomer by precipitation. Moreover, since the chains propagate outward from a central core, relatively high molecular weights can generally be achieved. A limitation of this

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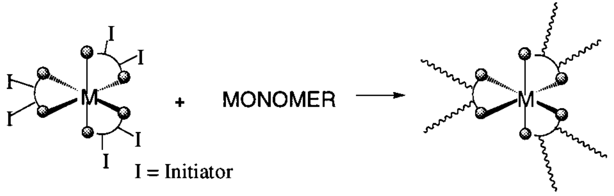
Divergent Synthesis: Metalloinitiators



Convergent Synthesis: Macroligand Chelation

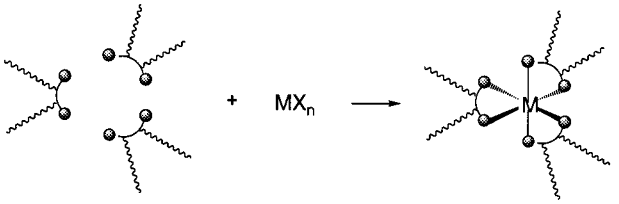


Figure 1. Synthetic approaches to metal complexes with macroligands.

reaction design is that it requires compatible organic and inorganic methodologies. Methods must be established both for preparing oftentimes sensitive functionalized ligands[15,16] and also for their attachment to metal ions.[7,17] Furthermore, once they are synthesized, complexes must be compatible with the polymerization conditions. The presence of the metal complex in the reaction mixture must not adversely affect the polymer chemistry, and likewise, the metal complex must not decompose under the conditions of the polymerization reaction. Thus far, inert Ru tris(bipyridine) have been widely compatible,[5,6,10] and labile metal ions such as Fe have been useful protecting groups for nucleophilic ligands during cationic polymerization.[7−9] Certain labile metal systems, however, do not survive the polymerization reactions.[7]

An alternative approach to achieving similar targets involves chelating preformed polymers with tailored binding sites to metal ions (Figure 1). This convergent approach is conceptually related to self-assembly strategies that have been widely exploited in inorganic supramolecular chemistry[18] and in metal-containing dendrimer synthesis.[19] Macroligand chelation is also the limiting case of metal ions serving as cross-linking agents in materials.[20] Here there is only a single point of convergence, rather than many as in most other cross-linked materials and ionomers.[21] Despite this prevalence of conceptually related multimetallic examples, the potential of metals to serve as functional templates for assembling low polydispersity linear polymers into different architectures has not been fully exploited. Furthermore, careful implementation of known inorganic methodologies in this fashion should allow more facile synthesis of block copolymer targets which have been difficult or impossible to make by standard organic methods. These macroligand chelation studies also address fundamental questions concerning the limitations of attachment of polymer chains at a point, rather than to a plane, as is exemplified by the anchoring of polymers to surfaces.[22] Energetic benefits of metal ion chelation are counterbalanced by additional steric constraints between neighboring polymers surrounding the metal center, changes in polymer chain conformation, and solvation that might be necessary to accommodate metal binding.

In this account we describe our exploratory efforts to prepare metal complexes with polystyrene macroligands by a self-assembly route. Specifically, polystyrene macroligands, bpyPS, **1**, and bpyPS$_2$, **2**, were generated from 4-chloromethyl-2,2′-bipyridine, bpy(CH$_2$Cl), and 4,4′-bis(chloromethyl)-2,2′-bipyridine, bpy(CH$_2$Cl)$_2$, respectively, via atom transfer radical polymerization (ATRP).[23] Bipyridine is present at the end or middle of the chains. These macroligands were used in place of small molecule α-diimine analogues in standard or modified preparations for chelating bpy ligands to Ru(II) centers. Targets with one and three bpy macroligands, (i.e., polymeric complexes with 1, 2, 3, and 6 pendant chains) were explored, thus generating a wide range of architectures. Since convergent methodologies often have upper molecular weight limits for efficient reactions,[24] a range of different molecular weights were probed. The upper molecular weight limit may also be affected by solvation.[25] Hence, different solvent systems were screened for certain reactions.

Experimental Section

Reagents and Solvents. Dichlorobis(2,2′-bipyridine)ruthenium(II) dihydrate (99%), silver hexafluorophosphate (99.99%), and anisole (99.7%) were purchased from Aldrich and used as received. *cis*-Ru(DMSO)$_4$Cl$_2$ was synthesized as described by Wilkinson et al.[26] Dichlorobis(1,10-phenanthroline)ruthenium(II) dihydrate was prepared from $RuCl_3 \cdot xH_2O$ and 1,10-phenanthroline (phen) by a modification of a literature procedure.[17,27] Styrene (Acros, assay ≥99.5) was purified by passing through a plug of neutral alumina followed by drying over CaH$_2$ and distillation under reduced pressure. Xylenes were purified by azeotropic distillation with 2-methoxyethanol followed by washing with water to remove the alcohol, then drying over CaH$_2$, and distillation under reduced pressure.[28] All other reagents and solvents were used as received unless indicated otherwise.

Initiators. 4,4′-Bis(chloromethyl)-2,2′-bipyridine[15] and 4-chloromethyl-2,2′-bipyridine[16] were prepared as previously described.

Catalysts. CuBr was purified as previously described.[29] The ligand, 4,4′-bis(tridecyl)-2,2′-bipyridine, bpy(C$_{13}$H$_{27}$)$_2$, was prepared using procedures described for similar compounds.[30] 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA) (97%) and CuCl (98+%) were obtained from Aldrich and were used without further purification.

Polymer Characterization. The polymers were characterized by gel permeation chromatography (GPC) in CHCl$_3$ using a Hewlett-Packard 1100 system equipped with a vacuum degasser, diode array detector, Polymer Labs 5μ Mixed C columns, Wyatt Technology Corp. DAWN mutiangle laser light scattering (MALLS) (5 mW polarized He−Ne laser, $\lambda = 633$ nm), and Optilab refractive index detectors and accompanying Wyatt Technology Corp. Astra software. The d*n*/d*c* for polystyrene, 0.145 mL/g, in CHCl$_3$ at 35 °C and 633 nm, was obtained from Wyatt Technology Corp. and was used in all calculations. ^{1}H NMR spectra were recorded on a GE QE 300 spectrometer in CDCl$_3$. UV/vis spectra were recorded for 30 μM CHCl$_3$ solutions using an HP 8452A diode array spectrophotometer.

Synthesis of Macroligands, bpyPS, 1, and bpyPS$_2$, 2. Bulk Polymerization Method A. Polymerizations in bulk styrene were performed using a modification of a procedure described by Matyjaszewski et al.[31,32] In a representative preparation for bpyPS$_2$, **2h**, the initiator, bpy(CH$_2$Cl)$_2$ (51.9 mg, 0.21 mmol), CuCl (41.0 mg, 0.41 mmol), and bpy(C$_{13}$H$_{27}$)$_2$ (0.427 g, 0.82 mmol) were combined in a Kontes tube. Styrene (8.82 g, 85 mmol) was added via syringe, and the mixture was immediately degassed by three freeze−pump−thaw cycles. The evacuated tube was then immersed in an oil bath maintained at 110 °C. After stirring for 1 day, the tube was opened, and THF was added to dissolve the dark brown viscous polymer. The greenish solution was passed through a neutral alumina column (diameter 1 cm; length ~15 cm). This procedure was repeated as necessary until a pale yellow solution was achieved. The solution was concentrated in vacuo, and the resulting residue was further purified by precipitation from THF into MeOH. The white polymer was collected on filter paper and was reprecipitated from CH_2Cl_2/hexanes. After collecting by filtration and drying in vacuo, a white polymer, **2h**, was obtained: 5.93 g, 67%. $M_n = 34\,250$, $M_w = 35\,010$, PDI = 1.02. ^1H NMR (300 MHz, $CDCl_3$): δ 7.2−6.9 (br m), 6.7−6.3 (br m), 2.3−1.2 (br m).

Bulk Polymerization Method B. Certain polymerizations in bulk styrene were performed using a alternate procedure described by Matyjaszewski et al.[34] In a representative preparation for bpyPS **1e**, the initiator, bpy(CH_2Cl) (13.0 mg, 0.063 mmol), CuBr (9.1 mg, 0.063 mmol), and HMTETA (14.4 mg, 0.063 mmol) were combined in a Kontes tube. Styrene (6.35 g, 61 mmol) was added via syringe, and the yellowish mixture was immediately degassed by three freeze−pump−thaw cycles. The evacuated tube was then immersed in an oil bath maintained at 110 °C for 1 day. The bpyPS product was isolated and purified as described in method A, except that the CH_2Cl_2/hexanes precipitation was omitted. A white polymer, **1e**, was obtained: 4.94 g, 78%. GPC: $M_n = 122\,700$, $M_w = 145\,000$, PDI = 1.18. ^1H NMR (300 MHz, $CDCl_3$): δ 7.2−6.9 (br m), 6.7−6.3 (br m), 2.3−1.2 (br m).

Solution Polymerization. A typical solution polymerization of styrene was performed by modification of known methods[34−36] as described below for **2c**. Bpy(CH_2Cl)$_2$ (42.8 mg, 0.17 mmol) and CuBr (49.0 mg, 0.34 mmol) were combined in a Kontes tube, and then styrene (625 mg, 6.00 mmol), HMTETA (78.7 mg, 0.34 mmol), and anisole (5 mL) were added via syringe. The mixture was immediately degassed by three freeze−pump−thaw cycles, and the evacuated tube was immersed in an oil bath maintained at 110 °C for 2 days. The viscous light brown reaction mixture was dissolved in THF, and the resulting green solution was passed through at least two separate neutral alumina plugs (~3 × 5 cm) to remove the blue catalyst.[33] The pale yellow solution was concentrated in vacuo. The crude product was further purified by precipitation from THF into MeOH. The resulting white polymer product, **2c**, was collected on filter paper and was dried in vacuo: 0.429 g, 64%. GPC: $M_n = 8065$, $M_w = 9517$, PDI = 1.18. ^1H NMR (300 MHz, $CDCl_3$): δ 7.2−6.9 (br m), 6.8−6.3 (br m), 2.4−1.2 (br m).

Synthesis of Polymeric Ru Complexes (5−9). a. Chelation of One Macroligand. $[RuL_2(bpyPS_n)]^{2+}$ (L = bpy, phen) Polymers, 5−7. A representative preparation is provided for $[Ru(bpy)_2(bpyPS_2)]^{2+}$, **6**, prepared from bpyPS$_2$, **2h**. $Ru(bpy)_2Cl_2{\cdot}2H_2O$ (8.4 mg, 16.1 μmol) was dissolved in MeOH (5 mL), and then $AgPF_6$ (25 mg, 0.099 mmol) was added. The purple-red solution was heated at reflux under N_2 for 6 h. The resultant reddish methanol solution containing a white precipitate was filtered via cannula into a 50 mL round-bottom flask containing DME (10 mL) and bpyPS$_2$, **2h** (0.554 g, 16.1 μmol). The reaction mixture was heated at reflux under N_2 for 2 days. The reaction was cooled, cannula filtered, and concentrated in vacuo. The orange-red residue was dissolved in $CHCl_3$ (25 mL) and washed with H_2O (3 × 50 mL). The organic layer was concentrated in vacuo to produce the orange product, **6**: 0.559 g, 99%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.2−6.9 (br m), 6.7−6.3 (br m), 2.3−1.2 (br m). GPC: $M_n = 33\,800$, $M_w = 35\,500$, PDI = 1.05. UV/vis: $\lambda_{max} = 460$ nm, $A = 0.232$ (30 μM in $CHCl_3$). (Note: for reactions run with excess $Ru(bpy)_2Cl_2{\cdot}2H_2O$, polymers were purified by passage through an alumina plug (~2 × 5 cm) before $CHCl_3/H_2O$ workup.)

b. Chelation of Three Macroligands. $[Ru(bpyPS_n)_3]^{2+}$ (8 and 9). A representative preparation is described for $[Ru(bpyPS)_3]^{2+}$, **8**, made from bpyPS, **1a**. A $CHCl_3$ solution of $Ru(DMSO)_4Cl_2$ (31.4 mg) was prepared in a 25 mL volumetric flask. A portion of the Ru solution (1.09 mL, 2.8 μmol) was added to bpyPS, **1a** (57.9 mg, 8.5 μmol), dissolved in DME (10 mL). The pale yellow-green solution was heated at reflux under N_2 for 2 days. $AgPF_6$ (26.4 mg, 0.104 mmol) was added to the deep purple reaction mixture. The resulting red mixture was heated at reflux under N_2 for 1 day, thus producing a brownish green, cloudy suspension. MeOH (4 mL) was added, and the reaction was heated at reflux for 4 h during which time the suspension clarified and a precipitate formed. After cooling, the reaction mixture was filtered via cannula, and the orange-red filtrate was concentrated in vacuo. The crude solid was dissolved in $CHCl_3$ (25 mL) and was washed with H_2O (3 × 50 mL). The organic layer was concentrated in vacuo to give an orange solid, **8**: 0.060 g, 100%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.3−6.9 (br m), 6.8−6.3 (br m), 2.0−1.2 (br m). GPC: $M_n = 18\,300$, $M_w = 19\,300$, PDI = 1.05. UV/vis: $\lambda_{max} = 460$ nm, $A = 0.441$ (30 μM in $CHCl_3$).

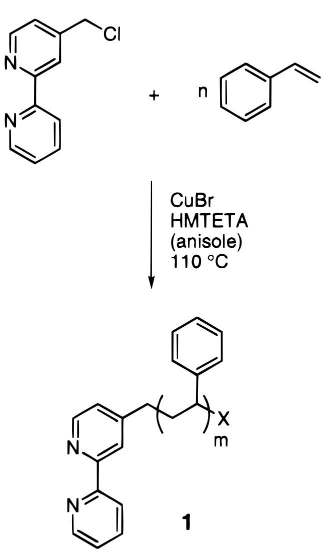


Figure 2. Synthesis of end-functionalized macroligands, bpyPS, **1**, by CuBr/HMTETA catalyzed ATRP using bpy(CH_2-Cl) as the initiator (X = Cl or Br).

Results and Discussion

Macroligand Synthesis. Bipyridine end-functionalized polystyrenes, bpyPS (Figure 2), of various molecular weights were synthesized in bulk styrene using bpy(CH_2Cl)[16] as the initiator and either CuCl/bpy-$(C_{13}H_{27})_2$[5] or CuBr/HMTETA as the catalyst system.[35,36] Bipyridine-centered polystyrenes, bpyPS$_2$, were made similarly using the difunctional initiator, bpy(CH_2Cl)$_2$[15] (Figure 3). Narrow polydispersities (<1.2) were typically observed. Polymers were purified by filtration through alumina to remove the Cu catalyst followed by precipitation from THF/MeOH. Because residual bpy$(C_{13}H_{27})_2$ ligand would compete with macroligands in subsequent metal binding reactions, an additional precipitation from CH_2Cl_2/hexanes was performed when CuCl/bpy-$(C_{13}H_{27})_2$ was employed as the catalyst. The bpyPS$_n$ polymers are insoluble under these conditions while the dialkylbipyridine remains in solution. The removal of bpy$(C_{13}H_{27})_2$ was confirmed by ^1H NMR spectroscopy. Representative GPC molecular weight data for the macroligands are provided in Table 1.

Though bulk polymerizations worked well for molecular weights higher than ~20K (**1d**, **1e**, **2d**, **2e**, **2g**−**2i**), they often exhibited poor control for lower monomer loadings. Insoluble solids were present in the reaction mixture when the styrene volume was reduced. The polymers obtained from these heterogeneous reactions always possessed much higher molecular weights than were anticipated. On the basis of literature precedent for solution ATRP,[35,36] anisole, dioxane, and xylenes were screened as solvents with the CuBr/HMTETA catalyst system. Although the reaction mixtures were

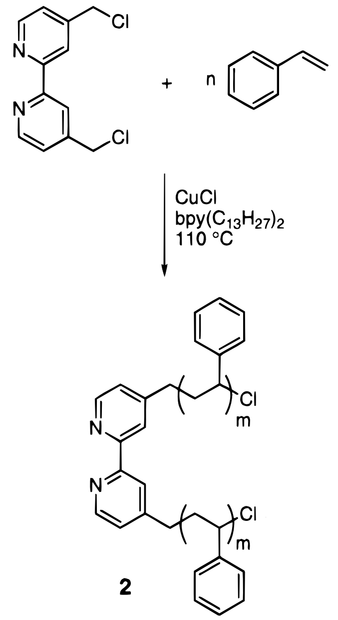


Figure 3. Synthesis of bpyPS$_2$ macroligands, **2**, by CuCl/bpy-(C$_{13}$H$_{27}$)$_2$ catalyzed ATRP using bpy(CH$_2$Cl)$_2$ as the initiator in bulk styrene.

Table 1. Molecular Weight Characterization[a] of Polystyrene Macroligands, bpyPS, 1, and bpyPS$_2$, 2, Prepared by Copper Catalyzed ATRP in Bulk Styrene or in Solution

bpyPS$_n$	$[M]_0/[I]_0$	calcd M_n[b] × 10^{-3}	M_n[a] × 10^{-3}	M_w[a] × 10^{-3}	PDI[a]	yield[c] (%)
1a[d]	77	8	6.8	7.2	1.06	20[i]
1b[d]	144	15	18.3	21.3	1.16	51
1c[d]	192	20	22.4	25.4	1.13	41
1d[e]	480	50	34.1	39.0	1.15	22[i]
1e[e]	968	100	122.7	145.0	1.18	78
2a[f]	29	3	5.5	5.7	1.05	48
2b[f]	58	6	7.7	9.0	1.17	50
2c[f]	35	4	8.1	9.6	1.18	64
2d[g]	288	30	16.3	17.2	1.05	72
2e[g]	384	40	20.8	21.8	1.04	56
2f[f]	144	15	19.5	23.5	1.20	55
2g[g]	230	24	24.2	25.1	1.03	65
2h[g]	405	43	34.3	35.0	1.02	67
2i[g]	480	50	63.0	68.1	1.08	73
2j[h]	29	3	10.3	18.5	1.8	5

[a] Molecular weight data determined by GPC in CHCl$_3$ at 25 °C with RI and MALLS detection. [b] Molecular weight calculated from monomer to initiator loading assuming 100% monomer conversion. [c] Yields are not corrected for incomplete monomer conversion. [d] Anisole; $[\mathrm{bpy(CH_2Cl)}]_0/[\mathrm{CuBr}]_0/[\mathrm{HMTETA}]_0 = 1{:}1{:}1$; 110 °C, 2 days. [e] Bulk; $[\mathrm{bpy(CH_2Cl)}]_0/[\mathrm{CuBr}]_0/[\mathrm{HMTETA}]_0 = 1{:}1{:}1$; 110 °C, 1 day. [f] Anisole; $[\mathrm{bpy(CH_2Cl)_2}]_0/[\mathrm{CuBr}]_0/[\mathrm{HMTETA}]_0 = 1{:}2{:}2$, 110 °C, 2 days. [g] Bulk; $[\mathrm{bpy(CH_2Cl)_2}]_0/[\mathrm{CuCl}]_0/[\mathrm{bpy(C_{13}H_{27})_2}]_0 = 1{:}2{:}4$, 110 °C, 1 day. [h] Xylenes; $[\mathrm{bpy(CH_2Cl)_2}]_0/[\mathrm{CuCl}]_0/[\mathrm{bpy(C_{13}H_{27})_2}]_0 = 1{:}2{:}4$; 110 °C, 2 days. [i] Reaction worked up 1 day after quenching and product twice purified.[33]

still heterogeneous, catalyst solubility was improved when these solvents were present. Though control was poor with xylenes (PDI = 1.8) (**2j**), the results were more favorable with anisole (**1a**−**1c**, **2a**−**2c**, **2f**).

Synthesis of Linear Ruthenium Polymeric Complexes. Ru end-functionalized linear polymers, **5**, are generated when one bpyPS is coordinated, whereas linear polymers with a Ru complex at the middle of the chain, **6** and **7**, are formed upon chelation of one bpyPS$_2$ (Figure 4). The simplest and most common methods for replacing the chlorides in Ru(bpy)$_2$Cl$_2$ with bpy derivatives involve refluxing this Ru reagent with the appropriate ligand in polar solvents such as MeOH, EtOH, or aqueous/alcohol mixtures.[37,38] However, when the macroligand bpyPS$_2$ was refluxed with Ru(bpy)$_2$Cl$_2$ even for 1 week, the reactions simply turned brown. There was little or no UV/vis spectroscopy evidence of the orange [Ru(bpy)$_2$(bpyPS$_2$)]$^{2+}$ product. Because the polystyrene macroligand is poorly soluble in polar media, reactions in other commonly used solvents such as DMF, DMF/alcohol, or CHCl$_3$/alcohol mixtures also failed.

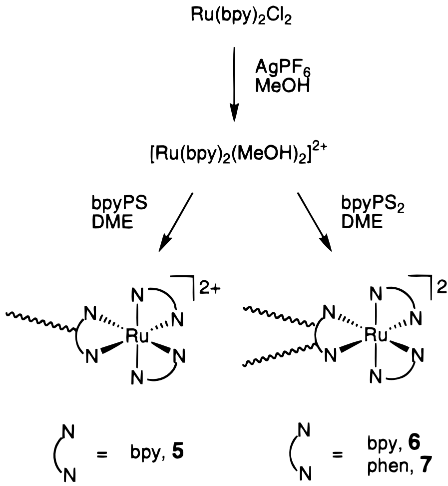


Figure 4. Synthesis of ruthenium polymeric complexes containing one macroligand, [Ru(bpy)$_2$(bpyPS)]$^{2+}$, **5**, and [Ru(L)$_2$(bpyPS$_2$)]$^{2+}$ (L = bpy, **6**; phen, **7**).

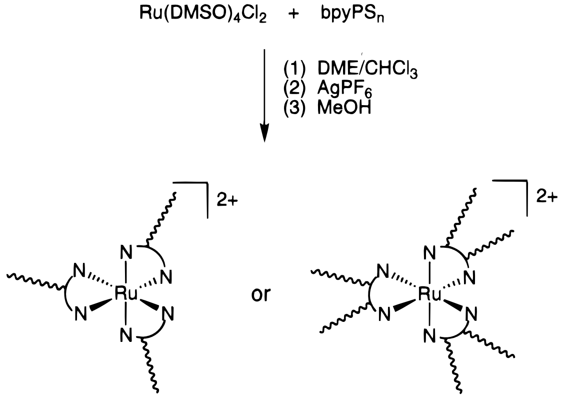
Another strategy for Ru complex synthesis uses silver salts to facilitate halide abstraction and, thus, ligand substitution.[39,40] This was crucial for generating polymeric Ru complexes as well.[13] The precursor, Ru(bpy)$_2$Cl$_2$, was refluxed with AgPF$_6$ in MeOH solution for 6 h to form the red Ru(bpy)$_2$(MeOH)$_2$ intermediate.[40] Subsequently, the appropriate polymeric ligand bpyPS or bpyPS$_2$ was added to this labile solvent intermediate as a DME solution.[39] Over time, the reaction mixtures developed the orange-red color characteristic of Ru tris(bipyridine) chromophores (~460 nm), thus signaling the formation of [Ru(bpy)$_2$(bpyPS$_n$)]$^{2+}$, **5** and **6**. To demonstrate that this method also extends to other ligand sets, the [Ru(phen)$_2$(bpyPS$_2$)]$^{2+}$ complex, **7**, was prepared in an analogous manner.

Polymers were characterized by gel permeation chromatography with in-line refractive index, multiangle laser light scattering, and diode array UV/vis detectors. With this configuration, it was confirmed that the Ru chromophores are associated with the polymers, and absolute molecular weights were obtained. Molecular weight data for [Ru(bpy)$_2$(bpyPS$_n$)]$^{2+}$ complexes made from different macroligands, as well as for [Ru(phen)$_2$(bpyPS$_n$)]$^{2+}$, **7**, are provided in Table 2. As expected, molecular weights of the polymeric Ru complexes generally increase only slightly compared with those of the starting macroligands. The absolute efficiency of chelation is difficult to establish in macroligand reactions when polymer starting material and product molecular weights are similar, since associated peaks are not separated in GPC chromatograms. Yet, since the inner- and outer-sphere environment surrounding the metal center is similar in polymeric complexes of a given series, UV/vis absorbances should estimate the relative reaction efficiency. Calculated M_n values for the polymeric complexes were determined using macroligand number-average molecular weights as determined by

Table 2. Molecular Weight[a] and UV/Vis[b] Characterization of $[RuL_2(bpyPS_n)]^{2+}$ Polymeric Complexes, 5−7, Prepared from the Designated Macroligand, bpyPS, 1, or $bpyPS_2$, 2[c]

	macroligand		ruthenium polymeric complex					
entry	$bpyPS_n$	$M_n \times 10^{-3}$	calcd $M_n \times 10^{-3}$	$M_n{}^a \times 10^{-3}$	$M_w{}^a \times 10^{-3}$	PDI[a]	$\lambda_{max}{}^b$ (nm)	A^b
1	**1a**	6.8	7.5	9.9	10.1	1.03	456	0.293
2	**1c**	22.4	23.1	23.2	25.9	1.12	457	0.302
3	**1d**	34.1	34.8	34.8	39.5	1.14	457	0.316
4	**1e**	122.7	123.4	115.9	141.7	1.22	460	0.199
5	**1e**[d]	122.7	123.4	136.6	155.4	1.14	455	0.520
6	**2b**	7.7	8.4	8.2	9.2	1.12	458	0.255
7	**2c**	8.1	8.8	8.8	9.6	1.09	460	0.262
8	**2e**	20.8	21.5	21.4	22.4	1.05	458	0.255
9	**2g**	24.2	24.9	25.5	26.3	1.03	458	0.255
10	**2g**[e]	24.2	25.1	24.4	25.9	1.06	446	0.311
11	**2h**	34.3	35.0	33.8	35.5	1.05	460	0.232
12	**2i**	63.0	63.7	67.0	72.7	1.08	458	0.103
13	**2i**[d]	63.0	63.7	64.5	69.8	1.08	458	0.384

[a] Molecular weight data determined by GPC in $CHCl_3$ at 25 °C with RI and MALLS detection. [b] Absorbances (A) and λ_{max} (nm) determined for 30 μM $CHCl_3$ solutions using calcd M_n to determine concentration. [c] $Ru(bpy)_2Cl_2$:$bpyPS_n$ = 1:1, L = bpy unless otherwise indicated. [d] $Ru(bpy)_2Cl_2$:$bpyPS_n$ = 5:1. [e] L = phen.



8 (n = 1) **9** (n = 2)

Figure 5. Synthesis of homoleptic ruthenium polymeric complexes containing three macroligands, $[Ru(bpyPS)_3]^{2+}$, **8**, and $[Ru(bpyPS_2)_3]^{2+}$, **9**.

GPC. These were used to prepare 30 μM $CHCl_3$ solutions for the determination of absorbances at λ_{max} of the MLCT band for Ru tris(bpy) chromophores (Table 2).

Absorbances and, thus, chelation efficiencies differ very little for $[Ru(bpy)_2(bpyPS_n)]^{2+}$ polymers prepared using a 1:1 loading of $Ru(bpy)_2Cl_2$ and a $bpyPS_n$ macroligand of molecular weight up to ∼35K (bpyPS, $A = \sim 0.30$; $bpyPS_2$, $A = \sim 0.26$) (Table 2, entries 1−3, 6−9, 11). However, polymeric complexes generated from higher molecular weight macroligands exhibit lower absorbance values (entries 4 and 12). The efficiency of chelation reactions of high molecular weight macroligands **1e** and **2i** (and, thus, presumably also of lower molecular weight ones) may be improved by using excess Ru reagent ($Ru(bpy)_2Cl_2$:$bpyPS_n$ = 5:1). Associated absorbances at λ_{max} increase considerably (Table 2, entries 5 and 13). Excess Ru reagent is readily separated from the $[Ru(bpy)_2(bpyPS_n)]^{2+}$ products during reaction workup. Factors that could contribute to differences in maximum absorbance values for polymeric complexes with one arm, **5**, and two arms, **6**, are the following. First, complexes could exhibit different extinction coefficients which would result in slightly different A values even for identical chelation efficiencies. Second, differences in the number of the bpy functionalities present in the macroligand fractions could also be a factor if initiation from bpy(CHCl) and $bpy(CH_2Cl)_2$ is not entirely and identically efficient. Finally, the bpyPS ligand with the more accessible chain end donor may simply chelate with greater efficiency than $bpyPS_2$ wherein the bidentate donor group is positioned at the center of the chain and is, thus, more hindered. The extent to which each of these factors contributes to differences in absorbance is difficult to distinguish for Ru derivatized linear polymers.

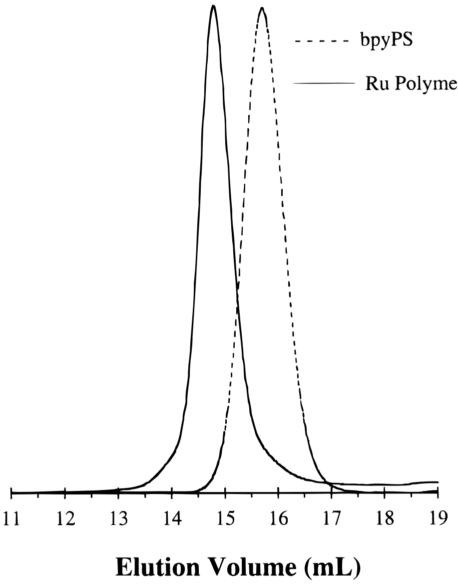


Figure 6. Overlay of the GPC traces ($CHCl_3$) of $[Ru(bpyPS)_3]^{2+}$, **8** (M_n = 18.3K, M_w = 19.3K, PDI = 1.05) and the bpyPS macroligand **1a** (M_n = 6.8K, M_w = 7.3K, PDI = 1.06) from which it was prepared.

Synthesis of Star-Shaped Ruthenium Polymeric Complexes. Chelation of three identical macroligands to ruthenium centers produces three-arm stars from bpyPS, **8**, whereas tris complexes of $bpyPS_2$ are six-arm metal-centered stars, **9** (Figure 5). A variety of standard literature procedures were attempted for the synthesis of $[Ru(bpyPS_2)_3]^{2+}$. Those involving reaction of $RuCl_3 \cdot xH_2O$ with $bpyPS_2$ in the presence of DMF,[41] aqueous HCl with H_3PO_3,[42] MeOH/DME with Pt and H_2,[43] or in EtOH[44] were all unsuccessful. Since both polystyrene macroligands and $Ru(DMSO)_4Cl_2$ are soluble in comparable media, chelation reactions with this Ru precursor were probed in toluene, $CHCl_3$, DME/MeOH, and

Table 3. Molecular Weight and UV/vis Characterization of Ruthenium Polymeric Complexes, $[Ru(bpyPS)_3]^{2+}$, 8, and $[Ru(bpyPS_2)_3]^{2+}$, 9, Synthesized from $[Ru(DMSO)_4Cl_2]$ and bpyPS, 1, or bpyPS$_2$, 2, Respectively

	macroligand		ruthenium polymeric complex				
bpyPS$_n$	$M_n \times 10^{-3}$	calcd $M_n \times 10^{-3}$	$M_n{}^a \times 10^{-3}$	$M_w{}^a \times 10^{-3}$	PDI^a	$\lambda_{max}{}^b$ (nm)	A^b
1a	6.8	20.8	18.3	19.3	1.05	460	0.441
1c	22.4	67.7	60.9	69.8	1.15	456	0.385
1d	34.1	102.6	60.3^c	70.2^c	1.16^c	460	0.500
1e	122.7		bimodal				
2a	5.5	16.8	16.5	17.2	1.04	465	0.373
2c	7.7	24.6	21.9	24.8	1.13	458	0.388
2d	16.3	49.4	40.2^c	43.5^c	1.08	465	0.306
2g	24.2		bimodal				

[a] Molecular weight data determined by GPC in $CHCl_3$ at 25 °C with RI and MALLS detection. [b] A = absorbance and λ_{max} (nm) determined for 30 μM solutions prepared using calcd M_n to determine concentration. Note: concentrations determined using calcd M_n overestimate A if M_n, M_w < calcd M_n and underestimate A if M_n, M_w > calcd M_n. [c] Evidence of shoulder corresponding to unreacted macroligand.

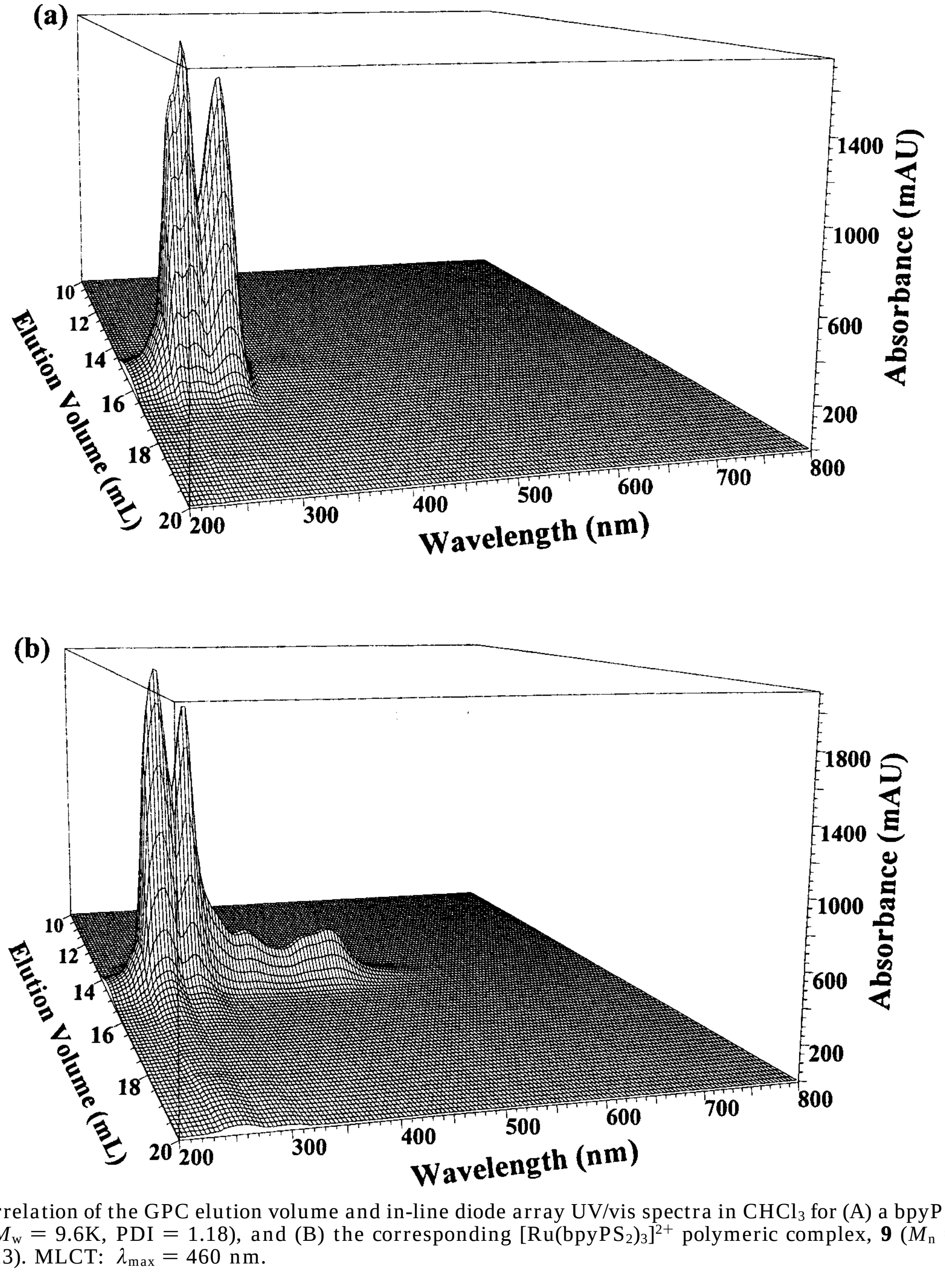


Figure 7. 3D correlation of the GPC elution volume and in-line diode array UV/vis spectra in $CHCl_3$ for (A) a bpyPS$_2$ macroligand, **2c** (M_n = 8.1K, M_w = 9.6K, PDI = 1.18), and (B) the corresponding $[Ru(bpyPS_2)_3]^{2+}$ polymeric complex, **9** (M_n = 21.9K, M_w = 24.8K, PDI = 1.13). MLCT: λ_{max} = 460 nm.

EtOH. But instead of orange tris products, purple solutions indicative of $[Ru(bpyPS_n)_2Cl_2]$ typically formed. Success with DME and $AgPF_6$ dehalogenation in $[Ru(bpy)_2(bpyPS_n)]^{2+}$ synthesis prompted us to try these conditions for the preparation of Ru tris(bpyPS$_n$) complexes as well. DME solutions of bpyPS$_n$ were combined with $Ru(DMSO)_4Cl_2$ dissolved in $CHCl_3$. Since extended reaction times of ∼1 week did not yield orange tris products, after refluxing for 2 days, $AgPF_6$ was added to dechlorinate the purple $[Ru(bpyPS_n)_2Cl_2]$ complex, thus generating a substitutionally labile $[Ru(bpyPS_n)_2(solvent)_m]^{2+}$ intermediate. Reactions were refluxed for an additional day to ensure complete tris complex formation, and then MeOH was added to precipitate suspended AgCl. After filtration and purification, the desired orange $[Ru(bpyPS_n)_3]^{2+}$ products were obtained (Figure 5).

Molecular weight and UV/vis absorbance data for selected Ru-centered stars are provided in Table 3. Absorbances of ∼0.3 and very minimal trailing in GPC traces indicate that reactions with low molecular weight macroligands are efficient (Table 3; **1a**, **1c**, **2a**, **2c**). A GPC overlay of a three-arm star, **8**, and the corresponding bpyPS macroligand **1a** is provided in Figure 6. This illustrates the expected tripling of the molecular weight upon metal-centered star polymer formation. The 3D GPC vs diode array UV/vis plots for a $bpyPS_2$ macroligand, **2c**, and its Ru-centered six-arm star, **9**, are compared in Figure 7. These plots illustrate the expected shift to lower elution volume for the star as compared with the macroligand and show that the Ru chromophores are associated with the eluting polymer fraction. By the convergent chelation approach, an upper molecular weight ceiling is reached above which star-shaped polymeric complex synthesis is no longer efficient. Moreover, the threshold molecular weight is influenced by the position of the bpy in the polystyrene chain. Synthesis of $[Ru(bpyPS)_3]^{2+}$ complexes works well for star molecular weights up to ∼65K (bpyPS ∼22K) (Table 3, **1c**). Reactions involving $bpyPS_2$, with the less accessible donor group at the center of the chain, are efficient for Ru-centered star molecular weights up ∼40K ($bpyPS_2$ ∼14K) (Table 3, **2d**). For reactions run with higher molecular weight macroligands, tris complexes still form, but even for long reaction times, GPC traces show evidence of unreacted macroligand.

Since the reaction medium influences polymer chain conformation, and steric demand of the ligand impacts chelation efficiency, different solvent systems were attempted. Interestingly, the solvents that worked best for forming tris(bpy) polymeric complexes, namely DME/$CHCl_3$ or DME, are in fact rather poor solvents for polystyrene.[45] Many solvents that are better suited for solubilizing polystyrene are in fact incapable of dissolving common Ru reagents. Others that seemed most promising for solubilizing both metal complex and macroligand, namely dioxane, cyclohexane/acetone, and THF, were tested. But a dark brown color developed in dioxane, $Ru(DMSO)_4Cl_2$ did not dissolve cyclohexane/acetone, and it was not possible to achieve the temperatures necessary to effect polymeric ligand substitution reactions in THF. The desired tris(bipyridine) products do form when DMF is substituted for DME in the standard procedure. But since DMF promotes the reduction of Ag^+ to Ag^0, a large excess of the silver reagent was required, and the reaction vessel became coated with a silver mirror, thus rendering this methodology impractical. In summary, the various solvents that were tested did not lead to higher molecular weight polymeric complexes than those achieved in DME. It may be possible to achieve higher molecular weight stars using macroligands that possess solubilities that are similar to common Ru precursors.

Conclusion

Polymeric metal complexes are generated by adapting methods for small molecule synthesis to make them compatible with macromolecular ligands. Longer reaction times and dehalogenation with $AgPF_6$ are required to effect ligand substitution. Ruthenium functionalization of linear polystyrenes proceeded smoothly for macroligands with molecular weights up to 100K. It is possible that even higher molecular weight materials could be produced. Reaction efficiencies increase when excess Ru reagent is used in reactions to form $[Ru(bpy)_2(bpyPS_n)]^{2+}$ products. Tris(bpy) polymeric complexes, in contrast, hit a threshold above which the reaction efficiency begins to drop off. This ceiling is determined by the steric demand of the $bpyPS_n$ ligand, namely its molecular weight, as well as the position of the bpy in the polystyrene chain. Extension of this modular macroligand chelation strategy to other kinds of polymers, ligands, and metal centers, including mixed ligand systems, opens up a wide range of possibilities for new functionalized macromolecular architectures. These materials that are equipped with a luminescent tag in a specific location of the polymer architecture could be useful for fundamental studies of structure−property relationships. Modified materials could be suitable for use as sterically and electronically tunable site isolated polymer supported catalysts. Replacing small molecule ligands with polymeric analogues introduces film-forming properties, ways of purifying catalysts by precipitation, and means of tuning the environment surrounding metal centers. Continued investigation of the scope of this highly modular metal template approach to polymer synthesis as well as exploration of the properties and applications of these materials will be addressed in future reports.

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