2972 *Macromolecules* **2008**, *41*, 2972−2974

Tris(1-pyrazolyl)borate (Scorpionate) Functionalized Polymers as Scaffolds for Metallopolymers

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Received February 11, 2008
Revised Manuscript Received March 27, 2008

Since their introduction in 1966 tris(1-pyrazolyl)borates (Tp), also known as scorpionates, have been extensively used as polydentate ligands with widespread applications in catalysis and materials chemistry.[1] Their polytopic analogues with multiple Tp ligands attached to a suitable backbone have recently attracted interest as potential building blocks for the assembly of new metal-containing polymers.[2] For instance, ditopic ligands, which feature two Tp (or related) functionalities that are bridged by a phenylene[3] or ferrocenylene[4] moiety, were reported by Niedenzu and Wagner. They are promising as precursors to linear rigid-rod coordination polymers through metal−ligand coordination. However, such a stepwise polymerization process provides little control and hence often leads to low molecular weights (MW), broad MW distributions, and sometimes to limited solubility. An intriguing alternative approach is to incorporate Tp ligands into well-defined polymeric structures, which may then be used as scaffolds for new metallopolymers with novel optical, electronic, or magnetic properties.[5] Polymers with, for example, multiple phosphine or polypyridyl binding sites continue to play important roles as supported reagents, catalysts, and linkers in organic synthesis,[6] as luminescent materials,[7] and in the assembly of supramolecular polymers.[8] The selective incorporation of Tp functionalities into polymeric structures is expected to greatly expand the variety of polymer-supported ligands and ultimately that of metal-containing polymers; at the same time, it provides the versatile Tp ligands with unique polymer properties such as enhanced stability and favorable processability.

We chose a polymer modification approach starting with poly(4-trimethylsilylstyrene). We have shown previously that 4-trimethylsilylstyrene can be polymerized by atom transfer radical polymerization (ATRP) to give functional polymers of narrow molecular weight and that excellent architectural control can be achieved.[9] The high selectivity of silicon−boron exchange reactions with BBr_3 then provides an excellent tool for attachment of the desired borate functionalities to polystyrene. As discussed in our recent work, the alternative route of direct polymerization of the respective boron monomers can in some cases be advantageous for the preparation of copolymers, but generally polymerization control is more difficult to achieve.[9d] Copolymers with different boron loadings were prepared by silicon/boron exchange to determine the optimal conditions for Tp functionalization. Poly(4-trimethylsilyl)styrene ($M_n = 16.4 \times 10^3$, PDI = 1.11) was treated with 0.25, 0.50, 0.75, and 1.00 equiv of BBr_3 (relative to $SiMe_3$ groups) in CH_2Cl_2 for 24 h (Scheme 1). Random replacement of the Me_3Si moieties is expected to take place under these conditions, and integration of the ^1H NMR signal of the residual $SiMe_3$ groups relative to the other aliphatic and aromatic protons suggested boron loadings of 24%, 48%, 73%, and 97%, respectively (see Figure S2 in the Supporting Information). Thus, the degree of boron functionalization is very close to that expected on the basis of the feed ratio of BBr_3. In-situ treatment of the resulting BBr_2 functionalized copolymer **1** with a slight excess of Me_3SiNMe_2 gave the $B(NMe_2)_2$-modified random copolymer **2**. An upfield shift of the ^{11}B NMR signal to $\delta = 32$ ppm (cf. **1**, $\delta = 56$ ppm) is consistent with attachment of the NMe_2 groups to boron, as is the observation of a new broad peak in the ^1H NMR at $\delta = 2.65$ ppm. Integration of the signal for the $B(NMe_2)_2$ moieties relative to the $SiMe_3$ signal is in excellent agreement with the degree of boron functionalization expected on the basis of the feed ratio of BBr_3 and consistent with that determined for the BBr_2-functionalized intermediate (see Figure S3 in the Supporting Information). The NMR data also confirm the high selectivity of these facile polymer modification procedures.

The products were isolated by free-drying from benzene and their conversion to polymers **3-Na** by treatment with pyrazole/sodium pyrazolide in THF was studied.[10] Polymers **2** were dissolved in THF, then 2 equiv of pyrazole (HPz) and 1 equiv of NaPz were added, and the mixtures were kept at 80 °C under a gentle flow of N_2 for efficient removal of $HNMe_2$. We found that the polymers with 24 and 48% loading remained soluble throughout the reaction period of 6 h. The polymer with 73% loading precipitated partially and very gradually, while the one with 97% functionalization precipitated almost immediately and almost quantitatively.[10] The THF-soluble polymers (24 and 48% functionalization) were directly studied by gel permeation chromatography (GPC) in DMF with 20 mM LiBr at 40 °C (RI detector), and the precipitates of the polymers with 74 and 97% loading were dissolved in DMF and also subjected to GPC analysis in DMF with 20 mM LiBr at 40 °C (RI detector). At 24% loading an average molecular weight of $M_n = 23.9 \times 10^3$ (PDI of 1.21) is observed, at 48% M_n is determined to 32.1×10^3 (PDI = 1.31), and at 73% loading M_n increases to 44.7×10^3 (PDI = 1.37). This is consistent with the expected increase in molecular weight of the polymer with increasing content of Tp moieties, and an almost linear increase in molecular weight with degree of Tp functionalization is obtained (see Figure S1 in the Supporting Information).[11] Column interactions likely contribute to the slight band broadening relative to the profile of the silylated precursor in THF ($M_n = 16.4 \times 10^3$; PDI = 1.11); band broadening was also observed for the silylated precursor in DMF, in which it is only poorly soluble. Finally, the polymer with 97% functionalization ($M_n = 40.9 \times 10^3$; PDI = 1.48) shows a high molecular shoulder. This is likely due to poor control of the reaction with pyrazole/sodium pyrazolide due to almost immediate precipitation of the (partially substituted) product.

An aminoborane-functionalized polymer **2** with 30% loading was chosen for the preparative synthesis of **3-Na**. The polymer **3-Na** was isolated by removal of volatile materials and extensively washed with ether. A large upfield shift of the ^{11}B NMR signal to $\delta = 1$ ppm confirms conversion to tetracoordinate borate functionalities and is consistent with the chemical shift measured for the molecular analogue, sodium 4-*tert*-butylphenyltris(pyrazolyl)borate (see Supporting Information). The product is well soluble in THF and acetone, indicating smooth reaction without significant cross-linking.[12]

To explore the ability of these novel Tp-functionalized polymers to bind to metal complexes, we chose to examine the formation of a complex of **3-Na** ($x = 0.3$) with the CpRu (Cp

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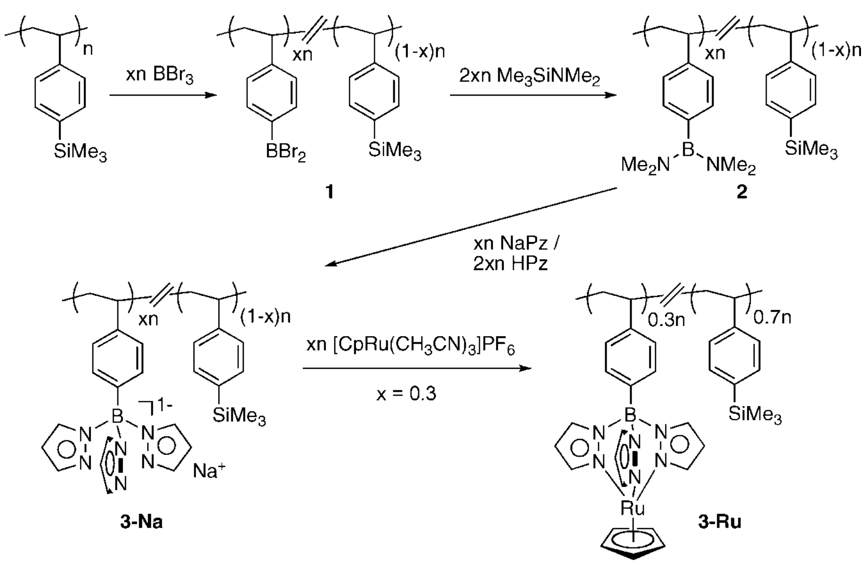
10.1021/ma800310v CCC: $40.75

Scheme 1. Synthesis of Tp-Functionalized Polymers (Pz = Pyrazolyl)



= cyclopentadienyl) fragment (Scheme 1). The mixed-ligand complexes $CpRuTp^R$ (Tp^R = substituted Tp ligands) are known to exhibit good stability toward air and moisture, are redox-active, and are readily accessible by reaction with $[CpRu(CH_3CN)_3]PF_6$.[13] To address the specific solubility characteristics of the polymeric precursor **3-Na**, we developed a procedure for the preparation of the Ru polymer **3-Ru**, in which a solution of **3-Na** in acetone was refluxed in the presence of $[CpRu(CH_3CN)_3]PF_6$ over a period of 12 h. The product **3-Ru** was isolated in high yield (84%) by precipitation into nitrogen-flushed methanol. The respective model compound $(4\text{-}^t BuC_6H_4BPz_3)RuCp$ (**4-Ru**), which resembles one repeat unit of the polymer chain, was also prepared for comparison (see Supporting Information).

The ^{11}B NMR signal for **3-Ru** remains in the tetracoordinate region at $\delta = -3$ ppm. The ^1H NMR of **3-Ru** reveals a singlet at $\delta = 4.06$ ppm that corresponds to the Cp ring protons (Figure 1). Integration of this signal is consistent with ~30% functionalization, indicating smooth and essentially quantitative complexation of the CpRu fragment to the Tp moieties without cleavage of the boron moieties from the polymer backbone. The B−N distance derived from the crystal structure of **4-Ru** is only slightly longer than that reported for $CpRu(HBPz_3)$[13] (Figure 2; see also the Supporting Information). Hence, the bulkier and more electron-donating Ph substituent does not significantly impact the bonding and in turn the complex stability. Indeed, the novel metallopolymer **3-Ru** is air-stable and so is the molecular species **4-Ru**.

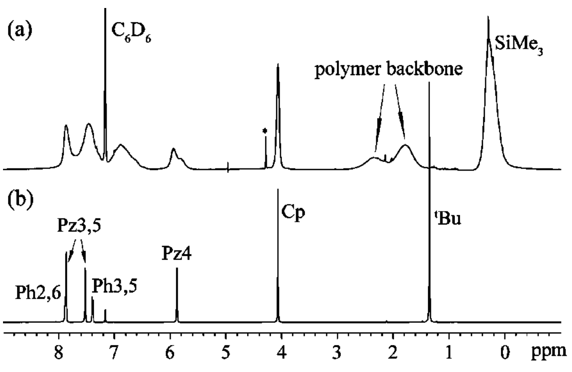


Figure 1. ^1H NMR spectra of (a) **3-Ru** and (b) **4-Ru** in C_6D_6 (* CH_2Cl_2).

GPC using RI detection in DMF gave $M_n = 27.6 \times 10^3$ and PDI = 1.19 for **3-Ru**. The molecular weight is slightly higher than that of the particular silylated precursor polymer used in this case ($M_n = 21.7 \times 10^3$) but still considerably lower than calculated for 30% functionalization. However, this is to be expected given that GPC is based on size exclusion, and only the MW but not the size increases dramatically upon attachment of the "heavy" metal units.

The thermal properties of the polymer were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC revealed a relatively high glass transition temperature of $T_g = 210$ °C for **3-Ru**, which is likely due to the more rigid nature of the CpRu moieties. TGA under N_2 demonstrated the high thermal stability of **3-Ru** with a single step decomposition starting at 350 °C (82% total weight loss at 800 °C).[14]

Cyclic voltammetry was used to further examine the redox properties of the metallopolymer **3-Ru** (Figure 3). With $Bu_4N[B(C_6F_5)_4]$ as the supporting electrolyte[15] a reversible oxidation process was observed at $E^{0\prime} = -77$ mV vs Cp_2Fe/Cp_2Fe^+, which

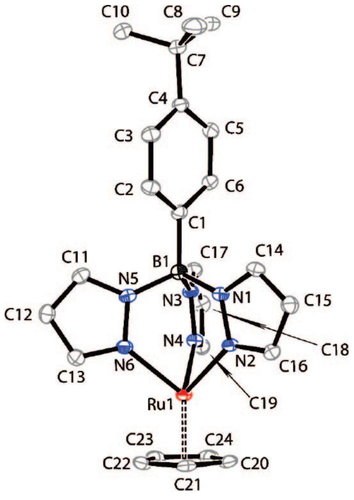


Figure 2. ORTEP plot of **4-Ru**.

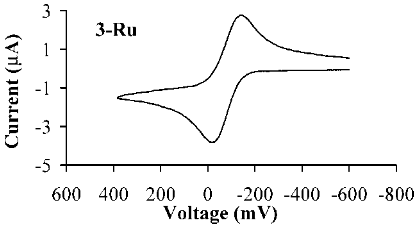


Figure 3. Cyclic voltammogram of **3-Ru** in CH_2Cl_2 with 0.1 M $Bu_4N[B(C_6F_5)_4]$ at 200 mV/s (vs Cp_2Fe/Cp_2Fe^+).

matches the potential for **4-Ru** and is comparable to $E^{0\prime} = -70$ mV (390 mV vs SCE) reported for $CpRu(HBPz_3)$.[13]

In conclusion, we have developed a versatile approach for the preparation of Tp-substituted polymers, where the loading is controlled by the feed ratio of BBr_3, and hence a series of functional polymers with varying degree of loading are accessible from one single polymer precursor. The remaining $SiMe_3$ groups can be advantageous in that they promote solubility in moderately polar solvents such as THF or acetone, which often need to be used in reactions of Tp ligands with transition metal complexes. Good solubility of **3-Na** in the reaction medium THF was achieved with up to ca. 50% Tp coverage. Even at 75% loading, smooth functionalization occurs, despite the gradual precipitation of the product polymer **3-Na** from the reaction mixture. The polymer with 75% loading is well soluble in DMF, and ^1H NMR and GPC analyses support its structural integrity. An area of further exploration will be to realize even higher loadings by use of more polar solvents or solvent mixtures in the pyrazole substitution step.

The successful preparation of the novel metallopolymer **3-Ru** demonstrates the synthetic utility of these Tp polymers; extension to other catalytically active metal complexes, attempts to realize different polymer architectures including block copolymers, and the application to supramolecular polymer chemistry are currently under way.

Acknowledgment. is made to the National Science Foundation (CAREER CHE-0346828, MRI-0116066, CRIF-0443538) and the Alfred P. Sloan foundation for support of this research. We thank Dr. K. Venkatasubbaiah and A. Doshi for acquisition of X-ray data.

Supporting Information Available: Experimental details for all polymers and model compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) For solubility reasons, the Na salt was chosen over the commonly used K salt. A reviewer noted that the solubility characteristics could also be optimized by using long alkyl side chains or a copolymerization method. Indeed, another approach would be to prepare Tp copolymers from styrene/trimethylsilylstyrene random copolymers. However, in contrast to our highly modular approach, multiple polymer precursors would be needed to achieve different loadings. Moreover, the remaining silyl groups have a dual function in that they themselves serve to further promote solubility in moderately polar solvents (in analogy to the alkyl side chain approach). Given the high stability of silicon−carbon bonds, no adverse effects are expected for most applications in materials chemistry or catalysis.

(11) The theoretical molecular weights at 24, 48, and 73% functionalization are 20.0, 23.6, and 27.4 × 10^3 Da, respectively, using a formula of BPz_3Na for the boron pendant groups. If three DMF molecules are assumed to coordinate to sodium for a hexacoordinate environment, these values increase to 24.9, 33.4, and 42.3 × 10^3 Da. The latter data are very close to those determined experimentally.

(12) Pyrazabole formation is typically observed for reactions of $RBBr_2$ species with pyrazole, which would lead to cross-linking in the case of polymers; however, reaction of the respective $B(NMe_2)_2$-substituted derivatives leads to selective formation of the desired Tp ligands; see refs 3 and 4.

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(14) The residue likely contains boron ceramic material; boron polymers are commonly used as precursors to boron carbide and boron nitride materials: Sneddon, L. G.; Pender, M. J.; Forsthoefel, K. M.; Kusari, U.; Wei, X. *J. Eur. Ceram. Soc.* **2005**, *25*, 91–97. This may also be related to the slightly low %C and %N for the elemental analysis of **4-Ru**.

(15) When conducted with 0.1 M $[Bu_4N]PF_6$ irreversible redox behavior was observed likely due to poor solvation of the charged polymer and deposition on the electrode.

MA800310V