Transition Metals as Templates for Multifunctional Initiators: Bulk Atom Transfer Radical Polymerization of Styrene Using Di-, Tetra- and Hexafunctional Ruthenium Tris(bipyridine) Reagents

James E. Collins and Cassandra L. Fraser*

*Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901*

New radical polymerization techniques[1] allow for the preparation of well-defined organic polymers with a wide range of different architectures[2] and compositions. While much effort has been devoted to determining the optimal combination of transition metal catalyst with different organic monomers and initiating systems,[2,3] considerably less is known about the compatibility of radical or other living polymerization methodologies with transition metal-based reagents. Recently we described the use of multifunctional metal tris(bipyridine) (bpy) reagents (M = Fe, Ru, Co, Zn) as initiators for living cationic polymerization of oxazoline monomers.[4] In contrast to most metalloinitiators in which the metal continues to play a key role in the propagating species, in this divergent approach the metal template is the "dead" part of the initiator and the polymer chains grow outward from the metal center. We refer to these new materials as metal core macromolecules (MCMs) to encompass both metal-centered star-shaped polymers prepared from reagents with three or more initiator functionalities and linear polymers with metal complexes at the center of the chain made from difunctional metalloinitiators. Monofunctional metalloinitiators lead to linear polymers with metal complexes on one chain end. These new materials may also be thought of as metal complexes with monodisperse macroligands.
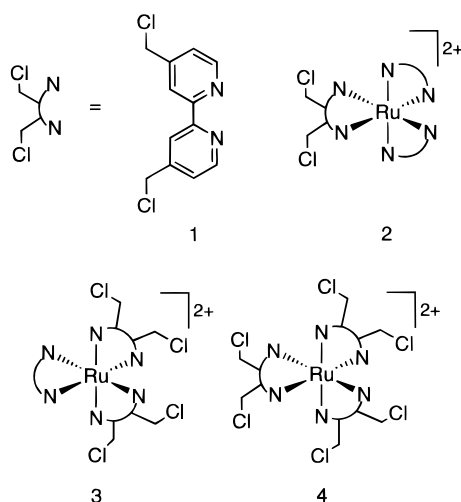
In this report 4,4′-bis(chloromethyl)-2,2′-bipyridine,[5] **1**, and inert Ru(II) complexes bearing one, two and three chloromethyl functionalized bpy ligands,[6] {(bpy)$_{3-n}$Ru[bpy(CH$_2$Cl)$_2$]$_n$}(PF$_6$)$_2$ (n = 1−3) (**2−4**), are used as initiators for the bulk atom transfer radical polymerization (ATRP) of styrene by the method of Matyjaszewski et al.[7] (eq 1). These reagents are designed to produce bpy-centered polystyrene, as well as Ru(II) core poly-

styrenes with two, four, and six arms, respectively. Since the metal binding sites and local polymer environments are well-defined and tunable in this approach and [Ru(bpy)$_3$]$^{2+}$ complexes exhibit fascinating photophysical properties[8] that are sensitive to different analytes, these Ru(II)-centered MCMs and related metal complexes are of interest for sensors,[9] for electroactive films,[10] and for a variety of other applications.[11] While planar multifunctional initiators based on main group reagents, namely hexafunctional phosphazenes and tetrafunctional siloxanes, have recently been reported,[12] to our knowledge this is the first use of transition metal ions as templates for ATRP initiators.
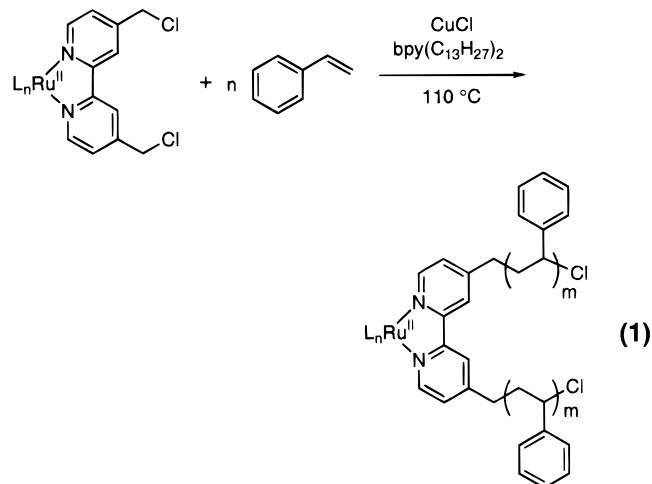
The difunctional halomethyl bpy initiator, **1**, was prepared from 4,4′-dimethyl-2,2′-bipyridine via a trimethylsilyl intermediate as previously described.[5] The dicationic ruthenium initiators were all made by reaction of the respective di-, tetra- and hexafunctional hydroxymethyl precursor complexes with oxalyl chloride/DMF in THF solution, and were isolated as their di-PF$_6$ salts.[6] The ligand **1** and the Ru^{II} complexes **2**-**4** all served as effective initiators for the bulk polymerization of styrene at 110 °C using CuCl and 4,4′-bis(tridecyl)-2,2′-bpy,[13] bpy(C$_{13}$H$_{27}$)$_2$, as the catalyst system (eq 1). Typical reagent ratios used in this preliminary study are as follows: initiator chloride:CuCl:bpyC$_{13}$H$_{27}$:styrene = 1:1:2:∼180 (2 mL styrene); (i.e. **1** or **2**:CuCl:bpyC$_{13}$H$_{27}$:styrene = 1:2:4:∼360; **3**:CuCl:bpyC$_{13}$H$_{27}$:styrene = 1:4:8:∼720; **4**:CuCl:bpyC$_{13}$H$_{27}$:styrene = 1:6:12:1080). Typically the reactions were cooled, THF was added, and the polymer solutions were filtered through paper into MeOH. Reactions run with the difunctional bpy initiator **1** yield pale green polymers, indicating the presence of chelated Cu(II) ion even after filtration and precipitation. Samples prepared from the Ru(II) initiators behave differently depending upon the degree of polymerization. Most samples readily precipitate from MeOH as flocculent pale orange solids, which were triturated once more with fresh MeOH before collection and drying. In some cases, lower MW polymers provided yellow suspensions after filtration into MeOH. The suspensions were clarified by collection on fine filter paper or by centrifugation in most cases. If not, they were simply concentrated to dryness and analyzed. It is important to note that while the former methods

Table 1. Bulk ATRP of Styrene Using Multifunctional Bipyridine and Ruthenium(II) Initiators[a]

| initiator	time (h)	yield[b] (%)	theor M_n[c] $\times 10^{-3}$	M_n[d] $\times 10^{-3}$	M_w[d] $\times 10^{-3}$	PDI[d]
bpy(CH$_2$Cl)$_2$	1.3	16	5.82	7.19	8.35	1.16
bpy(CH$_2$Cl)$_2$	4.1	40	14.6	14.0	15.0	1.09
bpy(CH$_2$Cl)$_2$	9	81	29.5	24.6	25.8	1.05
di	1	8.5	3.15	13.1	15.4	1.17
di	7.3	51	18.9	41.4	50.8	1.23
di	10.3	82	30.4	65.6	80.1	1.22
tetra	1	12.3	9.03	24.4	29.4	1.21
tetra	6	55.2	40.5	55.9	76.4	1.37
tetra	9	87.6	64.3	113	137	1.21
hexa	1	7.4	8.11	41.1	49.7	1.21
hexa	6.1	52	57.0	98.3	114	1.17
hexa	9.1	93	118	139	174	1.25

[a] Reaction Conditions: initiator Cl:CuCl:bpy(C$_{13}$H$_{27}$)$_2$:styrene = 1:1:2:~180; 110 °C. [b] Determined by gravimetry. [c] Theor M_n = yield × (M_n calculated for 100% conversion and initiator efficiency). [d] Determined by GPC in CHCl$_3$ with MALLS, RI, and UV/vis detection.

separate most of the MeOH-soluble Cu–bpy catalyst from the polymer products, concentration of the MeOH suspensions does not.

Since linear polystyrene standards do not always correlate well with more compact star and branched materials, the light scattering technique was used for determining star-shaped polymer MWs.[15] All polymers were analyzed as chloroform solutions[14] by gel permeation chromatography (GPC) equipped with online diode array UV/vis, multiangle laser light scattering (MALLS), and refractive index (RI) detectors for comparison with data obtained vs polystyrene standards. In this preliminary study all MWs are approximated using the refractive index increment (dn/dc) value for polystyrene (0.145 mL/g) in CHCl$_3$ solution, since literature precedent[16] and our experience with polyoxazoline MCMs[17] indicates that dn/dc values often vary little with the degree of branching in the MW ranges in which we are working.[18] Though MCMs with labile [Fe(bpy)$_3$]$^{2+}$ cores may be readily fragmented by chemical means which allows for the independent characterization of the liberated macroligands,[4] this is not possible for the inert Ru-centered star-shaped polymers. Representative data obtained for polymers made from the free bpy ligand **1** as well as from the Ru initiators **2**–**4** for different reaction times are collected in Table 1. Stock reaction mixtures were prepared and distributed into several reaction vessels which were stopped after the designated times. Yield and MW data given in Table 1 were obtained from crude reaction mixtures after evaporation of styrene.

All initiators generate polymers with narrow PDIs. While polystyrenes obtained from the bpy initiator **1** exhibit MWs close to the targeted values, all polymers made from Ru initiators show MWs that are higher than theoretical values. This is especially so for early time points in polymerization reactions. These observations are consistent with slow and inefficient initiation with the dicationic Ru initiators, which even at elevated temperature exhibit limited solubility in the nonpolar bulk styrene medium. Since polymer PDIs remain narrow, unreacted Ru initiators appear to be even less soluble as the reaction proceeds than at the onset.[19] MW data obtained by light scattering correlate well with that determined vs polystyrene standards for all samples. For example, reaction of the hexafunctional initiator, **4** with styrene (1:90 loading) for 1 d followed by purifica-

tion by precipitation yielded a polymer with the following MW data: MALLS (vs polystyrene): M_n = 58.0K (57.6 k); M_w = 64.5K (67.1K); PDI = 1.11 (1.16). ^{1}H NMR spectra of all polymers are typical for polystyrene. Neither signals corresponding to bpy protons nor the benzylic protons at the metal core are evident in the ^{1}H NMR spectra of the bpy- or Ru-centered polymers. All MCMs grown from multifunctional Ru^{II} initiators **2**–**4** exhibit electronic absorption spectra typical for [Ru(bpy)$_3$]$^{2+}$ chromophores with metal to ligand charge-transfer bands near ~460 nm. As powders or as films cast from methylene chloride or other solvents, all Ru polymers are luminescent, emitting at ~609 nm. The fact that polymerizations with multifunctional ligand and metal complex initiators **1**–**4** exhibit low PDIs and the [Ru(bpy)$_3$]$^{2+}$ chromophores are detected by diode array UV/vis spectra of eluting polymers is consistent with the targeted MCM structures.
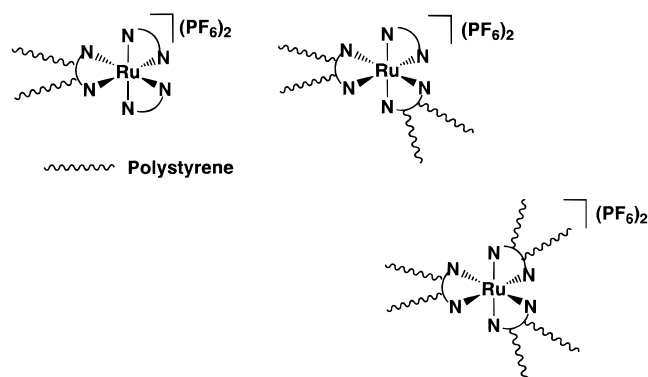
Light scattering also serves as a valuable analytical tool for the identification of impurities in the star-shaped polymer products and possible side reactions in these polymerizations. For example, some samples exhibit a trace amount of a very high MW material that is pronounced in the light scattering trace but is entirely absent in the RI trace. The UV/vis trace of this peak shows no evidence of the [Ru(bpy)$_3$]$^{2+}$ chromophore but it is consistent with polystyrene. In addition, low MW samples with Cu impurities give rise to negative peaks at longer retention times in the light scattering trace. For reactions run with the hexafunctional Ru initiator **4**, high MW shoulders appear in the RI and MALLS traces for longer reaction times. In some cases it is possible to isolate two different fractions from these samples exhibiting bimodal GPCs, a readily soluble lower MW fraction, and a higher MW material that is less soluble in THF. Both fractions show evidence of the [Ru(bpy)$_3$]$^{2+}$ chromophores. It has been suggested that intermolecular radical coupling reactions may give rise to these byproducts and that these may be eliminated or minimized with lower Cu catalyst loadings.[12]

This investigation illustrates that metal ions serve as versatile templates for polymerization initiators and, specifically, that these dicationic ruthenium metalloinitiators are compatible with the ATRP technique. Using these nonplanar reagents with different combinations of ligands, polymer architectures that would be difficult to access or easily "tune" using organic and main group reagents might be generated. Moreover, metalloreagents allow for the introduction of new properties into polymeric materials. The fact that the metal ions are in tunable environments makes these [Ru(bpy)$_3$]$^{2+}$-containing materials well suited for sensor applications

based on a luminescence quenching mechanism. A more detailed investigation of these and related Ru−tris(bipyridine) reagents as initiators for ATRP and other living polymerization reactions and further characterization of these new metal-containing materials are underway.

Experimental Section. Materials and Methods. The ligand 4,4′-bis(chloromethyl)-2,2′-bipyridine,[5] **1**, and the Ru(II) complexes {(bpy)$_{3-n}$Ru[bpy(CH$_2$Cl)$_2$]$_n$}(PF$_6$)$_2$ ($n = 1-3$; **2−4**)[6] were prepared as previously described. The ligand bpy(C$_{13}$H$_{27}$)$_2$ was prepared as described by Smith for similar compounds.[13] Styrene (Acros) was purified by passing through a plug of neutral alumina followed by drying over CaH$_2$ and distillation under reduced pressure. Copper(I) chloride was purified as described by Keller.[20] The polymers were characterized by GPC in CHCl$_3$ using a Hewlett-Packard 1100 system equipped with a vacuum degasser, a diode array detector, with a Polymer Labs "mixed c" guard column and two GPC columns, Wyatt Technology Corp (WTC) DAWN multiangle laser light scattering, and Optilab refractive index detectors and accompanying WTC Astra software. The dn/dc for polystyrene in CHCl$_3$ at 35 °C (0.145 mL/g) was obtained from WTC and was used in all calculations. ^{1}H NMR spectra were recorded on a GE QE 300 spectrometer in the solvents specified. UV/vis spectra were taken in CHCl$_3$ solution with an HP 8452A diode array spectrophotometer.

Polymerizations. According to the procedure described by Matyjaszewski et al.,[7] a solid mixture of the Ru(II) initiator (di, **2**, 0.0500 mmol; tetra, **3**, 0.025 mmol; and hexa, **4**, 0.0167 mmol), CuCl (0.100 mmol) and bpy-(C$_{13}$H$_{27}$)$_2$ (0.200 mmol) were combined in a Kontes tube. Styrene was added via syringe and the mixture was immediately degassed by the freeze−pump−thaw method (three cycles). The evacuated tube was then immersed in an oil bath maintained at 110 °C, and the initial time was recorded. Upon completion, reactions were cooled, exposed to air, diluted with THF (∼3 mL), and then were filtered through paper into stirring MeOH (50 mL). The resulting flocculent yellow-orange polymers were collected on filter paper, were triturated with MeOH (1×), and in some cases they were reprecipitated from toluene/hexanes. For studies monitoring polymerizations over time (Table 1), CuCl was used as received and styrene was purified by filtration through alumina. Stock solutions of monomer, catalyst and bpy ligand were prepared and distributed into separate tubes containing the appropriate Ru initiator, **2−4**. (The soluble bpy initiator **1** was dissolved in the stock solution prior to distribution.) Reactions were removed from the heat source at the indicated time. Yield and MW data reported in Table 1 were obtained for the entire reaction mixture after evaporation of unreacted styrene; samples were not purified by precipitation prior to MW characterization.

References and Notes

(1) For recent reviews see: (a) Matyjaszewski, K., Ed. *Controlled Radical Polymerizations*; ACS Symposium Series 685; American Chemical Society: Washington, DC, 1998. (b) Qiu, J.; Matyjaszewski, K. *Acta Polym.* **1997**, *48*, 169−80. (c) Hawker, C. J. *Trends Polym. Sci.* **1996**, *4*, 183. (d) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer,

G. K. *Trends Polym. Sci.* **1994**, *2*, 66. (e) Sawamoto, M.; Kamigaito, M.; *Trends Polym. Sci.* **1996**, *4*, 317.

(2) Multiarm materials by living radical polymerization methodologies: (a) Ueda, J.; Jatsuyama, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1998**, *31*, 557−62. (b) Hawker, C. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1456. (c) Gao, B.; Chen, X.; Ivan, B.; Kops, J.; Batsberg, W. *Macromol. Rapid Commun.* **1997**, *18*, 1095. (d) Kickelbick, G.; Miller, P. J.; Matyjaszewski, K. *Polym. Prepr.* **1998**, *39* (1), 284−5.

(3) For examples, see: (a) Matyjaszewski, K.; Wang, J.-L.; Grimaud, T.; Shipp, D. A. *Macromolecules* **1998**, *31*, 1527−34. (b) Xia, J.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 7697−700. (c) Matyjaszewski, K.; Gaynor, S.; Wang, J.-S.; *Macromolecules* **1995**, *28*, 2093−5. (d) Xia, J.; Matyjaszewski, K. *Polym. Prepr.* **1997**, *37* (2), 513. (e) Wei, M.; Matyjaszewski, K. *Polym. Prepr.* **1997**, *38* (1), 683. (f) Percec, V.; Barboiu, B.; Kim, H.-J. *J. Am. Chem. Soc.* **1998**, *120*, 305−16. (g) Ando, T.; Nishikawa, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1997**, *30*, 4507. (h) Barclay, G. G.; Hawker, C. J.; Ito, H.; Orellana, A.; Malenfant, P. R. L.; Sinta, R. F. *Macromolecules* **1998**, *31*, 1024-31. (i) Kwon, T. S.; Kumazawa, S.; Yokoi, T.; Kondo, S.; Kunisada, H.; Yuki, Y. *J. Macromol. Sci.−Pure Appl. Chem.* **1997**, *A34* (9), 1553−67.

(4) (a) Lamba, J. J. S.; Fraser, C. L. *J. Am. Chem. Soc.* **1997**, *119*, 1801−2. (b) Lamba, J. J. S.; McAlvin, J. E.; Peters, B. P.; Fraser, C. L *Polym. Prepr.* **1997**, *38* (1), 193.

(5) Fraser, C. L.; Anastasi, N. R.; Lamba, J. J. S. *J. Org. Chem.* **1997**, *62*, 9314−7.

(6) Collins, J. E.; Lamba, J. J. S.; Love, J. C.; McAlvin, J. E.; Peters, B. P.; Fraser, C. L. Manuscript submitted for publication.

(7) (a) Matyjaszewski, K.; Patten, T. E.; Xia, J. *J. Am. Chem. Soc.* **1997**, *119*, 674−80. (b) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614−5. (c) Wang, J.-S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901−10.

(8) (a) Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphrin Complexes* Academic Press: San Diego, CA, **1992**, p 138. (b) Balzani, V.; et al. *Comprehensive Supramolecular Chemistry*; Vol. 10, Chapter 23, pp 687−746. (c) *Solid State Luminescence. Theory, Materials and Devices*; Kitai, A. H., Ed.; Chapman and Hall: London, 1993.

(9) (a) Ziessel, R. F. *J. Chem. Educ.* **1997**, *74*, 673−9. (b) Shen, Y.; Sullivan, B. P. *J. Chem. Educ.* **1997**, 685−9. (c) Demas, J. N.; DeGraff, B. A. *J. Chem. Educ.* **1997**, *74*, 690−5.

(10) For example, see: Leasure, R. M.; Ou, W.; Moss, J. A.; Linton, R. W.; Meyer, T. J. *Chem. Mater.* **1996**, 264−73.

(11) For other examples see: (a) Meyer, G. J. *J. Chem. Educ.* **1997**, *74*, 652−6. (b) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163−70. (c) Yu, L.; Chan, W. K.; Peng, Z.; Gharavi, A. *Acc. Chem. Res.* **1996**, *29*, 13-21.

(12) Kickelbick, G.; Miller, P. J.; Matyjaszewski, K. *Polym. Prepr.* **1998**, *39* (1), 284−5.

(13) This ligand was prepared by a modification of the procedure described by Smith. Griggs, C. G.; Smith, D. J. *J. Chem. Soc., Perkin Trans. 1* **1982**, 3041.

(14) Though THF is the solvent typically used by Matyjaszewski et al. for GPC analysis it is less desirable for GPC with light scattering, as greater error is introduced into dn/dc measurements due to its volatility. GPC vs polystyrene standards using styragel columns (HR4, HR5) and THF as the mobile phase gave rise to peak shapes indicative of polymer interactions with the solid support. For a discussion of this issue for a different polymer system see: Liu, Q.; Konas, M.; Riffle, J. S. *Macromolecules* **1993**, *26*, 5572−6. Further investigations are merited to determine whether the solvent, the charged nature of these MCMs, or the columns are responsible for this observation.

(15) Bywater, S. *Adv. Polym. Sci.* **1979**, *30*, 90−116.

(16) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; John Wiley & Sons: New York, 1989; VII/437−447.

(17) McAlvin, J. E.; Fraser, C. L. Unpublished results. Related Ru(bpy)$_3$-centered polyoxazolines ($M_w = \sim$ 20K) with two, four, and six arms exhibit dn/dcs that are within experimental error of each other and the value measured for an analogous linear poly(2-ethyl oxazoline).

(18) The dependence of dn/dc on degree of polymerization for these polystyrene MCMs will be addressed in a subsequent full paper.

(19) Trace amounts of a THF insoluble red oil are evident in the bottom of the reaction flasks after polymerization.

(20) Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* **1946**, *2*, 1−4.