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### Polymerization of Diphenylacetylenes Having a Ferrocenyl Group and Polymer Properties

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## Polymerization of Diphenylacetylenes Having a Ferrocenyl Group and Polymer Properties

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### ABSTRACT

Polymerization of two diphenylacetylenes having a ferrocenyl group at *para* or *meta* position, 1-[*p*-ferrocenylphenyl]-2-phenylacetylene (*p*-FcDPA) and 1-[*m*-ferrocenylphenyl]-2-phenylacetylene (*m*-FcDPA) and properties of the formed polymers were investigated. Both monomers polymerized with TaCl<sub>5</sub>-*n*-Bu<sub>4</sub>Sn catalyst in good yields to give reddish brown polymers. Poly(*p*-FcDPA) was insoluble in any solvents. On the other hand, poly(*m*-FcDPA) was soluble in CHCl<sub>3</sub>, THF, anisole, *o*-dichlorobenzene, and so on, and its weight-average molecular weight ( $M_w$ ) was  $53 \times 10^4$  and fairly high. A free-standing film of poly(*m*-FcDPA) could be easily fabricated by solution casting. The onset temperature of weight loss ( $T_0$ ) of poly(*m*-FcDPA) in air was ca. 310°C, indicating moderate thermal stability. Poly(*m*-FcDPA) was electrochemically active, and showed redox cycles based on the ferrocene moiety in cyclic voltammetry.

**Key Words:** Metal-containing polymer; Substituted polyacetylene; Ferrocene; Metathesis polymerization; Transition metal catalyst; Redox-active polymer.

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## INTRODUCTION

Ferrocene is one of the most typical and stable organometallic compounds and belongs to a group of metallocene. It has attracted much attention for a long time due to its unique structure and properties.<sup>[1]</sup> Synthesis of various organometallic polymers has been examined because of their potential benefits as new materials with magnetism, optoelectronic properties, redox property, and thermal stability.<sup>[2]</sup> Among the organometallic polymers, ferrocene-containing polymers are of special interest due to its easy availability, and thermal and chemical stability.

There are many examples of ferrocene-containing polymers such as poly(vinylferrocene),<sup>[3]</sup> poly(ferrocenylene),<sup>[4]</sup> as well as polyamides, polyesters, and polyazomethines bearing ferrocenylene moieties. Recently, ferrocenylene-containing conjugated polymers,<sup>[5–7]</sup> (e.g., aryleneethynylene-type<sup>[6]</sup> and arylenevinylene-type<sup>[7]</sup> polymers) have been reported. Further, poly(ferrocenylene) consisting of only 1,1'-linkage has been synthesized by unique ring-opening polymerization of ferrocenophanes.<sup>[8]</sup>

On the other hand, there have been few reports regarding ferrocene-containing polyacetylenes.<sup>[9]</sup> Though the synthesis of poly(ethynylferrocene) have been attempted by using radical initiators, Ziegler–Natta catalysts, and MoCl<sub>5</sub>- and WCl<sub>6</sub>-based catalysts for a long time, only insoluble polymers or oligomers with molecular weight of a few thousand were obtained. In recent years, the synthesis of ferrocene-containing monosubstituted acetylene polymers<sup>[10]</sup> such as poly(ethynylferrocene) was achieved by using Schrock carbens in a living fashion.<sup>[10a]</sup> It has been found that poly(ethynylferrocene) is partly oxidized by iodine and dichlorodicyanoquinone to take mixed valence states which leads to semiconductivity ( $10^{-6}$ – $10^{-7}$  S cm<sup>-1</sup>).<sup>[11]</sup>

Previously, we reported that various diphenylacetylenes having ring substituents polymerized in good yields with TaCl<sub>5</sub>-based catalysts to afford high molecular weight polymers ( $M_w > 1 \times 10^6$ ). Interestingly, the formed polymers have excellent solubility, high thermal stability, and film-forming ability.<sup>[12]</sup> Such properties are important to develop practical applications. In the present study, two kinds of diphenylacetylenes having a ferrocenyl group at meta or para position were synthesized and their polymerization behavior and polymer properties were investigated.

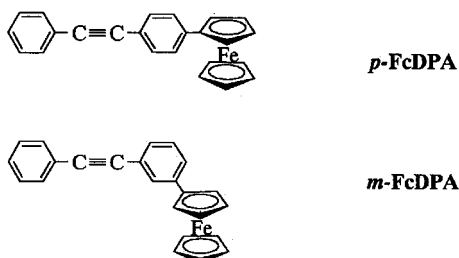
## EXPERIMENTAL

### Materials

TaCl<sub>5</sub> (Strem) and ferroceneboronic acid (Aldrich) were used as received. *n*-Bu<sub>4</sub>Sn was distilled twice from CaH<sub>2</sub> and used as toluene solution (200 mmol/L). Both monomers were synthesized according to Sch. 2 with reference to the literature.<sup>[12b,13,14]</sup> Dichloro[1,1'-bis(diphenylphosphino)ferrocene]palladium(II), PdCl<sub>2</sub>(dppf), was prepared by the method reported in the literature.<sup>[15]</sup> The coupling reaction of ferroceneboronic acid with aryl halides proceeded much faster with iodides than with bromides. Thus, the bromides were at first converted into the corresponding iodides. The detailed method for preparing the bromides has been described elsewhere.<sup>[12b]</sup>

## Ferrocene-Containing Poly(Diphenylacetylenes)

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**Scheme 1.** Monomers used in the present study.

**1-(*p*-Iodophenyl)-2-Phenylacetylene**

A mixture of 1-(*p*-bromophenyl)-2-phenylacetylene (3.0 g, 11.7 mmol), KI (20.6 g, 124 mmol), CuI (11.1 g, 58.5 mmol) and HMPA (70 ml) was stirred for 7 h at 160°C under nitrogen. The reaction was monitored by <sup>1</sup>H NMR (as the doublet peaks from ortho and meta protons of the bromine atom at 7.48 and 7.38 ppm, respectively, disappeared, those of the iodine atom in the desired compound at 7.70 and 7.25 ppm gradually increased). The reaction mixture was cooled to room temperature and the reaction was quenched by the addition of 2 N HCl (70 mL). Then the mixture was poured into benzene (100 mL) and stirred. The organic phase was washed three times with water and dried over anhydrous sodium sulfate. Benzene was evaporated to give a pale yellow solid (3.3 g) (the crude iodide was used in the next reaction without further purification).

**1-(*p*-Ferrocenylphenyl)-2-Phenylacetylene**

A mixture of the crude iodide obtained above (3.3 g), ferroceneboronic acid (2.5 g, 10.9 mmol), PdCl<sub>2</sub>(dppf) (79 mg, 0.106 mmol), and 3 N NaOH (16 mL) in 1,2-dimethoxyethane (40 mL) was refluxed with stirring for 12 h under nitrogen. The completion of the reaction was confirmed by <sup>1</sup>H NMR (the doublet peak of the iodide at 7.70 ppm disappeared). Subsequently, the reaction mixture was filtered to remove the insoluble residue. The filtrate was extracted with CHCl<sub>3</sub> and washed with water, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent, the crude product was purified by flash column chromatography (silica gel; eluent: a gradient from hexane/benzene 20/1 to hexane/benzene 2/1) and by the subsequent recrystallization (from diethyl ether) to give an orange solid in an overall yield of 20% (based on bromide). Mp. 173.0–175.0°C. IR (KBr) 3081, 3054, 3031, 1597, 1526, 1103, 1017, 999, 885, 843, 822, 756, 689, 583, 548, 540, 515, 500, 484 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.56–7.52 (m, 2H), 7.45 (s, 4H), 7.38–7.32 (m, 3H), 4.66 (t, 2H), 4.34 (t, 2H), 4.04 (s, 5H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 139.82, 131.59, 131.48, 128.29, 128.06, 125.76, 123.42, 120.29, 89.70, 89.35, 84.19, 69.66, 69.31, 66.46. Anal. Calcd for C<sub>24</sub>H<sub>18</sub>Fe: C, 5.01%; H, 79.57%; Fe, 15.42%. Found: C, 5.09%; H, 79.70%; Fe, 15.21%.

### 1-(*m*-Ferrocenylphenyl)-2-Phenylacetylene (*m*-FcDPA)

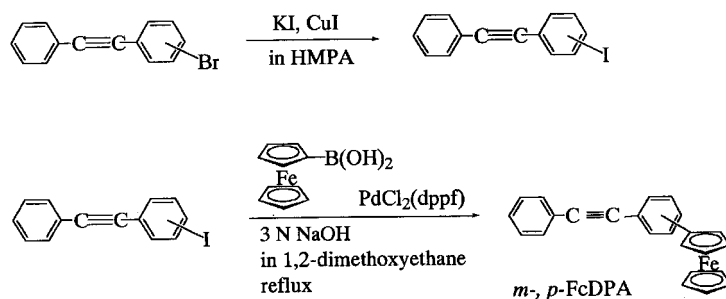
*m*-FcDPA was prepared from 1-(*m*-bromophenyl)-2-phenylacetylene as starting material by the same method as for the *para*-isomer described above; yield 22% (based on the bromide). Mp. 114.0–116.0°C. IR (KBr) 3081, 3056, 1499, 1489, 1105, 997, 897, 822, 791, 750, 687, 552, 540, 509, 490  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.64 (t, 1H), 7.60–7.56 (m, 2H), 7.45 (dt, 1H), 7.4–7.34 (m, 4H), 7.28 (d, 1H), 4.67 (t, 2H), 4.34 (t, 2H), 4.08 (s, 5H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  140.25, 132.21, 129.66, 129.44, 128.97, 128.94, 128.86, 126.64, 123.78, 123.71, 90.13, 89.70, 84.83, 70.23, 69.72, 67.05. Anal. Calcd for  $\text{C}_{24}\text{H}_{18}\text{Fe}$ : C, 5.01%; H, 79.57%; Fe, 15.42%. Found: C, 4.80%; H, 79.41%; Fe, 15.79%.

### Polymerization Procedures

Polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under dry nitrogen by using  $\text{TaCl}_5$ -*n*- $\text{Bu}_4\text{Sn}$  catalyst which has been most frequently employed for polymerization of diphenylacetylene derivatives. The monomer conversions could not be determined by gas chromatography because the boiling point of the monomers were too high. A detailed procedure of the polymerization has been described elsewhere.<sup>[12b]</sup> Polymers were isolated by precipitation into a large amount of methanol, and polymer yields were determined by gravimetry.

### Measurements

The molecular weights of the polymers were evaluated by GPC with the use of a polystyrene calibration [eluent,  $\text{CHCl}_3$ ; columns, Shodex K-802, K-803, K-804 for low molecular weight polymers, and Shodex K-805, K-806, K-807 for high molecular weight polymers (Showa Denko, Co., Japan)]. IR, UV, and NMR spectra were measured on a Shimadzu FTIR-8100 spectrophotometer, a Jasco V-530 spectrophotometer, and a JEOL EX-400 spectrometer, respectively. Thermogravimetric analyses (TGA) were conducted



Scheme 2. Synthesis of ferrocene-containing diphenylacetylene monomers.



in air on a Perkin–Elmer TGA-7 thermal analyzer at a heating rate of 10°C/min. Cyclic voltammograms were observed with an ALS-600A-n electrochemical analyzer. The film samples of the polymers were prepared by casting the solutions of poly(*m*-FcDPA) in CHCl<sub>3</sub> on In–Sn oxide (ITO)-coated quartz plates. The measurements were carried out in acetonitrile solution using *n*-Bu<sub>4</sub>NBF<sub>4</sub> (0.10 M) as supporting electrolyte, platinum working and counter electrodes, and a saturated calomel reference electrode (SCE).

## RESULTS AND DISCUSSION

### Polymerization of *p*-FcDPA and *m*-FcDPA

In general, the TaCl<sub>5</sub>-*n*-Bu<sub>4</sub>Sn catalyst works effectively in the polymerization of sterically crowded disubstituted acetylenes such as diphenylacetylene.<sup>[16]</sup> Hence, the polymerization of the present monomers were carried out using this catalyst (Table 1).

Polymerization of diphenylacetylene having ferrocenyl group at para position, *p*-FcDPA, afforded a polymer in 95% yield in toluene, but the polymer did not completely dissolve in any solvent. On the other hand, *m*-FcDPA, the meta isomer, gave a polymer soluble in CHCl<sub>3</sub> in 30–50% yield. However, only an oligomeric mixture ( $M_n < 1000$ ) was obtained, when toluene was used as polymerization solvent. This result is attributable to the poor solubility of the oligomer, which practically quenched the polymerization at an initial stage by precipitation of the product from the reaction solution. Therefore, it is expected that high-molecular-weight polymer can be obtained by using a good solvent of poly(*m*-FcDPA). It has been known that aromatic ethers, aliphatic hydrocarbons, and halogenated hydrocarbons are favorable solvents in the polymerization of diphenylacetylenes with TaCl<sub>5</sub>-based catalysts.<sup>[17]</sup> Hence, *o*-dichlorobenzene and anisole were examined as polymerization solvents (Table 1, runs 3, 4), because the oligomers of *m*-FcDPA were completely soluble in these solvents. Polymerization proceeded homogeneously in these solvents to afford poly(*m*-FcDPA) with  $M_w$  of  $30 \times 10^4$ – $50 \times 10^4$  in relatively good yields. The poly(*m*-FcDPA) obtained was soluble in CHCl<sub>3</sub>, THF,

**Table 1.** Polymerization of ferrocene-containing diphenylacetylenes by TaCl<sub>5</sub>-*n*-Bu<sub>4</sub>Sn<sup>a</sup>.

Run	Solvent	Polymer <sup>b</sup>		
		Yield (%)	$M_w/10^{3c}$	$M_n/10^{3c}$
<i>p</i> -FcDPA				
1	Toluene <sup>d</sup>	95		Insoluble
<i>m</i> -FcDPA				
2	Toluene	48		(Oligomers)
3	<i>o</i> -Dichlorobenzene	35	330	96
4	Anisole	30	530	260

<sup>a</sup> Polymerized in toluene at 80°C for 24 h;  $[M]_0 = 0.20$  M,  $[TaCl_5] = 20$  mM,  $[n - Bu_4Sn] = 40$  mM; <sup>b</sup> Methanol – insoluble product; <sup>c</sup> By GPC; <sup>d</sup>  $[M]_0 = 0.10$  M, for 7 days.

anisole, *o*-dichlorobenzene, and chlorobenzene, and provided a free-standing film by solution casting.

### Polymer Structure

The IR spectrum of poly(*m*-FcDPA) displayed no absorption around  $2200\text{ cm}^{-1}$  ( $\nu_{\text{C}=\text{C}}$ ) which is seen in the monomer (Fig. 1). A weak absorption band due to the C = C stretching of the double bonds in the main chain, and those of phenyl and cyclopentadienyl ring in the side groups of the polymer overlaps each other in a range of  $1400\text{--}1600\text{ cm}^{-1}$ . Further, a strong absorption due to the Ar-H deformation was seen at  $689\text{ cm}^{-1}$ . The bands characteristic of the ferrocenyl group are observed in both polymer and monomer; i.e., a band due to the vibration of Fe-cyclopentadienyl ring appears at  $496\text{ cm}^{-1}$ , and those due to the C-H in-plane and out-of-plane bendings of ferrocenyl ring at  $791$  and  $814\text{ cm}^{-1}$ , and  $1001$  and  $1105\text{ cm}^{-1}$ , respectively. Figure 2 illustrates the UV-visible spectrum of poly(*m*-FcDPA). Poly(*m*-FcDPA) has two absorption maxima at  $374$  and  $439\text{ nm}$ , and the cutoff wavelength is ca.  $490\text{ nm}$ . These absorption maxima are due to the conjugated double bonds along the main chain, which corresponds to the color of the polymer (reddish brown).

### Polymer Properties

The thermal stability of poly(*m*-FcDPA) was examined by TGA in air (Fig. 3). Poly(*m*-FcDPA) showed moderate thermal stability (onset temperature for weight loss ( $T_0$ ) ca.  $310^\circ\text{C}$ ), though inferior to poly(DPA) ( $T_0 = 500^\circ\text{C}$ ). Thus, the introduction of a ferrocenyl group on the phenyl ring proves to considerably lower the thermal stability. The TGA profile of poly(*m*-FcDPA) showed a large weight loss in the range  $310\text{--}400^\circ\text{C}$ .

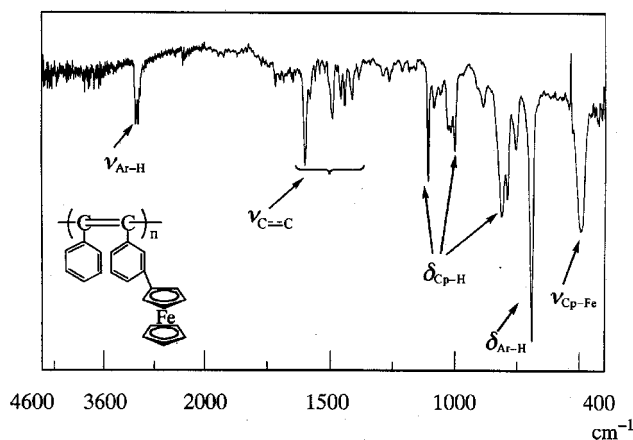


Figure 1. IR spectrum of poly(*m*-FcDPA) (sample from run 3, Table 1, KBr disk).

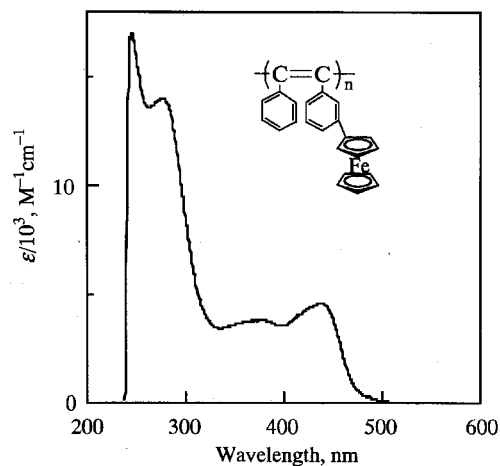


Figure 2. UV-vis spectrum of poly(*m*-FcDPA) (in CHCl<sub>3</sub>).

An inflection point is observed at 395°C and 47% wt loss which suggests the selective removal of the ferrocenyl groups (51% weight loss expected) below 400°C.

Cyclic voltammetry of poly(*m*-FcDPA) was examined to clarify its electrochemical behavior (Fig. 4). This polymer was electrochemically active, and reversible redox peaks originating from the Fe(II)/Fe(III) couple were observed. The maximum of current values became smaller as the oxidation–reduction process was repeated, but a constant maximum value and the same voltammetric profile were observed after several scans. Two oxidation peaks were observed at 0.7 and 0.9 V (vs. Ag/Ag<sup>+</sup>) in the first scan. The former seems to be the oxidation peak of one-electron oxidation which derives from the ferrocenyl group,

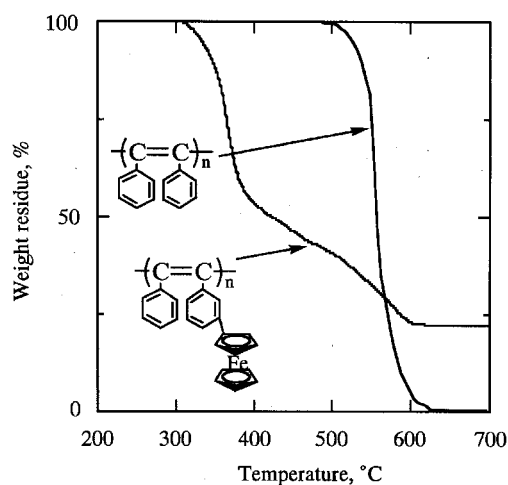
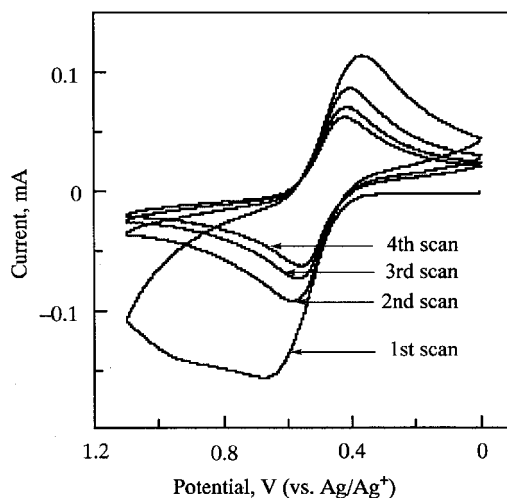


Figure 3. TGA curves of poly(*m*-FcDPA) and poly(DPA) (heating rate 10°C/min, in air).





**Figure 4.** Cyclic voltammogram of poly(*m*-FcDPA) (in acetonitrile containing *n*-Bu<sub>4</sub>NBF<sub>4</sub> as a supporting electrolyte (0.10 M), scan rate 0.10 V/s).

while the latter is probably that of the oxidation of the main chain. The constant currents of oxidation and reduction were reached at 0.6 and 0.4 V (vs. Ag/Ag<sup>+</sup>), respectively, which is close to the profile of ferrocene itself. This result indicates that the redox behavior of poly(*m*-FcDPA) are attributable to the Fe(II)/Fe(III) redox couple based on the ferrocene moieties independent of the conjugated polymer backbone.

## CONCLUSION

Two ferrocene-containing diphenylacetylenes, 1-[*p*-ferrocenylphenyl]-2-phenylacetylene (*p*-FcDPA) and 1-[*m*-ferrocenylphenyl]-2-phenylacetylene (*m*-FcDPA) were polymerized in the presence of TaCl<sub>5</sub>-*n*-Bu<sub>4</sub>Sn to give polymers in moderate yields. Poly(*p*-FcDPA) was insoluble in any solvents. On the other hand, poly(*m*-FcDPA) was soluble in CHCl<sub>3</sub>, THF, anisole, *o*-dichlorobenzene, etc, and its *M<sub>w</sub>* was as high as ca. 53 × 10<sup>4</sup>. Poly(*m*-FcDPA) was thermally fairly stable, and the onset temperature of wt loss in air was over 310°C. Poly(*m*-FcDPA) was electrochemically active, and the oxidation and reduction peaks were observed at 0.6 and 0.4 V (vs. Ag/Ag<sup>+</sup>), respectively, after scanning several redox cycles; the voltammograms were similar to that of ferrocene itself.

## ACKNOWLEDGMENTS

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