

Simple Synthetic Method of Preparing Conjugated Polymer Containing Ferrocene

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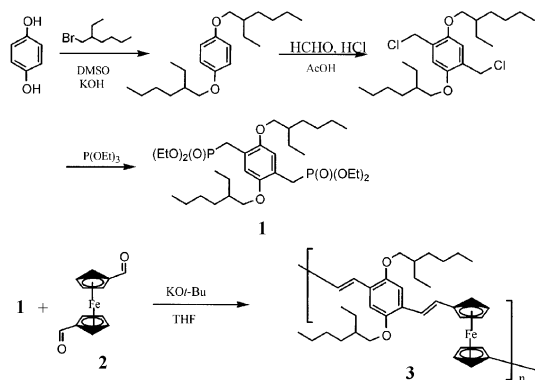
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Recently, inorganic/organic hybrid polymers have attracted much attention since they are expected to have novel properties resulting from the combination of both inorganic and organic characteristics. These include many interesting electrical, magnetic, and optical properties as inorganic characteristics, and good processibility and mechanical properties as organic features.¹⁻⁵ Several groups have recently reported new synthetic methods for preparing conjugated polymers containing inorganic or organometallic compounds, and these polymers showed many interesting properties useful for practical applications.⁶⁻¹¹ However, these synthetic methods involve tedious multiple step reactions and are usually applicable only to very specific polymer systems. Therefore, it is desirable to find a more general synthetic method to prepare conjugated polymers containing inorganic or organometallic compounds.

The synthetic method employed in our research to prepare processible conjugated polymers containing ferrocene is the Honer-Emmons reaction (phosphonate-aldehyde coupling reaction) as shown in Scheme 1. There are several advantages to producing conjugated polymers by this method compared to the conventional Wittig reaction, which has usually been used to generate conjugated polymers. First of all, it is relatively easy to prepare various alkyl dialkylphosphonate reagents from alkyl halides and they are usually very soluble in most organic solvents even when they have multiple phosphonate sites, while the insolubility of multifunctional Wittig reagents is a major drawback. Alkyl dialkylphosphonate can react with aldehydes and even with ketones to give coupled products having only a *trans* double bond. And by-product, salt of alkylphosphoric acid, can easily be removed by simple aqueous extraction. This type of reaction has been used to prepare short conjugated systems, and all *trans* configuration products have been easily prepared.^{12,13}

Long alkyl chains are introduced in the central phenyl ring of bisphosphonate reagent (**1**) to increase the solubility of

the resulting polymers. Ferrocene-1,1'-dialdehyde (**2**) was prepared from ferrocene according to the literature procedures.¹⁴ Bisphosphonate reagent (**1**) and ferrocene-1,1'-dialdehyde (**2**) were coupled in the presence of potassium *t*-butoxide as a base in a refluxing THF solution. The resulting polymer (**3**) was precipitated by addition of an excess amount of MeOH to the reaction mixture.¹⁵ As expected, **3** is very soluble in various organic solvents such as THF, CHCl₃, CH₂Cl₂, and toluene; it is slightly soluble in Et₂O and hexane and insoluble in alcohol and water. In order to compare and confirm the generation of polymer **3**, a simple model compound (**4**) of the conjugated polymer was also synthesized from bisphosphonate reagent and ferrocenealdehyde.¹⁶ UV-Vis. spectra of **3** and **4** shown in Figure 1 confirm the presence of ferrocene and the conjugated phenylene vinylene group. The UV-Vis. spectrum of **3** had a broader band in phenylene vinylene absorption region due to the longer conjugation length. The ¹H NMR spectrum also confirmed the formation of polymeric compound **3**. The peak corresponding to the unsubstituted cyclopentadienyl (Cp) ring at 4.15 ppm in the model analog compound **4** disappears in the polymeric compound **3**. All the other peaks were detected at exactly same chemical shifts both in **3** and **4**, but slightly broad for **3** due to the inhomogeneous magnetic environment in the polymeric materials. Cyclic voltammetry measurements also showed the presence of ferrocene units, and polymeric compound **3** had the lowest oxidation potential comparing to compound **4** as well as ferrocene itself because ferrocene units in polymer can interact through the conjugation and have a small band gap.



Scheme 1. Synthesis of Poly(phenylene vinylene ferrocene vinylene) (**3**).

	Ferrocene	4	polymer 3
Oxidation potential (E ^o) (mV vs. SCE)	307	298	276

Gel permeation chromatography (GPC) analysis of polymer **3** gave a weight-averaged molecular weight (M_w) of *ca.*

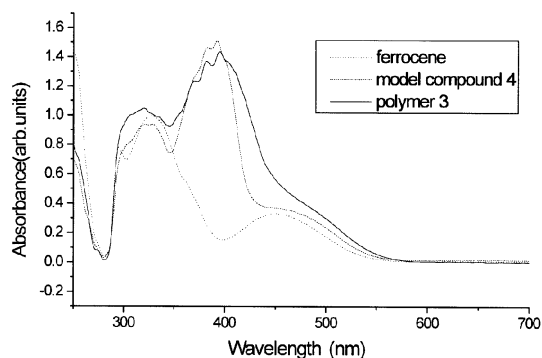


Figure 1. UV-Vis spectra of ferrocene, model compound **4**, and polymeric compound **3**.

7,400 with respect to the polystyrene standards. Based on the formula weight of repeating unit (542.6), the polymer with this weight-averaged molecular weight is calculated as *ca.* 14mer. However, the actual molecular weight and the degree of polymerization could be lower due to the rigid structure of the conjugated polymer compared to the polystyrene standard. Short oligomers can be removed from the polymer mixture by fractionation from the mixed solvents of THF and methanol to give the high molecular weight polymer (Mw = 29,000 with respect to the PS standard) with a polydispersity index (PDI) of 1.75.

Electrical conductivity of the thin films of conjugated polymer **3**, however, turned out to be very low. A value of 5×10^{-9} S/cm was measured for a spin-coated polymer thin film, and an iodine doping did not affect the conductivity significantly. This low conductivity is probably due to the presence of long alkyl side chains, which can enhance the solubility but also increase the distance between the polymer chains resulting in low interchain (chain-to-chain hopping) mobility of charge carriers. A similar effect has been reported in other conjugated polymer systems.⁷

A preliminary measurement of the third-order nonlinear optical (NLO) property in spin-coated thin film was taken using the degenerated four-wave mixing (DFWM) technique. The intensity of the conjugated signal from 0.12 μm thick film was measured to be $\chi^{(3)} = 1.24 \times 10^{-8}$ esu, compared to that of the liquid CS₂ reference ($\chi^{(3)} = 6.8 \times 10^{-13}$ esu).¹⁷ This value is comparable to and actually a few orders higher than those of conjugated poly(*p*-phenylene vinylene) (PPV) derivatives, which range from 10^{-12} to 10^{-9} esu depending upon the nature of the substituents.¹⁸ This might be due to the resonant effect caused by the absorption of incident light by the sample, and more detailed experiments at other wavelengths are under investigation.

In summary, we have shown that the Honer-Emmons reaction can be used as an excellent synthetic method to prepare processible conjugated polymers containing organometallic ferrocene compound and this method may be extended to synthesize many other conjugated polymers containing interesting inorganic and organometallic compounds. Poly(*p*-phenylene vinylene ferrocene vinylene) prepared by this method could be easily fabricated in a solid thin film by a simple spin-coating technique, and the preliminary experiments of third-order NLO property in solid thin films showed a very promising result.

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15. **Compound 1:** 1,4-bis(chloromethyl)-2,5-bis(2-ethylhexoxy)benzene was prepared from hydroquinone by employing slightly modified literature methods which have been used to make soluble poly(phenylene vinylene) (Ref. 7). The mixture of 1,4-bis(chloromethyl)-2,5-bis(2-ethylhexoxy)benzene (0.65 g, 1.51 mmol) and P(OEt)₃ (1.0 g, 6.02 mmol) was heated at 120 °C for 12h. The excess amount of P(OEt)₃ was removed under vacuum, and the residual liquid was purified by silica gel column (THF : HCl₃ = 1 : 15) to give 0.70 g (quantitative yield) of pure compound **1** as colorless liquid. ¹H NMR (CDCl₃, ppm): δ 0.91 (m, 12H, -CH₃), 1.24 (t, 12H, POCH₂CH₃), 1.43 (m, 16H, -CH₂-), 1.69 (m, 2H, -CH-), 3.24 (d, *J* = 20.1 Hz, 4H, -CH₂P-), 3.81 (d, *J* = 5.4 Hz, 4H, -OCH₂-), 4.02 (m, 8H, -POCH₂-), 6.95 (s, 2H, aromatic protons)
- Polymer 3:** Compound **1** (0.56 g, 0.87 mmol), compound **2** (0.21 g, 0.87 mmol) and KO^tBu (0.47 g, 4.2 mmol) in 50 mL of THF was refluxed for 12h under nitrogen atmosphere, and then solvent was evaporated under vacuum to make the volume less than 5 mL. The solution was diluted with 100 mL of methanol and stored in a refrigerator. The resulted red solid polymer was filtered and dried in air. ¹H NMR (CDCl₃, ppm): δ 0.88 (m, 12H, -CH₃), 1.21 (m, 16H, -CH₂-), 1.69 (m, 2H, -CH-), 3.96 (m, 4H, -OCH₂-), 4.29 (br. s, 4H, Cp), 4.49 (br. s, 4H, Cp), 6.89-7.06 (m, 6H, vinyl and aromatic protons)
16. **Compound 4:** Same procedure was used as preparing polymer **3** except employing ferrocene carboxaldehyde. ¹H NMR (CDCl₃, ppm): δ 0.88 (m, 12H, -CH₃), 1.21 (m, 16H, -CH₂-), 1.69 (m, 2H, -CH-), 3.96 (d, *J* = 5.1 Hz, 4H, -OCH₂-), 4.15 (s, 10H, Cp), 4.29 (s, 4H, Cp), 4.49 (s, 4H, Cp), 6.90 (d, 2H, 16.2 Hz, vinyl protons), 7.01 (s, 2H, aromatic protons), 7.06 (d, 2H, 16.2 Hz, vinyl protons); ¹³C NMR (CDCl₃, ppm): δ 11.18, 14.62, 23.58, 24.73, 29.72, 31.37, 40.28, 67.2, 69.31, 69.68, 71.90, 84.65, 110.36, 121.75, 126.82, 127.13, 151.02. Anal. Calcd for C₂₃H₅₈O₂Fe₂: C, 72.53; H, 7.75. Found: C, 72.72; H, 7.94.
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