

Synthesis of Nitropyridine-Based π -Conjugated Polymers and Their Chemical Properties

Byoung Ki Choi, Takakazu Yamamoto

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Received 24 January 2006; accepted 28 February 2006

DOI 10.1002/app.24416

Published online in Wiley InterScience (www.interscience.wiley.com).

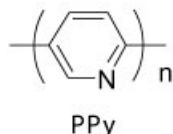
ABSTRACT: π -Conjugated poly(3-nitropyridine-2,5-diyl) (**PPy-3-NO₂**), poly(3,3'-dinitro-2,2'-bipyridine-5,5'-diyl) (**PBpy-3,3'-diNO₂**), and a poly(arylene ethynylene) type polymer consisting of a 3,3'-dinitro-2,2'-bipyridine unit (**PAE-1**) were synthesized by Cu-promoted Ullmann coupling reaction and Pd-catalyzed coupling reaction. **PPy-3-NO₂** and **PAE-1** were soluble in organic solvents such as DMSO, DMF, and chloroform, and gel permeation chromatography analysis showed a number average molecular weight (M_n) of 9,300 and 12,300, respectively. **PPy-3-NO₂** gave intrinsic viscosity, $[\eta]$, of 0.53 dL g⁻¹

in DMF. **PBpy-3,3'-diNO₂** had somewhat lower solubility. The polymers exhibited a UV-vis peak at about 430 nm. **PPy-NO₂** received electrochemical reduction at -1.5 V versus Ag⁺/Ag in acetonitrile, and gave an electrochemical redox cycle in a range from 0 to -1.1 V versus Ag⁺/Ag in an aqueous solution. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1763–1767, 2006

Key words: conjugated polymers; polyaromatics; poly(nitropyridine)s; reduction; UV-vis spectroscopy

INTRODUCTION

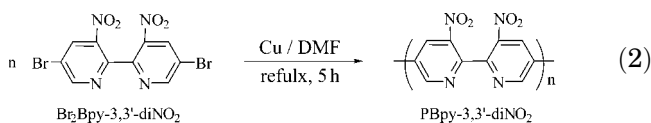
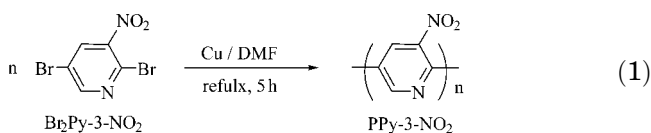
π -Conjugated poly(arylene)s are attracting much attention because of their interesting electronic and optical properties.^{1–3} Poly(pyridine-2,5-diyl)^{2–4} (**PPy**) is one of the most fundamental π -conjugated polymers,



and various π -conjugated polymers containing the pyridine unit or pyridine-based unit (e.g., copolymers of pyridine^{2–6} and quinoxaline^{2,3,7}) have been prepared. These polymers usually show electron-accepting properties because of the presence of electron-withdrawing imine⁸ nitrogen in the main chain. Because of π -electron-deficient properties, polypyridines serve as electron-transporting materials, and the pyridine-based polymers have been found useful for the electron-transporting and light-emitting layers of light emitting diodes.^{9,10} For enhancement of electron-accepting properties of polypyridines, introduction of electron-withdrawing substituents such as nitro and cyano groups is considered to be intriguing; however, such polypyridine derivatives have not much explored. Herein, we

report the preparation of poly(nitropyridine)s and their chemical properties including electrochemical response of the polymers.

Cu-promoted Ullmann coupling of halogenated aromatic compounds proceeds well especially when halogenated aromatic compounds have the nitro group.^{11,12} On this basis, we selected the polycondensation shown later for the preparation of poly(3-nitropyridine-2,5-diyl) (**PPy-3-NO₂**) and poly(3,3'-dinitro-2,2'-bipyridine-5,5'-diyl) (**PBpy-3,3'-diNO₂**). **PBpy-3,3'-diNO₂** may serve as a unique polymer chelating ligand for metals.



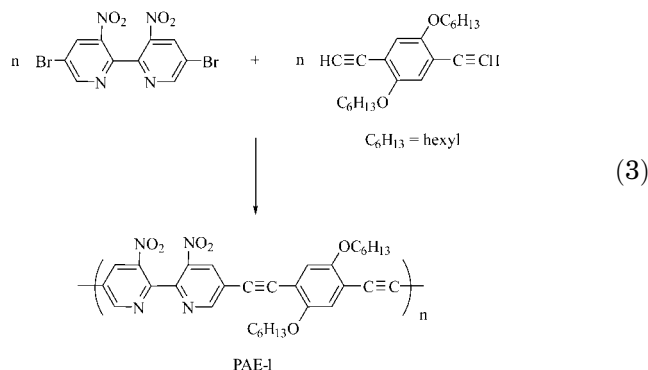
Direct nitration of **PPy** with mixed acid was examined; however, it was not successful. Nitration of π -electron deficient aromatic compounds such as pyridine generally did not proceed well because the nitration proceeds via electrophilic attack of NO₂⁺ at the aromatic ring.⁸

On the other hand, a poly(arylene ethynylene) type polymer (**PAE-1**) consisting of the 3,3'-dinitro-

Correspondence to: T. Yamamoto (tyamamot@res.titech.ac.jp).

Contract grant sponsor: Ministry of Education, Culture, Sports, and Science, Japan; contract grant number: 17067006.

2,2'-bipyridyl unit was prepared according to the following Pd-catalyzed polycondensation.¹³



Herein we report synthesis and chemical properties of the π -conjugated polymers composed of the nitropyridine units.

EXPERIMENTAL

Monomer synthesis

2,5-Dibromo-3-nitropyridine (**Br₂Py-3-NO₂**) was prepared from commercially available 2-amino-5-bromopyridine by modifying a literature method.¹⁴ A mixture of 5-bromo-2-hydroxy-3-nitropyridine¹⁴ (10.5 g, 48.0 mmol), POBr₃ (26.7 g, 93.1 mmol), and Br₂ (15.5 g, 97.2 mmol) was stirred for 5 h at 100°C. After cooling to room temperature, 40 mL of methanol and 118 mL of water was added. The precipitate was neutralized with aqueous ammonia at 5°C, separated by filtration, and washed with water. Purification by column chromatography on silica (eluent = 1 : 1 mixture of hexane and chloroform) gave a yellow powder of **Br₂Py-3-NO₂** in 75% yield.

¹H NMR (DMSO-*d*₆), δ (ppm): 8.83 (d, *J* = 2 Hz), 8.87 (d, *J* = 2 Hz).

Elemental analysis: (282 g mol⁻¹). Calcd: C, 21.3%; H, 0.7%; N, 9.9%; Br, 56.7%. Found: C, 21.3%; H, 0.5%; N, 9.9%; Br, 56.4%.

Controlled reaction of **Br₂Py-3-NO₂** with copper bronze gave 5,5'-dibromo-3,3'-dinitro-2,2'-bipyridyl (**Br₂Bpy-3,3'-diNO₂**). A mixture of copper bronze (190 mg, 3.0 mmol) and **Br₂Py-3-NO₂** (282 mg, 1.0 mmol) in 15 mL of DMF was heated at 100°C. When a spot of **Br₂Py-3-NO₂** on a thin layer silica chromatograph sheet (eluent = chloroform) disappeared after about 20 min, the reaction mixture was filtered, and the filtrate was added into aqueous ammonia. The precipitate was separated by filtration and purified by chromatography on silica gel (eluent = chloroform) to give a yellow powder of **Br₂Bpy-3,3'-diNO₂** in 70% yield. Recrystallization from hexane gave a yellow monoclinic crystal. Mp = 178–179°C.

¹H NMR (DMSO-*d*₆): δ (ppm): 9.01 (d, *J* = 2 Hz), 9.12 (d, *J* = 2 Hz).

Elemental analysis: (404 g mol⁻¹). Calcd: C, 29.7%; H, 1.0%; N, 13.9%; Br, 39.6%. Found: C, 30.0%; H, 1.0%; N, 13.8%; Br, 39.9%.

X-ray crystal structure of **Br₂Bpy-3,3'-NO₂** is depicted in Figure 1.

Preparation of polymers

Poly(3-nitropyridine-2,5-diyl) (PPy-3-NO₂)

A mixture of **Br₂Py-3-NO₂** (4.6 g, 16.4 mmol) and activated copper^{15,16} (7.3 g, 114.5 mmol) in DMF (120 mL) was stirred for 5 h at 120°C under N₂ atmosphere. (The activated copper prepared from CuSO₄ and Zn was washed with diluted nitric acid (0.02M) four times, methanol three times, and diethyl ether in this order under N₂. Vacuum-drying gave a copper powder with gold-like shine.) The reaction mixture was poured in cold water, and the precipitate was separated by filtration. The polymer was dissolved in formic acid and reprecipitated in aqueous ammonia. The brown polymer was separated by ultracentrifugation and filtration, washed with water and methanol, and dried under vacuum to yield **PPy-3-NO₂** (1.2 g, 60%).

¹H NMR (DMSO-*d*₆), δ (ppm): 9.6, 9.4.

Elemental analysis: (C₅H₂N₂O₂ + 0.1 H₂O)_n. Calcd: C, 48.5%; H, 1.8%; N, 22.6%. Found: C, 48.8%; H, 2.3%; N, 22.1%; Br, 0.6%. Number average molecular weight (*M_n*) = 9300 (gel permeation chromatography (GPC), polystyrene standards). *M_w*/*M_n* (*M_w* = weight average molecular weight) = 2.6. [η] (intrinsic viscosity) = 0.53 dL g⁻¹ in DMF.

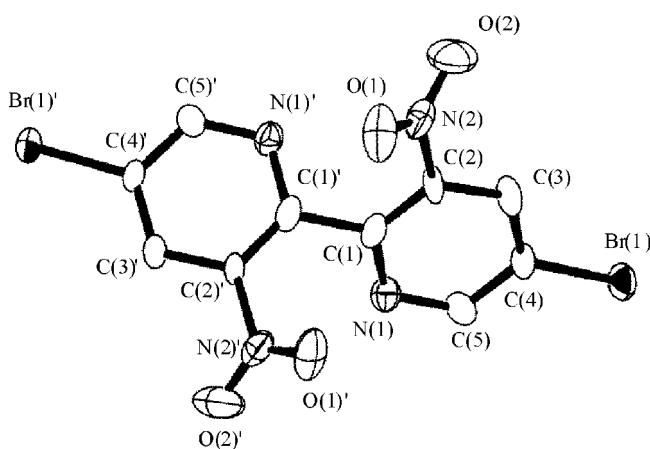


Figure 1 Molecular structure of **Br₂Bpy-3,3'-diNO₂**. Selected bond (Å) and angle (°): Br(1)-C(4): 1.87(1); O(1)-N(2): 1.21(2); O(2)-N(2): 1.24(2); N(1)-C(1): 1.35; N(2)-C(2): 1.47(2); C(1)-C(1)': 1.51(2); C(1)-C(2): 1.37. O(1)-N(2)-O(2): 127(2); N(1)-C(1)-C(1)': 113(2). The nitro group-containing plane is twisted in 45.9° toward the pyridine ring. Dihedral angle between the pyridine rings (N(1)-C(1)-C(1)'-C(2)') = 45°. Monoclinic. *R* = 0.052. *R_w* = 0.057.

Prolonged reaction time (40 h) led to partial loss of the nitro group, as indicated by analytical data (C, 54.3%; H, 2.7%; N, 19.7%).

Poly(3,3'-dinitro-2,2'-bipyridine-5,5'-diyl)
(PBpy-3,3'-diNO₂)

A mixture of **Br₂Bpy-3,3'-diNO₂** (500 mg, 1.24 mmol) and activated copper (550 mg, 8.68 mmol) in DMF (10 mL) was stirred for 5 h at 120 °C under N₂. Work-up of the polymer in a manner similar to that applied for **PPy-3-NO₂** gave **PBpy-3,3'-diNO₂** in 70% yield.

¹H NMR (DMSO-*d*₆), δ (ppm): 9.6, 9.4.

Elemental analysis: (C₁₀H₄N₄O₄ + 0.25 H₂O)_n: Calcd: C, 48.3%; H, 1.8%; N, 22.5%. Found: C, 48.5%; H, 2.6%; N, 22.1%. It is known that monomeric 2,2'-bipyridyl takes hydrated water. Prolonged reaction (10 h) led to partial loss of the nitro group as revealed by analytical data (C, 49.4%; H, 3.0%; N, 19.9%). GPC data for a DMF soluble part: *M_n* = 4100. *M_w*/*M_n* = 1.9.

PAE-1

A mixture of **Br₂Bpy-3,3'-diNO₂** (120 mg, 0.30 mmol), 2,5-di(hexyloxy)-1,4-diethynylbenzene¹⁷ (98 mg, 0.30 mmol), tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄; 20 mg, 0.017 mmol), and CuI (3.2 mg, 0.017 mmol) in a mixture of 10 mL of toluene and 2 mL of triethylamine was stirred for 15 h at 60 °C. After removal of solvents by evaporation, the polymer was dissolved in chloroform and reprecipitated into methanol, washed with methanol, and dried under vacuum to yield 168 mg (99%) of **PAE-1**.

¹H NMR (CDCl₃), δ (ppm): 8.94 (2H), 8.62 (2H), 7.10 (2H), 4.07 (4H), 1.88 (4H), 1.2–1.6 (12H), 0.91 (6H). GPC data: *M_n* = 12,300. *M_w*/*M_n* = 2.6.

Measurements

NMR, IR, UV-vis, and PL (photoluminescence) spectra were recorded on JEOL EX-400, JASCO IR-810, Shimadzu 3100 PC, and Hitachi F-4500 spectrometers, respectively. GPC traces were obtained with a Tosoh HLC-8120 GPC and a Shimadzu HIC-6A/LC-9A system using a DMF solution of LiBr (0.006M) (for **PPy-3-NO₂** and **PBpy-3,3'-diNO₂**) or chloroform (for **PAE-1**) as the eluent. An Ubbelohde viscometer was used to determine the intrinsic viscosity. Thermogravimetric analysis (TGA) was carried out with a Shimadzu TGA-50 thermogravimetric analyzer. Cyclic voltammetry of cast film of the polymer on a Pt plate or indium-tin-oxide (ITO) glass plate was performed with a Toyo Technica Solartron SI 1287 electrochemical interface, with a Hokuto Denko HA-501 galvanostat/potentiostat and a Hokuto Denko HB-104 function generator, or with a Hokuto Denko HABF501 potential/FG set.

RESULTS AND DISCUSSION

Synthesis of polymers

The dehalogenative polycondensation expressed by eqs. (1)–(3) gave **PPy-3-NO₂**, **PBpy-3,3'-diNO₂**, and **PAE-1** (Chart 1).

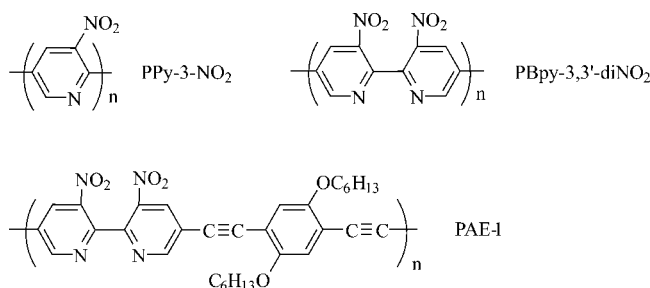


Chart 1 The synthesized polymers.

The ¹H NMR spectrum of **PBpy-3,3'-diNO₂** shows two peaks at δ 9.6 and 9.4 in a 1:1 ratio in DMSO-*d*₆. Because the reaction of **Br₂Py-NO₂** with copper gives symmetrical **Br₂Bpy-3,3'-diNO₂** in good yield (cf. the experimental part), presumably due to higher reactivity of the C—Br bond at the 2-position than that at the 5-position, **PPy-3-NO₂** is considered to contain the head-to-head unit (or the 2,2'-bipyridyl unit) as the main unit. ¹H NMR spectrum of **PPy-3-NO₂** is actually similar to that of **PBpy-3,3'-diNO₂**. However, **PPy-3-NO₂** showed higher solubility than **PBpy-3,3'-diNO₂**, probably due to containing an irregular unit, a head-to-tail unit. The molecular structure of the **Br₂Bpy-3,3'-diNO₂** monomer was confirmed by elemental analysis, IR, ¹H NMR, and X-ray crystallography exhibited in Figure 1.

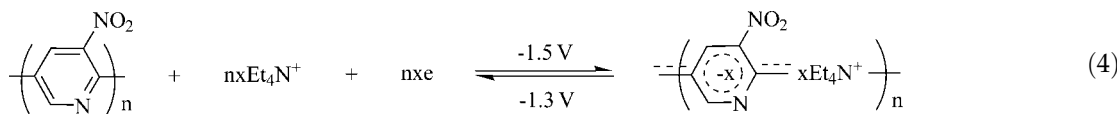
PPy-3-NO₂ and **PAE-1** were soluble in organic solvents such as chloroform, DMF, DMSO, *N*-dimethyl-2-imidazolidone, and acidic organic solvents, and showed *M_n* values of 9300 and 12,300, respectively, with an *M_w*/*M_n* value of about 2.6 in the GPC analysis. **PBpy-3,3'-diNO₂** was partly (about a half amount) soluble in the organic solvents, and a DMF soluble part gave *M_n* of 4100 with a *M_w*/*M_n* value of 1.9. Casting of **PPy-3-NO₂** from organic solvents gave a smooth film suited for electrochemical measurements.

Optical, electrochemical, and conductive properties

Because of expansion of the π-conjugation system, the polymers exhibited the UV-vis absorption peak in a visible region. **PPy-3-NO₂** and **PBpy-3,3'-diNO₂** showed the UV-vis absorption peaks at 400 nm (ε = 8300 M⁻¹ cm⁻¹) in formic acid, the position being located at a somewhat longer wavelength than that (373 nm)⁴ of nonsubstituted poly(pyridine-2,5-diyl) (**PPy**) and poly(2,2'-bipyridine-5,5'-diyl) (**PBpy**) probably because of the presence of a larger π-conjuga-

tion system in the monomeric unit by participation of the $-\text{NO}_2$ group in the π -conjugation. The UV-vis peak of **PPy-3-NO₂** appeared at 450 nm in DMF. **PAE-1** showed the UV-vis peak at 414 nm in chloroform; the UV-vis peak position is comparable to those of reported π -conjugated poly(arylene ethynylene)s.^{13,17,18} **PPy-3-NO₂** was photoluminescent and exhibited the photoluminescence peak at 510 nm with a quantum yield of about 30%. However, **PAE-1** was not photoluminescent.

Figure 2 depicts cyclic voltammograms of **PPy-3-NO₂** film on a Pt plate in two kinds of electrolytic



PBpy-3,3'-diNO₂ showed a similar response in electrochemical reduction (or *n*-doping) with reduction peak and its coupled *n*-dedoping peak at -1.8 and -1.5 V versus Ag^+/Ag , respectively. **PAE-1** gave the electrochemical reduction (*n*-doping) peak at -1.8 V versus Ag^+/Ag , with its coupled *n*-dedoping peak at -1.3 V versus Ag^+/Ag .

It is known that organic nitro compounds undergo various electrochemical proton-participated reduction (e.g., to hydroxylamines and to amines)¹⁹ in aqueous solutions and the electrochemical reaction(s) depend on the kind of the nitro compound and pH of the solution. As depicted in Figure 2 (middle and bottom), **PPy-3-NO₂** undergoes electrochemical reduction at about 1 V versus Ag^+/Ag (AgCl/Ag) at $\text{pH} = 4$ in the aqueous solution. When the sweeping is carried out in a range from 0 to -1.5 V versus Ag^+/Ag , flow of a large reduction current is observed as depicted in the figure (middle); the reduction current area corresponds to participation of about six electrons per the nitropyridine repeating unit in the redox process. However, the cyclic voltammogram changes with shifts of the reduction and its corresponding oxidation peaks in repeated scanings. This indicates that deep reduction of **PPy-3-NO₂** causes irreversible chemical change(s) on the polymer. To the contrary, sweeping in a range from 0 to -1.1 V versus Ag^+/Ag gives a reversible cycle, and the CV chart is exhibited in the bottom part of Figure 2. The electric current, however, is reduced in the case of the narrower scanning; the number of the participating electrons per the nitropyridine unit is reduced to 0.5. In this case, the cyclic voltammogram is stable for about 50 times scanning. These results suggest a possibility for usability of **PPy-3-NO₂** as an electrochemically active material in rechargeable battery. Polymer-based rechargeable battery has been the subject of many papers.^{1-4,20-22}

solutions. As exhibited in Figure 2, **PPy-3-NO₂** receives electrochemical reduction (or *n*-doping)¹⁻⁴ at -1.5 V versus Ag^+/Ag and its coupled oxidation (or *n*-dedoping) peak appears at -1.3 V versus Ag^+/Ag in a nonprotic solvent (CH_3CN). The reduction potential of **PPy-3-NO₂** locates at a higher potential by about 1.0 V than that observed with nonsubstituted **PPy**,⁴ and this electrochemical response of **PPy-3-NO₂** is reasonably explained by the electron-withdrawing effect of the nitro group. The electrochemical reduction of **PPy-3-NO₂** is considered to be expressed by the following equation.

PPy-3-NO₂ and **PAE-1** exhibit dc (direct current) conductivity of 3×10^{-9} and 6×10^{-9} S cm^{-1} , respectively, as measured with compressed powders even at the neutral state without doping. The electrical conductivity was considered to originate from electronic conduction (not ionic conduction), since the electric current did not show time dependence. Several π -conjugated polymers with functional pendants, such as the NO_2 group,¹² transition metal complex,⁴ and *N*-oxide group,²³ which seem to be able to generate carrier in the π -conjugated polymer chain by contribution of resonance structure(s), show certain electrical conductivity even without doping.

Treatment of a **PPy-3-NO₂** powder with sodium naphthalenide in THF afforded a reduced (or *N*-doped) polymer, which had a dc conductivity of 5.1×10^{-3} S cm^{-1} as measured with a compressed powder. Treatment of the reduced polymer with H_2O recovered the original **PPy-3-NO₂**, as proved by IR spectroscopy. The chemical reduction with Na is thus considered to occur at the π -conjugated main chain, and reduction of the NO_2 group is unlikely.

CONCLUSIONS

Polypyridines with the nitro substituent were synthesized by the dehalogenative polycondensations. Poly(3-nitro-pyridine-2,5-diyl) (**PPy-3-NO₂**) and the poly(arylene ethynylene) type polymer (**PAE-1**) were soluble in organic solvents, and they showed the UV-vis absorption peak at about 400 nm, revealing expansion of the π -conjugation system along the polymer chain. **PPy-3-NO₂** received electrochemical reduction at -1.5 V versus Ag^+/Ag , which was located at a higher potential by 1.0 V than reduction potential of nonsubstituted poly(pyridine-2,5-diyl) (**PPy**). **PPy-3-NO₂** showed reversible electrochemical reduction

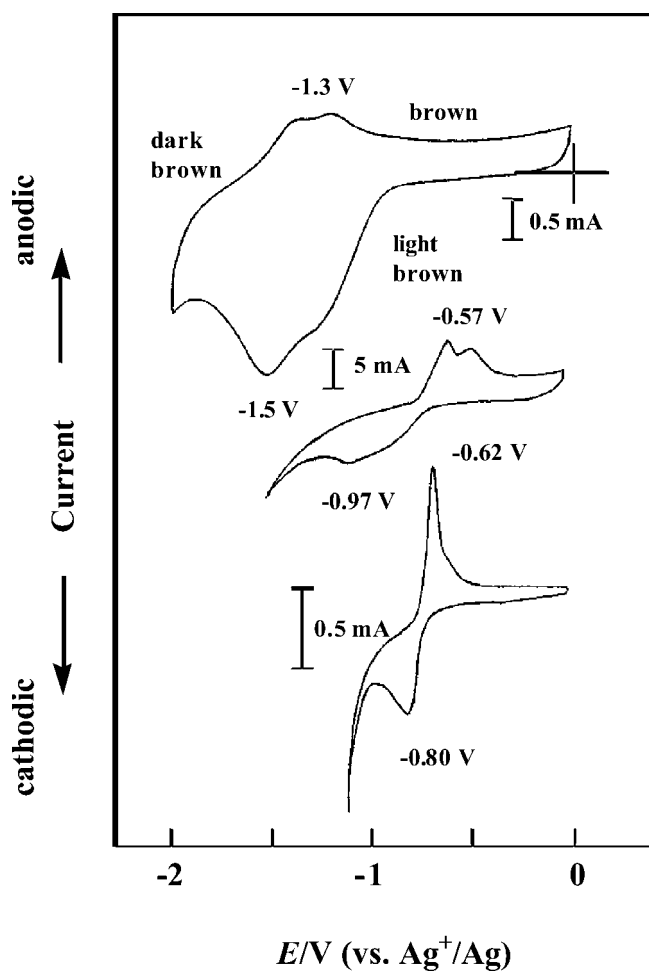


Figure 2 Cyclic voltammograms of PPy-3-NO₂ film in various media. Top: In an CH₃CN solution of [NEt₄]BF₄ (0.10M). Middle and bottom: In an aqueous buffer (McIlvaine's buffer) solution with pH value of 4. Scanning range: from 0 to -1.5 V versus Ag⁺/Ag for the middle figure and from 0 to -1.1 V versus Ag⁺/Ag for the bottom figure.

in an aqueous solution. The polymer showed certain electrical conductivity even in a neutral state. Because of the interesting chemical properties of poly(nitropyridine)s, they may find applications.

We are grateful to Professors T. Kanbara and H. Fukumoto for helpful discussion and experimental supports.

References

1. Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R. *Handbook of Conducting Polymers*, 2nd ed.; Marcel Dekker: New York, 1997.
2. Nalwa, H. S. *Handbook of Organic Conductive Molecules and Polymers*; Wiley: New York, 1997.
3. Hotta, S. *Electronic and Optical Properties of Conjugated Molecular Systems in Condensed Phases*; Research Signpost: Kerala, India, 2003.
4. Yamamoto, T.; Maruyama, T.; Zhou, Z.-H.; Ito, T.; Fukuda, T.; Yoneda, Y.; Begum, F.; Ikeda, T.; Sasaki, S.; Takezoe, H.; Fukuda, A.; Kubota, K. *J Am Chem Soc* 1994, 116, 4832.
5. Zhu, S. S.; Swager, T. M. *Adv Mater* 1996, 8, 497.
6. Lu, H.-F.; Chan, H. S. O.; Ng, S. C. *Macromolecules* 2003, 36, 1543.
7. Cui, Y.; Zhang, X.; Jenekhe, S. A. *Macromolecules* 1999, 32, 3824.
8. Newkome, G. R.; Paudler, W. W. *Contemporary Heterocyclic Chemistry*; Wiley: New York, 1982.
9. Gebler, D. D.; Wang, Y. Z.; Blatchford, J. W.; Jessen, S. W.; Lin, L.-B.; Gustafson, T. L.; Wang, H. L.; Swager, T. M.; MacDiarmid, A. G.; Epstein, A. J. *J Appl Phys* 1995, 78, 4264.
10. Dailey, S.; Halim, M.; Rebourt, E.; Horsburgh, L. E.; Samuel, I. D. W.; Monkman, A. P. *J Phys: Condens Matter* 1998, 10, 5171.
11. Fanta, P. E. *Chem Rev* 1946, 38, 139.
12. Yamamoto, T.; Muramatsu, Y.; Lee, B.-L.; Kokubo, H.; Sasaki, S.; Hasegawa, M.; Yagi, T.; Kubota, K. *Chem Mater* 2003, 15, 4384.
13. Weder, C. *Poly(arylene ethynylene)s From Synthesis to Application*; Springer: Berlin, 2005.
14. Batkowski, T. *Rocz Chem* 1967, 41, 729.
15. Gore, P. H.; Hughes, G. K. *J Chem Soc* 1959, 1615.
16. Yamamoto, T.; Kurata, Y. *Can J Chem* 1983, 61, 86.
17. Morikita, T.; Yamaguchi, I.; Yamamoto, T. *Adv Mater* 2001, 13, 1832.
18. Yamamoto, T.; Yamada, W.; Takagi, M.; Ooba, N.; Tomaru, S.; Kurihara, T.; Kaino, T.; Kubota, K. *Macromolecules* 1994, 27, 6620.
19. Kemula, W.; Krygowski, T. M. In *Encyclopedia of Electrochemistry of the Elements*; Bard, A. J., Lund, H., Eds.; Marcel Dekker: New York, 1973; Vol. 13, p 78.
20. MacInnes, D., Jr.; Dury, M. A.; Nigrey, P. J.; Nairns, D. P.; MacDiarmid, A. G.; Heeger, A. J. *J Chem Soc Chem Commun* 1981, 317.
21. Yamamoto, T. *J Chem Soc Chem Commun* 1981, 187.
22. Yamamoto, T.; Nishiyama, T.; Harada, G.; Takeuchi, M. *J Power Sources* 1999, 79, 281.
23. Yamamoto, T.; Lee, B.-L.; Hayashi, H.; Saito, N.; Maruyama, T. *Polymer* 1997, 38, 4233.