

Effect of Ferrocene Substituents and Ferricinium Additive on the Properties of Polyaniline Derivatives and Catalytic Activities of Palladium-Doped Poly(*m*-ferrocenylniline)-Catalyzed Suzuki–Miyaura Cross-Coupling Reactions

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ABSTRACT: Poly(aniline-*co-m*-ferrocenylniline) and ferricinium-doped poly(aniline-*co-m*-ferrocenylniline) were synthesized by a conventional chemical oxidative polymerization, then characterized by spectroscopic techniques and quantitative analyzes. Increasing of the percentages of *m*-ferrocenylniline in the copolymers resulted to a blue shift of UV–Vis absorption spectra. Broader EPR spectra indicated the loss of conjugation and crystallinity of copolymers. ¹H NMR spectra confirmed the presence of ferrocene moieties and ferricinium in the polymers. The CV measurements showed that the electron withdrawing power of ferrocene moieties could lead to the decreasing of electron delocalization on the polymer main chain. The VSM results showed that as-prepared copolymers were soft magnetic materials with very low magnetization. Pd-doped poly(*m*-ferrocenylniline) as catalysts were utilized in the Suzuki–Miyaura cross-coupling reactions to improve the catalytic activities. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 1489–1497, 2013

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INTRODUCTION

It is of special interest to investigate hybrid nanocomposites based on organic polymers which can be fabricated with various inorganic nanoparticles to create nanocatalysts with improvements in their properties for catalysis.^{1–6} In addition to the size and shape of nanocatalysts, it is apparent that some molecular factors such as the surface composition, charge transfer, and oxidation state of the stabilizing ligand layers can be used to control the catalytic activity and selectivity of nanocatalysts⁷ which can be chemically tuned with the redox property of appropriate ligands or polymers.⁸ Polyaniline⁹ is currently an excellent example of the most widely studied conducting polymers which can be synthesized by the oxidative polymerization of aniline in an aqueous acid solution with ease, either by using an electrochemical method or a chemical oxidant polymerization.^{10,11} In

order to modify the properties of polymers, substituted polyanilines can be made by adding various functional groups to the backbone of the polymers or incorporating external dopants binding to the polymer backbone.^{12–14}

The Suzuki–Miyaura cross-coupling reaction of aryl halides with arylboronic acids is a fundamental transformation in modern organic synthesis and offers a powerful method for the aryl–aryl formation.^{15,16} Palladium complexes and nanoparticles are one of the most useful catalysts for carbon–carbon cross-coupling reactions.^{3–5,17–20} Recently, conjugated conductive polyaniline used as a supporter for palladium nanoparticles (PdNPs) has been reported as excellent catalysts in the cross-coupling reactions.^{4,21–23} A number of studies investigated ligands containing ferrocene covalently bonded for the metal-assisted cross-coupling reactions of aryl halides with arylboronic

acids.^{24–39} As part of our efforts to synthesize a novel conjugated polymer, herein polyanilines based on the redox-active ferrocene moiety extended on the polymer backbone were synthesized, and their properties were investigated to improve the catalytic activities. The aims of this study were therefore to prepare and characterize poly(aniline-*co-m*-ferrocenylniline)(s) and ferricinium-doped poly(aniline-*co-m*-ferrocenylniline)(s), and investigate the Suzuki–Miyaura cross-coupling activities catalyzed by the nanocomposite conjugated polyaniline and poly(*m*-ferrocenylniline)-supported palladium nanocatalysts in toluene.

EXPERIMENTAL

Synthesis of Poly(aniline-*co-m*-ferrocenylniline)

m-Ferrocenylniline⁴⁰ was achieved by reduction reaction of *m*-ferrocenylnitrobenzene⁴¹ with Sn/HCl. To a mixture of aniline (0.51 g, 5.5 mmol) and *m*-ferrocenylniline (5, 10, 15, and 20 mol % of aniline) was added 1 M H₂SO₄ (7 cm³). A solution of ammonium peroxydisulfate (1.0 g, 4.4 mmol) in de-ionized water (2 cm³) was added to the suspension. The copolymerization was left stirring under ambient conditions for 24 h. The precipitate was filtered under vacuum and washed with de-ionized water. The resulting copolymer was dried by incubating at 80°C for 24 h.

Synthesis of Ferricinium-Doped Polyaniline

To a suspension of aniline (0.51 g, 5.5 mmol) in 1M H₂SO₄ (7 cm³) was slowly added 2 cm³ aqueous solution of ammonium peroxydisulfate (1.0 g, 4.4 mmol in de-ionized water). Then, the ferricinium species prepared by dissolving ferrocene (0.51 g, 2.7 mmol) in *conc.* H₂SO₄ (2 cm³) was added to the mixture and the reaction was allowed to proceed upon stirring under ambient conditions. After 24 h, a fine dark blue-green powder was filtered under vacuum and washed with de-ionized water. The resulting ferricinium-doped polyaniline was dried by incubating at 80°C for 24 h.

Synthesis of Ferricinium Doped Poly(aniline-*co-m*-ferrocenylniline)

The experimental procedure was similar to that for polyaniline. A mixture of monomers between aniline (0.51 g, 5.5 mmol) and *m*-ferrocenylniline (5, 10, 15, and 20 mol %) was added with 1M H₂SO₄ (7 cm³). Then, 1 g of ammonium peroxydisulfate in 2 cm³ of de-ionized water was added dropwise into the mixture solution. During the formation of copolymer, the ferricinium ion prepared by mixing ferrocene (0.51 g, 2.74 mmol) in 2 cm³ of *conc.* H₂SO₄ was then added. The copolymerization was allowed to proceed for 24 h. Then, a fine dark orange precipitate powder was obtained, separated by filtration, and washed several times with water. The resulting copolymer was dried by incubating at 80°C for 24 h.

Preparation of Palladium Nanoparticles (PdNPs)

PdNPs for Suzuki–Miyaura cross-coupling reactions were synthesized by combining palladium(II) acetate (2.2 mg, 0.01 mmol) with polyaniline or poly(aniline-*co-m*-ferrocenylniline) (0.1 mmol with respect to their monomer) in 5 cm³ of

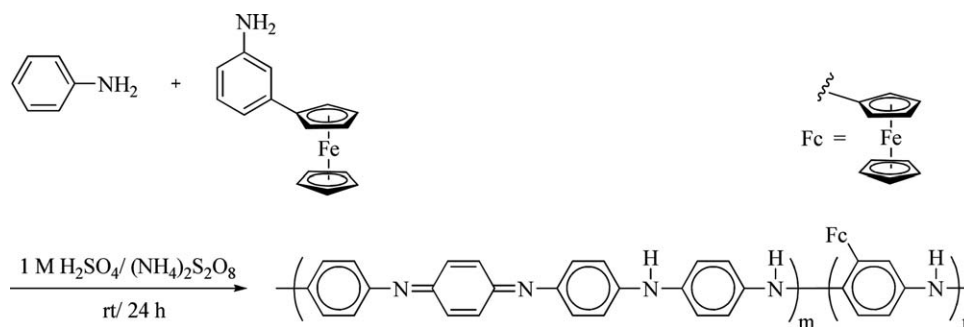
toluene. The mixture was kept under stirring at ambient temperature for 24 h.

Suzuki–Miyaura Cross-Coupling Reactions

Arylbromide (0.5 mmol) and arylboronic acid (0.5 mmol) were mixed into 10 cm³ of toluene. A solid of potassium hydroxide (112 mg, 2 mmol) and the PdNPs were added into the reaction flask. The reaction was refluxed for 20 h. After that, the PdNPs were removed by filtration, and then the filtrant was concentrated under vacuum. All cross-coupling products were characterized by ¹H NMR analysis.

General Characterization

UV–Visible absorption spectra of the sample solution were monitored over the wavelength of 300–800 nm using a HP-8453 Hewlett Packard UV–Visible scanning spectrophotometer with the path length of the quartz cell at 10 mm and dimethyl sulfoxide (DMSO) was used as a reference. A required amount of poly(aniline-*co-m*-ferrocenylniline)(s) (5 mg) and ferricinium-doped poly(aniline-*co-m*-ferrocenylniline)(s) (10 mg) was dissolved in DMSO (10 cm³) for the EPR measurements which were performed with a ground sample in a quartz tube. A Bruker (e500) spectrometer was used to operate at a frequency of 9.86 GHz, and the modulation amplitude used was set at 1.0 G. The microwave power for the EPR measurements of the polymers was set at 2.0 mW. The temperature dependence of the EPR signal intensities of the polymers in a solid state was measured at 298 K. In TEM measurements, the sample dispersed in water was dropped on a 300-mesh formvar coated copper grid. The images were acquired by a Tecnai G2 Sphera transmission electron microscope operated at 80 kV. All samples of polymer, ferricinium-doped polyaniline, poly(aniline-*co-m*-ferrocenylniline), ferricinium-doped poly(aniline-*co-m*-ferrocenylniline), poly(*m*-ferrocenylniline), and ferricinium-doped poly(*m*-ferrocenylniline) were examined by using ¹H NMR spectroscopy (300 and 500 MHz Bruker Avance) with a concentrated solution dissolved in dimethyl sulfoxide-*d*₆ (DMSO-*d*₆). The starting materials of Suzuki–Miyaura cross-coupling, *m*-ferrocenylniline, *m*-ferrocenylnitrobenzene, and all crude products were examined by using chloroform-*d* (CDCl₃) and methanol-*d*₄ (CD₃OD). Mass spectra were recorded on a Bruker Data Analysis Esquire-LC mass spectrometer, equipped with an electrospray source using ESI mode and Thermofinnigan Polaris Q 210179 mass spectrometer with direct probe controller 10493 using EI mode. An AUTOLAB-30 electrochemical analyzer was used to carry out the cyclic voltammetric measurements. In all cases, three electrodes were employed, consisting of working electrode and Pt wire serving as a counter electrode and the Ag/AgCl (saturated 3M KCl) serving as a reference electrode. The electrochemical experiments were carried out at 25°C. The coercivities (*H*_c), the remanent magnetizations (*M*_r), and the saturation magnetizations (*M*_s) of the as-prepared samples were performed by using the vibrating sample magnetometer (Lake-shore, Model 4500). The magnetic parameters (*H*_c, *M*_r, and *M*_s) of each sample were determined from the hysteresis loops produced by the vibrating sample magnetometry (VSM). The saturation magnetization was reached at an applied field of 7 kOe. The data of magnetization as a function of the applied field were plotted and also employed for calculations.



Scheme 1. The preparation of poly(aniline-*co-m*-ferrocenylaniline).

RESULTS AND DISCUSSION

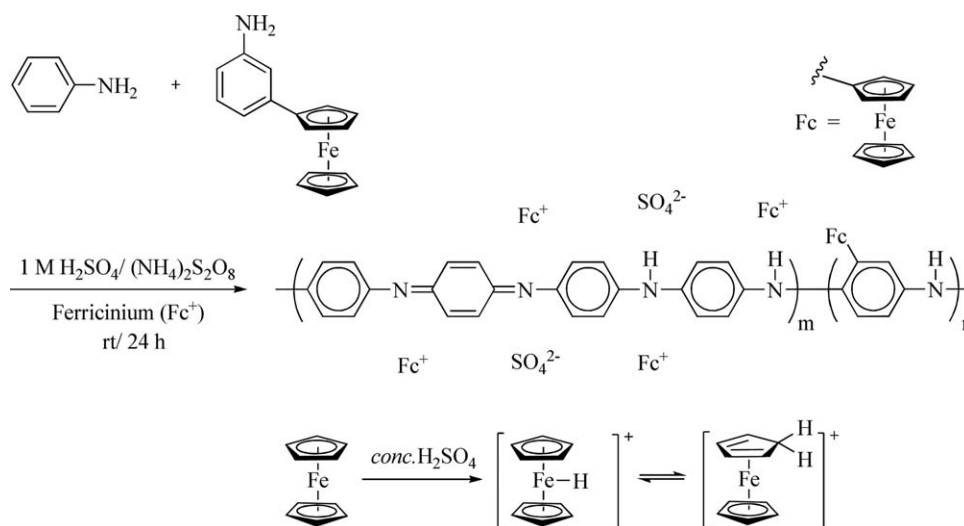
Poly(aniline-*co-m*-ferrocenylaniline)(s) and poly(*m*-ferrocenylaniline) were readily synthesized in diluted sulfuric acid by using ammonium peroxydisulfate as an oxidant. The structure of poly(aniline-*co-m*-ferrocenylaniline) is proposed as shown in Scheme 1; where Fc is a ferrocenyl substituent on the aromatic ring. Likewise, ferricinium-doped poly(aniline-*co-m*-ferrocenylaniline) was similarly prepared as described above with an external dopant of 50% molar ratio of ferricinium to aniline. The structure of the ferricinium-doped poly(aniline-*co-m*-ferrocenylaniline) is proposed as shown in Scheme 2; where Fc^+ is a ferricinium species.

UV-Visible spectra of the copolymers were recorded over the range of 300–800 nm as shown in Figure 1. The colorful solutions of poly(aniline-*co-m*-ferrocenylaniline) in DMSO were observed for various molar ratios of *m*-ferrocenylaniline to aniline: green for polyaniline, dark-brown for 5 and 10%, and orange for 15 and 20%. The strong absorption peak is shifted to a lower wavelength at 570 nm for the 5% molar ratio. It can be seen that the blue shift of absorption bands of the copolymers was observed as increasing the molar ratios of *m*-ferrocenylaniline. For 15 and 20% molar ratios of *m*-ferrocenylaniline, the UV-Visible spectra show a strong absorption band at 500 nm

which is a characteristic band of orange color of ferrocene moieties.

In order to study the influence of the external dopant of ferricinium ions to the absorption bands of copolymers, the UV-Visible spectra of ferricinium-doped copolymers in DMSO were also monitored. It should be noted that ferricinium ions in *conc.* H_2SO_4 exhibited a blue color. In Figure 2, the solution of ferricinium-doped polymers exhibited two distinct colors: brown-green and orange. The UV-Visible spectra of ferricinium-doped polyaniline show two absorption bands: the first region of absorption peaks is very broad over the wavelength of 550–700 nm, which is similar to characteristics of polyaniline as described above,^{42,43} and the second region is located at about 500 nm which is a characteristic of ferrocene obtained from the reduction from ferricinium ions to ferrocene by polyaniline. This indicated that polyaniline and ferricinium ions can be readily oxidized and reduced, respectively. In contrast, only one absorption band of ferricinium-doped poly(aniline-*co-m*-ferrocenylaniline) was observed at about 500 nm due to the ferrocenyl groups on the polymer backbone and ferricinium-derived ferrocene reduced by polyaniline.

Characteristic EPR spectra of solid polyaniline derivatives are shown in Figure 3. Intensities of the spectra of polyaniline



Scheme 2. The preparation of ferricinium-doped poly(aniline-*co-m*-ferrocenylaniline).

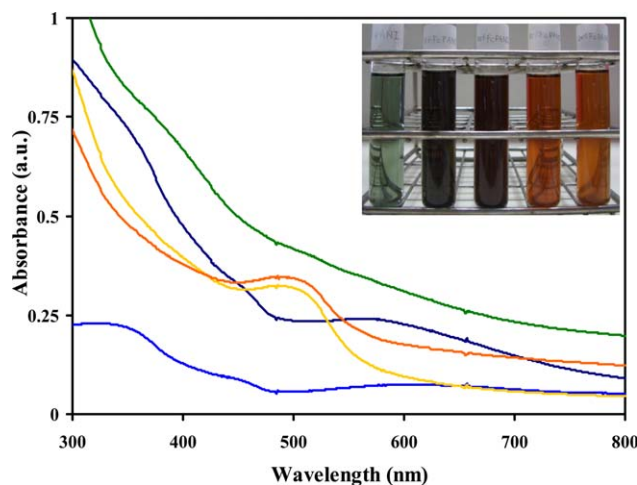


Figure 1. UV-Visible spectra of poly(aniline-*co-m*-ferrocenylaniline) for (—) 0%, (—) 5%, (—) 10%, (—) 15%, and (—) 20% molar ratios of *m*-ferrocenylaniline to aniline. Each solution contains a 5 mg of the sample dissolved in DMSO (10 cm³). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

derivatives decreased dramatically as increasing the percentages of *m*-ferrocenylaniline monomers in the structural backbone of poly(aniline-*co-m*-ferrocenylaniline). Compared to polyaniline, the EPR signal of poly(aniline-*co-m*-ferrocenylaniline)(s) became broader and non-symmetrical which strongly depended on the molar ratios of *m*-ferrocenylaniline to aniline. The *g*-values of copolymers were 2.0032, 2.0035, 2.0038, and 2.0039 corresponding to 5, 10, 15, and 20% molar ratio, respectively compared with the *g*-value of polyaniline at 2.0031. Based on the *g*-value obtained from the EPR measurements, it can be described that the addition of *m*-ferrocenylaniline had a minimal influence on the paramagnetic properties of poly(aniline-*co-m*-ferrocenylaniline). The decreasing intensities of EPR spectra of the

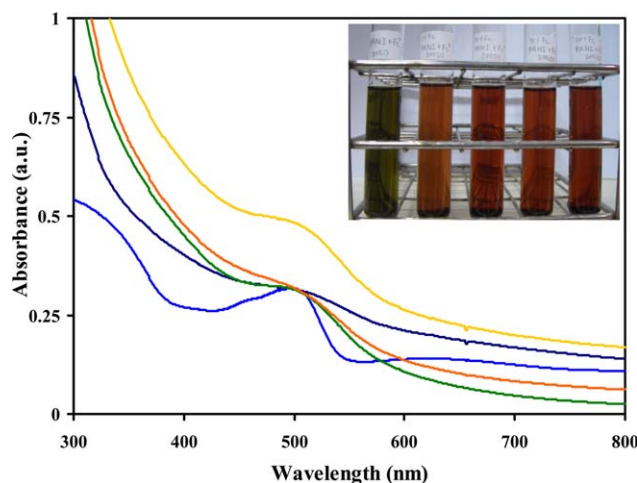


Figure 2. UV-Visible spectra of ferricinium-doped poly(aniline-*co-m*-ferrocenylaniline) for (—) 0%, (—) 5%, (—) 10%, (—) 15%, and (—) 20% molar ratio of *m*-ferrocenylaniline to aniline. Each solution contains a 10 mg of the sample dissolved in DMSO (10 cm³). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

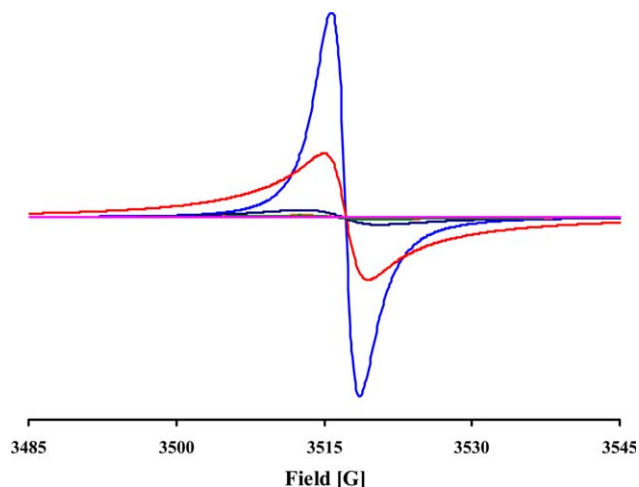


Figure 3. EPR spectra of poly(aniline-*co-m*-ferrocenylaniline)(s) for (—) 0%, (—) 5%, (—) 10%, (—) 15%, (—) 20% molar ratio of *m*-ferrocenylaniline to aniline, and (—) poly(*m*-ferrocenylaniline). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

copolymers may be due to the disorder and the disruption in the conjugation of polymer structures that may cause by the ferrocene moieties on the main chain of the copolymers.⁹

EPR spectra of ferricinium-doped poly(aniline-*co-m*-ferrocenylaniline) were recorded under the same conditions as those measurements of the undoped copolymers. The effect of the ferricinium ion as an external dopant on the EPR intensities of the synthesized-copolymers is shown in Figure 4. The *g*-values of all ferricinium-doped copolymers (2.0034) were close to the *g*-value of a free electron (2.0036) indicating that the spins over ring and nitrogen repeating units were free electron type and also more delocalized than that of the parent copolymers.

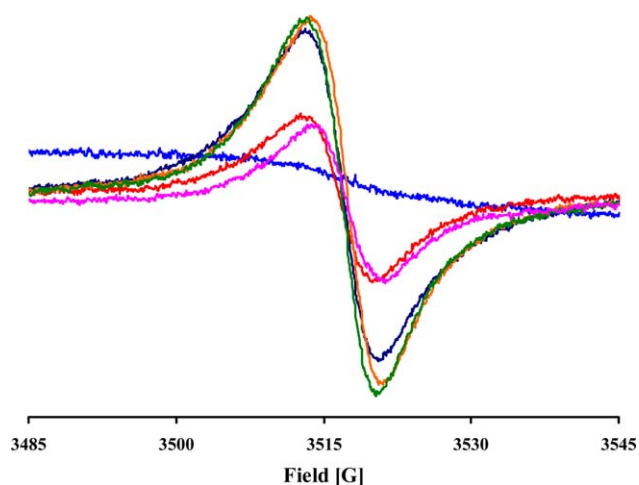


Figure 4. EPR spectra of ferricinium-doped poly(aniline-*co-m*-ferrocenylaniline)(s) for (—) 0%, (—) 5%, (—) 10%, (—) 15%, (—) 20% molar ratio of *m*-ferrocenylaniline to aniline, and (—) poly(*m*-ferrocenylaniline). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

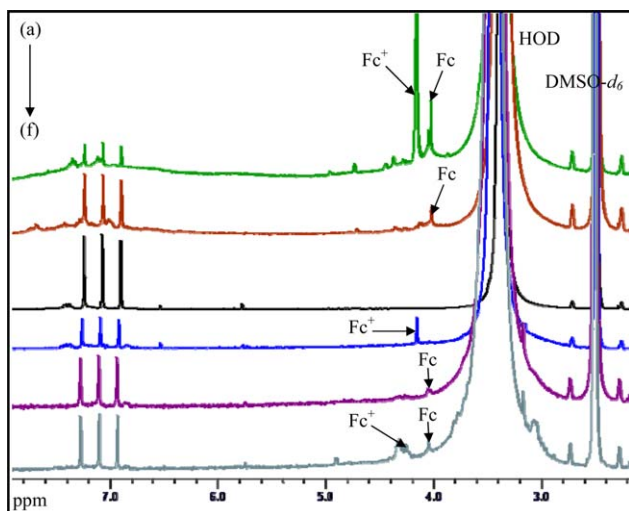


Figure 5. ^1H NMR spectra of (a) ferricinium-doped poly(aniline-*co*-20%*m*-ferrocenylaniline), (b) poly(aniline-*co*-20%*m*-ferrocenylaniline), (c) polyaniline, (d) ferricinium-doped polyaniline, (e) poly(*m*-ferrocenylaniline), and (f) ferricinium-doped poly(*m*-ferrocenylaniline). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

However, the *g*-values showed a remarkably small change in ferricinium-doped copolymers revealing that spin orbitals of heteroatoms which contributed to the dynamic defects of

ferricinium-doped polymer chains had an almost negligible effect.^{44,45}

The ^1H NMR spectra of polyaniline and its derivatives can be observed in $\text{DMSO-}d_6$ as shown in Figure 5. A triplet peak with the equal intensities at approximately δ 7.3–6.9 ppm was assigned as NH protons of polyaniline which were coupled to ^{14}N ($I=1$).⁴⁶ Polyaniline is a good conducting polymer which is easily oxidized and reduced reversibly.⁹ Therefore, the paramagnetic ferricinium ions could be reduced to ferrocene by polyaniline as observed by ^1H NMR data. Therefore, two bands in the region of δ 4.2–4.0 ppm were assigned to ferricinium-derived species (Fc^+) and ferrocene moiety on the main chain of polymers (Fc), respectively.

In order to compare the conductivity, the undoping and doping processes of the added ferricinium ions were investigated by CV measurements. The electrode was formed by mixing 50 wt% synthetic carbon powder (20 μm diameter), 40 wt % sample and 10 wt % mineral oil as binder before rolling into thin sheet of uniform thickness.^{47,48} The experiments were carried out by repeating potential cycles between -0.1 V and 0.8 V. The CVs at the scan rate of 5 mVs^{-1} of the polyaniline and poly(aniline-*co*-*m*-ferrocenylaniline)(s) with different molar ratios of *m*-ferrocenylaniline to aniline is shown in Figure 6. The peak current was decreased dramatically for 10% molar ratio of *m*-ferrocenylaniline. It can be described that both the steric hindrance to the conjugated length of the polymer and the electron withdrawing power of ferrocene moieties from the aromatic rings could lead

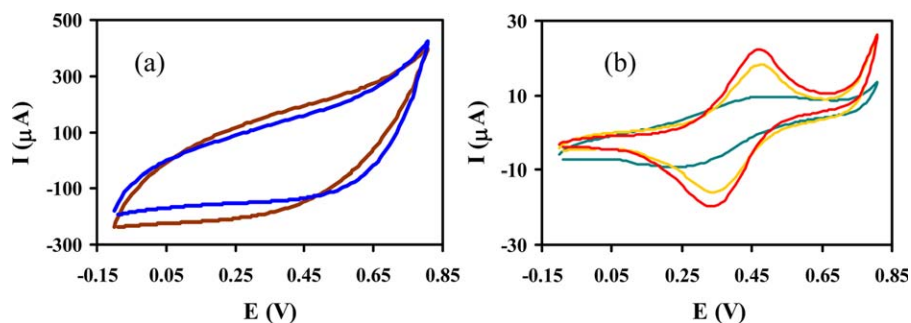


Figure 6. Cyclic voltammograms of poly(aniline-*co*-*m*-ferrocenylaniline)(s); (a) for (—) 0%, (—) 5%, (b) for (—) 10%, (—) 15%, and (—) 20% molar ratio of *m*-ferrocenylaniline to aniline in 0.1M KCl at the scan rate of 5 mVs^{-1} . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

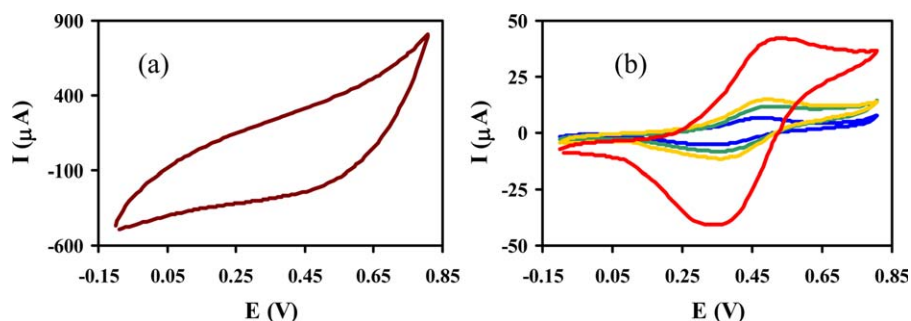


Figure 7. Cyclic voltammograms of ferricinium-doped poly(aniline-*co*-*m*-ferrocenylaniline) (a) for (—) 0%, (b) for (—) 5%, (—) 10%, (—) 15%, and (—) 20% molar ratio of *m*-ferrocenylaniline in 0.1M KCl at the scan rate of 5 mVs^{-1} . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

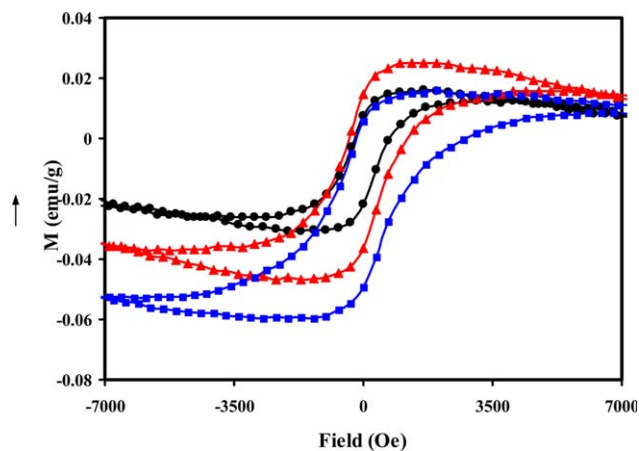


Figure 8. Hysteresis loops at 300 K of poly(aniline-*co-m*-ferrocenylaniline)(s) for (●) 5%, (▲) 10%, and (■) 20% of *m*-ferrocenylaniline by molar ratio to aniline. The magnetic parameters of 5, 10, and 20%, respectively: H_c (G) 476.74, 790.40, 1,474.4; M_s (emu/g) 23.265×10^{-3} , 35.930×10^{-3} , 37.923×10^{-3} ; M_r (emu/g) 14.472×10^{-3} , 25.238×10^{-3} , 27.272×10^{-3} . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to the decreasing of the electron delocalization.⁴⁹ It is believed that the ferrocene moiety plays a key role for increasing the oxidizing potential of polymers. However, the current was increased greatly as increasing the percentages of *m*-ferrocenylaniline. The peak potentials were shifted gradually towards the higher current as increasing the molar ratios of *m*-ferrocenylaniline in the copolymers. It was proposed that these potentials of the as-synthesized poly(aniline-*co-m*-ferrocenylaniline)(s) were obtained from the redox process of ferrocenyl moieties⁵⁰ as a part of the structure of poly(aniline-*co-m*-ferrocenylaniline)(s). Therefore, ferrocene and its derivatives were attractive for tuning the redox properties which it can be oxidized and reduced reversibly.

The CV measurements of ferricinium-doped poly(aniline-*co-m*-ferrocenylaniline) exhibited the redox behavior similarly to the undoped condition as shown in Figure 7. It is clear that the peak current of ferricinium-doped poly(aniline-*co-m*-ferrocenylaniline) was much lower compared to the ferricinium-doped polyaniline. Moreover, the currents were increased greatly as increasing the percentages of *m*-ferrocenylaniline in the copolymer. All CV voltammograms display chemically reversible ferrocene/ferricinium redox waves.⁵⁰ This was suggested that the ferrocene moieties of copolymers in all samples showed the similar redox potentials due to the lack of direct interactions between the metal centers.⁵¹ Compared to the undoped condition, the higher currents of the doped conditions were observed.

The electron localization effects of the magnetic states in the polyaniline copolymers have been investigated by several studies due to their interesting magnetic behaviors.⁵² Based on the hysteresis loops, the as-prepared poly(aniline-*co-m*-ferrocenylaniline) were soft magnetic materials because the magnetization values obtained from the final products were very low in the range from -0.06 to 0.02 emu/g as shown in Figure 8. As

increasing the molar ratio of *m*-ferrocenylaniline in the copolymers, the magnetic behavior from the hysteresis loops tended to increase the electron localization of the as-prepared poly(aniline-*co-m*-ferrocenylaniline)(s).

The general features of the catalytic cycles for Suzuki–Miyaura cross-coupling reactions are currently well understood and involved in the oxidative addition–transmetallation–reductive elimination sequence.^{15,16} In this study, the Suzuki–Miyaura cross-coupling reactions of aryl bromides and arylboronic acids were catalyzed by heterogeneous palladium nanocatalysts based on the dispersion in the poly(*m*-ferrocenylaniline) as shown in Figure 9. Therefore, ferrocene moieties on the main chain of polymers were expected to accelerate the rate of electron transfer to achieve a higher conversion and selectivity.

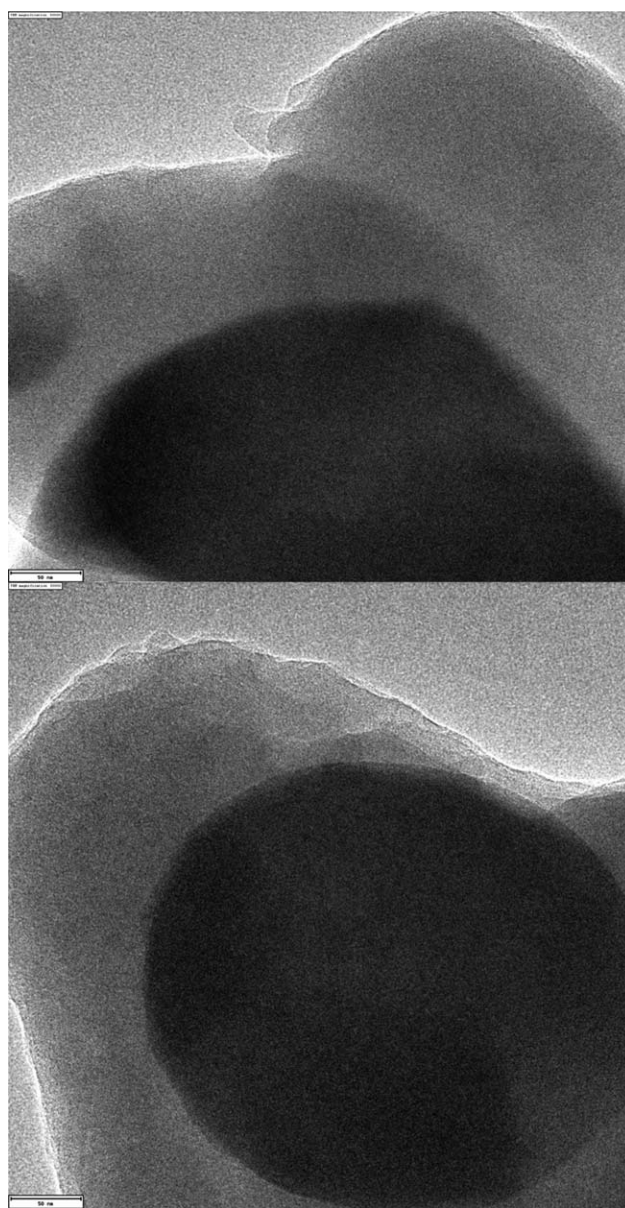
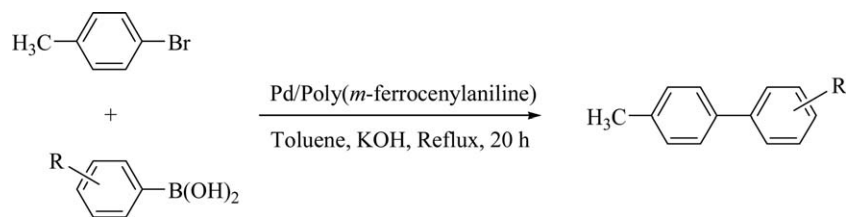


Figure 9. TEM image of Pd-doped poly(*m*-ferrocenylaniline). Bar is 50 nm.



Scheme 3. Suzuki–Miyaura cross-coupling reactions of 4-bromotoluene with arylboronic acids.

The Suzuki–Miyaura cross-coupling reactions of 4-bromotoluene with arylboronic acids were catalyzed by poly(*m*-ferrocenylaniline)-stabilized palladium nanocatalysts under a basic condition at a reflux condition (Scheme 3). The cross-couplings catalyzed by palladium nanocatalysts stabilized by polyaniline were used as a reference. The catalytic studies of Suzuki–Miyaura cross-coupling reactions were summarized in Table I. The results demonstrated the cross-coupling of 4-bromotoluene and arylboronic acids with PdNPs/polyaniline and PdNPs/poly(*m*-ferrocenylaniline) as a catalyst. It can be expected that the rate of reactions in the entry 2 may be lower than entry 1 due to the electronic and steric effects of the methyl group on the biphenyl ring. Due to this effect, the yields of the polyaniline experiments were expected to be increased from entry 2 to entry 4 which their arylboronic substrates were *o*-, *m*-, and *p*-

substituted benzene rings, respectively. Entries 1–3, the poly(*m*-ferrocenylaniline) experiments gave the excellent conversion and yield percentages higher than the polyaniline experiments while the comparable yields were obtained in both stabilizing ligands for entry 4. Therefore, the ferrocene moieties on the main chain of poly(*m*-ferrocenylaniline) accelerated the rate of reaction by presumably increasing the rate of electron transfer directly to the catalytic sites. Due to the electron withdrawing power of the substituent in entry 5, the yields were low for both stabilizing ligands. For the entry 6, it was surprising that ferrocene was obtained as a product instead of 4-ferrocenyltoluene. This can be proposed that the ferrocene group is liberated from ferrocenylboronic acid in the second transmetalation step⁵³ because no ferrocenylboronic acid was observed in ¹H NMR spectrum after the reaction was completed.

Table I. Suzuki–Miyaura Cross-Coupling of 4-Bromotoluene and Arylboronic Acids with Polyaniline (1) or Poly(*m*-ferrocenylaniline) (2) as Stabilizing Ligand

| Entry | R ₁ -X | R ₂ -B(OH) ₂ | Product | %Yield ^a | |
|-------|-------------------|------------------------------------|---------|---------------------|---------|
| | | | | PdNPs/1 | PdNPs/2 |
| 1 | | | | 81 | >99 |
| 2 | | | | 67 | >99 |
| 3 | | | | 92 | >99 |
| 4 | | | | 98 | >99 |
| 5 | | | | 26 | 24 |
| 6 | | | | 69 | 92 |

The reaction conditions were refluxed for 20 h with 4 equiv. KOH in toluene (10 cm³).

^aEstimated from ¹H NMR analysis.

CONCLUSIONS

A series of novel polyaniline derivatives and copolymers were successfully prepared by a simple oxidative polymerization. The molar ratios of aniline and *m*-ferrocenylaniline have a direct effect on optical, magnetic, and electrical properties of the copolymers. The Suzuki–Miyaura cross-coupling reactions of arylbromide with arylboronic acids in toluene were successfully examined by polyaniline-stabilized PdNPs and poly(*m*-ferrocenylaniline)-stabilized PdNPs as catalysts. For comparison, PdNPs catalysts containing ferrocene moieties were more effective than polyaniline-stabilized PdNPs in the Suzuki–Miyaura cross-coupling.

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