

Communications to the Editor

Metal Template-Assisted Block Copolymer Synthesis: Use of Solvent Polarity to Control Chain Conformation and Reactivity at the Metal Core

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When metals are bound to polymers, both inner and outer sphere environments may be engineered. As is illustrated by metalloproteins, macromolecular structure and electronic environment can play important roles in modulating properties, including access to and reactivity at the metal core. For example, the protective polymer shell of hemoglobin prevents iron porphyrin dimerization, whereas in other proteins, the polypeptides influence substrate specificity.¹ Analogous features have been incorporated into synthetic systems including molecularly imprinted polymers² and catalysts on solid supports.³ Although the polymer matrix and metal binding sites are not entirely uniform in these cases, site isolation and architectural control have been achieved in metal-centered dendrimers via iterative methods.⁴

Another approach to well-defined polymeric metal complexes⁵ involves the preparation of linear polymers with tailored binding sites by controlled polymerization,⁶ followed by their chelation to metal ions.⁷ This metal template-assisted polymer synthesis is highly modular and allows for systematic control over molecular weight, architecture, and metal position.⁸ Especially intriguing are block copolymer analogues⁹ such as metal-centered heteroarm stars, which are expected to form discrete higher order assemblies with chromophores localized at the microdomain boundaries. Luminescent $[\text{Ru}(\text{bpy})_3]^{2+}$ analogues are of interest as additives

(1) Bertini, I.; Gray, H. B.; Lippard, S. J.; Valentine, J. S., Eds.; *Bioinorganic Chemistry*; University Science Books: Mill Valley, CA, 1994.
(2) (a) Haupt, K.; Mosbach, K. *Chem. Rev.* **2000**, *100*, 2495. (b) Brunkan, N. M.; Gagné, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 6217. (c) Uezu, K.; Nakamura, H.; Kanno, J.; Sugo, T.; Goto, M.; Nakashio, F. *Macromolecules* **1997**, *30*, 3888.

(3) (a) Yang, X.-W.; Sheng, J.-H.; Da, C.-S.; Wang, H.-S.; Su, W.; Wang, R.; Chan, A. S. C. *J. Org. Chem.* **2000**, *65*, 295. (b) Bayston, D. J.; Fraser, J. L.; Ashton, M. R.; Baxter, A. D.; Polywka, M. E. C.; Moses, E. *J. Org. Chem.* **1998**, *63*, 3137. (c) Kobayashi, S.; Nagayama, S. *J. Am. Chem. Soc.* **1998**, *120*, 2985. (d) Bergbreiter, D. E.; Franchina, J. G.; Case, B. L. *Org. Lett.* **2000**, *2*, 393.

(4) Newkome, G. R.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689.
(5) For examples of other approaches to metal complexes see: *Metalloinertion*: (a) Lamba, J. J. S.; Fraser, C. L. *J. Am. Chem. Soc.* **1997**, *119*, 1801. (b) McAlvin, J. E.; Fraser, C. L. *Macromolecules* **1999**, *32*, 6925. (c) Collins, J. E.; Fraser, C. L. *Macromolecules* **1998**, *31*, 6715. (d) Schubert, U. S.; Eschbaumer, C.; Hochwimmer, G. *Tetrahedron Lett.* **1998**, *39*, 8643. *Polymer coupling*: (e) Peters, M. A.; Belu, A. M.; Linton, R. W.; Dupray, L.; Meyer, T. J.; Desimone, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 3380.

(6) (a) Szwarc, M.; van Beylen, M. *Ionic Polymerization and Living Polymers*; Chapman & Hall: New York, 1993. (b) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization: Principles and Practical Applications*; Marcel Dekker: New York, 1996. (c) Kennedy, J. P.; Jacob, S. *Acc. Chem. Res.* **1998**, *31*, 835 and references therein. (d) Matyjaszewski, K. *Chem. Eur. J.* **1999**, *5*, 3095.

(7) (a) Hecht, S.; Ihre, H.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1999**, *121*, 9239. (b) Naka, K.; Yaguchi, M.; Chujo, Y. *Chem. Mater.* **1999**, *11*, 849. (c) Naka, K.; Kobayashi, A.; Chujo, Y. *Macromol. Rapid Commun.* **1997**, *18*, 1025.

(8) (a) Wu, X.; Fraser, C. L. *Macromolecules* **2000**, *33*, 4053. (b) Wu, X.; Fraser, C. L. *Macromolecules*, in press.

(9) (a) Evans, C. C.; Bates, F. S.; Ward, M. D. *Chem. Mater.* **2000**, *12*, 236. (b) Ishizu, K.; Uchida, S. *Prog. Polym. Sci.* **1999**, *24*, 1439.

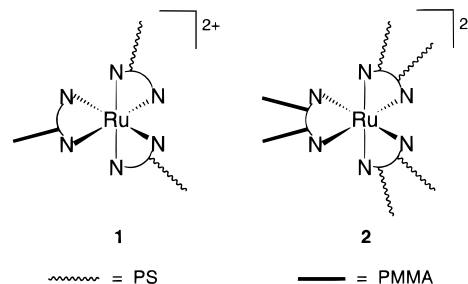


Figure 1. Schematic representation of polymeric $[\text{Ru}(\text{bpy})_3]^{2+}$ complexes with polystyrene (PS) and poly(methyl methacrylate) (PMMA) arms. (bpy = bipyridine).

Table 1. Molecular Weight Data^a for Polystyrene and Poly(methyl methacrylate) Macroligands, **3–6**, the Ru(II) Solvento Intermediates, **7** and **8**, and Heteroarm Stars, **1** and **2**

polymer	M_n	M_w	M_w/M_n
bpyPS	22400	25400	1.13
bpyPMMA	7000	7380	1.05
$[\text{Ru}(\text{bpyPS})_2(\text{S})_n]^{2+}$	39700	47200	1.19
$[\text{Ru}(\text{bpyPS})_2(\text{bpyPMMA})]^{2+}$	48800 ^b	55100 ^b	1.13
bpyPS ₂	4800	5100	1.06
bpyPMMA ₂	6600	7400	1.13
$[\text{Ru}(\text{bpyPS})_2(\text{S})_n]^{2+}$	7700	8300	1.08
$[\text{Ru}(\text{bpyPS})_2(\text{bpyPMMA}_2)]^{2+}$	13000 ^b	13900 ^b	1.07

^a Determined by GPC with multi-angle laser light scattering and refractive index detection. ^b Estimated using the dn/dc for polystyrene (0.145 mL/g).

for photonic materials and as probes of polymer interfaces.¹⁰ Although heteroleptic metal complexes with nonpolymeric ligands are commonplace, it was not certain that heteroarm stars would also be easily obtained by chelation. Different factors come into play when coordination chemistry is performed with polymeric ligands. Ligand field stabilization is counterbalanced by entropic losses and interchain repulsion upon convergence, the latter of which is particularly pronounced for dissimilar polymers, which often phase-separate when mixed. Moreover, solvation influences polymeric ligand conformation in a significant way.

In this study, strategic manipulation of solvent polarity was used to advantage in the assembly of ruthenium tris(bipyridine)-centered polystyrene–poly(methyl methacrylate) heteroarm stars, **1** and **2** (Figure 1). Macroligands for chelation reactions were prepared by copper-catalyzed atom transfer radical polymerization¹¹ using bpy ligand initiators. Bipyridine end- and center-functionalized polystyrenes, bpyPS, **3**, and bpyPS₂, **4**, were generated from 4-(chloromethyl)-2,2'-bipyridine¹² and 4,4'-bis-(chloromethyl)-2,2'-bipyridine,¹³ respectively.^{5c,8} Poly(methyl methacrylate) ligands, bpyPMMA, **5**, and bpyPMMA₂, **6**, (Table 1) were synthesized using bromoester bpy initiators made by esterification of the appropriate hydroxymethyl bpy¹⁴ with 2-bromoisobutryl bromide. Ruthenium-centered heteroarm star block copolymers were prepared by chelation of two bpyPS_n macroli-

(10) For a related metal-free example see: Tong, J.-D.; Ni, S.; Winnik, M. A. *Macromolecules* **2000**, *33*, 1482.

(11) Xia, J.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 7697.

(12) Savage, S. A.; Smith, A. P.; Fraser, C. L. *J. Org. Chem.* **1998**, *63*, 10048.

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

(14) Smith, A. P.; Corbin, P. S.; Fraser, C. L. *Tetrahedron Lett.* **2000**, *41*, 2787.

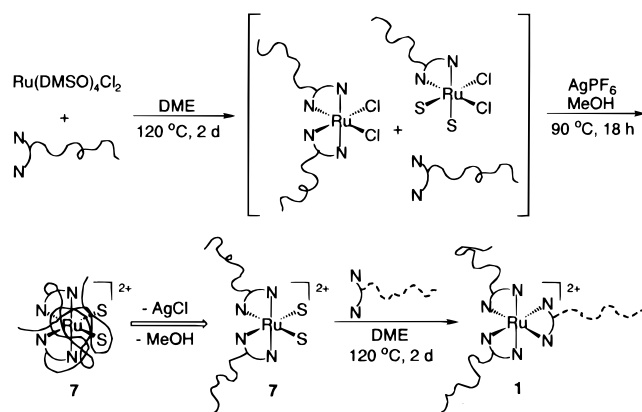


Figure 2. Synthesis of $[\text{Ru}(\text{bpyPS})_2(\text{bpyPMMA})]^{2+}$ (**1**) with illustration of the importance of MeOH addition in “protecting” the Ru center during $[\text{Ru}(\text{bpyPS})_2(\text{S})_n]^{2+}$ (**7**) formation and of its removal to “deprotect” the complex for bpyPMMA chelation. (— = PS; - - - = PMMA).

gands, followed by one bpyPMMA_n to the appropriate labile Ru intermediates (Figure 2). Reaction of $\text{Ru}(\text{DMSO})_4\text{Cl}_2$ with 2 equiv of bpyPS₂ ($M_n = 4800$) in dimethoxyethane (DME) produced $[\text{Ru}(\text{bpyPS})_2\text{Cl}_2]$ (MLCT: $\lambda_{\text{max}} = 571$ nm) after refluxing for ~ 1 week. For reactions with bpyPS of higher molecular weight ($M_n = 22\,400$), it was discovered that the formation of a Ru bis(bpy) intermediate could be accelerated if, after 2 days, MeOH and AgPF_6 were added to the mixture containing primarily $[\text{Ru}(\text{bpyPS})_2\text{Cl}_2]$, but also unreacted bpyPS and by inference, $[\text{Ru}(\text{bpyPS})_2(\text{S})_n]$ ($\text{S} = \text{MeOH}$ or DME). When Ag^+ was added in the absence of MeOH, a mixture of the desired $[\text{Ru}(\text{bpyPS})_2(\text{S})_n]^{2+}$ intermediate, **7**, and a $[\text{Ru}(\text{bpyPS})_3]^{2+}$ impurity resulted.^{8b} It is postulated that the polystyrene chains are more collapsed around the metal center in DME/MeOH relative to their conformation in DME, thus protecting the Ru bis(bpy) solvento complex and biasing unreacted bpyPS to coordinate with the sterically less crowded Ru intermediate bearing a single bpyPS. Even intentional addition of excess macroligand did not produce tris products when MeOH was present. In contrast, reactions with low molecular weight macroligand may not be accelerated by $\text{AgPF}_6/\text{MeOH}$ addition, possibly because they do not provide enough steric bulk to hinder Ru tris(bpy) formation.

Synthesis of substitutionally labile solvento intermediates, $[\text{Ru}(\text{bpyPS})_2(\text{S})_n]^{2+}$, **7** ($n = 1$) and **8** ($n = 2$), also proved necessary for the introduction of a third α -diimine ligand into the Ru coordination sphere (Figure 2) because reactions of bidentate ligands with $[\text{Ru}(\text{bpyPS})_2\text{Cl}_2]$ were unsuccessful. After filtration to remove AgCl , MeOH was evaporated. This presumably generates a less compact polymer conformation,¹⁵ thus “deprotecting” the Ru centers for reaction with bpyPMMA_n in

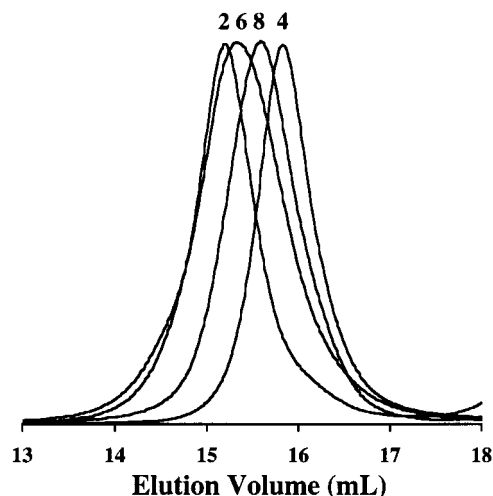


Figure 3. Overlay of the GPC traces for $[\text{Ru}(\text{bpyPS})_2(\text{bpyPMMA}_2)]^{2+}$ (**2**), $[\text{Ru}(\text{bpyPS})_2(\text{S})_n]^{2+}$ (**8**), and the macroligands, bpyPS₂ (**4**) and bpyPMMA₂ (**6**), from which they were made. (Note: PS-containing polymers elute later than bpyPMMA₂ of comparable molecular weight.) DME. After refluxing for 2 days, the heteroarm stars, $[\text{Ru}(\text{bpyPS})_2(\text{bpyPMMA}_n)]^{2+}$, **1** ($n = 1$) and **2** ($n = 2$), were produced. GPC coupled with in-line diode array UV/vis spectroscopic detection confirmed that Ru tris(bpy) chromophores were associated with the eluting polymer fractions (MLCT: $\lambda_{\text{max}} = \sim 460$ nm). The GPC traces for bpyPS₂, bpyPMMA₂, the corresponding Ru solvento intermediate, **8**, and the six-arm star product, **2**, are compared in Figure 3.

It has been demonstrated that the use of solvent polarity to influence chain conformation, and thus to turn reactions on and off, is important for achieving control in the assembly of heteroarm star polymers by a modular macroligand chelation approach. Other targets with different architectures and ligand sets, as well as structural characterization of luminescent block copolymer films,¹⁶ will serve as subjects of future reports.

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Supporting Information Available: Experimental details and characterization of compounds (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA001360P

(15) (a) Heise, A.; Hedrick, J. L.; Frank, C. W.; Miller, R. D. *J. Am. Chem. Soc.* **1999**, *121*, 8647. (b) Gitsov, I.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1996**, *118*, 3785.

(16) Preliminary investigations of polymer microstructure revealed a spherical morphology (25 nm diameter spheres with 50 nm center-to-center spacing) for annealed, thin, free-standing films of $[\text{Ru}(\text{bpyPS})_2(\text{bpyPMMA})]^{2+}$ (bpyPS: $M_n = 18\,300$; bpyPMMA: $M_n = 21\,300$; heteroarm star: $M_n = 51\,000$). Urbas, A. M.; Thomas, E. L.; Smith, A. P.; Wu, X.; Fraser, C. L. Unpublished results.