Metal Complexes with Polymeric Ligands: Modular Synthesis of Multifunctional Materials for Applications in Biomedicine and Nanotechnology

Jessica L. Bender, Robert M. Johnson, Adam P. Smith,
*and Cassandra L. Fraser**

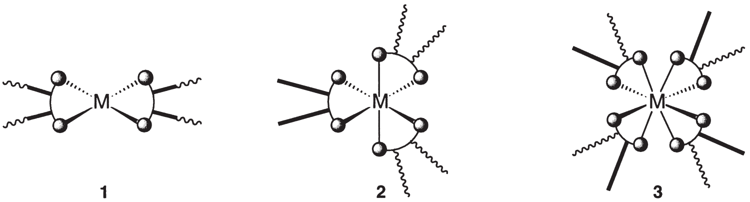
Department of Chemistry, University of Virginia, McCormick Road,
P.O. Box 400319, Charlottesville, VA 22904-4319, USA

Summary: Polymeric metal complexes exhibiting useful properties were prepared by chelating macroligands to labile and inert metal ions. The specific structures elucidated through this method, as well as potential applications for these complexes are described. By carefully selecting the appropriate metal ion and polymer, these materials can be tuned for a host of applications in fields ranging from biomedicine to nanotechnology.

Introduction

Although polymers most commonly feature covalent bonds at key positions in the macromolecular structure, hydrogen bond interactions between donors and acceptors[1] and coordinate bonds[2] are also receiving attention as structural motifs. A molecular design that employs metal ions as templates for polymer assembly serves as the focus of our research. This synthetic approach permits the selective positioning of metals within the polymer structure, namely, at the chain ends or center of star or linear architectures.[3] Initiation, termination, coupling and chelation methods are employed individually, or in combination, to prepare these types of metal-containing materials.[4] Chelation serves as a present emphasis because it is modular and versatile. Various macroligand subunits and non-polymeric donor groups may be mixed and matched to generate an array of new materials that may be utilized as surface coatings, sensors, catalysts and light emitting materials. Of particular interest are block copolymer systems (Figure 1) that form patterned structures with discretely located metal functionalities. As in biological systems, these materials, when appropriately designed, may be hierarchically structured and can become dynamic, in response to stimuli.

CCC 1022-1360/00/$ 17.50+.50/0

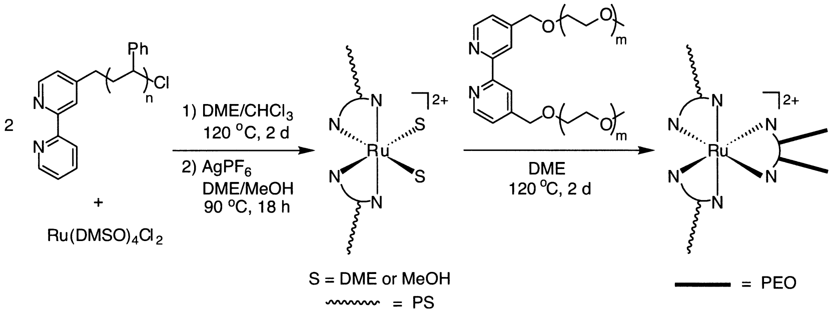


1 **2** **3**

Figure 1. Schematic representation of a star block copolymer (**1**) and heteroarm stars from two different macroligands (**2**) or block copolymer macroligands (**3**).

Research Highlights

Block copolymeric metal complexes have been prepared through various methodologies, including sequential monomer addition to metal complex initiators,[5] and chelation of two different kinds of homopolymeric macroligands to inert metals.[6] Even more elaborate architectures are possible through the coordination of *block copolymeric* macroligands to metal ions. For bidentate ligands of the type depicted in compound **3**, the donor group bridges the blocks. Other macroligands have a donor group attached to only one block, either at the chain end (for a monofunctional initiator), or at the center of the structure (difunctional initiators, see compound **1**). Controlled ring opening and atom transfer radical polymerizations, along with polymer coupling methods, were extended to suitably derivatized bipyridine (bpy) or beta-diketonate ligand reagents to produce polymers with tailored binding sites. These ligands were then chelated to different metal centers to generate materials with functional crosslinks. For example, a robust ruthenium-centered heteroarm star was synthesized by the coordination of two bpy end-functionalized polystyrene (PS) chains, followed by chelation of a single bpy-centered poly(ethylene oxide) (PEO) macroligand to $Ru(DMSO)_4Cl_2$ (Scheme 1). In contrast to non-polymeric complexes, this luminescent, amphiphilic material and other macromolecular analogues can be conveniently cast as films. Interestingly, in ordered block polyoxazoline films, nano-scale metal cluster formation occurs upon annealing.[7] This is analogous to templated mineralization processes in nature. Iron materials also bleach upon exposure to heat, light and chemical reagents such as acid, base and peroxides, which could perhaps be harnessed for sensors or novel triggered-release drug delivery systems.[8] Ruthenium tris(bipyridyl) polymeric systems exhibit red-orange luminescence and are being tested as oxygen sensors,[9] whereas new site-isolated polymeric lanthanide complexes exhibit red and green emission upon photoexcitation.[10] Narrow bandwidth emission and long excited state lifetimes in the millisecond range make these lanthanide materials potentially useful for photoluminescent displays, time-resolved fluoroimmunoassays (TR-FIA), as well as other photonic and bioanalytical technologies.[11]



bpyPS	$[Ru(bpyPS)_2(S)_2]^{2+}$	$bpyPEO_2$	$[Ru(bpyPS)_2(bpyPEO_2)]^{2+}$
M_n = 18 330	M_n = 31 550	M_n = 8 690	M_n = 38 050
M_w = 21 330	M_w = 36 510	M_w = 10 150	M_w = 43 590
PDI = 1.16	PDI = 1.16	PDI = 1.17	PDI = 1.15
			(Estimated using PS dn/dc = 0.145)

Scheme 1. Chelation of two bpyPS ligands and one $bpyPEO_2$ macroligand to ruthenium to generate a heteroarm star polymer, $[Ru(bpyPS)_2(bpyPEO_2)]^{2+}$.

Conclusion

A multitude of materials with selectively positioned metal binding sites have been prepared using a modular chelation approach and a toolkit of macroligands with bipyridine and beta-diketonate donor groups. These systems exhibit interesting behavior in response to heat, light and chemical agents. Block copolymer analogues self assemble to adopt morphologies that are organized on the nanometer scale. Properties of the metal complexes are maintained in these ordered materials. Additional characterization of these complexes in solution phase and as thin films will serve as subjects of future investigations.

[1] S. C. Zimmerman, F. Zeng, D. E. C. Reichert, S. V. Kolotuchin, *Science* **1996**, *271*, 1095.
[2] F. Zeng, S. C. Zimmerman, *Chem. Rev.* **1997**, *97*, 1681.
[3] C. L. Fraser, A. P. Smith, *J. Polym. Sci*, *Part A*: *Polym. Chem.* **2000**, *38*, 4704.
[4] For related work in this area, see: (a) M. Matsumi, Y. Chujo *Organometallics* **2001**, *20*, 2425. (b) K. D. Ley, C. E. Whittle, M. D. Bartberger, K. S. Schanze, *J. Am. Chem. Soc.* **1997**, *119*, 3423. (c) U. S. Schubert, G. Hochwimmer, *Macromol. Rapid Commun.* **2001**, *22*, 274. (d) B. Clapham, T. S. Reger, K. D. Janda, *Tetrahedron* **2001**, *57*, 4637.
[5] J. E. McAlvin, C. L. Fraser, *Macromolecules* **1999**, *32*, 1341.
[6] C. L. Fraser, A. P. Smith, X. Wu, *J. Am. Chem. Soc.* **2000**, *122*, 9026.
[7] C. Park, J. E. McAlvin, C. L. Fraser, E. L. Thomas, manuscript submitted.
[8] P. S. Corbin, M. P. Webb, J. E. McAlvin, C. L. Fraser, *Biomacromolecules* **2001**, *2*, 223.
[9] Z. J. Fuller, R. W. Cutts, C. L. Fraser, J. N. Demas, unpublished results.
[10] (a) J. L. Bender, P. S. Corbin, D. H. Metcalf, F. S. Richardson, C. L. Fraser, manuscript in preparation. (b) J. L. Bender, P. S. Corbin, J. E. McAlvin, S. R. Shenoy, D. H. Metcalf, F. S. Richardson, C. L. Fraser, manuscript in preparation.
[11] (a) N. Sabbatini, M. Guardigli, *Coord. Chem. Rev.* **1993**, *123*, 201. (b) M. Elbanowski, B. Makowska, *J. Photochem. Photobiol. A: Chem.* **1996**, *99*, 85. (c) I. Hemmilä, *J. Alloys Comp.* **1995**, *225*, 480.