

Synthesis of transition-metal-containing poly(pyrazabole)s*

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Abstract: Novel organoboron polymers containing transition metals (Ni, Pd, Pt) and pyrazaboles in the main chain were prepared by Cu-catalyzed coupling polymerization. The Ni- and Pt-containing polymers showed MLCT (metal-to-ligand charge transfer) absorption, whereas the Pd-containing polymer did not demonstrate the absorption. Only the Pd-containing polymer exhibited the emission spectrum with a vibronic structure. These differences in the optical properties were studied in detail.

Keywords: organoboron polymers; transition metals; pyrazaboles; Heck–Sonogashira coupling; optical properties.

INTRODUCTION

We have synthesized various organoboron polymers by way of hydroboration polymerization [1–3]. Recently, we prepared novel organoboron polymers containing pyrazabole [4]. These polymers are highly stable against air and moisture. Furthermore, they exhibit strong emission in a short wavelength region, and the emission spectra have the vibronic structure typical of pyrazabole moiety. Generally, pyrazabole is regarded as an electron-withdrawing molecule because of the strong electron affinity of boron atoms [5]. Moreover, it is reported that the boron atom in pyrazabole can relay the electrons of neighbor pyrazole rings [5]. Further functionalization is necessary, in order to investigate this property of the poly(pyrazabole)s. On the other hand, transition-metal complexes of π -conjugated polymers constitute a potentially important class of polymers for polymer electronics. When the metal is bridged between organic conjugated spacers, we could obtain the metal-polyynes with a rigid rod conjugated architecture that gives rise to a number of interesting properties such as liquid crystal [6] and third-order nonlinear optical behavior [7,8]. Their innovative characteristics in optics and electronics are due to a synergy of delocalization effects of the organic spacer and mobility of d-metal electrons, that give rise to metal-to-ligand charge transfer (MLCT) effects [9]. Thus, these physical properties would be tailored by changing the transition metal or the organic spacer. In this study, we investigate the combination of transition metals and pyrazaboles to offer the novel organoboron polymers with improved properties.

EXPERIMENTAL

Materials and instruments

Tetrahydrofuran (THF) and diisopropylamine were distilled before use. ¹H, ¹¹B and ³¹P NMR spectra were recorded in CDCl₃ on a JEOL EX-270 instrument. infrared (IR) spectra were obtained on a

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Perkin-Elmer 1600 spectrometer. Gel permeation chromatographic (GPC) analysis was carried out on a TOSOH G3000HXL by using THF as an eluent after calibration with polystyrene standards. UV-vis spectra were recorded on a JASCO V-530 spectrophotometer. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer. Cyclic voltammetry was recorded on a BAS CV-50W Electrochemical Analyzer. *Trans*-dichlorobis(tributylphosphine)-palladium (**1a**) [10], Pt (**1b**) [10] and Ni (**1c**) [10], and 2,6-diethynyl-4,4,8,8-tetrahexylpyrazabole (**2**) [4] were prepared according to the reported procedure. Other reagents were commercially available and purified before use. All reactions were performed under nitrogen atmosphere.

Pd-PZB (**3a**)

To a mixture of *trans*-dichlorobis(tributylphosphine)palladium(II) (**1a**) (0.175 g, 0.30 mmol), 2,6-diethynyl-4,4,8,8-tetrahexylpyrazabole (**2**) (0.163 g, 0.30 mmol), CuI (0.005 g, 0.026 mmol) and 10 ml of THF, 5 ml of diisopropylamine was added at room temperature. After refluxing for 12 h, the solvents were removed in vacuo. The residue was poured into *t*-butyl methyl ether, and the ammonium salt was removed from the solution by filtration. The orange solid (0.288 g, 91 %) was reprecipitated from methanol and dried. NMR data (solution in CDCl₃): δ (¹H, ppm) = 7.39 (4H, Pz), 2.01–0.75 (106H, hexyl, butyl); δ (¹¹B, ppm) = –0.19; δ (³¹P, ppm) = 12.08. IR (cm^{–1}) = 2115 (ν -C≡C-).

Pt-PZB (**3b**)

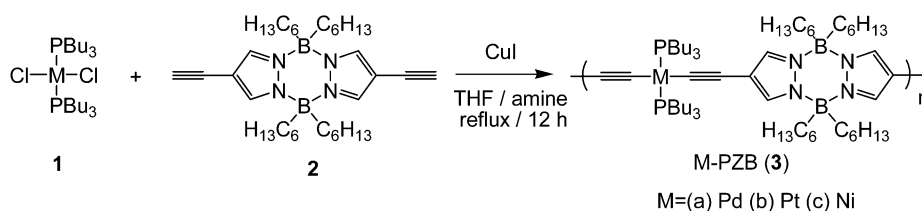
The reaction was carried out by following the procedure described above. The polymerization between 0.201 g (0.30 mmol) of Pt-complex (**1b**) and 0.163 g (0.30 mmol) of **2** gave the corresponding polymer **3b** (0.323 g, 94 %). NMR data (solution in CDCl₃): δ (¹H, ppm) = 7.39 (4H, Pz), 2.13–0.79 (106H, hexyl, butyl); δ (¹¹B, ppm) = –5.93; δ (³¹P, ppm) = 4.39. IR (cm^{–1}) = 2119 (ν -C≡C-).

Ni-PZB (**3c**)

Coupling reaction between 0.107 g (0.20 mmol) of Ni-complex (**1c**) and 0.109 g (0.20 mmol) of **2** followed by reprecipitation into methanol gave the Ni-containing polymer **3c** (0.05 g, 25 %). NMR data (solution in CDCl₃): δ (¹H, ppm) = 7.39 (4H, Pz), 2.11–0.75 (106H, hexyl, butyl); δ (¹¹B, ppm) = –0.14; δ (³¹P, ppm) = –8.14. IR (cm^{–1}) = 2100 (ν -C≡C-).

RESULTS AND DISCUSSION

Synthesis of the metal-containing poly(pyrazabole)s was carried out by Cu-catalyzed dehydrohalogenation as described in Scheme 1. To a solution of metal complex (**1**) and the diethynyl derivative of pyrazabole (**2**) in THF, amine was added as a base and the reaction mixture was refluxed for 12 h under nitrogen atmosphere. The insoluble salts were removed, and the resulting polymers M-PZB (**3a–c**) were further purified by reprecipitation into methanol. The number-average molecular weights of the obtained polymers were estimated from the result of GPC based on polystyrene calibration curves. As shown in Table 1, the molecular weight and the polymer yield of Ni-PZB (**3c**) were relatively low compared to other polymers. These results can be accounted by low stability of the Ni complex (**1c**), which caused a decomposition of the monomer in some extent during the polymerization. The obtained polymers were further characterized by ¹H, ¹¹B, and ³¹P NMR spectra.



Scheme 1 Polymerization.

Table 1 Polymerization results.

Polymer	M_n^a	M_w^a	M_w/M_n^a	Yield (%) ^b
Pd-PZB (3a)	10 000	20 000	2.0	91
Pt-PZB (3b)	17 000	57 000	3.3	94
Ni-PZB (3c)	5500	11 200	2.0	25

^aMeasured by GPC (THF). Polystyrene standards.^bIsolated yields after reprecipitation into MeOH.

Optical properties

The UV–vis absorption spectra of these polymers are shown in Fig. 1. Strong absorption bands around 350 nm were observed in Pt-PZB (3b) and Ni-PZB (3c), however, not shown in the case of Pd-PZB (3a). These bands can be attributed to MLCT absorption, which is the charge transfer from transition metal to alkynyl bonds. This peculiarity of Pd-PZB (3a) was also observed in the fluorescence emission spectra (Fig. 2). The distinct vibronic structure appeared in the spectrum of Pd-PZB (3a), whereas the gentle-sloped peaks were observed in Pt-PZB (3b) and Ni-PZB (3c). This vibronic structure was accepted to be derived from the vibronic mode of pyrazole ring [5]. That is, it is characteristic to the emission spectra of poly(pyrazabole)s. These differences in emission spectra should be assigned to the electron state of the polymer main chain. In Pd-PZB (3a), the electrons related to emission should be localized on the pyrazabole moieties, whereas the electrons on Pt-PZB (3b) and Ni-PZB (3c) are assumed to be delocalized on the main chain. It is also recognized that the extension of π -conjugation through the transition metals is more effective in the latter two polymers. The relative fluorescence quantum efficiencies of these polymers were lower than 1 %.

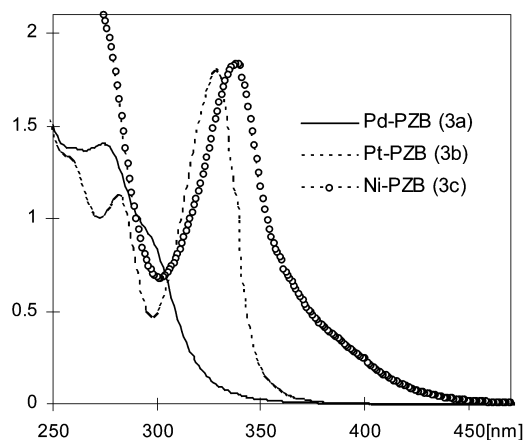


Fig. 1 UV–vis absorption spectra of the polymers (3a–c) in chloroform at room temperature.

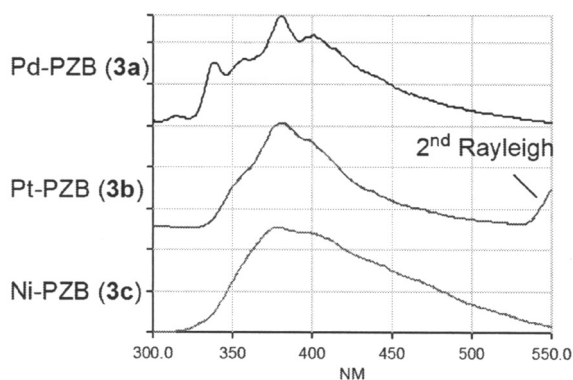


Fig. 2 Fluorescence emission spectra of the polymers (**3a–c**) at 1.0×10^{-5} M in chloroform, excited at 300 nm.

To understand the complicate difference in $d\pi\text{-}p\pi^*$ interaction, further information on the electron density was collected. The electrochemical behavior of these polymers was studied by cyclic voltammetry using 0.1 M THF solution of tetra-*n*-butylammonium perchlorate. As represented in Fig. 3, the cyclic voltammograms of the polymers showed reversible cycles at $E^0 = +0.9$ V [Pd-PZB (**3a**)], $+0.83$ V [Pt-PZB (**3b**)], and $+0.61$ V [Ni-PZB (**3c**)], respectively. This result is consistent with the fact that the electron density on Pd is the highest, and lowest on Ni. From evaluation of the length of the alkynyl bond in IR measurement, it was getting longer in an order of Pt-PZB (**3b**) < Pd-PZB (**3a**), < Ni-PZB (**3c**). The electron density on the boron atom was also estimated by ^{11}B NMR spectra. As a result, the boron atom in Pt-PZB (**3b**) had the highest density, and lowest in Ni-PZB (**3c**). These results recognize that the electron density on the boron atom becomes higher as the length of the alkynyl bond is short (Table 2). However, this relation is inconsistent with the trend of the electron density on metals. Eventually, it is difficult to understand the relation between the optical property and the electron state. Whereas, it should be mentioned that an interaction is significant for the optical properties, between transition metals and electron-withdrawing pyrazaboles. Further studies using model compounds are now in progress.

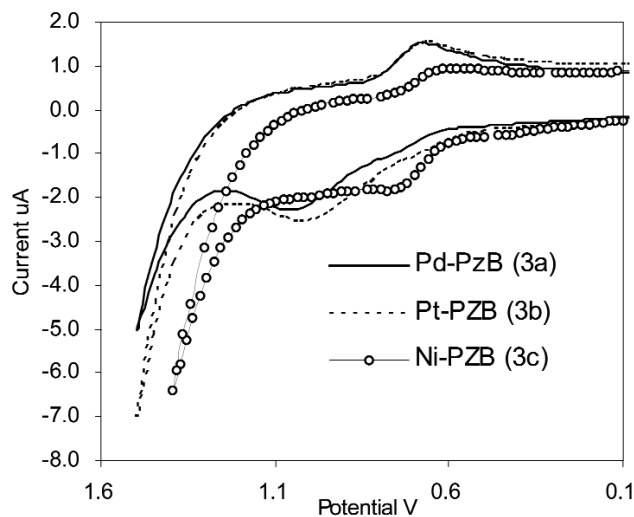


Fig. 3 Cyclic voltammograms of the polymers (**3a–c**) recorded in 0.1 M THF solution of tetra-*n*-butylammonium perchlorate using Pt electrode (vs. Ag/Ag^+) at the sweep rate of 100 mV/s.

Table 2 Results of CV, IR, and ^{11}B NMR measurements.

Polymer	E^0 (V) ^a	IR (cm ⁻¹) ^b	^{11}B NMR (δ , ppm)
Pd-PZB (3a)	+0.9	2115	-0.19
Pt-PZB (3b)	+0.83	2119	-5.93
Ni-PZB (3c)	+0.61	2100	-0.14

^aMeasured by cyclic voltammetry in 0.1 M *n*-Bu₄NClO₄.^bWavenumbers of alkynyl bonds.

CONCLUSIONS

Novel poly(pyrazabole)s containing transition-metal complex were synthesized. The obtained polymers had high molecular weight and showed good solubility in common organic solvents. The absorption and the emission spectrum of Pd-containing polymers showed specific properties compared with other polymers. The interaction between transition metals and pyrazaboles is considered to be significant in these polymers.

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