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Synthesis and Properties of Novel Poly(*p*-phenylenevinylene)s Containing a Tricarbonyl(arene)chromium Unit in the Main Chain

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Summary

Novel π-conjugated polymers based on poly(*p*-phenylenevinylene)s (PPVs) containing a tricarbonyl(arene)chromium unit in the main chain were synthesized by Horner-Wadsworth-Emmons olefination. The structures of the polymers were supported by ^{1}H NMR and IR spectra. The polymers obtained were soluble in common solvents such as THF, CH_2Cl_2, $CHCl_3$ and toluene. The molecular weights of the polymers were determined by GPC. Their thermal, optical, and electrochemical properties were investigated in detail.

Introduction

In recent years, a great deal of interest has been focused on the synthesis of novel π-conjugated polymers [1] because of their unique properties, such as electrical conductivity [2], electroluminescence [3], liquid crystallinity [4], third-order nonlinear optical properties [5], and chemical sensing [6]. Among these polymers, π-conjugated polymers which contain transition metal complexes are of increasing interest [7], because they not only enable the physical properties of the resulting materials to be tuned easily by the exchange of a ligand coordinated to the metal center, but can also be converted to various kinds of functional organic polymers by polymer reactions. Therefore, a number of polymers having organometallic units in the main chain or in the side chain have been prepared so far. Polymers which contain the transition metals π-coordinating to the phenylene units in the polymer backbones (e.g., cyclopentadienyliron [8], cyclopentadienylruthenium [8e,9], tricarbonylmolybdenum [10], and tricarbonylchromium [11]) have been synthesized, and have exhibited interesting properties.

A tricarbonylchromium unit is a very attractive functional group because it is able to change the reactivity of an aromatic group from nucleophilicity to electrophilicity [12]. Namely, a tricarbonylchromium-coordinated phenylene unit has the potential to act as a strong acceptor. However, little work has been carried out on the synthesis of polymers having a tricarbonylchromium unit [11]. In addition, most of the tricarbonyl(arene)chromium, (η^6-arene)Cr(CO)$_3$, containing polymers prepared so far are insoluble in common organic solvents. The present research is focused on the synthesis and properties of soluble conjugated copolymers based on poly(*p*-phenylenevinylene)s (PPVs) having a tricarbonyl(arene)chromium unit as an acceptor in the main chain.

Experimental

General

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX270 instrument at 270 and 67.5 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 THF at room temperature. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer, and samples were analyzed in THF at room temperature. Gel permeation chromatography (GPC) was carried out on a TOSOH UV-8011 and RI-8000 (Shodex K-803L column) using chloroform as an eluent after calibration with standard polystyrene. Thermogravimetric analysis (TGA) was made on a Seiko EXSTAR 6000 instrument (10 $^{\circ}$C/min). Cyclic voltammetry was carried out on a BAS-CV50W.

Materials

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen. Sodium hydride (60% dispersion in mineral oil), triethyl phosphite, hexacarbonylchromium, α,α'-dibromo-*p*-xylene (**1**) were obtained commercially and used without further purification. Tetraethyl *p*-xylylenediphosphonate (**2**) [13], tricarbonyl[tetraethyl [(η^6-1,4-phenylene)bis(methylene)]bis[phosphonate]] (**3**) [14], and 2,5-bis(alkoxy)-1,4-benzenedicarboxaldehyde (**4**) [15], and the model compound (**7**) [14] were prepared as described in the literature.

Polymerization

A typical procedure is as follows [16]. A 50 mL Pyrex flask was charged with **3** (51 mg, 0.10 mmol), **4** (0.10 mmol), sodium hydride (0.22 mmol), THF (5.0 mL), and a stirring bar under a flow of nitrogen. The reaction mixture was heated to reflux temperature for 24 h. After cooling to room temperature, the reaction was quenched by addition of 1.0 M hydrochloric acid. The organic layers were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was evaporated under vacuum and the residue was reprecipitated from a large amount of MeOH to give the corresponding polymer (**5**) as a red solid.

5a. Yield: 22 mg, 46%. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 1.01 (m, 6H), 1.25 (m, 4H), 1.85 (m, 4H), 4.06 (m, 4H), 5.70 (m, 2.8H), 6.75 (m, 2H), 7.15 (m, 2H), 7.54 (m, 3.2H); IR (film): 1954, 1876, 959 cm^{-1}.

5b. Yield: 36 mg, 60%. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 0.88 (br, 6H), 1.23-1.53 (m, 20H), 1.86 (m, 4H), 4.02 (m, 4H), 5.69 (m, 2 H), 6.72 (m, 2H), 7.12 (m, 2H), 7.55 (m, 4H); IR (film): 1959, 1890, 964 cm^{-1}.

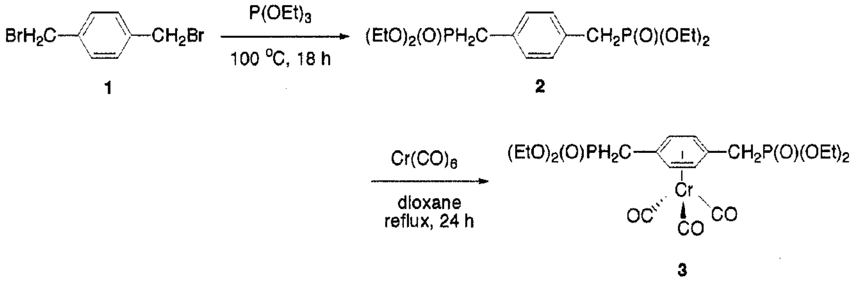
5c. Yield: 35 mg, 50%. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 0.87 (br, 6H), 1.26-1.51 (m, 36H), 1.87 (m, 4H), 4.05 (m, 4H), 5.68 (m, 3.3H), 6.73 (m, 2H), 7.10 (m, 2H), 7.49 (m, 2.7H); IR (film): 1956, 1890, 959 cm^{-1}.

Polymer (**6**) was obtained following the same method. Yield: 40 mg, 70%. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 0.88 (m, 6H), 1.26-1.54 (m, 36H), 1.86 (m, 4H), 4.06 (m, 4H), 7.14 (m, 4H), 7.53 (m, 6H); IR (film): 962 cm^{-1}.

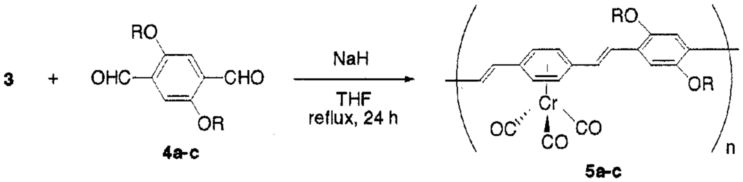
Results and Discussion

We prepared the diphosphonate monomer (**3**), which has an electron withdrawing tricarbonylchromium tripod. The synthetic route is shown in Scheme 1 [14]. The procedure for the polymer synthesis by Horner-Wadsworth-Emmons olefination [16] is outlined in Scheme 2, and the results are summarized in Table 1. Thus, the polymerization of **3** with 2,5-dialkoxy-1,4-diformylbenzene (**4**) in THF in the presence of NaH at a reflux temperature for 24 h under a nitrogen atmosphere provided the corresponding polymers (**5**) in a moderate yield. Polymers (**5a-c**) were red solids, which were soluble in common organic solvents such as THF, $CHCl_3$, CH_2Cl_2, and toluene. The molecular weight values for the polymers (**5**) were determined by gel permeation chromatography (GPC) in a $CHCl_3$ eluent using a calibration curve of polystyrene standards. For example, the polymer (**5c**) (R = *n*-dodecyl) had the number-average molecular weight (M_n) of 10800, which corresponded to a degree of polymerization of 15, with a polydispersity of 2.9 (Table 1, run 3).

Scheme 1



Scheme 2



R = **a** *n*-butyl, **b** *n*-octyl, **c** *n*-dodecyl

Table 1. Polycondensation of **3** with **4a-c**[a] and optical properties of the polymers (**5a-c**)

polym.	yield (%)[b]	M_w[c]	M_n[c]	M_w/M_n[c]	UV λ_{max} (nm)[d]	PL λ_{max} (nm)[d,e]
5a	46	5100	3500	1.4	433	523
5b	60	5600	2600	2.2	440	512
5c	50	31300	10800	2.9	427	520

[a] A mixture of **3** (0.10 mmol), **4** (0.10 mmol), NaH (0.22 mmol), and THF (5.0 mL) in a 50 mL Pyrex flask was heated at reflux temperature for 24 h under a nitrogen atmosphere. [b] Isolated yields after reprecipitation into MeOH. [c] GPC ($CHCl_3$), polystyrene standards. [d] Absorption and emission spectra were recorded in dilute THF solutions. [e] Excited at 420 nm.

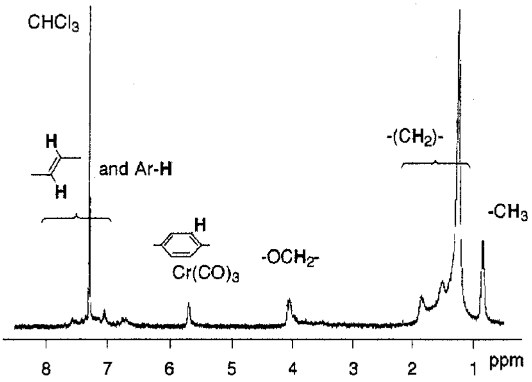
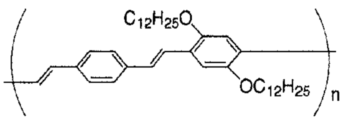


Figure 1. ^1H NMR spectrum of the polymer (**5c**) in $CDCl_3$.

These polymers were characterized by the ^1H NMR and IR spectra. In the ^1H NMR spectrum of **5c** in $CDCl_3$ (Figure 1), the peak at 5.7 ppm is attributed to the protons of the phenylene unit coordinated to chromium. The peaks at 6.6-7.6 ppm are attributed to the protons connected to the benzene rings and carbon-carbon double bonds. **5c** was found to consist of 65% chromium coordinated phenylene and 35% phenylene moieties according to the ^1H NMR integral ratio. The ^{13}C NMR spectra of the polymers were not clearly obtained, due to their relatively low solubility. The IR spectrum of **5c** in the film state exhibited strong absorption peaks at 1956 and 1890 cm^{-1} due to the stretching vibrations of the metal carbonyls. There was also an additional absorbance at 959 cm^{-1} due to *trans*-vinylene out-of-plane the CH bending mode, indicating that the carbon-carbon double bond formation had taken place.

The polymers (**5a-c**) were very stable under air in the solid state. The thermal stability of the polymer (**5c**) was investigated by thermo-gravimetric analysis (TGA), the results of which are shown in Figure 2. A weight loss of **5c** began at a temperature of around 250 ^oC under nitrogen at a heating rate of 10 ^oC/min, and was completed at around 500 ^oC. The decomposition of the polymer (**5c**) involved two steps. The completion of the first step may be assigned to thermal dissociation and the oxidation of tricarbonyl-chromium moieties, and the second step can be attributed to the decomposition of the polymer backbone. On the other hand, the polymer (**6**) as a reference polymer was synthesized under the same reaction condition (M_w = 3900,



Polymer (6)

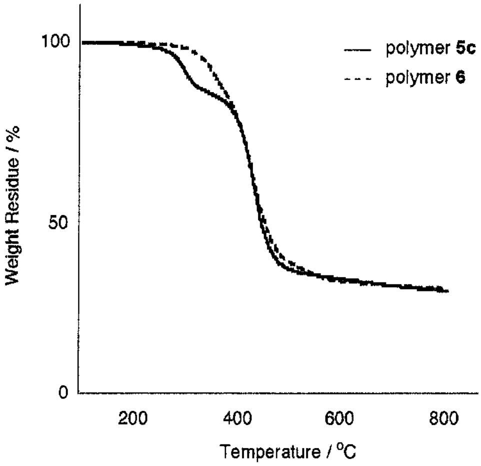


Figure 2. Thermogravimetric analysis (TGA) of the polymers (**5c**) and (**6**) under nitrogen (10 °C/min).

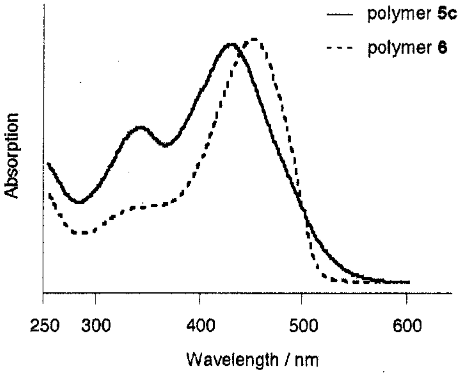
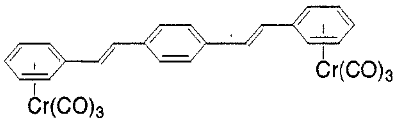


Figure 3. UV-visible spectra of the polymers (**5c**) and (**6**) in THF solution.

M_n = 2700), and was subjected to TGA analysis under an atmosphere of nitrogen. The polymer (**6**) showed only one onset of the decomposition around 290 °C. Both **5c** and **6** gave similar curves, except for the first decomposition of the tricarbonylchromium unit in the polymer **5c**.

We investigated the optical properties of the polymer obtained. The results are listed in Table 1. Figure 3 shows the UV-vis absorption spectra of the polymers (**5c**) and

(**6**). The polymer (**5c**) had an absorption maximum at 427, whereas the polymer (**6**) showed a maximum at 448 nm. This result suggests that the coplanarity of each monomer unit in **5** is poorer due to steric hindrance caused by the tricarbonylchromium unit in the polymer chain [11e]. However, the absorption peak of **5c** exhibited a red-shift of 20 nm in comparison with that of the model compound (7) (λ_{max} = 408 nm) [14]. This finding clearly indicates the extended π-delocalization length through the polymer backbone. In the fluorescence spectra, a weak emission λ_{max} of **5a-c** was observed in a visible green region with an excitation wavelength at 420 nm (Table 1). The quantum efficiency of **5c** and **6** were 0.01 and 0.30, respectively [17]. The absorption and fluorescence spectra of **5a-c** in the solid state were very similar to those in solution.



Model compound (7)

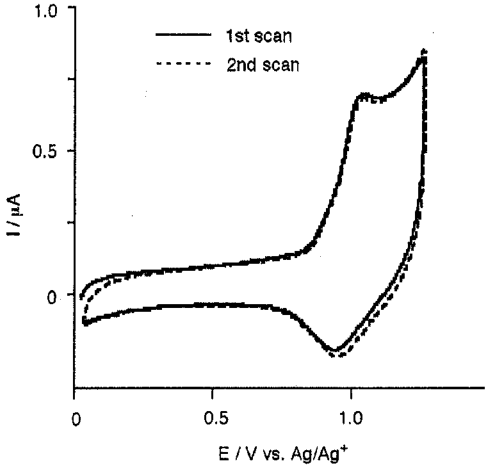


Figure 4. Cyclic voltammogram of **5c** measured in 0.1 M CH_2Cl_2 solution of Bu_4NPF_6 using Pt electrode (vs. Ag/Ag^+) at the sweep rate of 50 mV/s.

The electrochemical activity of the polymer (**5c**) was investigated using cyclic voltammetry at room temperature in a conventional three-electrode cell in a CH_2Cl_2 solution containing 0.1 M Bu_4NPF_6 at 50 mVs^{-1} (Pt electrode vs. Ag/Ag^+). The result is that the solution of **5c** gave a single oxidation peak at about 0.98 V reversibly, while no oxidation peaks appeared for the polymer (**6**) under the same condition. These results indicate that one electron oxidation process occurs on the (η^6-arene)$Cr(CO)_3$ moiety. In addition, an anodic shift of the oxidation potential for the tricarbonyl(arene)chromium unit in the polymer chain was observed compared with that of 7 (0.85 V) [14]. It clearly indicates that the tricarbonyl(arene)chromium unit incorporated in the π-conjugated system caused stabilization against electrochemical oxidation.

In conclusion, the Horner-Wadsworth-Emmons olefination of the $Cr(CO)_3$-coordinated diphosphonate (**3**) with 2,5-dialkoxy-1,4-diformylbenzene (**4**) gave the corresponding alternating conjugated copolymers (**5a-c**) having a tricarbonyl(arene)chromium unit as an acceptor in the main chain in moderate yields. The polymers obtained were stable under air, and soluble in common solvents. The polymers showed an extension of π-delocalization according to the UV-vis absorption spectrum in comparison with that of the model compound (7). Further studies on the synthesis of novel π-conjugated polymers which have a tricarbonyl(arene)chromium unit as an acceptor are now underway.

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17. The quantum yield (F_{unk}) of unknown sample was calculated by the following equation: $F_{unk} = F_{std}[A_{std}F_{unk}/A_{unk}F_{std}][n_{D,unk}/n_{D,std}]^2$ 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].