Synthesis and Properties of PPV-Based ($\eta^6$-Arene)Cr(CO)$_3$-Containing Polymers Having Alkyldiphenylamine or Triarylamine in the Main Chain

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Summary

Novel poly(p-phenylenevinylene)-based ($\eta^6$-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$_2$Cl$_2$. The polymer showed interaction between the electron-withdrawing ($\eta^6$-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 $\pi$-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 \( \text{H}_6 \)-coordinated to the tricarbonylchromium fragment, \( \text{Cr(CO)}_3 \), is highly deficient because \( \text{Cr(CO)}_3 \) is strongly electron-withdrawing [6]. Namely, the \( (\text{H}_6 \)-arene)tricarbonylchromium, \( (\text{H}_6 \)-arene)\( \text{Cr(CO)}_3 \), can act as an electron acceptor. Furthermore, the \( (\text{H}_6 \)-arene)\( \text{Cr(CO)}_3 \) 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 \( (\text{H}_6 \)-arene)\( \text{Cr(CO)}_3 \)-containing conjugated polymers so far [11]. Recently, we reported the first soluble \( (\text{H}_6 \)-arene)\( \text{Cr(CO)}_3 \)-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 \( (\text{H}_6 \)-arene)\( \text{Cr(CO)}_3 \) units in the main chain are described.

**Experimental**

**General**

\(^1\)H 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\(_4\)Si 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 °C min\(^{-1}\)). Cyclic voltammetry (CV) was carried out with a BAS CV-50W Electrochemical Analyzer in CH\(_2\)Cl\(_2\) solution of 0.1 M Bu\(^n\)\( _4\)NPF\(_6\) 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[(\( \text{H}_6 \)-1,4-phenylene)bis(methylene)]bis[phosphonate]}chromium (1) [13], tetraethyl[1,4-phenylenebis(methylene)]bisphosphonate (1') [14], N-dodecylphénylamine [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.