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Synthesis and Properties of PPV-Based (η^6-Arene)Cr(CO)3-Containing Polymers Having Alkyldiphenylamine or Triarylamine in the Main Chain

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Summary

Novel poly(*p*-phenylenevinylene)-based (η^6-arene)Cr(CO)3-containing polymers including the alkyldiphenylamine or triarylamine units in the main chain were synthesized by the Horner-Wadsworth-Emmons coupling reaction. The structures of the polymers were confirmed by NMR and FT-IR spectra. The polymers were soluble in common organic solvents such as THF, $CHCl_3$, and CH_2Cl_2. The polymer showed interaction between the electron-withdrawing (η^6-arene)Cr(CO)3 unit and the unshared electron pair on the nitrogen atom along the polymer backbone.

Introduction

Recently, conjugated polymers have received much attention due to their potential applications in electrical and optical functional materials [1]. For example, since the first report on poly(*p*-phenylenevinylene) (PPV) in 1990 [2], PPVs and its derivatives have been extensively studied and used as light-emitting diodes (LEDs) for displays and other purposes. The synthesis of novel conjugated polymers, in which transition metal and other main group elements are incorporated, is also of considerable importance due to the enormous opportunities to change the properties of the resulting materials. Therefore, a number of conjugated polymers containing transition-metals in the polymer backbone or in the side chain have been synthesized [3].

On the other hand, chemical and physical properties of triarylamine-containing polymers are the subjects of current interest in view of their great potential for use in advanced materials such as hole-transporting materials in organic photoconductors and electroluminescent devices [4]. In addition, their physical properties and solubility can easily be improved by modification of the phenyl moieties, and they have thermal as well as air stability. These derivatives are important building blocks for constructing the π-conjugated polymer.

Considering that the polymer having an electron-accepting unit can improve the electron injection to the material, construction of the conjugated polymer containing electron-donating and electron-accepting moieties can balance the properties of electron injection and transportation [5]. It has been shown that the electron density of aromatic groups η^6-coordinated to the tricarbonylchromium fragment, $Cr(CO)_3$, is highly deficient because $Cr(CO)_3$ is strongly electron-withdrawing [6]. Namely, the (η^6-arene)tricarbonylchromium, (η^6-arene)$Cr(CO)_3$, can act as an electron acceptor. Furthermore, the (η^6-arene)$Cr(CO)_3$ unit is attractive from the standpoints of redox activity [7], nonlinear optical property [8], ligand exchange reactions [9], and catalysis [10]. However, little work has been carried out on the synthesis of (η^6-arene)$Cr(CO)_3$-containing conjugated polymers so far [11]. Recently, we reported the first soluble (η^6-arene)$Cr(CO)_3$-containing conjugated polymers, which showed air and thermal stabilities, conductivity, and redox activity [12]. Here, the synthesis and properties of novel conjugated polymers based on PPV containing triarylamine and (η^6-arene)$Cr(CO)_3$ units in the main chain are described.

Experimental

General

^1H NMR spectra were recorded on a JEOL EX400 instrument at 400 MHz. 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 $CHCl_3$ or in the film state at room temperature. Gel permeation chromatography (GPC) was carried out on a TOSOH UV-8011 and RI-8000 (Shodex K-803L column) using $CHCl_3$ as an eluent after calibration with standard polystyrene. Thermogravimetric analysis (TGA) was done on a Seiko EXSTAR 6000 instrument (10 $^\circ C$ min^{-1}). Cyclic voltammetry (CV) was carried out with a BAS CV-50W Electrochemical Analyzer in CH_2Cl_2 solution of 0.1 M $Bu^n{}_4NPF_6$ 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.

Materials

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen. Sodium hydride (60% dispersion in mineral oil), diphenylamine, 1-bromododecane, 1-bromo-4-butylbenzene, 1,10-phenanthroline, phosphorus oxychloride, and dehydrated *N,N*-dimethylformamide, were obtained commercially, and used without further purification. Tricarbonyl{tetraethyl[(η^6-1,4-phenylene)bis(methylene)]bis[phosphonate]}chromium (**1**) [13], tetraethyl[1,4-phenylenebis(methylene)]bisphosphonate (**1'**) [14], *N*-dodecyldiphenylamine [5b], and 4-butyl-*N,N*-diphenylaniline [4g] were prepared as described in the literature. All reactions were performed under a nitrogen atmosphere using a standard Schlenk technique.

Preparation of Monomers

4,4'-(Dodecylimino)dibenzaldehyde (**2a**)

N,N-Dimethylformamide (1.8 g, 1.9 mmol) and phosphorus oxychloride (3.8 g, 2.3 mmol) are mixed under a flow of nitrogen. After stirring at 0 °C for 1 h and 25 °C for 1 h, *N*-dodecyldiphenylamine (0.93 g, 5.0 mmol) in 3.0 mL of 1,2-dichloroethane was added slowly. The mixture was heated at 90 °C for 24 h, cooled to room temperature, and poured into a crushed ice. The organic layer was separated and washed with saturated aqueous Na_2CO_3 and water. The combined organic layer was dried over anhydrous $MgSO_4$. The organic solvents were evaporated and the crude viscous oil was purified through a silica gel column using hexane:ethyl acetate (v/v = 1/1) as an eluent. The aimed compound (**2a**) was obtained in 41% yield as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.88 (t, J = 7.0 Hz, 3H), 1.26-1.57 (m, 20H), 3.83 (t, J = 7.5 Hz, 2H), 7.17 (d, J = 6.7 Hz, 4H), 7.80 (d, J = 6.7 Hz, 4H), 9.89 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 14.1, 22.7, 26.9, 27.5, 29.3, 29.5, 29.6, 31.9, 52.5, 120.6, 130.5, 131.5, 151.8, 190.3. Anal. Calcd for $C_{26}H_{35}NO_2$: C ,79.35; H, 8.96; N, 3.56. Found: C, 79.08; H, 9.07; N, 3.54.

4,4'-[(4-Dodecylphenyl)imino]bisbenzaldehyde (**2b**)

N,N-Dimethylformamide (1.8 g, 1.9 mmol) and phosphorus oxychloride (3.8 g, 2.3 mmol) are mixed under a flow of nitrogen. After stirring at 0 °C for 1 h and 25 °C for 1 h, 4-butyl-*N,N*-diphenylaniline (1.5 g, 5.0 mmol) in 3.0 mL of 1,2-dichloroethane was added slowly. The mixture was heated at 90 °C for 24 h. Then, following work-up procedure was same as **4a**, where the crude product was purified through a silica gel column using hexane:ethyl acetate (v/v = 7/2) as an eluent. The aimed compound (**2b**) was obtained in 91% yield as a white solid.

^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.96 (t, J = 7.2 Hz, 3H), 1.28-1.58 (m, 4H), 2.63 (t, J = 7.5 Hz, 2H), 7.01-7.25 (m, 8H), 7.77 (d, J = 6.7 Hz, 4H), 9.88 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 14.0, 22.4, 33.5, 35.2, 122.4, 127.0, 130.0, 131.0, 131.2, 141.3, 142.8, 152.0, 190.4. Anal. Calcd for $C_{26}H_{23}NO_2$: C ,80.64; H, 6.48; N, 3.92. Found: C, 80.64; H, 6.63; N, 3.86.

Polymerization

A typical procedure is as follows. A 50 mL Pyrex flask was charged with **1** (175 mg, 0.35 mmol), **2a** (135 mg, 0.35 mmol), NaH (30.8 mg, 0.77 mmol), THF (5.0 mL), and a stirring bar under a flow of nitrogen. The reaction was carried out at 60 °C for 24 h with stirring under a nitrogen atmosphere. The reaction mixture was quenched with 1.0 M hydrochloric acid after cooling to room temperature. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$. The combined organic layer was evaporated under vacuum and the residue was reprecipitated from a large amount of MeOH to give the corresponding polymer (**3a**) as an orange solid. The polymers (**3b**, **4a**, and **4b**) were also synthesized by the same procedure.

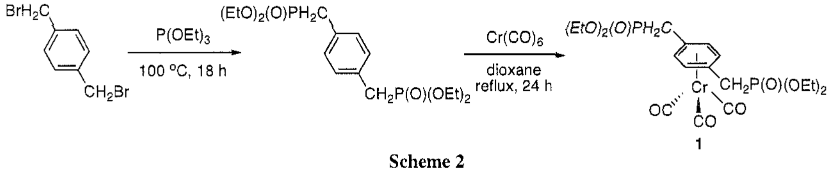
Polymer (**3a**): 65%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.88 (m, 3H), 1.26-1.56 (m, 20H), 3.75 (m, 2H), 5.65 (m, 2.3H), 6.45 (m, 2H), 6.98 (m, 2H), 7.01-7.50 (m, 9.7H). IR (KBr): 1959, 1890, 962 cm^{-1}.

Polymer (**3b**): 60%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.95 (m, 3H), 1.26-1.56 (m, 4H), 2.61 (m, 2H), 5.64 (m, 2.4H), 6.50 (m, 2H), 6.92 (m, 2H), 7.05-7.46 (m, 13.6H). IR (KBr): 1970, 1894, 960 cm^{-1}.

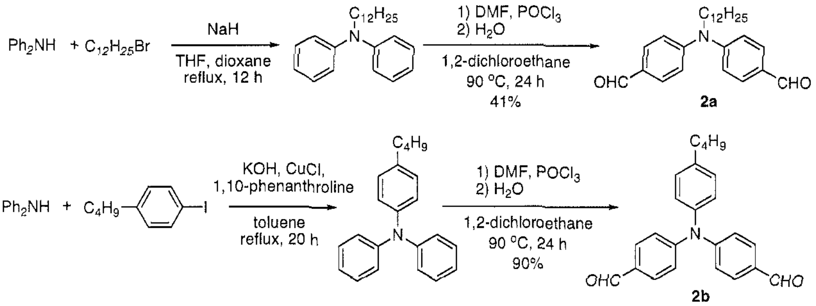
Polymer (**4a**): 20%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.88 (m, 3H), 1.26-1.55 *(m, 20H), 3.72 (m, 2H), 6.78 (m, 2H), 6.90 (m, 2H), 7.06-7.48 (m, 8H). IR (KBr)*: 967 cm^{-1}.

Polymer (**4b**): 50%. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 0.95 (m, 3H), 1.24-1.61 (m, 4H), 2.61 (m, 2H), 6.56 (m, 2H), 6.86 (m, 2H), 7.08-7.47 (m, 12H). IR (KBr): 967 cm^{-1}.

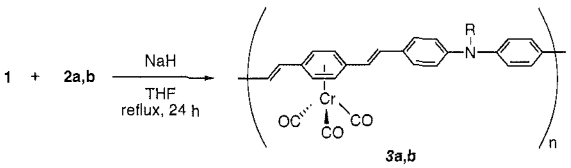
Scheme 1



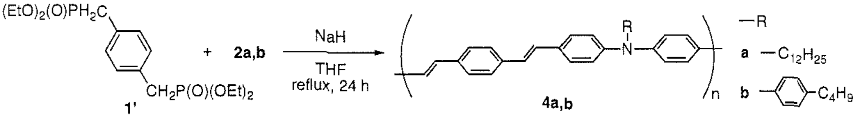
Scheme 2



Scheme 3



Scheme 4



Results and Discussion

Tricarbonyl{tetraethyl[(η^6-1,4-phenylene)bis(methylene)]bis[phosphonate]}-chromium (**1**) was prepared according to published procedures (Shceme 1) [13]. The monomers of 4,4'-(dodecylimino)dibenzaldehyde (**2a**) and 4,4'-[(4-dodecylphenyl)imino]bisbenzaldehyde (**2b**) were synthesized as shown in Scheme 2. The procedure for the polymer synthesis by Horner-Wadsworth-Emmons olefination [15] is outlined in Scheme 3, and the results of the polymerization are summarized in Table 1. For example, treatment of **1** with **2a** in the presence of NaH as a base at 60 °C for 24 h under nitrogen produced the corresponding polymer (**3a**) in 65% yield as an orange solid after work-up. As a reference, polymers **4a** and **4b**, without a

$Cr(CO)_3$ moiety, were also prepared by the same coupling reaction of tetraethyl[1,4-phenylenebis(methylene)]bisphosphonate (**1'**) with **2a** or **2b** (Scheme 4, Table 1). The reactivity of **1** was relatively higher than that of **1'** (Table 1). This result indicates that the benzylic position of **1** is activated by the electron withdrawing $Cr(CO)_3$ unit. The polymers **3a** and **3b** were soluble in common organic. The number-average molecular weights of **3a** and **3b** were found to be 5500 and 6500 by gel permeation chromatography (GPC) using polystyrene standards, which correspond to degree of polymerization of 9 and 11, respectively.

Table 1. Results of Polymerization

run	monomer	polymer	M_w[a]	M_n[a]	M_w/M_n[a]	yield (%)
1	**1/2a**	**3a**	9200	5500	1.6	65
2	**1'/2a**	**4a**	25000	6700	3.7	20
3	**1/2b**	**3b**	12400	6500	1.9	60
4	**1'/2b**	**4b**	3700	2500	1.5	50

[a] GPC ($CHCl_3$), polystyrene standards.

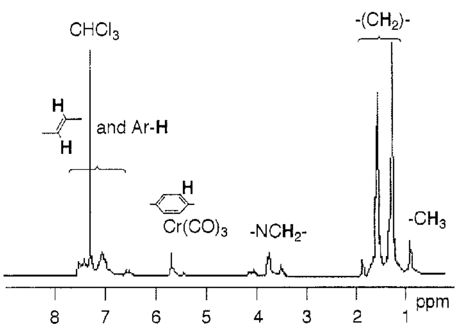


Figure 1. ^1H NMR spctrum of **3a** in $CDCl_3$.

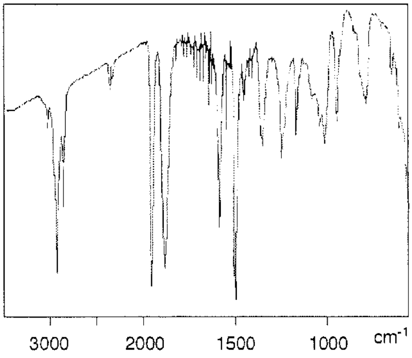


Figure 2. IR spectrum of **3a** in the film state.

The ^1H NMR spectrum of the polymer (**3a**) is shown in Figure 1. The peaks of the phenyl protons coordinated to $Cr(CO)_3$ appeared at 5.7 ppm. The peaks corresponding to the olefinic protons were observed at 6.5 and 6.8 ppm. The protons of aryl units appeared at 7.0-7.5 ppm, and they were overlapped with aromatic protons of the phenylene units from the thermal- or photo-dissociation of $Cr(CO)_3$ moieties. This result indicates that **3a** consists of approximately 60% chromium-coordinated phenylene and 40% normal phenylene units as determined by calculation from a proton integral ratio. The structures of the polymers obtained were also confirmed by IR spectra. In Figure 2, the absorption of the out-of-plane bending mode of *trans*-vinylene appeared at 962 cm^{-1}. According to the absence of that of *cis*-vinylene at around 700 cm^{-1}, *trans*-olefins were formed predominantly through this polycondensation reaction [15]. In addition, strong absorption of the stretching mode of coordinated carbon monoxide was observed at 1959 and 1890 cm^{-1}, respectively.

The optical properties of the polymers obtained was investigated by UV-vis absorption measurement in a CHCl3 solution at room temperature (Table 2), and the spectra of **3a** and **4a** are shown in Figure 3. The absorption maxima corresponding to a π-π* transition in the polymer chain were observed at 421 nm and 419 nm for **3a** and **4a**, respectively. Although the absorption maxima were almost same, the absorption onset of **3a** (522 nm) was red-shifted in comparison with respect to that of **4a** (486 nm) which is without a chromium complex coordinated to the phenylene moiety. In our previous work, due to the steric hindrance of the $Cr(CO)_3$ unit in the polymer backbone, the polymers containing the coordinated $Cr(CO)_3$ unit have a shorter conjugated length compared with the polymers without $Cr(CO)_3$ [12]. The present result of the red-shift of the absorption spectrum of **3a** implies that the donor-acceptor effect between the unshared electron pair on the nitrogen atom and the electron-withdrawing (η^6-arene)$Cr(CO)_3$ moiety overcomes the steric effect of the $Cr(CO)_3$ unit.

Table 2. Optical Properties of the Polymers[a]

polymer	absorption (nm)	emission (nm)[b]	Φ_{PL}[c]
3a	421	477	0.029
4a	419	476	0.31
3b	435	480	0.028
4b	426	480	0.32

[a] All experiments were performed in $CHCl_3$. [b] Excited at the absorption maximum wavelength. [c] Fluorescence quantum yield.

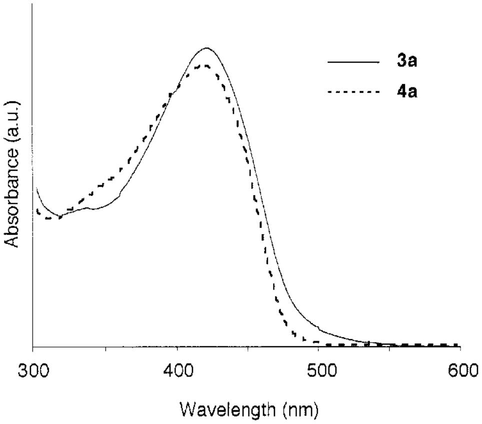


Figure 3. UV-vis absorption spectra of **3a** and **4a** in $CHCl_3$.

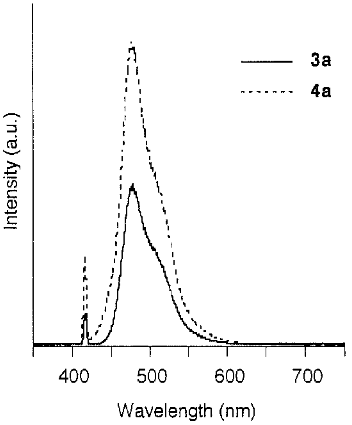


Figure 4. Fluorescence emission spectra of **3a** and **4a** in $CHCl_3$ (420 nm excitation).

The fluorescence emission of the polymers was investigated in dilute CHCl3 solution at room temperature at the excitation wavelength of the absorption maximum. The polymers **3a** and **3b** emitted a bluish green light with a photoluminescence maximum at approximately 480 nm (Table 2). The emission spectra of the polymers **3a** and **4a** are shown in Figure 4. The fluorescence quantum efficiency was measured in dilute CHCl3 solution (absorbance was below 0.05) relative to that of 9-anthracenecarboxylic acid in CH_2Cl_2 as a standard [16], and its value was found to be

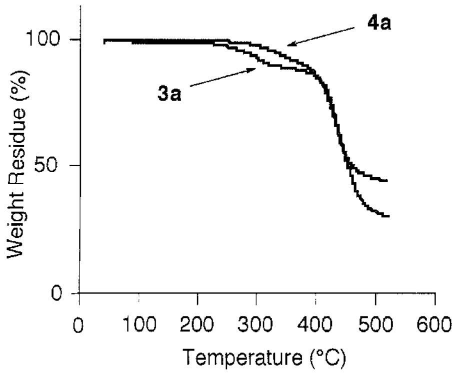


Figure 5. TGA traces (10 °C/min) of **3a** and **4a** under nitrogen.

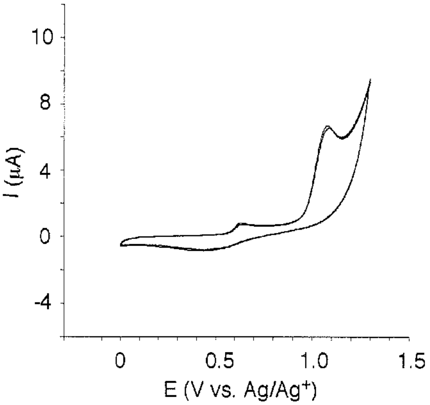


Figure 6. Cyclic voltammogram of **3a** in CH_2Cl_2 containing Bu_4NPF_6 as a supporting electrolyte at scan rate of 100 mV/s. 1st and 2nd cycles are shown.

0.03. While the polymers **4a** and **4b** showed moderate quantum yield (Table 2), the emissions of **3a** and **3b** were highly quenched by the presence of $Cr(CO)_3$. This result implies that an intramolecular charge transfer between the coordinated $Cr(CO)_3$ unit and the conjugated polymer chain occurs in the excited state.

Thermogravimetric analysis (TGA) was carried out for **3a** and **4a** under nitrogen at a heating rate of 10 °C min^{-1} (Figure 5). In the case of the polymer **3a**, pyrolysis took place in two steps. The first step is attributed to the liberation of carbon monoxide from the chromium center, while the second step is attributed to the decomposition of the polymer backbone. The polymer **4a** showed a higher decomposition temperature, being stable up to approximately 350 °C under the same conditions. Both **3a** and **4a** gave similar curves except for the first decomposition of the $Cr(CO)_3$ unit in the polymer **3a**. In addition, the weight loss of this first step, i.e., the escape of carbon monoxide from **3a**, is in close agreement with the calculated value of the amount of carbon monoxide incorporated in the polymer **3a**.

The electrochemical behavior of the polymer **3a** was investigated by cyclic voltammetry. The measurement was performed in 0.1 M CH_2Cl_2 solution containing $Bu^n{}_4NPF_6$ at a scan rate of 100 mV s^{-1}. As shown in Figure 6, the polymer **3a** exhibited two broad reversible oxidation peaks at 0.63 V and 1.08 V vs. Ag/Ag^+, while the oxidation peak appeared at 0.67 V for the polymer **4a** under the same conditions. These results indicate that this first oxidative wave could be attributed to the oxidation of an arylamine unit and the second one to the oxidation of chromium. In addition, the polymer **3a** was found to be electrochemically stable for repeated scanning.

In conclusion, novel π-conjugated polymers containing (η^6-arene)$Cr(CO)_3$ and triarylamine units in the main chain based on PPV were synthesized by Horner-Wadsworth-Emmons coupling reaction in moderate yield. The polymers were soluble in common organic solvents and characterized by NMR and FT-IR spectra. In the UV-vis spectra, the polymers showed a slight red-shift compared to the model reference polymer without a $Cr(CO)_3$ moiety, while the (η^6-arene)$Cr(CO)_3$-containing polymer previously reported showed a blue-shift. This result suggests an interaction between the electron-withdrawing (η^6-arene)$Cr(CO)_3$ unit and the unshared electron pair on the nitrogen atom along the polymer backbone. Cyclic voltammetry showed reversible oxidation peaks derived from the arylamine and the (η^6-arene)Cr(CO)$_3$ units. Further studies on the synthesis and properties of novel π-conjugated polymers possessing a (η^6-arene)Cr(CO)$_3$ unit in combination with other heteroatoms are now underway.

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16. The quantum yield (Φ_{unk}) of unknown sample was calculated by the following equation: $\Phi_{unk} = \Phi_{std}[A_{std}F_{unk}/A_{unk}F_{std}][n_{D,unk}/n_{Dstd}]^2$ where A_{std} and A_{unk} are the absorbance of the standard and unknown sample, respectively, F_{std} and F_{unk} are the corresponding relative integrated fluorescence intensities, and n_D is the refractive index [CH_2Cl_2 (n_D = 1.424) and $CHCl_3$ (n_D = 1.446) were used].