

Synthesis and characterization of organometallic conjugated polymers containing tricarbonyl(arene)chromium unit and platinum

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Abstract

Novel organometallic conjugated polymer containing (η^6 -arene)Cr(CO)₃ and platinum in the main chain was synthesized by dehydrohalogenation coupling reaction of (η^6 -1,4-diethynylbenzene)tricarbonylchromium with *trans*-(PBu₃)₂PtCl₂. The polymer was soluble in common organic solvents and has the number-average molecular weight of 31,000 by GPC analysis. The polymer exhibited an absorption peak derived from π – π^* interaction at 358 nm in the UV–Vis spectrum, which showed a red shift of approximately 90 nm compared to that of the model compound. The photochemical ligand exchange reaction of the polymer was also investigated.

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1. Introduction

In recent years, a wide variety of transition-metal-containing polymers have been synthesized for the potential applications in areas such as conducting and optoelectronic materials [1]. Among these polymers, the first conjugated poly-yne polymers including Ni, Pd, and Pt were synthesized by Hagihara and co-workers [2] by means of a dehydrohalogenation reaction using CuX as a catalyst, and the polymers obtained exhibited liquid crystallinity [3]. In general, incorporation of the transition-metal atom into the conjugated polymer backbone with alkynyl linkages does not result in an effective conjugation due to the orbital mismatch

between a d-orbital of the transition-metal and a π -orbital of the alkynyl moiety.

Recently, we reported the preparation of π -conjugated organoboron polymers [4,5] containing transition-metal complexes, such as Fe [6], Ru [7], Pd [8], and Pt [9] via hydroboration polymerization. A remarkable extension of π -conjugation length was observed according to the bathochromic shift of the absorption spectra of these polymers resulting from the donor–acceptor effect between the electron-donating transition-metal complex and the electron-accepting boron atom.

On the other hand, it is well known that the tricarbonylchromium fragment, Cr(CO)₃, has the strongly electron-withdrawing character and it activates the η^6 -coordinated arene ligand toward nucleophilic substitution [10–12]. In other words, the tricarbonyl(arene)chromium complex, (η^6 -arene)Cr(CO)₃, can act as an electron acceptor, since the electron density of η^6 -coordinated arenes in a Cr(CO)₃ unit is highly

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deficient. Furthermore, there has also been much interest in $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complexes due to their redox activity [13–16], ligand exchange reaction [17], possible application in nonlinear optical molecules [18], and use as a catalyst [19]. However, little research has been performed regarding the synthesis of a conjugated polymer containing a $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ unit in the main chain [20–23]. Wright [20] reported the first synthesis of poly(*p*-phenylene-ethynylene) (PPE) including a $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ moiety in the main chain by means of the Stille coupling reaction of $(\eta^6\text{-1,4-dichlorobenzene})\text{Cr}(\text{CO})_3$ with organostannane reagents. According to the thermogravimetric analysis (TGA), these polymers showed thermal stability; however, they showed low solubility in common organic solvents. Recently, we reported the synthesis of the first soluble $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ -containing π -conjugated polymers by the Sonogashira coupling reaction for PPE [24,25] or the Horner–Emmons–Wadsworth coupling reaction for poly(*p*-phenylenevinylene) (PPV) [26,27], which showed redox activity and conductivity. In this paper, we report on the synthesis and properties of the novel transition-metal-containing conjugated polymer alternately having a $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ unit as the acceptor and platinum as the donor in the main chain.

2. Results and discussion

Monomers $(\eta^6\text{-1,4-diethynylbenzene})\text{tricarboxyl-chromium}$ **1** [28] and *trans*-(PBu_3)₂PtCl₂ **2** [29] were prepared according to synthetic procedures previously reported. Polycondensation of **1** with **2** was carried out in the presence of a catalytic amount of CuI in THF–HNEt₂ at reflux temperature for 24 h, as shown in Scheme 1. After the work-up procedures, the copolymer **3** was obtained in a quantitative yield with a number-average molecular weight of 31,700 and a polydispersity of 1.9 determined by gel permeation chromatography (GPC) using polystyrene standards (CHCl_3 eluent). The polymer **3** had good solubility in common organic solvents and could be processed into transparent and uniform thin films by casting or spin-coating from toluene. In addition, the reference polymer **4** without a $\text{Cr}(\text{CO})_3$ complex coordinated to the phenylene moieties ($M_w = 71,000$, $M_n = 39,000$) and the model compound **5** were also prepared (Chart 1).

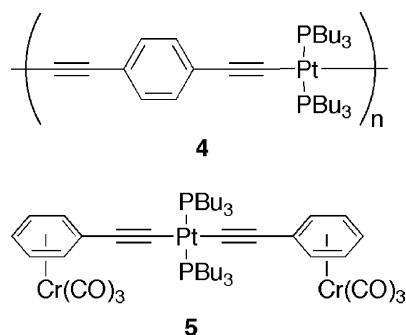


Chart 1.

The structure of the polymer **3** was confirmed by NMR and FT-IR spectra. In the ¹H NMR spectrum of **3** in CDCl_3 solution (Fig. 1), the peak corresponding to the terminal alkyne proton of the monomer **1** disappears completely, and the peaks of the butyl group are observed in the range of 0.9–2.1 ppm. The aromatic proton peaks of the phenylene unit η^6 -coordinated to $\text{Cr}(\text{CO})_3$ moieties appear at 5.3 ppm. In addition, the peaks around 7.1 ppm are derived from aromatic protons of the phenylene units by the thermal- or photo-dissociation of the $\text{Cr}(\text{CO})_3$ moieties. This result indicates that the polymer **3** consists of 70% chromium-coordinated phenylene and 30% normal phenylene units as

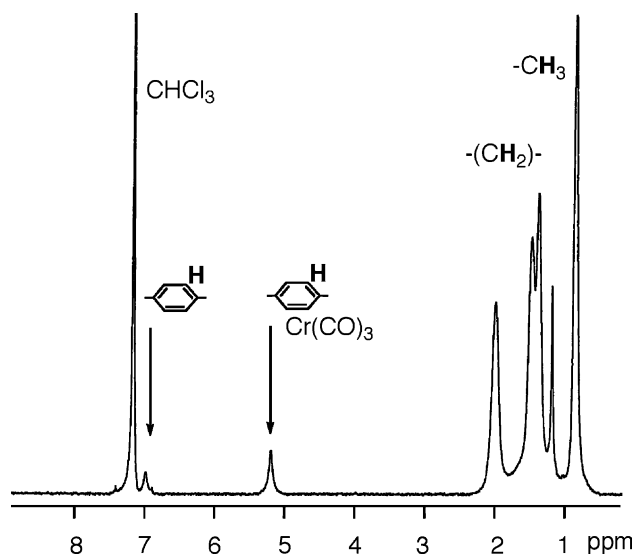
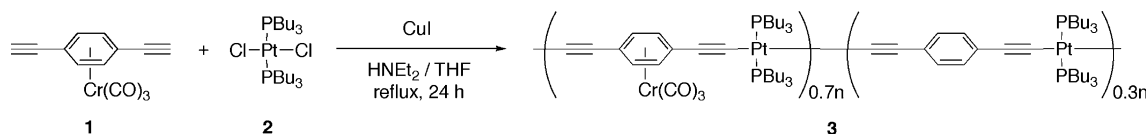


Fig. 1. ¹H NMR spectrum of the polymer **3** in CDCl_3 .



Scheme 1.

determined by calculation from a proton integral ratio. The polymerization under UV light or UV irradiation to the polymer **3** resulted in the complete removal of tricarbonylchromium groups from the polymer chain [25]. In the ^{13}C NMR spectrum of **3**, typical signals for acetylenic carbons are found at 96.4 and 110.9 ppm, and the peak of the coordinated carbonyl carbon appears at 231.0 ppm. In the IR spectrum, **3** shows characteristic absorption bands at 1958 and 1891 cm^{-1} (stretching vibrations of coordinated carbon monoxide), and at 2108 cm^{-1} corresponding to the weak stretching vibrations of the internal carbon–carbon triple bond.

The optical property of the polymer obtained was investigated by the UV–Vis absorption measurement in a dilute CHCl_3 solution at room temperature, and the spectrum is shown in Fig. 2. The absorption maximum of the polymer **3** corresponding to the π – π^* transition in the conjugated polymer backbone was observed at 358 nm ($\log \epsilon = 4.58$), and the broad absorption peak due to metal-to-ligand charge transfer (MLCT) band was also observed around 430 nm. The UV–Vis absorption spectrum of the model compound **5** (Chart 1) is shown in Fig. 2. The UV–Vis spectrum of **5** in a CHCl_3 solution exhibited a π – π^* transition band at 270 nm ($\log \epsilon = 4.66$). In addition, absorption of **5** showed ligand-to-metal charge transfer (LMCT) band and MLCT band at 328 and 400 nm, respectively. This large bathochromic shift of the absorption maximum of **3** suggests the effective extension of π -delocalization length along the polymer backbone by the donor–acceptor effect.

The measurement of the thermogravimetric analysis (TGA) was carried out for **3** and **4** under nitrogen at a heating rate of 10 $^\circ\text{Cmin}^{-1}$ (Fig. 3). In the case of **3**, pyrolysis took place in two steps. The first step started at

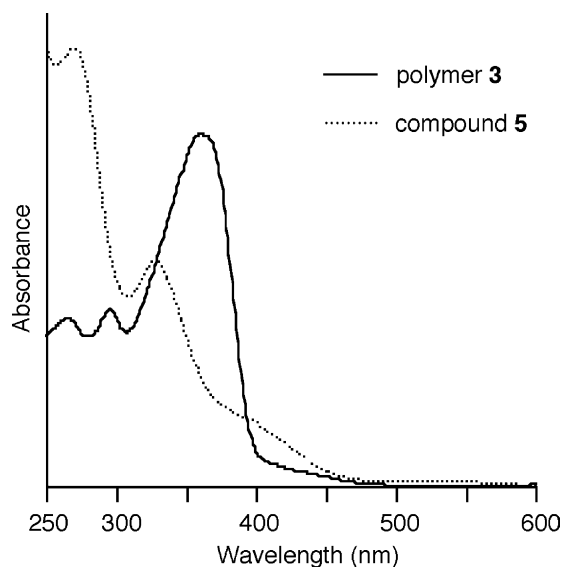


Fig. 2. UV–Vis absorption spectra of the polymer **3** and the compound **5**.

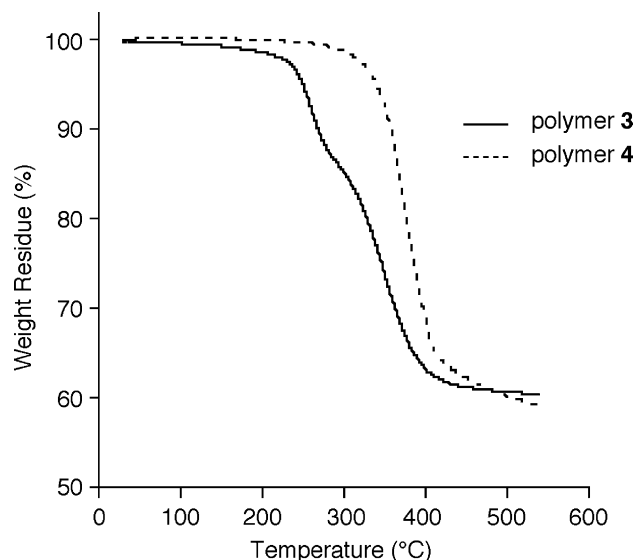


Fig. 3. TGA curves of the polymers **3** and **4** under nitrogen (10 $^\circ\text{Cmin}^{-1}$).

230 $^\circ\text{C}$, which was attributed to the liberation of carbon monoxide from the chromium center, while the second step started around 310 $^\circ\text{C}$, which was attributed to the decomposition of the polymer backbone. The decomposition of the polymer **4** set in at 320 $^\circ\text{C}$ and was completed at 420 $^\circ\text{C}$ under the same conditions. Both **3** and **4** gave similar curves except for the first decomposition of the $\text{Cr}(\text{CO})_3$ unit in the polymer **3**. In addition, the weight loss observed in the first step, i.e., the escape of carbon monoxide from **3**, was in close agreement with the calculated value of the amount of carbon monoxide incorporated in **3** measured by ^1H NMR.

The electrochemical behavior of the polymer **3** was investigated by cyclic voltammetry. The measurement was performed in CH_2Cl_2 solution containing 0.1 M $\text{Bu}^n_4\text{NPF}_6$ at a scan rate of 100 mVs^{-1} . As shown in Fig. 4, the polymer **3** showed broad oxidation peaks at 0.52 and 1.07 V vs. Ag/Ag^+ , respectively. The oxidation of **4** occurred at 0.69 V, and that of **5** occurred at 0.58 and 0.78 V, respectively. This result confirms that the first oxidation peak of **3** and **5** arises from the oxidation of the chromium center and the second arises from the platinum center. Due to the electron-withdrawing characteristic of the $\text{Cr}(\text{CO})_3$ unit and the first oxidation of chromium through the conjugated polymer chain, the oxidation potential of platinum in the polymer **3** was shifted anodically in comparison with that of the polymer **4**. These results indicate a strong interaction between two metal centers via the rigid rod conjugated bridge.

The ligand exchange reaction of the $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ complex under thermal [30], electrochemical [31,32], and photochemical conditions [33–35] has been investigated. Interestingly, electron poor η^6 -coordinated phenylene is converted to electron rich phenylene when

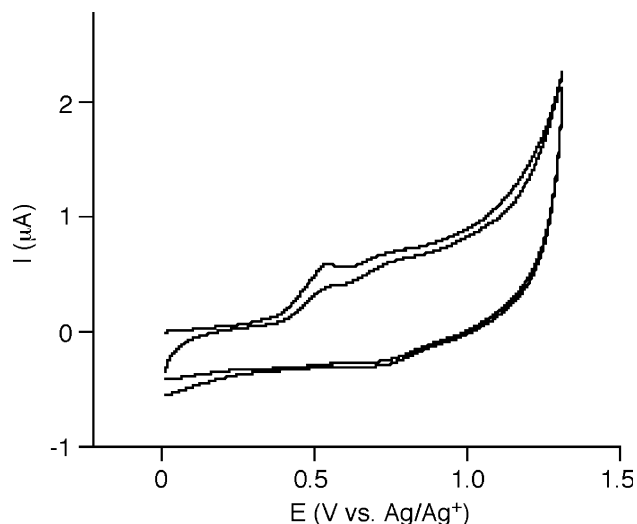


Fig. 4. Cyclic voltammogram of the polymer **3** in CH_2Cl_2 solution containing 0.1 M Bu_4NPF_6 using Pt electrode (vs. Ag/Ag^+) at the sweep rate of 100 mV s^{-1} . 1st and 2nd cycles are shown.

only one carbonyl ligand is replaced by a donor ligand such as trialkylphosphine [10]. We examined the carbonyl ligand replacement of the polymer **3** under photochemical conditions. As shown in Scheme 2, ligand exchange from CO to PPh_3 was completed after irradiating the solution of **3** for 2 h. In the ^1H NMR spectrum of the resulting polymer **6** (Fig. 5), the signals of the coordinated phenylene protons appear at 4.4 ppm. This shift to the high magnetic field compared to **3** is due to the electron-donating feature of the phosphine ligand. According to the proton integral ratio, the polymer **6** consists of 35% $\text{Cr}(\text{CO})_2(\text{PPh}_3)$ -coordinated phenylene and 65% normal phenylene units in the polymer chain due to photo-dissociation of chromium moieties. In the IR spectrum of **6**, the CO stretching frequency shifted to a shorter wavelength (1886 and 1844 cm^{-1}) relative to **3** (1958 and 1891 cm^{-1}).

In conclusion, a novel conjugated organometallic polymer containing $(\eta^6\text{-arene})\text{Cr}(\text{CO})_3$ and platinum in the main chain was synthesized by the dehydrohalogenation reaction. The obtained polymer was soluble in common organic solvents and characterized by NMR and FT-IR spectra. The polymer **3** showed an effective extension of π -delocalization length through the polymer chain. Cyclic voltammogram indicated an interaction between two metal centers via the conjugated bridge in the polymer chain. One of carbonyl ligands of the polymer **3** can be easily replaced by the phosphine ligand by photo-irradiation.

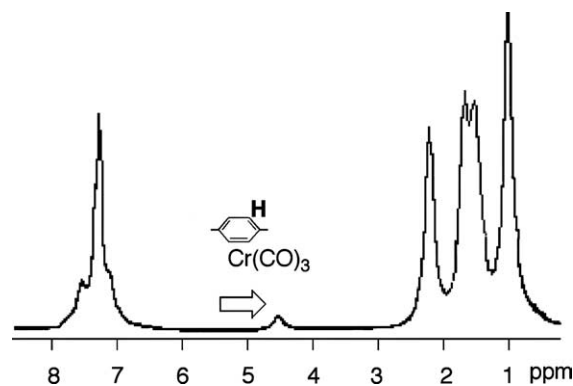


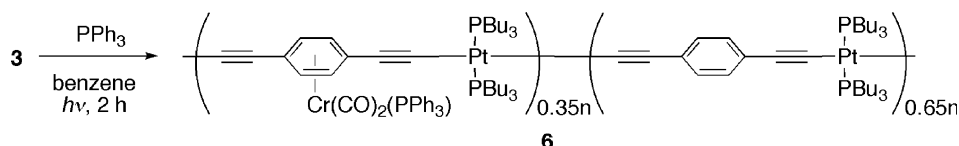
Fig. 5. ^1H NMR spectrum of the polymer **6** in CDCl_3 .

3. Experimental

^1H and ^{13}C NMR spectra were recorded on a JEOL EX400 instrument at 400 and 100 MHz, respectively. Samples were analyzed in CDCl_3 , and the chemical shift values were expressed relative to Me_4Si as an internal standard. IR spectra were obtained on a Perkin–Elmer 1600 spectrometer. UV–Vis spectra were obtained on a JASCO V-530 spectrophotometer, and samples were analyzed in CHCl_3 at room temperature. Fluorescence emission spectra were recorded on a Perkin–Elmer LS50B luminescence spectrometer, and samples were analyzed in CHCl_3 at room temperature. Gel permeation chromatography (GPC) was carried out on a TO-SOH UV-8011 and RI-8000 (Shodex K-803L column) using CHCl_3 as an eluent after calibration with standard polystyrene. Thermogravimetric analysis (TGA) was made on a Seiko EXSTAR 6000 instrument ($10^\circ\text{C min}^{-1}$). Cyclic voltammetry was carried out with a BAS CV-50W Electrochemical Analyzer in CH_2Cl_2 solution of 0.1 M Bu_4NPF_6 as a supporting electrolyte. Platinum wire auxiliary electrode and Ag/AgCl RE-5 reference electrode were used in the CV measurement. Elemental analysis was performed at the Microanalytical Center of Kyoto University.

3.1. Materials

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen. Diethylamine was distilled from KOH under nitrogen. CuI was obtained commercially, and used without further purification. $(\eta^6\text{-1,4-Diethynylbenzene})\text{tricarbonylchromium}$ **1** [28], $\text{trans}(\text{PBu}_3)_2\text{PtCl}_2$ **2** [29], and $(\eta^6\text{-ethynylbenzene})$



Scheme 2.

tricarbonylchromium [36] were prepared as described in the literature.

3.2. Polymerization

A 50 mL Pyrex flask was charged with **1** (26 mg, 0.10 mmol), **2** (67 mg, 0.10 mmol), CuI (1.0 mg, 5.0×10^{-3} mmol), THF (1.0 mL), HNEt₂ (1.0 mL), and a stirring bar under a flow of nitrogen. The reaction was carried out at reflux temperature for 24 h with stirring under a nitrogen atmosphere. After filtration of the precipitated ammonium salt, the filtrate was concentrated and dried in vacuo. The residue was dissolved in CHCl₃ and the resulting solution was poured into a large amount of MeOH to obtain the corresponding polymer **3** in quantitative yield (95 mg, 0.10 mmol) as a yellow powder.

¹H NMR (CDCl₃, 400 MHz): δ 0.91 (br, 18H), 1.54 (m, 24H), 2.08 (br, 12H), 5.30 (br, 2.8H), 7.12 (br, 1.2H); ¹³C NMR (CDCl₃, 100 MHz): δ 13.9, 23.0, 24.4, 26.3, 96.4, 110.9, 125.7, 130.2, 234.2. IR (KBr): 2108, 1958, 1891 cm⁻¹.

The polymer **4** was also synthesized by polycondensation between 1,4-diethynylbenzene and **2** following the procedure same as the polymer **3** (>99% yield). Spectral data of **4** matched the literature values [2,37].

3.3. Synthesis of the model compound **5**

A 50 mL Pyrex flask was charged with (η^6 -ethynylbenzene)tricarbonylchromium [36] (52 mg, 0.22 mmol), **2** (67 mg, 0.10 mmol), CuI (1.0 mg, 5.0×10^{-3} mmol), THF (2.0 mL), HNEt₂ (2.0 mL), and a stirring bar under a flow of nitrogen. The reaction mixture was refluxed for 8 h with stirring under a nitrogen atmosphere. After cooling, the precipitated ammonium salts were filtered off. The filtrate was evaporated and the residue was purified by column chromatography (SiO₂, hexane/Et₂O = 7/1) to provide 90 mg (0.085 mmol, 85%) of **5** as an orange solid.

¹H NMR (CDCl₃, 400 MHz): δ 0.95 (t, J = 7.2 Hz, 18H), 1.46 (m, 24H), 1.95 (br, 12H), 5.11 (t, J = 6.4 Hz, 2H), 5.30 (m, 8H); ¹³C NMR (CDCl₃, 100 MHz): δ 14.1, 26.4, 26.6, 28.9, 92.7, 94.7, 105.8, 128.7, 130.8, 132.4, 233.4. IR (KBr): 2118, 1963, 1881 cm⁻¹. Anal. Calc. for C₄₆H₆₄Cr₂O₆P₂Pt: C, 51.44; H, 6.01. Found: C, 51.90; H, 6.41%.

3.4. Photochemical ligand exchange reaction of the polymer **3**

The polymer **3** (42 mg) and triphenylphosphine (20 mg, 0.070 mmol) were dissolved in 5.0 mL of benzene, and the solution was irradiated by a 400 W high pressure mercury lamp for 2 h under a continuous flow of nitrogen. The reaction mixture was filtered, and the

filtrate was evaporated. The residue was dissolved in CHCl₃ and the resulting solution was poured into a large amount of MeOH to give the corresponding polymer **6** (25 mg) as a brown powder.

¹H NMR (CDCl₃, 400 MHz): δ 0.82 (br, 18H), 1.50 (m, 24H), 2.04 (br, 12H), 4.41 (br, 1.3H), 7.08–7.48 (m, 18H). IR (KBr): 2109, 1886, 1844 cm⁻¹.

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