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Polymerization of 2-Ethyl-2-oxazoline Using Di-, Tetra-, and Hexafunctional Ruthenium Tris(bipyridine) Metalloinitiators

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ABSTRACT: Ruthenium reagents with two, four, and six chloromethyl functionalities, $[(bpy)_nRu\{bpy(CH_2Cl)_2\}_{3-n}](PF_6)_2$ ($n = 0-2$), were employed as multifunctional metalloinitiators for the cationic polymerization of 2-ethyl-2-oxazoline to generate orange, glassy polymers with narrow molecular weight (MW) distributions. MWs were determined by GPC vs PMMA standards and for selected samples by GPC with multiangle laser light scattering (MALLS) detection. In-line diode array UV/vis spectroscopic analysis coupled with GPC MW determination confirms the presence of $[Ru(bpy)_3]^{2+}$ chromophores in the eluting polymers. Polymers are luminescent, and they exhibit thermal properties analogous to the metal-free PEOX counterparts ($T_g \sim 54$ °C; onset of thermal decomposition at 365−385 °C). Unlike reactions run with a labile hexafunctional Fe initiator, reactions wherein MWs > 100K and degrees of polymerization (dp) >200 are attainable, Ru-centered polymers reach an upper MW limit of ~25K regardless of the number of functionalities on the initiator (difunctional, dp = ~125; tetrafunctional, dp = ~63; hexafunctional, dp = ~42 per initiator site). High monomer loadings and concentrations and elevated reaction temperatures were explored to surmount this barrier, and control experiments using different combinations of components found in typical Ru reaction mixtures are also described. Though M_n vs percent conversion plots are roughly linear for the Ru initiators, observed MWs are lower than expected values based on monomer/initiator loading. This may be due to poor correlation of polyoxazolines with linear PMMA standards and/or to competing chain transfer side reactions during the polymerization. Linear first-order kinetics plots were obtained. Comparison of rate constants obtained from the slopes of these plots reveals the trend expected for the targeted structures: hexa > tetra > di.

Introduction

As is clearly demonstrated by metalloproteins and enzymes, metal complexes in well-defined polymeric environments have the potential to carry out a wide range of functions as reactive and responsive materials, both individually or as molecular assemblies.[1] Though there are numerous ways of preparing metal-containing polymers,[2] there remains, however, a considerable gap between the structural and functional control observed in natural systems and that which is within the purview of the synthetic chemist, in terms of both molecular design and synthesis. The development of new and convenient approaches to metal complexes with well-defined macroligands, wherein the polymer composition, molecular weight (MW), and architecture may be readily manipulated, begins to close that gap. Moreover, gaining a better understanding of the principles governing aggregation of metal-containing macromolecules[3] allows for rational synthesis and inspires new uses for such functional assemblies.

The combination of inorganic chemistry with living polymerization offers numerous ways to address this challenge. Recently, we have explored the metalloinitiator approach to metal ions with well-defined macroligands.[4−6] Polymers are grown in a divergent fashion from suitably derivatized metal complex initiators[4,7] and are readily separated from unreacted monomer by precipitation. By varying the number of pendent initiator sites on the ligands, a wide variety of linear and star-shaped architectures are accessible.[5,6] Compositional control is achieved using different reaction mechanisms and monomers to generate a variety of homopolymer and block copolymer targets.[8] Another way of making these kinds of metal-centered macromolecules involves the chelation of metal ions to preformed polymers with tailored binding sites.[9,10] Coupling approaches have also been utilized.[11] Though metal tris(bipyridine) complexes have been employed as the test system in many of these studies, ultimately it should be possible to extend these findings to other metals and ligand sets as well.

In a preliminary account we described the use of derivatized metal tris(bipyridine) complexes as initiators for oxazoline polymerizations.[4] Though Fe(II) and other labile metal initiators are easy to prepare by chelation of metal ions to 4,4′-bis(halomethyl)-2,2′-bipyridine[12] and other bpy analogues,[13,14] more inert Ru reagents proved far more elusive. The electrophilic chloromethyl-substituted bpy ligands were not compatible with elevated temperatures and polar, nucleophilic aqueous or alcohol solvents typically required to effect ligand substitution at this more inert metal center. Milder preparations utilizing silver salts to facilitate chloride ligand removal in the presence of more labile triflate ligands or neutral chelating solvents such as DME did produce the desired functionalized Ru products; however, yields dropped considerably during purification. Difficulty in accessing Ru reagents in high yield rendered detailed study of their polymer chemistry impractical.

Despite these complications, the synthesis of Ru-centered polymers remained an important goal for a variety of reasons. First, inert metal systems were expected to maintain their structural integrity during MW characterization by standard chromatographic

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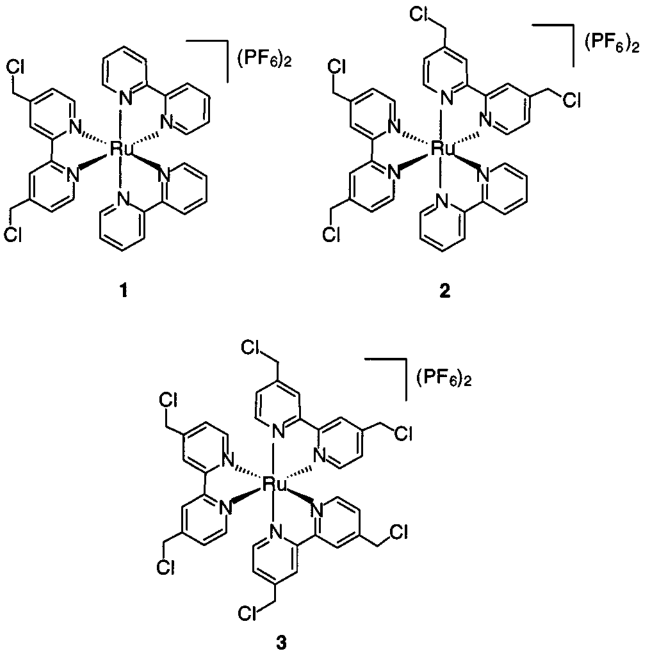


1 **2** **3**

Figure 1. Ruthenium metalloinitiators (**1**−**3**).

techniques. The metal chromophores may be tracked as the polymer elutes from the GPC column. This is in contrast to Fe and other labile metal systems that fragment partially or entirely during GPC analysis. Second, with inert metals it is possible to prepare heteroleptic complexes. Metal complexes with mixed ligand sets, some functionalized with initiator groups and some not, are of interest for tuning both the architectures and the optical properties of these types of polymer systems. Finally, Ru complexes are noted for their luminescent properties which have been previously exploited for a wide variety of applications.[15] We were especially interested in preparing chromophore-tagged amphiphilic block copolymers of different architectures for their selective insertion into membranes and for studying their assembly in thin films. These goals prompted us to develop new routes to Ru α-diimine complexes with halomethyl bipyridine ligands.[7] Specifically, robust hydroxymethyl bpy precursor complexes with two, four, and six functionalities were prepared and were subsequently converted to chloromethyl derivatives (Figure 1) on the metal center using oxalyl chloride/DMF. Difunctional reagents should allow for the preparation of metal-centered linear polymers whereas tetra- and hexafunctional reagents are expected to generate four- and six-arm stars, respectively, upon reaction with monomers (Figure 2). This account documents our findings using these di-, tetra-, and hexafunctional Ru reagents as initiators for the polymerization of 2-ethyl-2-oxazoline (EtOX) in an attempt to form Ru complexes with two, four, and six polymeric arms. Surprisingly, there exist striking differences between reactions run with inert Ru reagents and those employing labile Fe complexes as initiators.

Experimental Section

General Considerations. (**a**) **Materials**. 2-Ethyl-2-oxazoline (Aldrich) and acetonitrile were purified by distillation from CaH_2. Dipropylamine was used as received (Aldrich). The initiators, $[(bpy)_nRu\{bpy(CH_2Cl)_2\}_{3-n}](PF_6)_2$ ($n = 0-2$) (**1**−**3**), were prepared as previously described.[7]

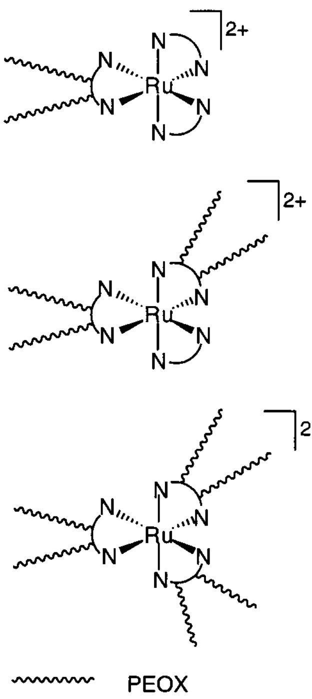


Figure 2. Schematic representation of Ru-centered polymers with two, four, and six arms.

(b) Instrumentation. ^1H NMR spectra were recorded on a GE QE 300 spectrometer in $CDCl_3$. UV/vis spectra of polymers were obtained for $CHCl_3$ solutions using a Hewlett-Packard 8452A diode array spectrophotometer. IR spectra were obtained as KBr pellets with a Nicolet Impact 400D FTIR spectrometer. Molecular weight determination was performed by GPC either in (1) $CHCl_3$ at 25 °C using multiangle laser light scattering (MALLS) ($\lambda = 633$ nm), refractive index, and diode array UV/vis detection or (2) DMF containing 0.4% Et_3N at 50 °C vs PMMA standards. Polymer Labs 5μ mixed C columns and Wyatt Technologies Inc. and Hewlett-Packard instrumentation and software were used. Refractive increments were obtained as previously described.[4a] Luminescence spectroscopic measurements were recorded using a Perkin-Elmer luminescence spectrometer LS50B (excitation slit = 5 nm; emission slit = 2.5 nm; scan rate = 100 nm/ min). Thermal measurements were performed using a TA Instruments DSC 2920 modulated DSC and a TA Instruments TGA 2020 thermogravimetric analyzer as previously described.[8] Yields have not been corrected for unreacted monomer unless otherwise indicated.

General Polymerization Procedure. To a dry Kontes flask equipped with a stirbar and under a nitrogen atmosphere was added the Ru initiator (**1**, 24.9 mg, 2.61×10^{-2} mmol; **2**, 13.7 mg, 1.30×10^{-2} mmol; **3**, 10.0 mg, 8.69×10^{-3} mmol). Dry CH_3CN (0.80 mL) and 2-ethyl-2-oxazoline monomer (1.55 g, 15.6 mmol) were added, and the reaction vessel was sealed and heated to 80 °C in an oil bath. After stirring for ~1.5 days, the reaction was allowed to cool to room temperature, dipropylamine (42.2 mg, 0.417 mmol) was added, and the reaction was stirred for an additional 1 day at room temperature. The orange solutions were then concentrated to dryness, followed by redissolution in a minimal amount of CH_2Cl_2 for precipitation from Et_2O. The polymers were collected by centrifugation. After the filtrate was decanted, the residues were redissolved in CH_2Cl_2 and then were concentrated in vacuo to yield the Ru-centered polymers as red-orange glassy solids. Typical yields: 300−400 mg, 19−26% (uncorrected for unreacted monomer). The ^1H NMR spectra for $[bpy_2Ru(bpyPEOX_2)]^{2+}$, **4**, $[bpyRu(bpyPEOX_2)_2]^{2+}$, **5**, and $[Ru(bpyPEOX_2)_3]^{2+}$, **6**, are indistinguishable. ^1H NMR (300 MHz, $CDCl_3$): δ 3.2−3.6 (br m, $-(N(CH_2)_2)-$), 2.1−2.5 (br m, $-(C(O)CH_2)-$), 1.0−1.4 (br m, $-(C(O)CH_2CH_3)$. UV/vis ($CHCl_3$) λ_{max}, nm: **4**, 455; **5**, 460; **6**, 465. IR (KBr), cm^{-1}: **4**, 2982, 2941, 2882 (CH aliphatic), 1655 (C=O); **5**, 2945, 2986 (CH aliphatic), 1653 (C=O); **6**, 2980, 2940 (CH aliphatic), 1636 (C=O).

^{1}H NMR Experiment (Low Monomer Loading). Reactions were run according to the general polymerization procedure described above using the following reagent loadings and reaction conditions: **3** (55.7 mg, 4.84×10^{-2} mmol), EtOX (0.246 g, 2.48 mmol), CD_3CN (2.0 mL); 80 °C. Aliquots were removed at the designated times and were diluted with additional CD_3CN. The 300 MHz ^{1}H NMR spectra were recorded (32 scans, 3 s delay). See Figure 3 for a comparison of ^{1}H NMR spectra of the hexafunctional initiator, **3**, and those monitoring the formation of a low-MW $[Ru(bpyPEOX_2)_3]^{2+}$ polymer, **6,** at two different times during the course of the reaction.

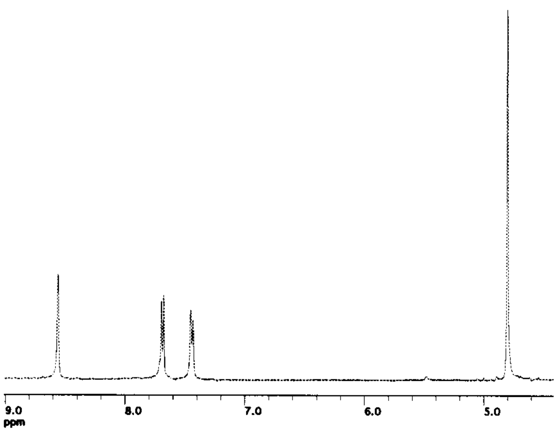
Reactions with Iodide Initiators. The general procedure was followed except that NaI was added to the reaction mixture. An example of typical reagent loadings and reaction conditions is as follows: **3** (10 mg, 8.5×10^{-3} mmol), EtOX (0.507 g, 5.11 mmol), NaI (31 mg, 0.204 mmol), CH_3CN (1.8 mL); 80 °C, 1 day. Yield: 0.167 g, 32%. Representative MW data for **6**: $M_n = 21\,390$, $M_w = 24\,800$, PDI = 1.16.

Reactions with Triflate Initiators. Triflate reactions were run according to the general procedure described above using the following reagent loadings and reaction conditions: **3** (21.5 mg, 1.86×10^{-2} mmol), EtOX (1.10 g, 11.2 mmol), AgOTf (35 mg, 0.134 mmol), CH_3CN (3.0 mL); 80 °C, 1 day. Yield: 1.067 g, 95%. Representative MW data for **6**: $M_n = 18\,400$, $M_w = 20\,600$, PDI = 1.12.

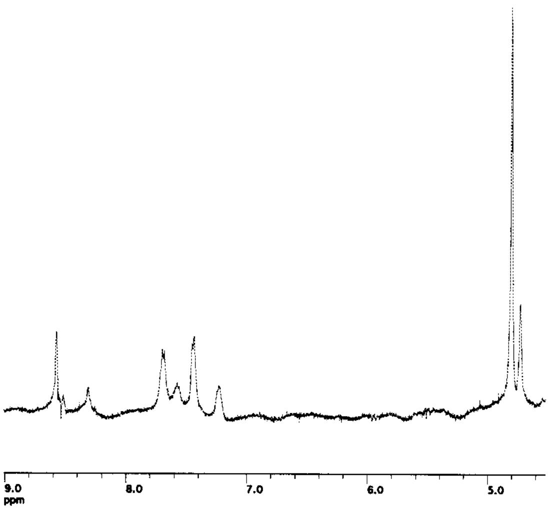
Control Reactions. All reactions were run at 80 °C for 1 day using the reagent loadings indicated below. Reaction solutions were concentrated in vacuo and then were subjected to GPC and ^{1}H NMR analysis. (A) EtOX autopolymerization in CH_3CN*:* EtOX (0.786 g, 7.93 mmol), CH_3CN (2.4 mL). Yield: 0.4%. (B) NaI control*:* NaI (0.077 g, 0.514 mmol), EtOX (0.786 g, 7.93 mmol), CH_3CN (2.4 mL). Yield: 0.1%. (C) $NaPF_6$ control*:* $NaPF_6$ (3 mg, 1.79×10^{-2} mmol), EtOX (0.492 g, 4.96 mmol), CH_3CN (1.5 mL). Yield = 4.9%. $M_n = 3654$, $M_w = 13\,539$, PDI = 3.91. (D) $[Ru(bpy)_3]^{2+}$with no initiator: $[Ru(bpy)_3](PF_6)_2$ (12 mg, 1.40×10^{-2} mmol), EtOX (0.786 g, 7.92 mmol), CH_3CN (2.4 mL). Yield: 1.8%. (E) $[Ru(bpy)_3]^{2+}$with benzyl chloride initiator: $[Ru(bpy)_3](PF_6)_2$ (0.035 g, 4.07×10^{-2} mmol), benzyl chloride (0.028 mL, 0.024 mmol), EtOX (2.38 g, 24 mmol), CH_3CN (5.0 mL). Yield = 2.22 g, 92%. $M_n = 9800$, $M_w = 10\,800$, PDI = 1.10.

Molecular Weight vs Percent Conversion Experiment. Equimolar amounts (6.0×10^{-2} mmol) of the metalloinitiators (**1**, 0.057 g; **2**, 0.063 g; **3**, 0.069 g) were added to three separate Kontes flasks. To each tube was added CH_3CN (3.6 mL) and 2-ethyl-2-oxazoline (3.6 mL, 36 mmol). The mixtures were stirred and sealed under nitrogen and then were immersed in an oil bath maintained at 80 °C. Aliquots were removed at the designated times and then were concentrated in vacuo for ~1 day to determine percent conversion by gravimetric analysis. (Note: it was confirmed by ^{1}H NMR that entrapped monomer comprises <5% of the remaining residue after concentration of aliquots.) Molecular weight determination was performed by GPC vs PMMA standards (mobile phase = DMF with 0.4% triethylamine).

A. Initiator



B. Reaction, t = 7 h.



C. Reaction, t = 36 h.

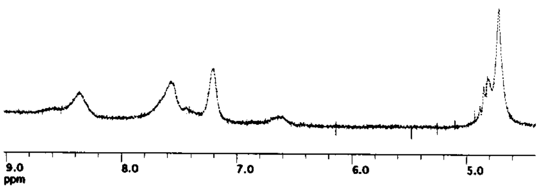
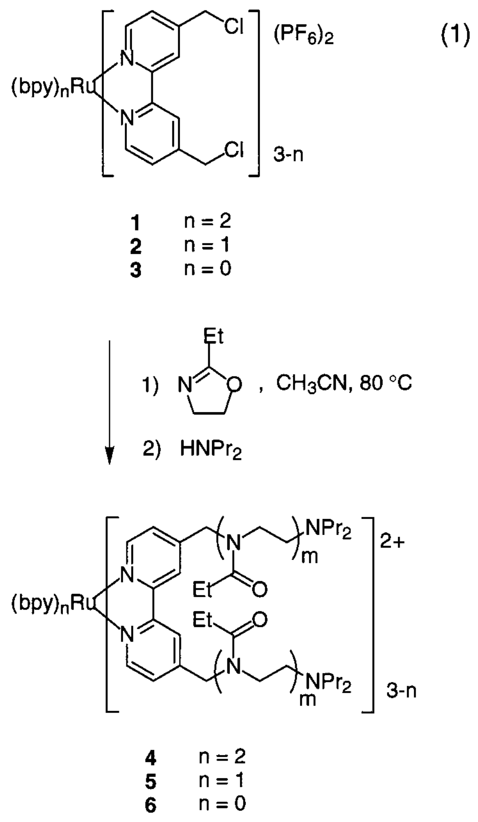


Figure 3. Comparison of aromatic and benzylic regions of the ^{1}H NMR spectrum (300 MHz, CD_3CN) of $[Ru\{bpy(CH_2Cl)_2\}_3](PF_6)_2$ (**3**) and spectra monitoring a reaction to produce a low molecular weight analogue of $[Ru(bpyPEOX_2)_3](PF_6)_2$ (**6**) ([EtOX]/[Cl] = 7) (A, initiator; B, reaction *t* = 7 h; C, reaction *t* = 36 h).

Results and Discussion

Reaction of the di-, tetra-, and hexafunctional ruthenium tris(bipyridine) initiators (**1**−**3**) with 2-ethyl-2-oxazoline in CH_3CN at 80 °C, followed by termination with dipropylamine and precipitation in CH_2Cl_2/Et_2O, affords orange polymers that become glassy upon drying in vacuo (eq 1). The resulting polymers, $[bpy_2Ru(bpyPEOX_2)]^{2+}$, **4**, $[bpyRu(bpyPEOX_2)_2]^{2+}$, **5**, and $[Ru(bpyPEOX_2)_3]^{2+}$, **6**, are soluble in CH_2Cl_2, $CHCl_3$, water, methanol, ethanol, DMF, and acetonitrile but are insoluble in diethyl ether and nonpolar solvents such as hexanes. Polymer products retain the $[Ru(bpy)_3]^{2+}$ chromophores and their luminescent properties (UV/vis, 460 nm; emission, 609 nm). Thermal data are consistent with results previously obtained for poly(2-ethyl-2-oxazolines).[8] Analysis by modulated differential scanning calorimetry (MDSC) reveals a glass transition at approximately 54 °C. Thermogravimetric analysis under N_2 shows that the onset of thermal decomposition occurs in the range 365−385 °C.



1 n = 2
2 n = 1
3 n = 0

4 n = 2
5 n = 1
6 n = 0

As was true for Fe-containing polymers,[8] ^{1}H NMR spectra of high-MW $[(bpy)_nRu(bpyPEOX_2)_{3-n}]^{2+}$ systems contain polymer backbone resonances; however, signals arising from bipyridine and bpyCH_2– core protons are not evident in CD$_3$CN solution. For a low-MW polymer prepared from the hexafunctional initiator, a very broad resonance centered at 4.72 ppm is observed, which is attributable to the "benzylic" protons on the bipyridines at the core. Thus, it was not possible to obtain useful information about initiator efficiency under normal polymerization conditions. Instead, the hexafunctional initiator, **3**, was combined with EtOX at very low loading (~7 equiv per initiator site) in CD$_3$CN solution at 80 °C, and the reaction was monitored over the course of the reaction by ^{1}H NMR spectroscopy. Comparison of spectra corresponding to the metalloinitiator and the resulting oligomers confirms the growth of the oligomeric chains from the halomethyl sites on the metalloinitiator (Figure 3). In the initiator, **3**, "benzylic" methylene protons, bpyCH_2Cl, exhibit a characteristic resonance at 4.80 ppm (s, 12 H) whereas the bipyridine protons are evident at 8.57 (s, 6 H), 7.68 (d, 6 H), and 7.44 ppm (d, 6H). As the reaction with monomer proceeds, signals attributable to bipyridine protons broaden and exhibit an upfield shift to 8.36, 7.56, and 7.21 ppm. The initiator peak at 4.80 ppm begins to vanish, and a new signal, corresponding to the bpy methylene, bpyCH_2NRR′, appears at 4.72 ppm. Though reactions with chloride initiators often proceed by a covalent mechanism, comparison with spectral data for other oxazoline polymerizations suggests that multiplets at 4.85 and 4.88 ppm may correspond to cationic oxazolinium species.[16–18] It must be noted that a broad resonance centered at 4.81 ppm remains in the spectrum of the oligomer. This may be attributed either to unreacted chloride sites or to core protons arising from oligomers with oxazolinium species on the remote chain ends. This, combined with the fact that it is not possible to remove the ligands from the inert Ru center to analyze the polymer arms independently of the metal ion, makes it difficult to conclude with absolute certainty that all halide sites on the metalloreagents have reacted with monomer to produce polymer chains. However, since initiation is quite efficient even under these conditions of low monomer loading and high dilution for the hexafunctional reagent, **3,** it is expected to be even more effective under normal polymerization conditions and for reactions employing initiators with fewer numbers of functionalities. It is also important to note that these dicationic Ru initiators are likely to be more electrophilic than benzyl chloride and, thus, better initiators for oxazoline polymerizations.

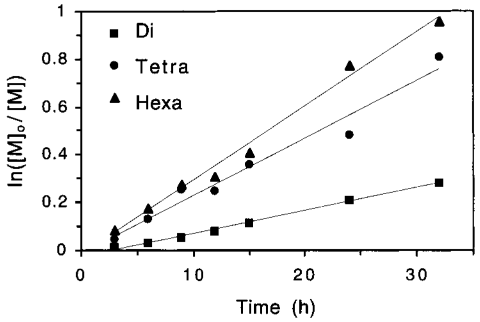


Figure 4. Comparison of first-order kinetics plots for reactions initiated with equimolar amounts of the difunctional **1**, tetrafunctional, **2**, and hexafunctional, **3**, Ru metalloreagents. $[EtOX]_0 = 5.0$ M; $[\mathbf{1}]_0 = [\mathbf{2}]_0 = [\mathbf{3}]_0 = 8.3$ mM.

Further evidence suggesting that initiation is proceeding as expected may be found by comparing the first-order kinetics plots for the multifunctional reagents **1**–**3** (Figure 4). Propagation rate constants, k_p, calculated from the slopes of these plots[17a] are comparable to what has been observed previously for oxazoline polymerizations:[17a] hexa (**3**), $k_p = 1.03 \times 10^{-3}$ L mol^{-1} s^{-1}; tetra (**2**), $k_p = 8.06 \times 10^{-4}$ L mol^{-1} s^{-1}; di (**1**), $k_p = 3.33 \times 10^{-4}$ L mol^{-1} s^{-1}. This demonstrates that the rate of monomer consumption is roughly proportional to the number of chloride sites on the initiators, as is anticipated for polymerization reactions that are initiating from all or most sites.

Molecular weights of Ru-centered poly(2-ethyl-2-oxazolines) were determined by gel permeation chromatography (GPC). Both linear and star-shaped Ru polymers present special difficulties for MW characterization. Though consistent MW data are obtainable for metal-free linear bpy-centered oxazolines in CHCl$_3$ solution, $[(bpy)_nRu(bpyPEOX_2)_{3-n}]^{2+}$ products often gave inconsistent results particularly as the GPC columns age over months of use. It has been noted previously that PEOX has a tendency to interact with standard cross-linked polystyrene size exclusion columns–peaks rise sharply on the high-MW side and trail on the low-MW side.[8,16] For metal-free polyoxazolines this problem has been addressed by using THF/MeOH solvent mixtures,[16] *N*-methylpyrrolidone pretreated with P$_2$O$_5$,[19] DMF containing triethylamine,[20] or various aqueous solutions. After screening CHCl$_3$, THF/MeOH, and DMF as GPC solvents, DMF containing 0.3% Et$_3$N proved to be the most reliable for routine characterization of the Ru-centered polymers. Representative MW data reported versus poly(methyl methacrylate) (PMMA) standards are collected in Table 1, and GPC traces for polymers generated from the di-, tetra-, and hexafunctional initatitors are provided in Figures 5–7. Because MWs of star-shaped polymers do not always correlate well

Table 1. Representative Molecular Weight Data for Ruthenium Tris(bipyridine)-Centered Poly(2-ethyl-2-oxazolines)[a]

initiator	time (h)	$M_n{}^b \times 10^{-3}$	$M_w{}^b \times 10^{-3}$	PDI[b]
di[c]	12	2.51	2.55	1.02
di[d]	42	4.33	4.49	1.04
di	26	6.15	7.12	1.16
di[e]	50	12.33	14.13	1.15
tetra	26	8.23	10.73	1.30
tetra[f]	43	14.85	16.92	1.14
tetra	50	22.12	24.13	1.09
hexa	20	6.30	7.84	1.24
hexa	36	10.23	12.44	1.22
hexa[g]	51	22.68	24.67	1.09

[a] di = **1**, tetra = **2**, hexa = **3**. Loading: [monomer]/[Cl] = 300. [b] GPC in DMF containing 0.3% Et_3N at 50 °C vs PMMA standards. [c] Loading: [monomer]/[Cl] = 15. [d] Loading: [monomer]/[Cl] = 20. [e] MALLS ($CHCl_3$): M_n = 18.8K, M_w = 20.2K, PDI = 1.08, d*n*/d*c* = 0.0918. [f] MALLS ($CHCl_3$): M_n = 23.7K, M_w = 24.0K, PDI = 1.08, d*n*/d*c* = 0.0940. [g] MALLS ($CHCl_3$): M_n = 19.4K, M_w = 20.4K, PDI = 1.05, d*n*/d*c* = 0.0933.

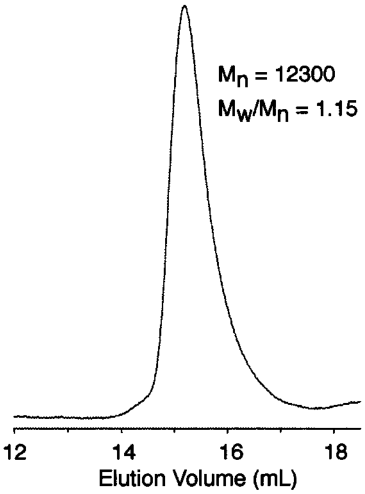


Figure 5. GPC trace of $[bpy_2Ru(bpyPEOX_2)]^{2+}$ (**4**) (reaction time: 50 h; GPC conditions: DMF/0.4% Et_3N, 50 °C).

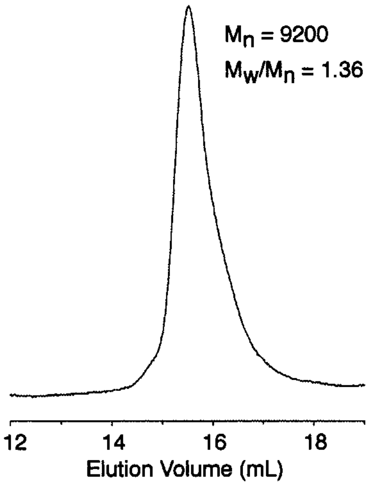


Figure 6. GPC trace of $[bpyRu(bpyPEOX_2)_2]^{2+}$ (**5**) (reaction time: 15 h; GPC conditions: DMF/0.4% Et_3N, 50 °C).

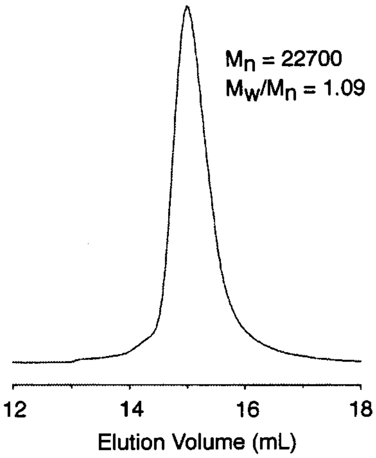


Figure 7. GPC trace of $[Ru(bpyPEOX_2)_3]^{2+}$ (**6**) (reaction time: 50 h; GPC conditions: DMF/0.4% Et_3N, 50 °C).

with linear standards, certain samples were also characterized by GPC with multiangle laser light scattering (MALLS) and RI detection for comparison. Since light scattering measurements are poorly compatible with mixed solvent systems, it was not possible to obtain consistent data using DMF/Et_3N or THF/MeOH. Thus, data were obtained in $CHCl_3$ and were repeated at least three times to ensure reproducibility. In contrast to the labile core Fe systems, the inert Ru-centered poly(oxazolines) do not fragment on the GPC columns. Electronic absorption spectra recorded with an in-line diode array detector as the polymers elute from the column indicate the presence of the $[Ru(bpy)_3]^{2+}$ chromophores (Figure 8).

Interestingly, Ru and Fe initiators exhibit markedly different polymerization chemistry. Using the hexafunctional iron initiator, $[Fe\{bpy(CH_2Cl)_2\}_3](PF_6)_2$, narrow polydispersity materials were obtained up to M_w = ~120K (dp = 200 per initiator site; overall dp = 1200).[4c] Even higher MW materials can be achieved but with broadening of the MW distributions. In contrast, the Ru-centered polymers reach an upper MW limit of ~25K regardless of the number of functionalities on the initiator (dp **4** = ~125; dp **5** = ~63; dp **6** = ~42 per initiator site). Generally, polydispersity indices (PDIs) increase but remain reasonably narrow over the course of the reactions, as is illustrated by molecular weight vs percent conversion plots for initiators **1**−**3** (Figures 9−11). Roughly linear plots are obtained; however, it should be noted that the measured MWs are depressed relative to the values that would be expected for a living polymerization in which MWs are controllable by reaction stoichiometry. This could be attributable to poor correlation of linear and star Ru-containing PEOXs with PMMA standards or to competing chain transfer reactions. Literature precedent suggests that oxazoline polymerizations are "living" only for lower MWs. Certain reactions generating linear PEOXs become less controlled (PDIs > 1.3) above ~40K.[21] In some cases, where low-MW Ru polymers were targeted, it was possible to drive reactions to completion to produce polymers of the expected MW. However, narrower PDIs were typically observed for reactions run in the presence of excess monomer (100−300 equiv per initiator site). Unreacted EtOX is recovered in the colorless filtrate fractions upon polymer precipitation. Molecular weights increase very gradually up until ~50 h without significant broadening of polydispersity. (Figures 5−7 and 9−11). However after ~36 h, a slight shoulder begins to emerge on the high-MW side GPC traces of certain eluting polymers. Previously, this feature has been attributed to coupling between reactive chain ends and enamines formed by chain transfer to monomer.[22] However, the fact that MW vs percent conversion plots are essentially linear and the PDIs of these reactions remain relatively narrow

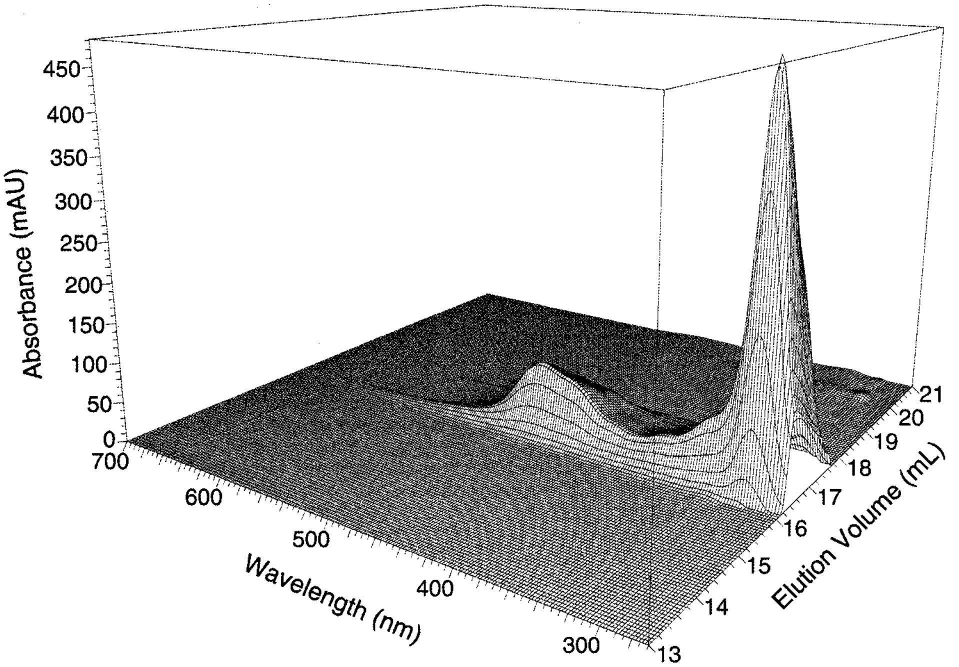


Figure 8. A 3D plot of an in-line diode array UV/vis spectrum of $[Ru(bpyPEOX_2)_3]^{2+}$ (**6**) (MLCT: $\lambda_{max} = 460$ nm) as it elutes from the GPC column (DMF/0.4% Et_3N, 50 °C).

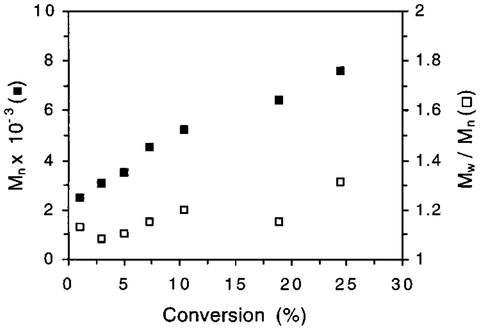


Figure 9. Number-average molecular weight, M_n, vs percent conversion plot for a polymerization initiated with $[bpy_2Ru\{bpy(CH_2Cl)_2\}](PF_6)_2$, **1**, as the initiator.

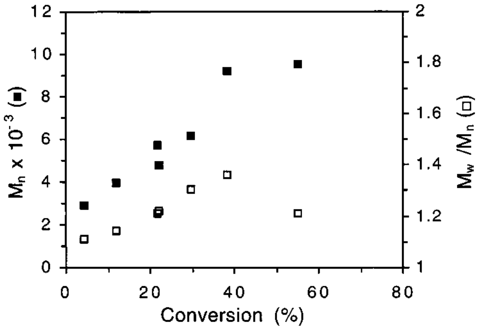


Figure 10. Molecular weight vs percent conversion plot for a polymerization employing $[bpyRu\{bpy(CH_2Cl)_2\}_2](PF_6)_2$, **2**, as the initiator.

seem to suggest that chain transfer is a minimal occurrence at the early stages of the reaction.

Since polymerizations with Ru reagents differ so dramatically from reactions employing Fe initiators, a variety of reaction conditions were explored in attempt to surmount the MW barrier observed for ruthenium. Experiments varying the ratio of solvent to monomer revealed that polymer products are most monodisperse for EtOX/CH_3CN ratios of ~0.5−2.5. Reaction times greater than 50 h, high monomer loadings, and elevated reaction temperatures (100 °C) were ineffective in producing higher MW polymers, and often they resulted in more polydisperse materials. Counterions more reactive than chloride, namely iodide and triflate, were investigated in attempt to produce a more reactive propagating species. Changing from Cl to I in situ using NaI[23] led to increased rates of reaction; however, no significant changes in upper MW, polydispersity, or yields were observed. Moreover, addition of NaI produced a darker reaction mixture, and the polymer developed a brownish color. Highly reactive triflate initiators prepared in situ by the method of Sogah[24] were also ineffective in surmounting the ~25K MW barrier. Monomer conversion was highly efficient, and reaction rates were considerably faster for these reactive triflate initiators, which are believed to proceed via a cationic oxazolinium ion mechanism. MWs of polymers obtained for triflate reactions were even more significantly depressed relative to what would be expected for a living polymerization, which may imply that chain transfer is more significant for these reactions.

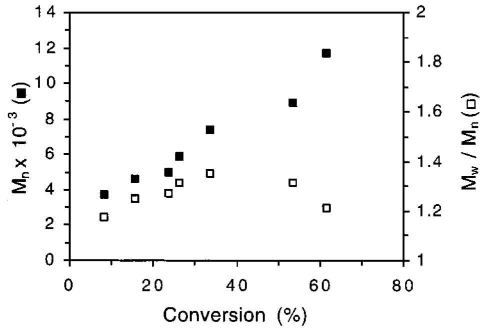


Figure 11. Molecular weight vs percent conversion plot for a polymerization employing $[Ru\{bpy(CH_2Cl)_2\}_3](PF_6)_2$, **3**, as the initiator.

Control studies were performed with different combinations of reaction components in order to ensure that other features of the Ru metalloinitiator system were not responsible for the distinctive chemistry that is observed. It was reconfirmed that EtOX does not autopolymerize in CH_3CN under the standard reaction conditions. Reactions were also run with EtOX and either NaI, $NaPF_6$, or $[Ru(bpy)_3](PF_6)_2$ in molar quantities, concentrations, temperatures, and reaction times comparable to those employed in the multifunctional initiator reactions using **1**−**3**. Reaction products were analyzed by GPC and ^1H NMR. Reactions with NaI and Ru tris(bpy) resulted in oligomers with extremely low mass recovery (<1% yield). On the other hand, reactions run in the presence of $NaPF_6$ showed more significant amounts of low-MW, broad polydispersity materials (yield 4.9%, $M_n = 3600$, PDI = 3.71). It has been shown previously[22] by Litt and co-workers that inorganic salts can initiate the polymerization of 2-oxazolines. However, it should be noted that the polymers obtained in this manner exhibit very different MWs and PDI from those observed for reactions run with Ru initiators. Finally, $[Fe(bpy)_3](PF_6)_2$ was introduced as an additive in reactions with Ru chloride initiators in order to determine whether some feature of the more labile iron reagent might be playing a fortuitous role in reactions with Fe initiators. Yet again, no changes were observed in the properties of the Ru-containing polymers that were obtained.

Since Ru(II) complexes are noted for their electron transfer (ET) capability, we were also curious whether interaction between Ru centers and cationic propagating species might be occurring to inhibit, terminate, or otherwise influence oxazoline polymerization reactions. The fact that reactions proceed in a reasonably controlled fashion at the onset and only after a time do they reach at a limiting MW does not seem consistent with typical distance-dependent ET processes. Electron transfer processes would be expected to be more of a factor just after initiation when the Ru centers and cationic propagating species are in closer proximity. Moreover, ethyloxazoline polymerizations employing benzyl chloride initiators were unaffected by $[Ru(bpy)_3](PF_6)_2$. Polymerizations proceeded to completion, and high-MW, narrow-PDI materials were obtained, which provides further evidence against ET as a side reaction leading to termination.

Conclusion

This study demonstrates that low-polydispersity $[Ru(bpy)_3]^{2+}$-centered polymers are readily obtained using di-, tetra-, and hexafunctional metalloinitiators with electrophilic chloromethyl substituents. Polymers exhibit luminescence properties typical of Ru tris(bipyridine) chromophores and thermal properties similar to metal-free poly(2-ethyl-2-oxazolines). Comparison of kinetics data for the three Ru reagents and a ^1H NMR experiment conducted with the hexafunctional reagent and low loading seem to indicate that initiation is reasonably efficient for these reactions. However, since molecular weight is not readily controlled by reaction stoichiometry and the polymer chains stop growing over the course of the reaction, the cationic polymerization of 2-ethyl-2-oxazoline with these Ru reagents is not living over the MW range that is normally observed for reactions employing metal-free initiators. It is also intriguing that inert Ru and labile Fe metalloinitiators exhibit quite different polymerization chemistries. The precise origin of the ∼25K MW ceiling noted in Ru reactions is not known. It is possible that a trace impurity or as yet undetected decomposition product present in the Ru reagents is responsible for the unique chemistry that is observed. The puzzling fact that a similar MW barrier is reached regardless of the number of initiator functionalities suggests that molecular size or possibly aggregation might be playing a role.

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