Ruthenium-Centered Heteroarm Stars by a Modular Coordination Approach: Effect of Polymer Composition on Rates of Chelation

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ABSTRACT: Bipyridine end- and center-functionalized polymer chains, bpyA and bpyA$_2$, respectively, were chelated to Ru(II) centers to form Ru(bpyA$_n$)$_2$Cl$_2$ complexes **1**−**6** where A = polystyrene (PS), n = 1 (**1**), n = 2 (**2**); A = poly(methyl methacrylate) (PMMA), n = 1 (**3**), n = 2 (**4**); A = poly(ϵ-caprolactone) (PCL), n = 2 (**5**); and A = poly(ethylene glycol) PEG, n = 2 (**6**). Intermediates **1** and **5** were subsequently reacted with a second type of bpy macroligand to generate [Ru(bpyA$_n$)$_2$(bpyB$_2$)]$^{2+}$ heteroarm star copolymers for the following combinations: A$_n$,B = PCL$_2$,PS (**7**), PCL$_2$,PEG (**8**), PS,PLA (**9**), where PLA = poly(lactic acid), and PS,PEG (**10**). Rates of chelation were affected by macroligand composition, molecular weight, and architecture and paralleled the solubility parameter series for PCL, PLA, PMMA, PS, and PEG in dimethoxyethane (DME). Rates decreased with increasing M_n and were lower for bpyA$_2$ relative to end-functionalized bpyA of comparable molecular weights within each compositional class.

Introduction

Block copolymers are of great interest for their self-assembly properties.[1] Important applications for these structured materials with nanoscale periodicities are in photonics.[2] Aggregation of high molecular weight block copolymers can lead to patterned structures with domain sizes suitable for interaction with visible light. Other times, particularly for lower molecular weight block copolymers, matched homopolymers are blended into block copolymer templates in order to swell domains to suitable sizes.[3,4] Often dopants are incorporated to enhance nonlinear properties, increase dielectric contrast, or to serve as optical collectors, amplifiers, or simply as probes of the photonic crystal structure.[5−7] For example, poly(methyl methacrylate) (PMMA) opaline films have been doped with fluorescent dyes to provide crystals that exhibited an incomplete photonic band gap (PBG).[8]

Polymeric metal complexes (PMCs)[9] developed by our group are also of interest for use as photonic crystal dyes for block copolymer assemblies. Preliminary results with high molecular weight polystyrene (PS):PMMA block copolymers and blends as templates demonstrate that homopolymer Ru PMC dyes segregate to matched template domains; luminescence from specific domains may be detected by near field scanning optical microscopy (NSOM) techniques.[10] With site-isolated block copolymer PMCs, it should be possible to position metals within a single microdomain (Figure 1A)[11] or at domain boundaries (Figure 1B)[12] either upon self-assembly or when used as dopants in matched high molecular weight BCP templates.

To study the self-assembly and optical properties of block copolymer PMC dyes in these and other applications, it is first necessary to develop efficient syntheses of the materials of interest. In support of these long-term goals of investigating materials properties, in this study we report on reaction parameters affecting heteroarm star block copolymer metal complex formation for an expanded materials set. These findings illustrate that reaction rates for coordination reactions involving polymeric ligands differ markedly from analogous transformations with nonpolymeric systems.

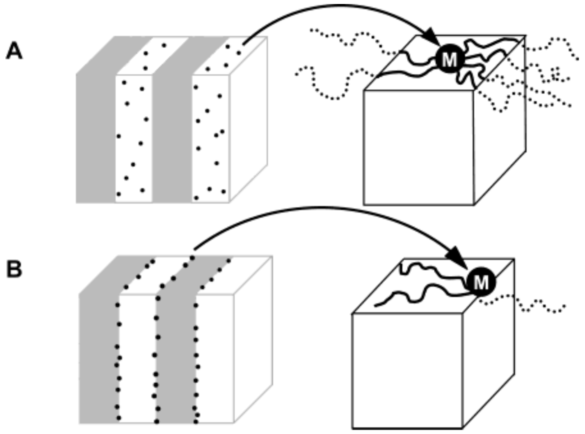

Figure 1. Schematic representation of the metal placement predicted for (A) a metal-centered star block copolymer and (B) a metal-centered heteroarm star in microphase-separated films.

In addition to divergent methods involving sequential monomer addition to metalloinitiators,[13] polymeric metal complexes may be generated by a modular chelation approach. To date, a number of macroligand building blocks have been achieved (Figure 2), and these may be mixed and matched in metal coordination reactions. One way to generate block copolymer PMCs involves chelation of macroligands that are themselves block copolymers.[14,15] When inert metals such as Ru(II) are utilized as synthetic templates, heteroleptic complexes can also be generated through sequential chelation of different homopolymer ligands. As a first demonstration of metal-centered heteroarm stars by this approach, we described the synthesis of [Ru(bpyPS$_n$)$_2$(bpyPMMA$_n$)]$^{2+}$ analogues with polystyrene and poly(methyl methacrylate) macroligands, bpyPS$_n$ and bpyPMMA$_n$ (n = 1 or 2), coordinated to a ruthenium core.[12] Dehalogenation of Ru intermediates with Ag$^+$ salts to form more reactive solvento intermediates and attention to the ways in which polymer conformation could change in solvents

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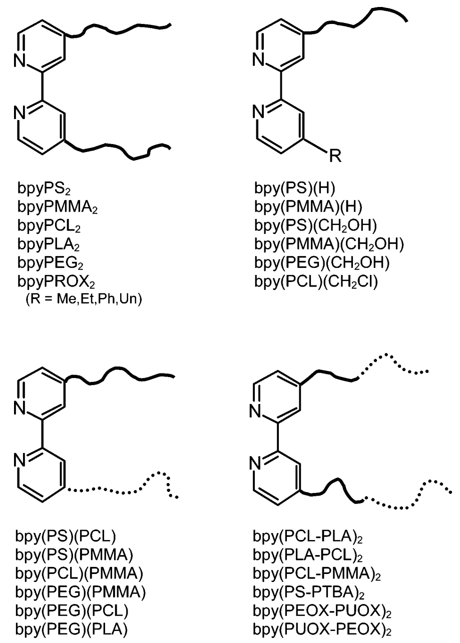

Figure 2. Bipyridine macroligands.[9,11,18,27,36]

of different polarity (i.e., to alternately protect and expose the metal center) were crucial to the success of the synthesis. It was further reported that these materials self-assemble into nanopatterned films.[16] Here we expand upon this study by exploring systems of different compositions, architectures, and donor position, paying particular attention to the way that reaction rates are influenced by these parameters.

Experimental Section

Materials. Reagents were obtained from Aldrich Chemical Co. and used as received unless otherwise indicated. THF was dried and purified by distillation over Na$^+$/benzophenone ketyl. Acetonitrile, diisopropylamine, and methyl methacrylate (MMA) were distilled from CaH$_2$ prior to use. Dry *N*,*N*-dimethylformamide (DMF) was obtained from Aldrich in Sureseal bottles. The macroligands bpyPS,[17] bpyPS$_2$,[17] bpyPMMA,[12] bpyPMMA$_2$,[12] bpyPEG$_2$,[9] bpyPLA$_2$,[18] and bpyPCL$_2$[18] were prepared as previously reported (PS = polystyrene; PMMA = poly(methyl methacrylate); PEG = poly(ethylene glycol); PLA = poly(lactic acid); PCL = poly(ϵ-caprolactone)).

Methods. UV/vis spectra were obtained in CHCl$_3$ using a Hewlett-Packard 8452A diode-array spectrophotometer. Polymer molecular weights were determined by gel permeation chromatography (GPC) in CHCl$_3$ using a Hewlett-Packard 1100 system equipped with a vacuum degasser, a diode array detector with a Polymer Labs 5μ “mixed C” guard column and two “mixed C” GPC columns, a Wyatt Technology Corp. DAWN multiangle laser light scattering (MALLS) (5 mW polarized He−Ne laser, λ = 633 nm), and an Optilab refractive index detector and diode-array UV/vis detection along with accompanying Wyatt Technology Corp. Astra software. The incremental refractive indices (d*n*/d*c* values) for PMMA (0.059 mL/g)[19] and PS (0.145 mL/g) were obtained from Wyatt Technology Corp., while the d*n*/d*c* values for PCL (0.056 mL/g) and PLA (0.030 mL/g) were determined in microbatch mode as previously reported.[18] These values were used to calculate MALLS molecular weights unless otherwise indicated. Reaction temperatures refer to oil bath settings.

Homopolymeric Ruthenium Complexes with Two Bipyridine Macroligands. Ru(bpyPS)$_2$Cl$_2$ (1), Ru(bpyPS$_2$)$_2$Cl$_2$ (2), Ru(bpyPMMA)$_2$Cl$_2$ (3), Ru(bpyPMMA$_2$)$_2$Cl$_2$ (4), Ru(bpyPCL$_2$)$_2$Cl$_2$ (5) and Ru(bpyPEG$_2$)$_2$Cl$_2$ (6). General Procedure for Kinetics Study. A CHCl$_3$ solution of Ru(DMSO)$_4$Cl$_2$ was prepared, and then a portion of it was delivered to a dimethoxyethane (DME) solution of 2 mol equiv of the macroligand to provide a 15:1 DME:CHCl$_3$ solvent system with an overall Ru(DMSO)$_4$Cl$_2$ concentration of ~0.35 mM. The resulting pale yellow solution was heated under N$_2$ at 120 °C. Aliquots were removed at timed intervals, (e.g., for **5**, approximately every 6 h for the first day, then every 12 h for the next 5 days), and dried to constant weight in vacuo to monitor reaction progress. UV/vis absorption spectra were measured for each aliquot, and the molar absorptivities for the lowest energy absorption (MLCT, ~565 nm) were plotted vs time.

Dehalogenation of Ru(bpyA$_n$)$_2$Cl$_2$ Complexes. The intermediate bis(bpy) Ru(II) dichlorides, **1**−**6** (formed in kinetics experiments and remaining after aliquot removal described above), were dissolved in DME and combined with 5 mol equiv of AgPF$_6$ to provide [AgPF$_6$] ~ 2.6 mM. The resulting reaction mixtures were stirred under nitrogen at 90 °C in the dark. Aliquots were removed at timed intervals, (e.g., for **3**, every 50 min for 4 h), and the degree of dehalogenation was determined with UV/vis analysis, by monitoring the disappearance of the MLCT absorption at ~565 nm for the Ru(bpyA$_n$)$_2$Cl$_2$ intermediates.

Ruthenium Complexes with Three Macroligands. The dehalogenated bis(bpy) solvento intermediates, Ru(bpyA$_n$)$_2$(DME),[20,21] were reacted with 1 equiv of a second type of macroligand in DME solution at 120 °C. Aliquots were drawn at timed intervals (e.g., for **7**, every 12 h for the first 2 days and then every 1−2 days until a maximum absorbance value was achieved), and the degree of chelation for the third macroligand was monitored via UV/vis and GPC. A representative procedure is provided for [Ru(bpyPCL$_2$)$_2$(bpyPS$_2$)]$^{2+}$, **7**.

[Ru(bpyPCL$_2$)$_2$(bpyPS$_2$)]$^{2+}$ (7). A sample of bpyPS$_2$ (35.9 mg, 2.0 μmol, M_n = 18 220) and the solvento intermediate, [Ru(bpyPCL$_2$)$_2$(DME)]$^{2+}$ (37.0 mg, 2.0 μmol), were refluxed in DME for ~12 days. The solvent was removed in vacuo, and then the crude product was dissolved in CHCl$_3$, washed with H$_2$O (2 × 100 mL), and concentrated in vacuo. The product was purified by precipitation from CH$_2$Cl$_2$/hexanes to afford an orange solid: 7.0 mg (69%).[22] M_n = 34 500, M_w = 38 100, PDI = 1.10.

[Ru(bpyPCL$_2$)$_2$(bpyPEG$_2$)]$^{2+}$ (8). The PCL−PEG heteroarm star, **8**, was prepared from [Ru(bpyPCL$_2$)$_2$(DME)]$^{2+}$ (30.4 mg, 1.5 μmol) as described above for **7** using bpyPEG$_2$ (5.4 mg, 1.5 μmol, M_n = 3600) in place of bpyPS$_2$: 3.1 mg (71%).[22] GPC:[23] M_n = 23 200, M_w = 27 600, PDI = 1.19.

[Ru(bpyPS)$_2$(bpyPLA$_2$)]$^{2+}$ (9). The PS−PLA heteroarm star, **9**, was prepared from [Ru(bpyPS$_2$)$_2$(DME)]$^{2+}$ (43.7 mg, 1.2 μmol) as described above for **7** using bpyPLA$_2$ (23.1 mg, 1.2 μmol, M_n = 19 300) in place of bpyPS$_2$: 49.3 mg (74%).[22] GPC:[24] M_n = 51 800, M_w = 58 000, PDI = 1.12.

[Ru(bpyPS)$_2$(bpyPEG$_2$)]$^{2+}$ (10). The PS−PEG complex, **10**, was prepared from [Ru(bpyPS$_2$)$_2$(DME)]$^{2+}$ (43.7 mg, 1.2 μmol) as described above for **7** with the exception that bpyPEG$_2$ (4.4 mg, 1.2 μmol, M_n = 3700[25]) was used in place of bpyPS$_2$, and the product was not isolated via aqueous workup, but by precipitation (CH$_2$Cl$_2$/hexanes): 31.4 mg (65%).[22] GPC:[26] M_n = 38 100, M_w = 43 600, PDI = 1.15.

Results and Discussion

A metal-template approach was recently utilized in the synthesis of ruthenium-centered PS−PMMA heteroarm star polymers, [Ru(bpyPS$_n$)$_2$(bpyPMMA$_n$)]$^{2+}$. In short, this method involved the chelation of two bpyPS$_n$ ligands to Ru(II) in DME, followed by dehalogenation to generate a more reactive solvento intermediate, and subsequent chelation of one bpyPMMA$_n$ macroligand.[12] Because of the greater steric bulk associated with ligands bearing polymeric substituents, the formation of Ru(bpyPS$_n$)$_2$Cl$_2$ by the convergence of two macroligands at the metal center required the implementation of both a high temperature and a long reaction time. For example, the chelation of 2 equiv of bpyPS$_2$ (M_n = 4800) to Ru(DMSO)$_4$Cl$_2$ required refluxing at 120 °C for 6 days in DME to drive the formation of Ru(bpyPS$_2$)Cl$_2$

Table 1. Observed Rate Constants, Approximate Reaction Times, and Molar Absorptivities for the Formation of Selected $Ru(bpyA_n)_2Cl_2$ Complexes

complex	ligand M_n (kDa)	reaction time[a] (days)	k_{obs}	$\epsilon_{max} \times 10^{-3}$ [b] (M^{-1} cm^{-1})	chelation efficiency[c]
$Ru(bpyPS)_2Cl_2$, **1**	19.5	4	0.89	5.65	0.61
$Ru(bpyPS_2)_2Cl_2$, **2**	9.9	5	1.03	6.57	0.71
	18.2	4	0.83	3.68	0.40
	34.3	11	0.40	4.50	0.49
$Ru(bpyPMMA)_2Cl_2$, **3**	7.0	15	0.40	9.43	1.03
	21.4	25	0.26	7.77	0.84
$Ru(bpyPMMA_2)_2Cl_2$, **4**	6.6	5	0.89	6.54	0.71
	12.2	6	0.71	7.76	0.84
	24.5	10	0.48	6.05	0.66
	58.8	12	0.39	4.31	0.47
$Ru(bpyPCL_2)_2Cl_2$, **5**	4.4	4	1.16	5.58	0.61
	10.4	5	1.05	4.63	0.50
$Ru(bpyPEG_2)_2Cl_2$, **6**	3.7	28	0.20	9.03	0.98

[a] Approximate time required for maximum molar absorptivity at ~565 nm to be achieved. [b] Determined at $\lambda_{max} \sim 565$ nm. [c] Estimated as $\epsilon_{MLCT}Ru(bpyA_n)_2Cl_2/\epsilon_{MLCT}Ru(bpy)_2Cl_2$.

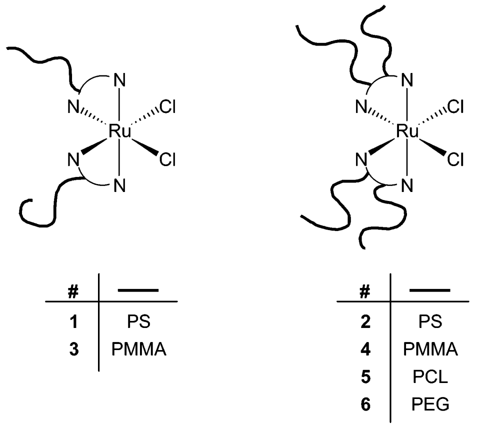

Figure 3. Polymeric ruthenium(II) bis(bipyridine) dichloride complexes, $Ru(bpyA_n)_2Cl_2$ ($n = 1, 2$), **1**−**6**.

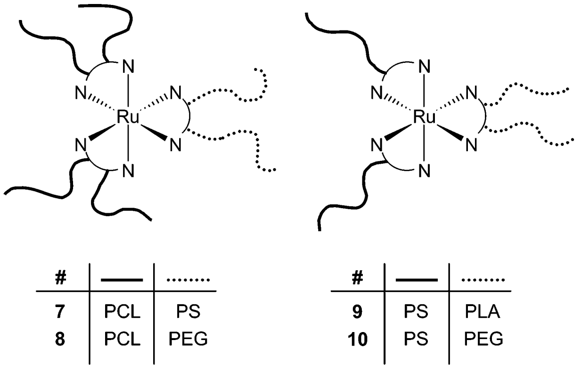

Figure 4. Ruthenium(II) tris(bipyridine)-centered heteroarm stars, $[Ru(bpyA_n)_2(bpyB_2)]^{2+}$ ($n = 1, 2$), **7**−**10**.

to completion. A benefit of this slower method is that the bis(bpy) product is formed free of tris(bpy) impurities, which, under certain conditions, are evident in faster reactions involving silver-promoted dehalogenation.[27,28] To determine how polymer composition affects the rate of reaction and if even higher molecular weight macroligands can be driven to completion with longer reaction times, here, this study is expanded to include $bpyPCL_2$, $bpyPMMA_2$, $bpyPEG_2$, and $bpyPS_2$ macroligands in the formation of other $Ru(bpyA_n)_2Cl_2$ (Figure 3) and $Ru(bpyA_n)(DME)$ intermediates and $Ru(bpy)_3^{2+}$-centered heteroarm stars (Figure 4).

Synthesis of $Ru(bpyA_n)_2Cl_2$ Intermediates. To determine the optimum reaction time for the generation of a series of $Ru(bpyA_n)_2Cl_2$ samples, **1**−**6**, $Ru(DMSO)_4Cl_2$ was combined with 2 equiv of a bipyridine-functionalized macroligand in a refluxing 15:1 $DME:CHCl_3$ solvent mixture. Aliquots were drawn at timed intervals (typically every 12 h), and a UV/vis absorption spectrum was recorded for each sample. The amount of time to reach completion was defined as the point at which the extinction coefficient reached a plateau. The time points for all reactions fit well to pseudo-first-order kinetics plots ($r^2 > 0.90$), where k_{obs} represents the observed rate constant. Mono-bpy ruthenium intermediates form at a much faster rate than the bis complexes; absorption bands for the mono-bpy complexes at ~400 nm reached a maximum in less than 1 day and slowly decreased as the bis complexes formed. Thus, it is assumed that the observed rate constants reflect rates of chelation of the second macroligand. Rates for the generation of a series of $Ru(bpyA_n)_2Cl_2$ complexes **1**−**6** of different sizes are provided in Table 1.

Upon inspection of the data several trends emerge. For the series of $bpyPMMA_2$ macroligands, the rate of $Ru(bpyPMMA_2)_2Cl_2$ (**4**) formation decreased steadily with increasing macroligand molecular weight. This is most likely due to the presence of added steric bulk that limits access to the bipyridine binding site or makes it more difficult for the bpy to adopt the proper (cis) configuration for metal coordination. In addition, the maximum value of ϵ generally decreased with increasing molecular weight for each class. For example, the maximum obtainable molar absorptivity (9430 M^{-1} cm^{-1}) for a $Ru(bpyPMMA)_2Cl_2$ complex (**3**) with a 7030 Da bpyPMMA macroligand was greater than that for the Ru(II) bis(bpy) dichloride (7770 M^{-1} cm^{-1}) with a higher molecular weight bpyPMMA chain (21 360 Da). While it is possible that molar absorptivities differ for PMCs of the same composition but different molecular weights, this trend may also be indicative of lower formation constants for the reactions with higher molecular weight macroligands. Decomposition of a fraction of the metal intermediate could also be occurring over extended reaction times. Similar trends in chelation rates were observed for $bpyPCL_2$ and $bpyPS_2$ macroligands (Table 1, compound sets **2** and **5**). With these two systems, the amount of time needed to reach the maximum ϵ_{MLCT} increased over the series with increasing molecular weight. The maximum attainable ϵ_{MLCT} values for all polymeric $Ru(bpy)_2Cl_2$ complexes **1**−**6** are lower than that reported for a small molecule analogue (e.g., $Ru(bpy)_2Cl_2 \cdot 3H_2O$ in CH_2Cl_2: λ_{max} (ϵ) = 555 nm (9200 M^{-1} cm^{-1})).[29]

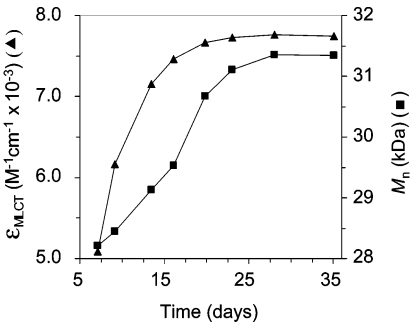

Figure 5. Molar absorptivity (ϵ_{MLCT}) (▲) and M_n (■) as a function of reaction time in the generation of Ru(bpyPMMA)$_2$Cl$_2$, **3** (bpyPMMA: M_n = 21 360, M_w = 23 250, PDI = 1.09).

Monitoring the molecular weights of the polymeric Ru(II) complexes as they formed also provided insight into optimum reaction times. For Ru(bpyPMMA)$_2$Cl$_2$ **3** (bpyPMMA M_n = 21 360) both the molecular weight and ϵ_{MLCT} (λ_{max} = 562 nm) reached a plateau after a reaction time of ~25 days (Figure 5). This contrasts with a reaction time of less than 1 day for the chelation of 2 equiv of nonpolymeric 4,4′-dimethyl-2,2′-bipyridine to Ru(DMSO)$_4$Cl$_2$ under similar conditions. Molecular weight measurements for the polymeric complex suggested somewhat inefficient chelation, as the maximum M_n of 31 400 is lower than the calculated molecular weight (21 360 × 2 = 42 720). However, this discrepancy may be, in part, a consequence of determining the molecular weight data for this star-shaped sample vs linear PMMA standards. Though normally helpful in this regard, MALLS measurements provided erroneous data for Ru(bpyA$_n$)$_2$Cl$_2$ complexes **1**−**6** because they absorb in the region of the laser wavelength (λ = 633 nm).

Solvent also plays a role in reaction kinetics for different polymer chains. For example, the chelation of bpyPEG$_2$ to Ru(DMSO)$_4$Cl$_2$ to form Ru(bpyPEG$_2$)Cl$_2$, **6**, proceeded at a much faster rate (k_{obs} = 0.20 vs k_{obs} ~ 0.05) when a 15:1 mixture of DME:CHCl$_3$ was utilized in place of DME alone. In fact, in the absence of CHCl$_3$, after ~15 days, the major product was the mono-bpy ruthenium complex Ru(bpyPEG$_2$)(DMSO)$_2$Cl$_2$ (λ_{max} = 402 nm).[30] Though problematic for bis(bpy) complex formation, it may be possible to exploit mono-bpy intermediates and the reduced rate in DME to prepare Ru(II) complexes with three different kinds of bipyridyl macroligands[31,32] for increased architectural complexity. For example, PMCs with three or more blocks could lead to even more elaborate microstructures with selectively positioned chromophores for probing morphology. Responsive materials of this type present new possibilities for fundamental studies in block copolymer physics and more nearly approximate the sophisticated hierarchically organized responsive metal-containing materials found in natural systems. A comparison of solubility parameter values (δ) for PEG (21.3),[33] DME (17.6), and CHCl$_3$ (19.0) may offer one explanation for the reduced rate.[19] The closer the solubility parameter value of the polymer chain is to the solvent, the greater the miscibility. Therefore, CHCl$_3$ is a better solvent for PEG, and in it, the bipyridine binding site may be more accessible for coordination. A similar observation was made for PMMA samples **3** and **4**—a DME/CHCl$_3$ solvent mixture resulted in a faster rate of chelation relative to reactions run in DME alone.

A comparison of bpyPCL$_2$, bpyPS$_2$, and bpyPMMA$_2$ in the mixed 15:1 DME:CHCl$_3$ solvent system indicated that chelation rates for macroligands of similar molecular weights (10.4, 9.9, and 12.2 kDa, respectively) were comparable. For example, the rate for bpyPCL$_2$ (k_{obs} = 1.05; M_n = 10 370) was only slightly faster than that for bpyPS$_2$ (k_{obs} = 1.03; M_n = 9900); nonetheless, rates again followed δ value trends (DME, 17.6;[19] PCL, 19.7;[33] PS, 21.1[34]), with more dramatic differences observed for bpyPEG$_2$. Specifically, a bpy-centered PEG chain (M_n = 3700) chelated to Ru(II) centers (Table 1, **6**) at a significantly slower rate (k_{obs} = 0.20) than a bpyPMMA$_2$ macroligand (k_{obs} = 0.89) of double the molecular weight (M_n = 6600) (Table 1, **4**). Aside from solubility parameter differences for these materials, PEG ether groups may function as competitive chelating ligands for the metal. This, too, could account for slower product formation in reactions with bpyPEG$_2$.

The location of the bipyridine ligand within the polymer chain correlated with rate differences as well. The chelation of bpyPMMA$_2$ (M_n = 6600) reached a maximum ϵ value twice as fast as that of bipyridine end-functionalized polymer, bpyPMMA, of similar molecular weight (M_n = 7000) (Table 1, compounds **4** and **3**, respectively). However, the maximum molar absorptivity for the bpy end-functionalized PMMA sample (9430 M^{-1} cm^{-1}) was much larger than that calculated for the 6.6 kDa bpyPMMA$_2$ macroligand (6540 M^{-1} cm^{-1}). This suggests that after a certain point chelation of the bpy-centered polymer "stops" while the reaction continues for bpyPMMA. It required 5 days for the difunctional macroligand to reach a molar absorptivity of 6540 M^{-1} cm^{-1}, while the monoarmed macroligand reached a similar ϵ value (6390 M^{-1} cm^{-1}) after just over 3 days. A similar result was observed when bpyPS (M_n = 19 500) and bpyPS$_2$ (M_n = 18 200) were compared in the formation of Ru(bpyPS)$_2$Cl$_2$, **1**, and Ru(bpyPS$_2$)Cl$_2$, **2**, respectively; the monofunctional sample reached the limit of bpyPS$_2$ chelation (~3700 M^{-1} cm^{-1}) after only 1 day vs 4 days for the bpy-centered macroligand. In summary, chelation of bpy end-functionalized polymers is faster and more efficient than that of macroligands with bpy at the center of the chain.

Synthesis of Ru(bpyA$_n$)$_2$(bpyB$_m$) Products. Ruthenium bis(bpy) dichloride complexes, Ru(bpyA$_n$)$_2$Cl$_2$, were subsequently dehalogenated in order to prepare more reactive solvento reagents, Ru(bpyPS$_n$)$_2$(DME), for the addition of a third polymeric bpy ligand to form heteroarm stars. These labile intermediates have previously been prepared by stirring Ru(bpyPS$_n$)$_2$Cl$_2$ precursors (**1** and **2**) with excess AgPF$_6$ in a MeOH/DME solvent mixture at 90 °C for 1 day.[27] While this methodology was effective for the chelation of relatively inert PS ligands, it did not extend well to the preparation of solvento intermediates with Ru PCL and PMMA polymers, which have more reactive ester linkages. By monitoring the dehalogenation reaction by GPC, the effect of reaction conditions on the polymer backbone was determined. For both PCL and PMMA, low molecular weight shoulders emerged after approximately 3 h and polydispersities (PDIs) steadily increased. The formation of lower molecular weight chains may be due to silver-mediated transesterification between the polymer backbones and MeOH. Indeed, when dehalogenation reactions were run in the absence of MeOH with only DME solvent, low molecular weight contaminants were not detected until reaction times of 1 day, although

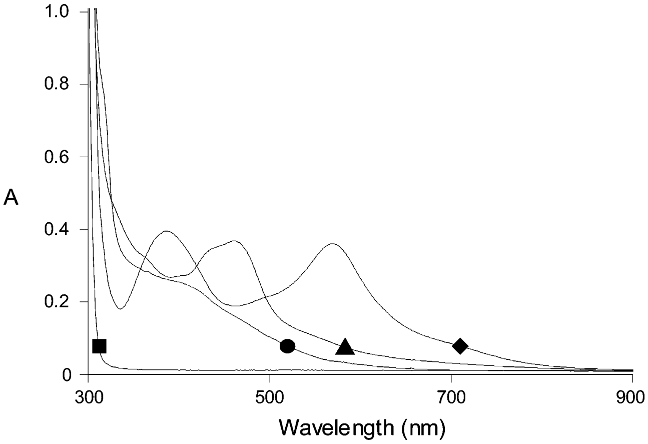

Figure 6. Overlay of UV/vis absorption spectra for Ru(bpyPCL$_2$)$_2$(bpyPS$_2$)$^{2+}$ (▲), the dehalogenated intermediate, Ru(bpyPCL$_2$)$_2$(DME) (●), the precursor bis(bpy) dichloride, Ru(bpyPCL$_2$)$_2$Cl$_2$ (◆), and the corresponding macroligand, bpyPCL$_2$ (■).

PDIs continued to increase beyond this time. UV/vis absorption spectra of aliquots were monitored for the disappearance of the Ru(bpyPS$_n$)$_2$Cl$_2$ MLCT band at ~530 nm and the emergence of features attributable to the DME intermediate[20,21] (see Figure 6). By coupling GPC analysis with UV/vis absorption measurements, a dehalogenation reaction time of 1 h was determined to be sufficient for all samples in DME solvent at 90 °C, even for the bpyPS$_n$ macroligands. After this time, there was no evidence of a Ru(bpyA$_n$)$_2$Cl$_2$ absorption band in the 530 nm regime, and little to no broadening of molecular weight distributions was observed.

Once routes to Ru(bpyA$_n$)$_2$(DME) samples were developed, a second kind of macroligand was added to produce Ru(bpy)$_3$-centered heteroarm stars, **7**−**10**. Molecular weight data for these final polymeric Ru tris(bpy) products, corresponding Ru(bpyA$_n$)$_2$(DME) intermediates and individual bpy macroligands, are provided in Table 2. Aliquots were again taken throughout the course of the reactions for analysis by UV/vis spectroscopy. Plots of the extinction coefficient at $\lambda_{\max}$ (~460 nm) as a function of time for the formation of [Ru(bpyPCL$_2$)$_2$(bpyPS$_2$)]$^{2+}$, **7**, from Ru(bpyPCL$_2$)$_2$(DME) ($M_n = 19\,800$) and bpyPS$_2$ ($M_n = 18\,220$) (▲) and for [Ru(bpyPCL$_2$)$_2$(bpyPEG$_2$)]$^{2+}$, **8**, from Ru(bpyPCL$_2$)$_2$(DME) ($M_n = 19\,800$) and bpyPEG$_2$ ($M_n = 3720$) (■) in DME at 120 °C are compared in Figure 7. The extinction coefficients steadily increase until they reach a plateau at reaction times of ~12 days for **7** and ~10 days for **8** (i.e. times where data points used to determine k_{obs} begin to deviate from linearity in the regression analyses). Like Ru(bpyA$_n$)$_2$Cl$_2$, this is another example where reaction rates for bpyPEG$_2$ macroligands in DME are slower than for bpyPS$_2$ ones of much higher molecular weight. For an overlay of the UV/vis absorption spectra for **7**, the dehalogenated intermediate, Ru(bpyPCL$_2$)$_2$(DME), the bis(bpy) dichloride (**5**), and the corresponding macroligand, bpyPCL$_2$, see Figure 6.

Other Ru(II)-centered complexes with two bpyPS ligands and either one polyether or polyester ligand were synthesized by combining Ru(bpyPS)$_2$(DME) with bpyPLA$_2$ or bpyPEG$_2$, to form **9** and **10**, respectively. The resulting heteroarm stars were characterized by GPC equipped with in-line diode array UV/vis detection. A representative overlay of the GPC traces for [Ru(bpyPS)$_2$(bpyPLA$_2$)]$^{2+}$, **9**, the bis intermediate, [Ru(bpyPS)$_2$(DME)]$^{2+}$, and the bpyPS macroligand subunit appears in Figure 8. The expected increase in molecular weight is apparent as the product shifts to lower elution volume. In addition, the metal-to-ligand charge-transfer (MLCT) fingerprint for the Ru(bpy)$_3$ core was evident for both [Ru(bpyPS)$_2$(bpyPLA$_2$)]$^{2+}$ (**9**) and [Ru(bpyPS)$_2$(bpyPEG$_2$)]$^{2+}$ (**10**) as well as for tris complexes [Ru(bpyPCL$_2$)$_2$(bpyPS$_2$)]$^{2+}$ (**7**) and [Ru(bpyPCL$_2$)$_2$(bpyPEG$_2$)]$^{2+}$ (**8**). The fact that the absor-

Table 2. Summary of GPC Molecular Weights[a] for Representative Ruthenium-Centered Heteroarm Stars, the Corresponding Ru(II) Solvento Intermediates, and Macroligand Precursors

polymer	M_n (kDa)[a]	M_w (kDa)[a]	M_w/M_n[a]
bpyPCL$_2$	12.3 (10.4)	15.5	1.26
bpyPS$_2$	18.2	22.4	1.23
[Ru(bpyPCL$_2$)$_2$(DME)]$^{2+}$	19.8	23.4	1.18
[Ru(bpyPCL$_2$)$_2$(bpyPS$_2$)]$^{2+}$, **7**	34.5	38.1	1.10
bpyPCL$_2$	12.3 (10.4)	15.5	1.26
bpyPEG$_2$	3.7[b]		1.15[b]
[Ru(bpyPCL$_2$)$_2$(DME)]$^{2+}$	19.8	23.4	1.18
[Ru(bpyPCL$_2$)$_2$(bpyPEG$_2$)]$^{2+}$, **8**[c]	23.2	27.6	1.19
bpyPS	18.3	21.3	1.16
bpyPLA$_2$	25.3	26.0	1.03
[Ru(bpyPS)$_2$(DME)]$^{2+}$	31.6	36.5	1.16
[Ru(bpyPS)$_2$(bpyPLA$_2$)]$^{2+}$, **9**[d]	51.5	59.5	1.15
bpyPS	18.3	21.3	1.16
bpyPEG$_2$[e]	8.7	10.1	1.17
[Ru(bpyPS)$_2$(DME)]$^{2+}$	31.6	36.5	1.16
[Ru(bpyPS)$_2$(bpyPEG$_2$)]$^{2+}$, **10**[f]	38.1	43.6	1.15

[a] Determined using MALLS/RI detection. Values in parentheses were determined by ^{1}H NMR spectroscopic analysis. [b] Molecular weight data provided for commercially available poly(ethylene glycol), monomethyl ether (vs PEG standards). [c] Estimated using the dn/dc value for PCL (0.056 mL/g). [d] Calculated using a dn/dc of 0.107 mL/g.[24] [e] Measured vs PS standards. [f] Estimated using the dn/dc value for PS (0.145 mL/g).

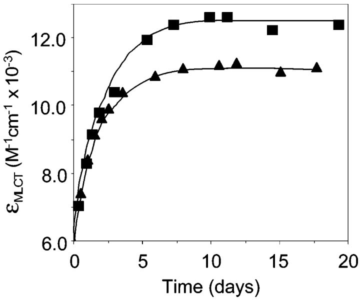

Figure 7. Molar absorptivity (ϵ_{MLCT}) as a function of time for the formation of [Ru(bpyPCL$_2$)$_2$(bpyPS$_2$)]$^{2+}$, **7** (▲), and [Ru(bpyPCL$_2$)$_2$(bpyPEG$_2$)]$^{2+}$, **8** (■).

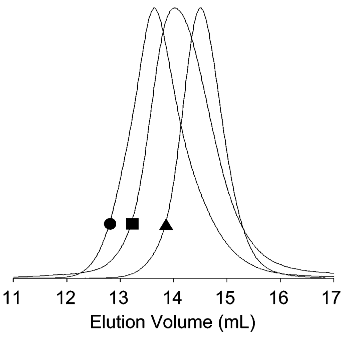

Figure 8. Overlay of the GPC traces for [Ru(bpyPS)$_2$(bpyPLA$_2$)]$^{2+}$ (**9**, $M_n = 51\,500$) (●), [Ru(bpyPS)$_2$(DME)]$^{2+}$ ($M_n = 31\,600$) (■), and bpyPS ($M_n = 18\,300$) (▲). The corresponding bpyPLA$_2$ macroligand $M_n = 25\,300$ (GPC not shown).

bance coincides with the eluting polymer peak confirms that the chromophore is bound to the polymer chains.

Molecular weight data collected in Table 2 for complexes **7**−**10** illustrate that chelation of 2 equiv of bpyA_n, followed by dehalogenation, produced [Ru(bpyA_n)$_2$(DME)]$^{2+}$ products that are roughly double the molecular weight measured for bpyA_n. Addition of the second kind of bpy macroligand (bpyPS$_2$ for **7**; bpyPEG$_2$ for **8** and **10**; bpyPLA$_2$ for **9**) likewise yielded materials with molecular weights that increased in the expected ways. For both solvento intermediates and tris products, measured molecular weights are slightly lower than values estimated by addition of the molecular weights of the component parts. Reasons for these discrepancies may stem from underestimation of star polymer molecular weights when they are determined vs linear standards or from the fact that molecular weights were estimated using d*n*/d*c* values corresponding to the majority block. Moreover, because it is difficult to separate starting materials from products when both are polymers, reaction products are analyzed together with any residual starting materials. The absence of shoulders in GPC traces and UV/vis spectral data suggests that these chelations are quite efficient and unreacted starting materials are minimal. Nonetheless, any residual starting materials could serve to depress the average molecular weights that are measured. As is expected for reactions that couple chains to form block copolymers, the PDIs for homoblock copolymer solvento star polymer intermediates and heteroarm tris(bpy) products are typically comparable to or less than macroligand starting materials.[35]

Conclusions

Ruthenium-centered polymeric metal complexes of variable structure and architecture were synthesized by combining different bpy macroligands. The extension of these synthetic methods to other bpy macroligands in an ever expanding “tool kit” will lead to new functional materials of increasing complexity. For example, synthesis of a Ru tris(bpy) analogue with three different bpy subunits, some of which are di- or triblock copolymers, could lead to assembly structures with elaborate and as yet undescribed morphologies. The selective positioning of luminescent metals in discrete locations within these complex film architectures could serve as a useful probe of periodic structure. The use of Ru and other block copolymer metal complexes in this capacity and as dopants in photonic crystals will serve as the subjects of future investigations.

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(24) Molecular weight data estimated using a d*n*/d*c* value of 0.107 mL/g measured by a single injection method that assumed 100% mass recovery from the columns.

(25) The molecular weight of the commercially available monomethylated ether, poly(ethylene glycol) 2000, was obtained from Fluka ($M_n = 1768$), and the M_n of the bpyPEG$_2$ macroligand was calculated therefrom.

(26) Molecular weight data estimated using the d*n*/d*c* value for PS (0.145 mL/g) in $CHCl_3$.

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