

Synthesis and Properties of Conjugated Copolymer Based on Poly(*p*-phenylenevinylene) Containing Tricarbonyl(arene)chromium and Thiophene Units in the Main Chain

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(Received January 14, 2003; Accepted March 19, 2003)

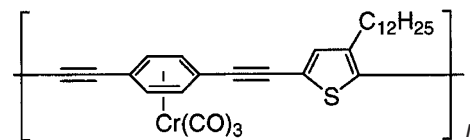
ABSTRACT: A novel Poly(*p*-phenylenevinylene)-type (PPV-type) conjugated copolymer containing tricarbonyl-(arene)chromium and thiophene units in the main chain was synthesized by Horner–Wadsworth–Emmons coupling reaction. The structure of the polymer was confirmed by ¹H NMR and IR. The polymer was soluble in common organic solvents. The polymer exhibited an absorption maximum at 454 nm in the UV-vis absorption spectrum. The thermal stability and redox property of the polymer were studied in detail.

KEY WORDS Conjugated Polymer / Tricarbonyl(arene)chromium / Thiophene Horner–Wadsworth–Emmons Olefination / Poly(*p*-phenylenevinylene) /

Considerable attention has been given to the synthesis of novel conjugated polymers due to their interesting electrical and optical properties.¹ Since the first report on poly(*p*-phenylenevinylene) (PPV) in 1990,² PPVs and its derivatives have been the most extensively studied and have been used as light-emitting diodes (LEDs) for displays and other purposes. Polymers containing transition-metals are also of considerable importance, because of the requirements for advanced materials in molecular electronics,³ molecular optics,⁴ catalytic processes,⁵ and so on. A number of the well-defined conjugated polymers containing transition-metals π -coordinated to phenylene units in the polymer backbone have been synthesized.⁶

It is well-known that the tricarbonylchromium fragment, Cr(CO)₃, is strongly electron-withdrawing and activates the η^6 -arene ligand towards nucleophilic attack.⁷ Namely, since the electron density of arenes η^6 -coordinated to a Cr(CO)₃ unit is highly deficient, the tricarbonyl(arene)chromium, (η^6 -arene)Cr(CO)₃, complex can act as an electron acceptor. In addition, the (η^6 -arene)Cr(CO)₃ unit is attractive from the standpoints of redox activity,⁸ nonlinear optical properties,⁹ ligand exchange reactions,¹⁰ and catalytic applications.¹¹ The preparation of a conjugated polymer containing a (η^6 -arene)Cr(CO)₃ unit in the main chain as an intermolecular donor-acceptor system should be of great interest; however, little work has been carried out on the synthesis of such polymers so far.¹² In addition, most of the (η^6 -arene)Cr(CO)₃-containing polymers prepared to date are insoluble in common organic solvents, and their properties have not been studied

in detail. Recently, we reported that the first soluble (η^6 -arene)Cr(CO)₃-containing π -conjugated polymer **1** showed photoluminescence, redox activity, and conductivity.¹³ In this paper, the synthesis and properties of the PPV-type π -conjugated polymer containing (η^6 -arene)Cr(CO)₃ and thiophene units in the main chain are described.



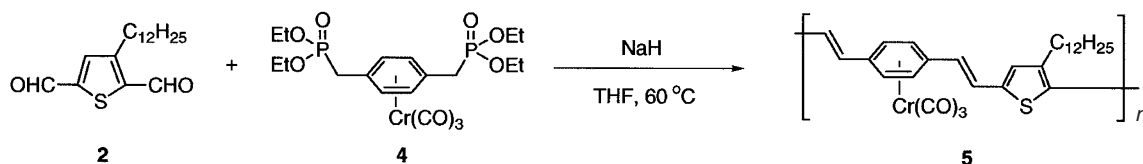
polymer 1

EXPERIMENTAL

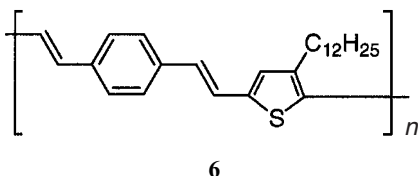
General

¹H NMR spectra were recorded on a JEOL JNM-EX270 instrument at 270 MHz. Samples were analyzed in CDCl₃, and the chemical shift values were expressed relative to Me₄Si as an internal standard. IR spectra were obtained on a PerkinElmer 1600 spectrometer. UV-Vis spectra were obtained on a JASCO V-530 spectrophotometer, and samples were analyzed in CHCl₃ 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 CHCl₃ as an eluent after calibration with standard polystyrene. Thermogravimetric analysis

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Scheme 1.

Table I. Results of Polycondensation^a

Run	Monomer	Polymer	Yield/% ^b	M_n^c	M_w^c	M_w/M_n^c
1	2/4	5	90	8000	9700	1.2
2	2/3	6	73	6400	8400	1.3

^aA mixture of **2** (0.35 mmol), **4** or **3** (0.35 mmol), NaH (0.77 mmol), and THF (5.0 mL) in a 50 mL Pyrex flask was heated at 60 °C for 24 h under a nitrogen atmosphere. ^bIsolated yields after reprecipitation into MeOH. ^cGPC (CHCl₃), polystyrene standards.

(TGA) was made on a Seiko EXSTAR 6000 instrument (10 °C min⁻¹). Cyclic voltammetry (CV) was carried out with a BAS CV-50W Electrochemical Analyzer in CH₂Cl₂ solution of 0.1 M Buⁿ₄NPF₆ as a supporting electrolyte. Platinum wire auxiliary electrode and Ag/AgCl RE-5 reference electrode were used in the CV measurement.

Materials

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen. Sodium hydride (60% dispersion in mineral oil), triethyl phosphite, hexacarbonylchromium, and *α,α'*-dibromo-*p*-xylene were obtained commercially, and used without further purification. 2,5-Diformyl-3-dodecylthiophene **2**¹⁴ and tricarbonyl{tetraethyl[(*tr*⁶-1,4-phenylene)bis(methylene)]bis[phosphonate]}chromium **4**¹⁵ were prepared as described in the literature. All reactions were performed under a nitrogen atmosphere using a standard Schlenk technique.

Polymerization

A typical procedure is as follows. A 50 mL Pyrex flask was charged with **2** (108 mg, 0.35 mmol), **4** (180 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 CHCl₃. 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. The polymer **6** was also synthesized by the same procedure.

Polymer 5. Yield: 162 mg, 90%. ¹H NMR (270 MHz, CDCl₃): δ 0.88 (m, 3 H), 1.26 (m, 16 H), 1.59 (m, 4 H), 2.63 (m, 2 H), 5.60 (m, 2.3 H), 6.42 (m,

2 H), 6.86 (m, 2 H), 7.13 (m, 1 H), 7.44 (m, 1.7 H). IR (KBr): 1960, 1887, 944 cm⁻¹.

Polymer 6. Yield: 97 mg, 73%. ¹H NMR (270 MHz, CDCl₃): δ 0.88 (m, 3 H), 1.26 (m, 16 H), 1.62 (m, 4 H), 2.64 (m, 2 H), 6.83 (m, 4 H), 7.12 (m, 1 H), 7.43 (m, 4 H). IR (KBr): 942 cm⁻¹.

RESULTS AND DISCUSSION

Synthesis and Characterization of Polymers

2,5-Diformyl-3-dodecylthiophene **2**¹⁴ and tricarbonyl{tetraethyl[(*tr*⁶-1,4-phenylene)bis(methylene)]bis[phosphonate]}chromium **4**¹⁵ were prepared according to published procedures. The procedure for the polymer synthesis by Horner–Wadsworth–Emmons olefination¹⁶ is outlined in Scheme 1, and the results are summarized in Table I. Treatment of **2** with **4** in the presence of NaH as a base at 60 °C for 24 h under nitrogen produced the corresponding polymer **5** in 90% yield as a red solid after work-up. The polymer **5** was soluble in common organic solvents such as THF, CHCl₃, and CH₂Cl₂ due to the alkyl substituent at the 3-position of a thiophene ring. On the other hand, the reaction of **4** with 2,5-diformylthiophene resulted in an insoluble product. As a reference polymer, the polymer **6** was also obtained by the same method in 73% yield.¹⁷ The number-average molecular weights of **5** and **6** were found by gel permeation chromatography (GPC) using polystyrene standards to be 8000 and 6700, respectively, which correspond to degrees of polymerization of 16 and 18. The ¹H NMR spectrum of the polymer **5** is shown in Figure 1. The peaks of phenyl protons coordinated to Cr(CO)₃ appeared at 5.7 ppm. The peaks corresponding to olefinic protons were observed at 6.5 and 6.8 ppm. The peaks at around

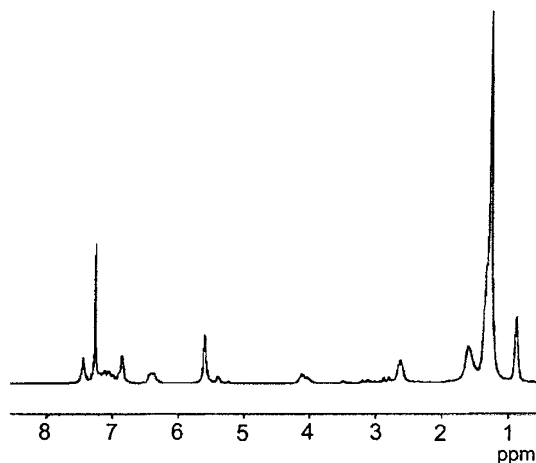


Figure 1. ^1H NMR spectrum of **5**.

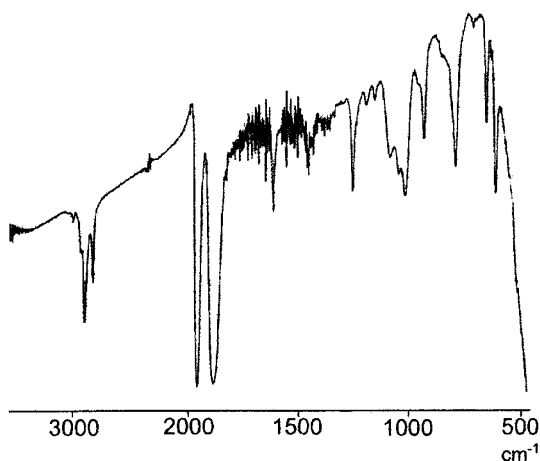


Figure 2. IR spectrum of **5**.

7.0 ppm were derived from 4-position of a thiophene ring. Phenyl protons appeared at around 7.4 ppm by thermal- or photo-dissociation of tricarbonylchromium moieties. Polymer **5** was found to consist of 65% chromium-coordinated phenylene and 35% phenylene moieties. The structures of the polymers obtained were confirmed by IR spectra. In Figure 2, the absorption of the out-of-plane bending mode of *trans*-vinylene appeared at 944 cm^{-1} , and strong absorption of the stretching mode of coordinated carbon monoxide was observed at 1960 and 1887 cm^{-1} .

Optical Property

The optical property of the polymers obtained was investigated by UV-vis absorption measurement in a CHCl_3 solution at room temperature, and the spectra are shown in Figure 3. The absorption maxima corresponding to a $\pi\text{-}\pi^*$ transition in the polymer chain were observed at 454 nm ($\epsilon = 1.8 \times 10^4$) and 487 nm ($\epsilon = 3.1 \times 10^4$) for **5** and **6**, respectively. The absorption maximum of **5** was blue-shifted about 30 nm in comparison with that of **6**. This result indicates that

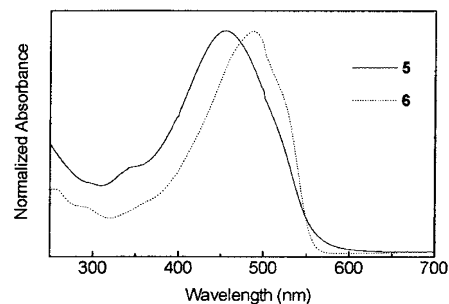


Figure 3. Absorption spectra of **5** and **6** in CHCl_3 .

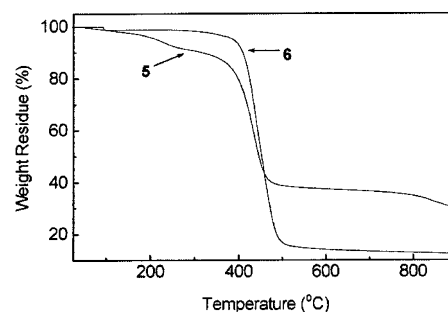


Figure 4. Thermogravimetric analysis (TGA) of **5** and **6** under nitrogen ($10^\circ\text{C min}^{-1}$).

the polymer **5** containing coordinated $\text{Cr}(\text{CO})_3$ has a shorter conjugated length due to the steric hindrance of the $\text{Cr}(\text{CO})_3$ unit.¹³ On the other hand, compared to the absorption maximum of the polymer **1** ($\lambda_{\text{max}} = 375\text{ nm}$, $\epsilon = 3.7 \times 10^4$), λ_{max} of **5** showed a red-shift of about 80 nm . In addition, the UV-vis absorption spectra of the polymer films were also recorded. The absorption spectra of **5** and **6** in the solid state were slightly red-shifted compared to those in solution, which indicates the rigidity of the polymer backbone resulted in no remarkable change between in the solid state and in solution.

Thermal Property

The measurement of thermogravimetric analysis (TGA) was also carried out for **5** and **6** under nitrogen (Figure 4). In the case of the polymer **5**, the pyrolysis took place in two steps. The first step started at 210°C , which could be attributed to the liberation of carbon monoxide coordinated to the chromium center; the second, which started at 370°C , could be attributed to the decomposition of the polymer backbone. For the polymer **6**, the decomposition also set in at 370°C and was complete at 420°C .

Electrochemical Property

The electrochemical behavior of the polymer **5** was investigated by cyclic voltammetry. The measurement was performed in $0.1\text{ M Bu}^n_4\text{NPF}_6$ in dry CH_2Cl_2 at room temperature using a scan rate of 100 mV s^{-1} . As

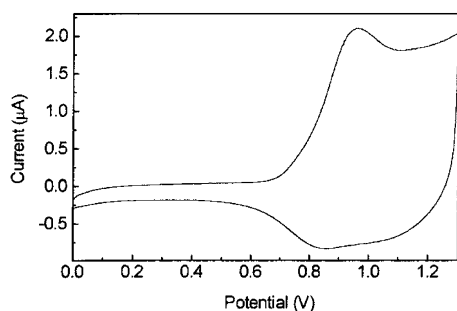


Figure 5. Cyclic voltammogram of **5** measured in 0.1 M CH₂Cl₂ solution of Buⁿ₄NPF₆ using Pt electrode (vs. Ag/Ag⁺) at the sweep rate of 100 mV s⁻¹.

shown in Figure 5, the polymer **5** exhibited a single broad oxidation peak at about 0.93 V vs. Ag/Ag⁺ 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. The polymer **5** was electrochemically stable for repeated scanning in a solution. On the other hand, the film of **5** in CH₃CN showed irreversible oxidation peak due to the ligand exchange reaction of (phenylene)Cr(CO)₃ to (CH₃CN)₃Cr(CO)₃.^{8c}

CONCLUSION

Novel π -conjugated polymer containing (η^6 -arene)Cr(CO)₃ and thiophene units in the main chain based on PPV was synthesized by Horner–Wadsworth–Emmons olefination. The polymer was soluble in common organic solvents and characterized by NMR and IR spectra. The polymer **5** exhibited an absorption maximum at 454 nm, which showed a red shift of about 80 nm compared to that of the polymer **1** reported in our previous work. The cyclic voltammogram showed a single oxidation peak for the (η^6 -arene)Cr(CO)₃ unit reversibly. Further studies on the synthesis and properties of novel π -conjugated polymers possessing a (η^6 -arene)Cr(CO)₃ unit are now underway.

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