

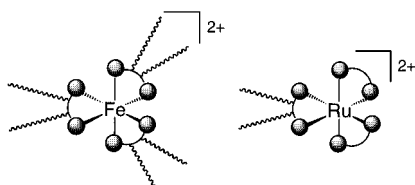
Synthesis of Metal-Centered Star-Shaped Polyoaxolines Using Fe(II) and Ru(II) Tris-bipyridine Derivatives as Multifunctional Initiators

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Due to their varied structures, physical properties, and reactivities, metal complexes often play key roles in macromolecules.¹ They serve as templates for self-assembly,² as cross-links, or as part of the polymer backbone. Since metal ions may be labile or inert, may be electron donors or acceptors, and are often chromophoric, magnetic, or conducting centers, they allow for the introduction of a variety of features into polymers. Thus, metal-containing materials are of interest as sensors, as storage and switching devices,³ as supported catalysts,⁴ and as models of structural proteins and enzymes,^{4a,5} among other uses in nanotechnology. Although it is well documented that living polymerizations allow for exquisite control over molecular weight (MW) and architecture in organic polymers,⁶ there have been few reports of their extension to transition metal-containing materials. In a few cases, metal-containing monomers have been used for living polymerizations⁷ and monodisperse polymers have been functionalized with metals subsequent to polymerization.⁸ However, the use of metalloinitiators or terminators as structural templates in living polymerization reactions remains largely unexplored.^{7,9}



Herein is described the synthesis of metal-centered star-shaped polymers (MCSPs), namely, Fe(II) and Ru(II) tris-bipyridine-(bpy)-centered polyoaxolines by a multifunctional initiator

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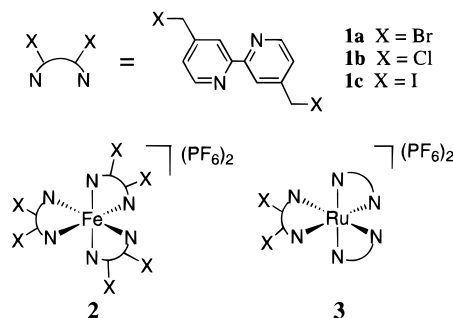
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strategy. It will also be demonstrated that the reactivity of [Fe-(bpy)₃]²⁺ may be exploited to produce dramatic changes in the properties of Fe(II) core materials. Since living oxazoline polymerizations are initiated by electrophilic reagents (e.g., benzyl bromide)¹⁰ and are run in polar CH₃CN solutions, they were expected to be compatible with cationic metal complex cores. Thus, the ligand (4,4'-bromomethyl)-2,2'-bipyridine (bpyBr₂, **1a**) and some of its complexes (**2a** and **3a**)^{11,12} were selected as model systems for testing the metalloinitiator approach (eq 1). Complexes **2** and **3** probe the compatibility



of the polymerizations with both labile and inert metal centers and with different numbers of functionalities at the cores. Also, materials of these metal complexes are of great interest for their reactivities and photophysical properties.^{5d,e,13} The ligand **1a**¹² was used to prepare the labile hexafunctional compound [Fe-(bpyBr₂)₃](PF₆)₂ (**2a**); however, the inert, difunctional complex [Ru(bpy)₂(bpyBr₂)](PF₆)₂ (**3a**) proved difficult to access in sufficiently high purity for use as an initiator. Instead, the less-reactive dichloride analog **1b**¹² was used to prepare a difunctional Ru(II) complex (**3b**), which was converted to the diiodide initiator **3c** (X = I) *in situ* using NaI.^{10a} The Fe(II) preinitiator **2b** was also prepared and treated in an analogous manner for comparison.

(7) Here, “metalloinitiator” refers to cases where the metal complex remains behind as part of the dead or nonliving end of the polymer chain. This may be contrasted with coordination polymerizations wherein metals are essential components of the living chain end. For examples of both concepts, as well as the use of metal-containing monomers, see: Schrock, R. R. In *Ring Opening Polymerization*; Brunelle, D. J., Ed.; Hanser: Munich, 1993; Chapter 4.

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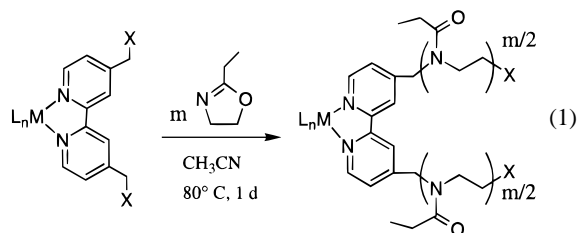
(9) Another class of monodisperse macromolecules are metal-containing dendrimers. These highly branched molecules are typically prepared by self-assembly or iterative routes. In contrast, star polymers possess linear arms and are accessed in a single step from multifunctional reagents. See: ref 2. (a) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759–833. (b) Bhyrappa, P.; Young, J. K.; Moore, J. S.; Suslick, K. S. *J. Am. Chem. Soc.* **1996**, *118*, 5708–11. (c) Ardoin, N.; Astruc, D. *Bull. Soc. Chim. Fr.* **1995**, *132*, 875–909.

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In a typical polymerization, the ligands (**1**) or the metalloinitiators (**2** and **3**) were combined with 2-ethyloxazoline in CH_3CN at 80°C for 1 day (eq 1). Analysis of the resulting polymers by ^1H NMR indicated the disappearance of the halide initiator functionalities. Glassy polymer products were obtained which retain the color of the respective initiators (UV-vis): **1**, pale yellow; **2**, violet; **3**, orange. MW data for the polymers were determined by gel permeation chromatography (GPC) (Table 1). The labile Fe star polymers fragment during GPC which allows for independent characterization of the liberated macroligand arms.¹⁴ (Polymer arms of Fe star: [monomer]/[initiator site] = 125; calcd MW = 25k; found M_w = 28k.) MW data for the Fe polymer were also obtained using multiangle laser light scattering (MALLS). (Fe star from **2c**: [monomer]/[initiator site] = 125; calcd MW = 76k; found M_w = 77k.)¹⁵ The kinetically inert Ru-centered polymer remains intact during GPC analysis, and the chromophores are detected in the eluted polymer. Low polydispersities (PDIs) were observed for all of the polymers. However, since the MWs for metal-free polymers prepared from **1** are approximately two times the anticipated values, a polymer coupling reaction may be occurring after the reaction is complete.¹⁶

In addition to developing methodologies for growing polymers from metalloinitiators, a second important goal is to identify ways in which MCSPs might be disassembled. Such "star burst" reactions which separate the metal from its macroligands are not only important for the characterization of MCSPs but also allow for their chelation to different metal centers. Metal complexation can protect sensitive functionality during polymerization. And since these reactions may be accompanied by dramatic changes in color or other physical properties, they could be important for the application of MCSPs as environmentally responsive materials. For the Fe star polymer, disassembly was achieved under a variety of different conditions (eq 2). Since the Fe(II) core polymers fragment during GPC, these materials may be sensitive to shear. In addition, aqueous basic and acidic reagents can also effect "star burst" reactions. While the Fe(II) cores remain intact upon termination of the living chains with amines,^{10b,17} reaction with aqueous K_2CO_3 yields a colorless solution with concomitant deposition of a rust-colored solid. Addition of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$

(14) In some cases, a high MW shoulder is observed with a UV-vis trace and a MW corresponding to the intact Fe star.

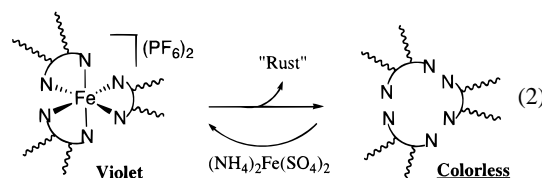
(15) Microbatch MALLS MWs represent an average for the entire sample and vary with both experimental technique and sample handling.

(16) Similar coupled products were obtained using $[\text{Zn}(\text{bpyX}_2)_3]^{2+}$ which may fragment during polymerization.

Table 1. Molecular Weight Data for Polyoxazolines^a

initiator	calcd $M_w/10^3$ ^b ([mon]/[X]) ^c	$M_w/10^3$	PDI ^d
$[\text{Fe}(\text{bpyBr}_2)_3]^{2+}$	60 (100)	16 ^e	1.06
macroligands ^f	20 (100)	14	1.27
$[\text{Fe}(\text{bpyI}_2)_3]^{2+}$	76 (125)	28 ^e	1.07
macroligands ^f	25 (125)	22	1.08
$[\text{Ru}(\text{bpy})_2(\text{bpyI}_2)]^{2+}$	40 (200)	22 ^g	1.04
bpyBr_2	25 (125)	46	1.03
bpyI_2	25 (125)	41	1.09

^a GPC MW characterization in CHCl_3 using RI and MALLS detectors. Values reported for M_w and PDIs represent averages of at least two runs. ^b Calculated molecular weight based on monomer and initiator loadings. ^c [Monomer]/[halide initiator sites]. ^d PDI = polydispersity index = M_w/M_n . Error: ± 0.02 to ± 0.06 . ^e Sample fragments after injection. Macroligand arms are detected. ^f Liberated from Fe star polymer with K_2CO_3 , in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$, 80°C , 14 h. ^g Reaction was quenched prior to completion.



to previously liberated bpy-centered polyoxazolines regenerates the distinctive violet color of $[\text{Fe}(\text{bpy})_3]^{2+}$ (UV-vis). It was also observed that films of the Fe polymer undergo thermal bleaching when heated to $\sim 210^\circ\text{C}$. This process is at least partially reversible since the violet color returns upon cooling. Blends of $[\text{Fe}(\text{bpy})_3]^{2+}$ and linear polyoxazolines exhibit a similar, even sharper violet to clear transition which is also reversible. This behavior is not observed for the $[\text{Fe}(\text{bpy})_3]^{2+}$ complex alone under the same conditions.

These results demonstrate the viability of the multifunctional initiator strategy as a way into a variety of metal-centered macromolecular structures. Extension of this concept to other metal complexes and reactions promises to broaden the scope of living polymerization methodologies and to yield new materials with intriguing and useful properties.

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Supporting Information Available: Additional experimental details, UV-vis spectra of **2** and Fe polymer, GPC data vs PS standards, GPC chromatogram, and Zimm plot of Fe polymer with reports (10 pages). See any current masthead page for ordering and Internet access instructions.

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