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Metal-Centered Heteroarm Polymers: Chelation of Polystyrene-*b*-polycaprolactone with a Bipyridine Donor at the Block Junction

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Introduction. The development of convenient syntheses of block copolymers and systematic control over their properties remains a goal in materials research. Particularly interesting are the microstructures that block copolymers form[1]—spherical, cylindrical, lamellar, and even more elaborate ones—and how this microphase separation is related to polymer composition and architecture.[2] Sophisticated nanoscale block copolymer assemblies are being exploited in numerous applications including waveguides,[3] electrode coatings,[4] electronic and optoelectronic devices,[5] as biomineralization mimics,[6] and for lithography.[7]

The combination of living/controlled polymerization with metal chelation permits even greater diversity in block copolymer synthesis. Using a modular metal template approach, different metals and macroligand subunits may be readily interchanged, resulting in the formation of stimuli responsive materials with site-isolated metal centers. If the metal resides in a specific location in the molecular architecture, this correlates with discrete positioning of metals in block copolymer morphologies. For example, star block copolymers resulting from bpy$(AB)_n$[8] coordination (bpy = bipyridine; AB = block copolymer) form assemblies with metals embedded in one microdomain and not the other,[9] whereas systems with donor groups at the block junctions position metals at the domain boundaries. The latter have been achieved by chelating two different kinds of macroligand to inert metal centers (e.g., bpyA_n and bpyB_n to Ru(II)).[10] Because labile systems, on the other hand, are likely to exchange ligands, it may be impossible to make distinct products by this route. Here we describe an alternative approach to metal-centered heteroarm polymers that addresses this issue and extends our work with homofunctional halide[11] and alcohol[12] bipyridyl initiators. Inspired by the work of Jérôme[13] and Sogah,[14] a dual functional ligand initiator, 4-chloromethyl-4′-hydroxymethyl-2,2′-bipyridine, bpy(CH_2Cl)(CH_2OH), was used in a tandem atom transfer radical polymerization (ATRP)−ring-opening polymerization (ROP) sequence to generate polystyrene (PS)−polycaprolactone (PCL) copolymers with bpy binding sites at the block interface. The coordination of bpy(PS)(PCL) subunits to Ru, Fe, and Pt centers to form linear and star-shaped structures is described.

Results and Discussion. Previously, we demonstrated that polystyrene macroligands can be generated from 4,4′-bis(chloromethyl)-2,2′-bipyridine with high molecular weight control using ATRP.[11] Similarly, 4,4′-bis(hydroxymethyl)-2,2′-bipyridine served as a viable initiator for the ROP of ϵ-caprolactone and lactide monomers to produce degradable polyesters with bipyridine binding sites.[12] Because these two methods are orthogonal, they may be combined without protection and activation of an initiating functionality, or modification of a propagating end,[15] as is often required in other block copolymer syntheses. Thus, the dual functional initiator bpy(CH_2Cl)(CH_2OH), **1**, which was prepared in 23% yield[16] by reacting 4,4′-bis(chloromethyl)-2,2′-bipyridine with aqueous calcium carbonate in refluxing dioxane,[17] was subjected to various ATRP and ROP reaction sequences and conditions (e.g., catalyst, solvent, temperature) in order to optimize molecular weight control.

Table 1. Summary of GPC Molecular Weights[a] for Representative bpy-Functionalized PS and PCL Macroligands

polymer	M_n (kDa)	M_w (kDa)	M_w/M_n
bpy(CH_2OH)(PS), **2**	6.0	7.4	1.23
bpy(CH_2Cl)(PCL), **3**	5.5	6.5	1.19
bpy(PS)(PCL), **4a**[b]	57.3	64.7	1.13
bpy(PCL)(PS), **4b**[c]	161.4	225.0	1.39

[a] Molecular weights were determined by gel permeation chromatography (GPC) ($CHCl_3$, 25 °C, 1.0 mL/min) using multiangle laser light scattering (λ_{max} = 633 nm, 25 °C) and refractive index (λ_{max} = 633 nm, 40 °C) detection. The incremental refractive indices (d*n*/d*c* values) of the respective homopolymers (PS = 0.145 mL/g; PCL = 0.056 mL/g) were used unless otherwise indicated. [b] The d*n*/d*c* value for this copolymer was estimated to be 0.063 mL/g by a single injection method that assumed 100% mass recovery from the GPC columns. [c] The d*n*/d*c* value for PS was used in the calculation of molecular weight.

Because initiators with pendant hydroxyl groups are compatible with ATRP,[18] extension of CuBr/HMTETA-catalyzed methodology to the unsymmetrical, dual-functional initiator **1** proved relatively straightforward. A polystyrene sample, bpy(CH_2OH)(PS), **2**, prepared by this method exhibited a narrow polydispersity (Table 1). Tin-mediated polymerizations of lactide and ϵ-caprolactone monomers that were previously effective with bpy$(CH_2OH)_2$ initiators[12] were also attempted with **1**; however, no polymer growth was observed. These procedures, which involved reaction of the chloro alcohol with $Sn(Oct)_2$ (Oct = 2-ethylhexanoate) in bulk monomer at ∼110−130 °C, may promote intermolecular ether formation or bipyridine N-alkylation. The appearance of additional bpy peaks in the ^1H NMR spectrum of the crude product lends support to these hypotheses. In an effort to circumvent any problems associated with ligand sensitivity to elevated temperatures, room temperature aluminum-mediated polymerizations were tested.[19] This procedure proved to be an attractive alternative as chloride-functionalized poly(ϵ-caprolactone), bpy(CH_2Cl)(PCL), **3**, was successfully synthesized (Scheme 1).

End-functionalized homopolymers, bpy(CH_2OH)(PS), **2**, and bpy(CH_2Cl)(PCL), **3**, serve as macroinitiators for subsequent reactions, namely ϵ-caprolactone polymerization from the alcohol of **2**, or generation of PS from the chloride of **3**. Because electrophilic chloride functionalities may be more sensitive than alcohols under the reaction conditions, we suspected that growing the polystyrene block first, followed by the poly(ϵ-caprolactone) chain, would form the targeted diblock more

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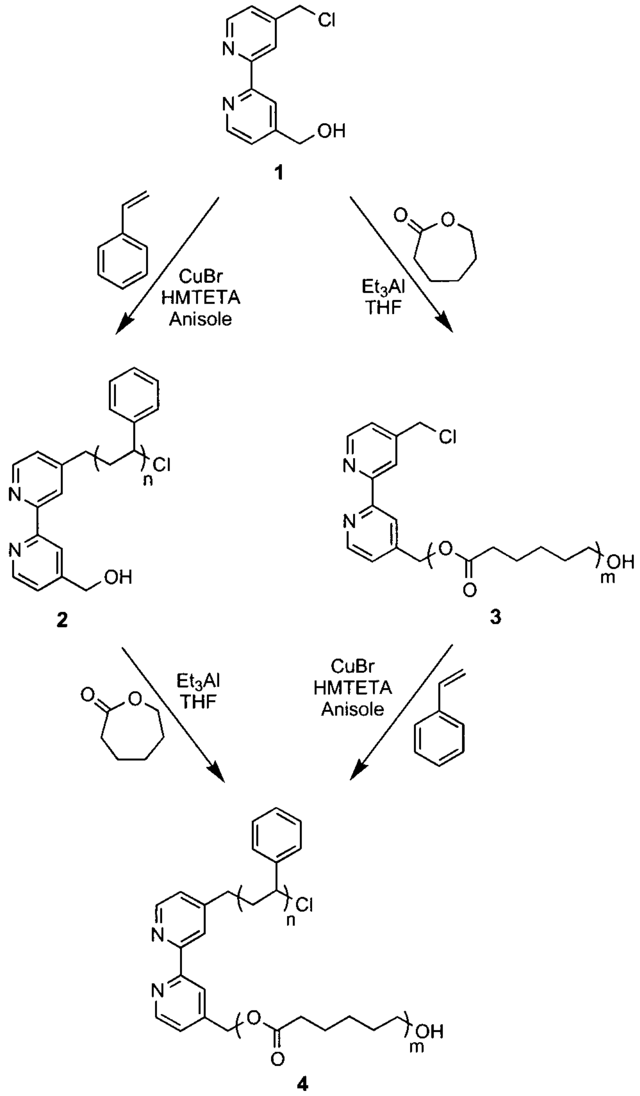
Scheme 1. Two Routes for the Preparation of a bpy-Centered PS−PCL Diblock, bpy(PS)(PCL), 4a, and bpy(PCL)(PS), 4b[8]



efficiently. However, attempts to prepare the product in this manner were initially unsuccessful and usually resulted in the adventitious growth of low molecular weight poly(ϵ-caprolactone) chains from something other than the PS macroinitiator. After adopting a more rigorous purification protocol to remove contaminant Cu salts[20] and/or residual MeOH, ϵ-caprolactone was productively polymerized from **2** to yield the targeted bpy-centered diblock, bpy(PS)(PCL), **4a**[8] (Table 1). Comparison of the GPC traces indicated both consumption of macroinitiator and the anticipated increase in molecular weight for the diblock product (Figure 1). Further, the ^{1}H NMR spectrum contains resonances corresponding to the backbones of both polymer blocks. By integrating distinct peaks (i.e., PS Ar**H** and PCL OC**H**$_2$) and factoring in the M_n of the PS macroinitiator measured by GPC (6000 g mol^{-1}), a molecular weight of 59 500 g mol^{-1} was calculated for the diblock, which is consistent with that measured by GPC (57 300 g mol^{-1}).

The chloride-functionalized PCL homopolymer was also used as a macroinitiator for the growth of a polystyrene second block. For one trial, the homopolymeric polyester ($M_n = 5500$, $M_w = 6500$, PDI = 1.19), **3**, initiated styrene polymerization to generate a diblock product ($M_n = 161\,400$, $M_w = 224\,900$, PDI = 1.39) of higher molecular weight than anticipated on the basis of monomer loading ($M_n = 10\,400$). This discrepancy correlates with only ~6% viable chloride active sites remaining after PCL polymerization. Given the relatively high reactivity of the bipyridyl chloride functionality, this is perhaps not unexpected. The bimodal GPC trace for the diblock product also indicated the presence of a significant amount of inactive macroinitiator. Interestingly, this impurity could be separated from the product by taking advantage of the solubility differences of the two components; acetonitrile selectively dissolved the polycaprolactone, which was removed from the desired PCL−PS diblock by filtration. The higher polydispersity index of 1.39 for bpy(PCL)(PS), **4b**,[8] suggests diminished control for this sequence relative to bpy(PS)(PCL), **4a** (PDI ~ 1.13), in which the PS chain was grown first. An attempt to simultaneously prepare the diblock copolymer in a one-pot reaction from the dual-functional initiator also resulted in uncontrolled polymerization.

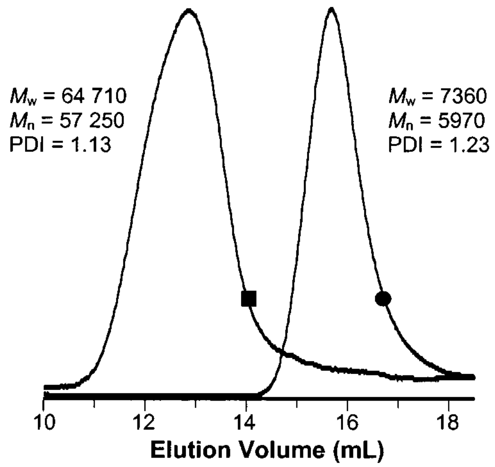
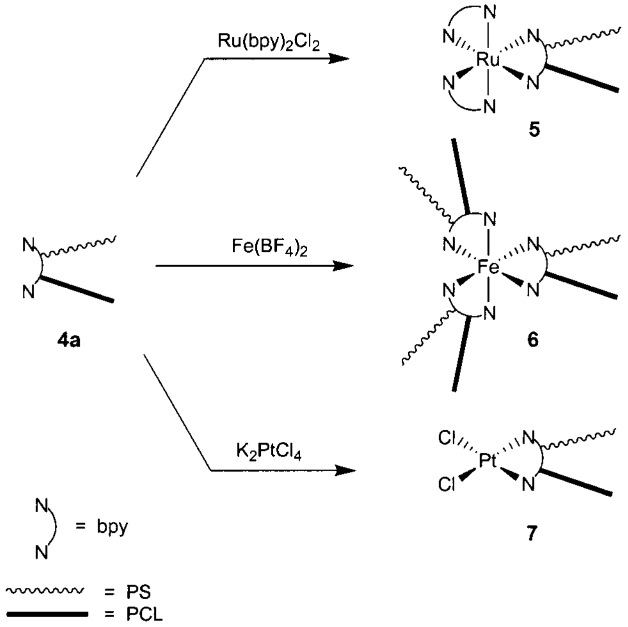


Figure 1. Overlay of the GPC traces for a bpy(PS)(PCL) diblock, **4a** (■), and the bpy(CH$_2$OH)(PS) macroinitiator, **2** (●), from which it was grown.

Metal Chelation. The utility of the metal template approach to block copolymers was previously demonstrated in the synthesis of ruthenium-centered heteroarm stars by sequential coordination of bpyPS$_n$ and then bpyPMMA$_n$ homopolymeric macroligands.[10] Although the synthesis of block copolymer macroligands with metal binding sites at the block junction is more difficult than their bpy-centered homopolymer counterparts, they were worth pursuing because coordination of just one ligand provides a metal-centered block copolymer in a single step. This was demonstrated with the chelation of bpy(PS)(PCL), **4a**, to a dehalogenated Ru(bpy)$_2$Cl$_2$ complex to yield $[\mathrm{Ru(bpy)_2\{bpy(PCL)(PS)\}}]^{2+}$, **5** (Scheme 2), which exhibited the expected MLCT red-orange chromophore at ~460 nm by UV/vis analysis. The presence of a luminescent block connection point may assist in the determination of polymer microstructure through microscopy. Studies of this nature are underway.

Because of the large stability constant for iron tris(bpy) complexes and the lability of these systems, it may not be possible to generate iron-centered heteroarm stars uniquely by using two or more different homopolymer macroligands. That is, in contrast to Ru(II), for Fe(II) it is difficult to stop at a $[\mathrm{M(bpyA}_n)_2\mathrm{X}_2]^{2+}$ intermediate.[21] Furthermore, even if $[\mathrm{Fe(bpyA}_n)_2(\mathrm{bpyB}_n)]^{2+}$ could be formed, ligand exchange could produce

Scheme 2. Chelation of bpy(PS)(PCL), 4a, to M(II) Salts To Generate $[Ru(bpy)_2\{bpy(PS)(PCL)\}]^{2+}$, 5, $[Fe\{bpy(PS)(PCL)\}_3]^{2+}$, 6, and $Pt\{bpy(PS)(PCL)\}Cl_2$, 7



$[Fe(bpyA_n)(bpyB_n)_2]^{2+}$ and the respective homopolymer stars, $[Fe(bpyA_n)_3]^{2+}$ and $[Fe(bpyB_n)_3]^{2+}$. However, when bpy-centered diblocks, bpy(A)(B), are used, homoleptic heteroarm stars are readily accessible, even for labile metal ions. To illustrate this point, an iron-centered six-arm star with three PS and three PCL chains, **6**, was generated through reaction of three bpy(PS)(PCL) diblock subunits, **4a**, with $Fe(BF_4)_2$ (Scheme 2). The red-violet color corresponding to an MLCT absorbance of ~530 nm appeared immediately. Because the macroligand is unsymmetrical, both facial and meridional isomers are possible for the topologically chiral (i.e., Λ and Δ) metal centers. It remains to be seen whether energetic preferences for polymer chain assembly are transmitted to the metal center, biasing coordination toward a *fac* or *mer* arrangement. UV/vis analysis of the block copolymer in chloroform solution indicated efficient macroligand chelation; the extinction coefficient of 9284 M^{-1} cm^{-1} (λ_{max} = 533 nm) was in close agreement with that for the dimethyl bpy small molecule analogue, $[Fe(bpyMe_2)_3]^{2+}$, where $bpyMe_2$ = 4,4′-dimethyl-2,2′-bipyridine ($\epsilon = 9300$ M^{-1} cm^{-1}).[22]

Because of the relatively inert nature of $Pt(bpy)Cl_2$ complexes, they can be generated free of bis-bpy impurities, while at the same time retaining the potential for further substitution of the chloride groups. The bpy-centered diblock, bpy(PS)(PCL), **4a**, was stirred with the platinum salt, K_2PtCl_4, to form a yellow $Pt\{bpy(PS)(PCL)\}Cl_2$ complex, **7**. The absorption spectrum in $CHCl_3$, λ_{max} (ϵ) = 399 nm (3012 M^{-1} cm^{-1}), was in agreement with that reported for $Pt(bpy)Cl_2$, λ_{max} (ϵ) = 398 nm (3100 M^{-1} cm^{-1}).[23] Further elaboration of $Pt(bpy)Cl_2$ at the block connection point should be possible by reaction with additional ligands (or macroligands), attachment to surfaces, or through interaction with biomolecules.

Conclusions. Block junctions of linear PS−PCL polymers were decorated with inert, luminescent $[Ru(bpy)_3]^{2+}$ chromophores and more reactive $Pt(bpy)Cl_2$ fragments. Homoleptic, labile iron-centered heteroarm stars were generated by the chelation of bpy-centered PS−PCL diblock subunits. Bpy(PS)(PCL) was best prepared by growing the PS block first from the more reactive halide, followed by generation of the PCL block from the OH site. Elaboration of this modular synthesis concept to other polymer compositions and block architectures as well as detailed studies of the properties of these systems will serve as subjects of future reports.

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Supporting Information Available: Experimental details for compounds **1**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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