SHORT COMMUNICATIONS

Synthesis of Poly(3-nitropyridine-2,5-diyl) and Poly(3,3′-dinitro-2,2′-bipyridine-5,5′-diyl) and Electrochemical Response

Byoung-Ki Choi, Hiroshi Takahashi, Takaki Kanbara, and Takakazu Yamamoto[†]

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

π-Conjugated poly(arylene)s attract much attention owing to electronic and opitical properties as well as increasing applications.[1] Poly(pyridine-2,5-diyl),[2] PPy, is a most fundamental π-conjugated polymer, and various π-conjugated polymers containing the pyridine unit or

PPy
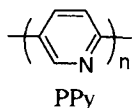
pyridine-based unit (*e.g.*, poly(pyridinevinylene) type polymers[3] and poly(quinoline)s[4]) have been prepared. These polymers usually possess electron-withdrawing properties due to the presence of electron-withdrawing imine nitrogen in the main chain. Because of electron-withdrawing properties, polypyridines should serve as electron-transporting materials, and polymers for the electron-transporting and light-emitting layers of light emitting diode (LED) have been found useful.[5] For enhancement of electron-withdrawing properties of polypyridines, the introduction of electron-withdrawing substituents such as nitro and cyano groups is considered, but such polypyridine derivatives have not been reported. Herein we report the preparation of nitrated poly(pyridine-2,5-diyl) and chemical properties including electrochemical response of the polymer.

Several π-conjugated poly(arylene)s have been prepared by oxidative polymerization of aromatic compounds and organometallic polycondensation of dihalo- or dimetallated aromatic compounds.[1,2,4] Both methods are not suited for the preparation of the nitrated polymer. The oxidative polymerization is suited for the polymerization of electron-donating aromatic compounds such as pyrrole and thiophene,[1] while the nitro group often leads to side reaction in organometallic processes. Cu-promoted Ullmann coupling of halogenated aromatic compounds proceeds well especially when halogenated aromatic compounds have nitro substituents in the ortho- and para-positions with respect to halogen atoms.[6] On this basis, we selected the following polycondensation 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 which are considered applicable due to the presence of the nitro group. PBpy-3,3′-diNO₂ may serve as a unique polymer chelat-

---

[†] To whom correspondence should be addressed.

$$(1)$$
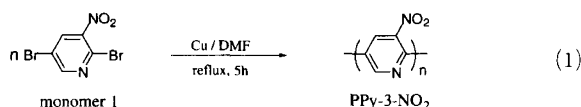
ing ligand for metals.

Direct nitration of PPy with mixed acid was examined. The nitration of electron-withdrawing aromatic compounds such as pyridines generally did not proceed well,[7] and the direct nitration of PPy was unsuccessful.

EXPERIMENTAL

Monomer Synthesis

3-Nitropyridine and 3,3′-dinitro-2,2′-bipyridine were prepared according to the literature.[8,9] 2,5-Dibromo-3-nitropyridine, monomer 1, was prepared by modifying a literature method.[10] A mixture of 5-bromo-2-hydroxy-3-nitropyridine[10] (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℃. After cooling to room temperature, 40 mL of methanol and 118 mL of distilled water were added. The precipitate was neutralized with aqueous ammonia at 5 ℃, separated by filtration, and washed with water. A light yellow powder was obtained by separation using a silica gel column (eluent = 50% hexane, 50% chloroform). The product yield was 75%. *Anal.* Found: C 21.3%; H 0.5%; N 9.9%; Br 56.4%. Calcd for C₅H₂Br₂N₂O₂ : C 21.3%; H 0.7%; N 9.9%; Br 56.7%.

Controlled reaction of monomer 1 with copper bronze gave 5,5′-dibromo-3,3′-dinitro-2,2′-bipyridine, monomer 2. Copper bronze (190 mg, 3 mmol) and monomer 1 (282 mg, 1 mmol) in *N,N*-dimethylformamide (DMF) (15 mL) were heated at 100℃. The reaction was monitored by thin layer chromatography (TLC) (eluent = CHCl₃). When a spot of the starting material disappeared after about 20 min, the reaction mixture was filtered, and the filtrate was added to aqueous ammonia. The precipitate was separated by filtration and purified by column chromatography on silica gel (eluent = CHCl₃). Evaporation of the solvent under vacuum yielded a yellow powder of 5,5′-dibromo-3,3′-dinitro-2,2′-bipyridine, monomer 2 (141 mg, 70% yield). Recrystallized from hexane gave a light yellow monoclinic crystal. Mp = 178—179℃. *Anal.* Found: C 30.0%; H 1.0%; N 13.8%; Br 39.9%. Calcd for C₁₀H₄Br₂N₄O₄ : C 29.7%; H 1.0%; N 13.9%; Br 39.6%. In-
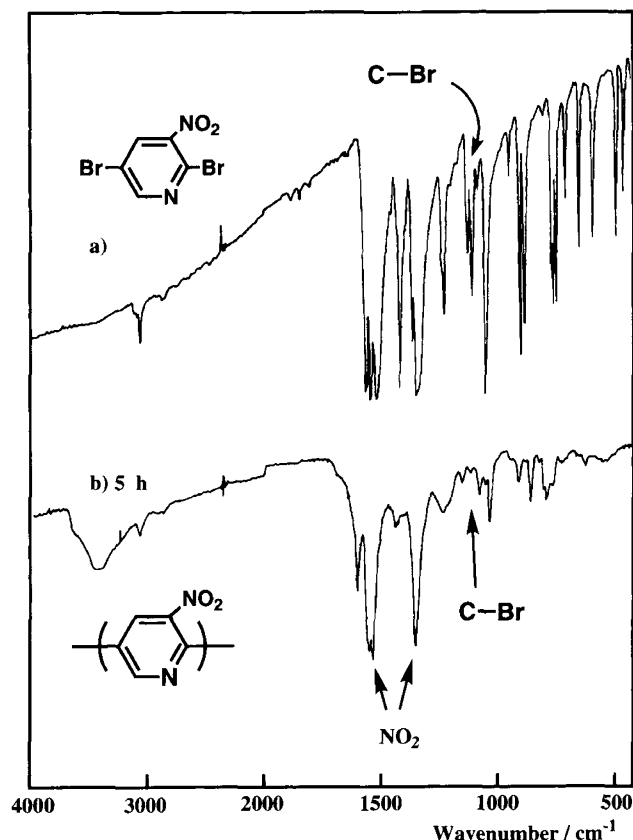
Figure 1. IR spectra of a) monomer 1 and b) PPy-3-NO₂ (polymerization for 5 h).

frared (IR) (KBr, cm⁻¹): 3066, 1592, 1545, 1531 ($NO_{2\,asym}$), 1429, 1346($NO_{2\,sym}$), and 1236. ¹H NMR (400 MHz, DMSO-d_6, ppm): δ: 9.12 (2H, H at the 6,6′-position), 9.01 (2H, H at the 4,4′-position). X-Ray crystallographic analysis clearly indicated the structure of monomer 2 and detailed X-Ray crystallographic data will be reported elsewhere.

Polymerization

Under nitrogen atmosphere, monomer 1 (4.6 g, 16.4 mmol) and DMF (120 mL) were added to activated copper[11] (7.3 g, 114.5 mmol). After 5 h stirring under reflux, the mixture was poured into cold water, and the precipitated polymer was separated by filtration. The polymer was dissolved in formic acid and reprecipitated by adding into aqueous ammonia. The brown polymer was separated by filtration, washed with water and methanol, and dried under vacuum to yield PPy-3-NO₂ (1.2 g, 60% yield). *Anal.* Found: C 48.8%; H 2.3%; N 22.1%; Br 0.6%. Calcd for ($C_5H_2N_2O_2$+0.1 $H_2O)_n$: C 48.5%; H 1.8%; N 22.6%. The discrepancy between calculated and found values may be, at least in part, due to high thermal stability of the polymer. IR (KBr, cm⁻¹) : 3070, 1599, 1545, 1526 ($NO_{2\,asym}$), 1440, 1345($NO_{2\,sym}$), and 1232. ¹H NMR (400 MHz, dimethyl sulfoxide (DMSO)-d_6, ppm): δ: 9.6 (1H), H at the 6-position), 9.4 (1H, H at the 4-position). Prolonged reaction time (40 h) led to partial loss of the nitro group, as shown by analytical data (C 54.3%; H 2.7%; N 19.7%) and IR spectroscopy. Monomer 2 (500 mg, 1.24 mmol) and DMF (10 mL) were added to activated copper (550 mg, 8.68 mmol) under a

nitrogen atmosphere. After 5 h reflux, the product was separated by a method similar to that for PPy-3-NO₂, and dried under vacuum to yield PBpy-3,3′-diNO₂ (212 mg, 70% yield). IR (KBr, cm⁻¹) : 3070, 1599, 1539, 1522 ($NO_{2\,asym}$), 1456, 1341($NO_{2\,sym}$), and 1232. ¹H NMR (400 MHz, DMSO-d_6): δ: 9.6 (2H, H at the 6, 6′-position), 9.4 (2H, H at the 4, 4′-position). Anal. Found : C 48.5%; H 2.6%; N 22.1%. Calcd For ($C_{10}H_4N_4O_4$+0.25 $H_2O)_n$: C 48.3%; H 1.8%; N 22.5%. It is known that monomeric 2,2′-bipyridine takes hydrated water. Prolonged reaction time (10 h) led to partial loss of the nitro group, as revealed by analytical data (C 49.4%; H 3.0%; N 19.9%) and IR spectroscopy.

Measurements

IR spectra and ¹H NMR spectra were recorded on a JASCO IR-810 spectrometer and a JEOL EX-400 spectrometer, respectively. UV-visible spectra were measured with a SHIMADZU UV-3100 PC spectrometer. Elemental analysis was carried out with a Yanagimoto CHN Autocorder Type MT-2 and a Yazawa halogen analyzer or a Yanaco SX-Elements Micro analyzer. Gel permeation chromatography (GPC) analysis was carried out with a Tosoh high performance liguid chromatography (HLC) 8120 equipped with polystyrene gel columns (TSK gel G 2500, G 4000, and G 5000), using a DMF solution of LiBr (0.006 M) as the eluent. An Ubbelohde viscometer was used to determine intrinsic viscosity, [η], of PPy-3-NO₂ at 30℃. DMF was used as the solvent.

Cyclic voltammograms were obtained with a Hokuto Denko HA-501 galvanostat/potentiostat and a Hokuto Denko HB-104 function generator or a Hokuto Denko HABF 501 potential/FG set, using an acetonitrile solution of [NEt₄][BF₄] (0.1 M). Electrical conductivity was measured using an Advantest R 8340 A Ultra High Resistance meter (for dc conductivity) by a 2-probe method. For measurement of direct current (dc) conductivity, a pellet specimen was obtained by compressing (4×10^8 Pa) the powdery polymer. Chemical reduction was carried out by stirring the polymer powder dispersed in the sodium-naphthalenide in tetrahydrofuran (THF), and the reduced powder was collected under nitrogen, and dried under vacuum.

RESULTS AND DISCUSSION

The polycondensation expressed by eq 1 proceeded well in DMF under reflux. Polymerization was completed in 5 h, and elongation of reaction time led to loss of the nitro group, judging from analytical and IR data. Elemental analysis and IR spectroscopy data of the polymer obtained in the 5 h polymerization were consistent with the structure of the polymer containing hydrated water. As shown in Figure 1, the IR spectrum of PPy-3-NO₂ exhibited strong absorption peaks at 1520 cm⁻¹ (NO₂, asymmetry) and 1340 cm⁻¹ (NO₂, symmetry). ν(C −Br) peaks of the monomer at 1123 and 1108 cm⁻¹ almost completely disappeared after polymerization. The ¹H NMR spectrum of PPy-3-NO₂ showed two peaks at δ 9.6 and 9.4 in a 1 : 1 ratio in DMSO-d_6.

In contrast to the limited solubility of PPy,[2] PPy-3-NO₂ had good solubility in polar solvents including DMSO, DMF, N-methyl-2-pyrrolidinone (NMP), and N,-
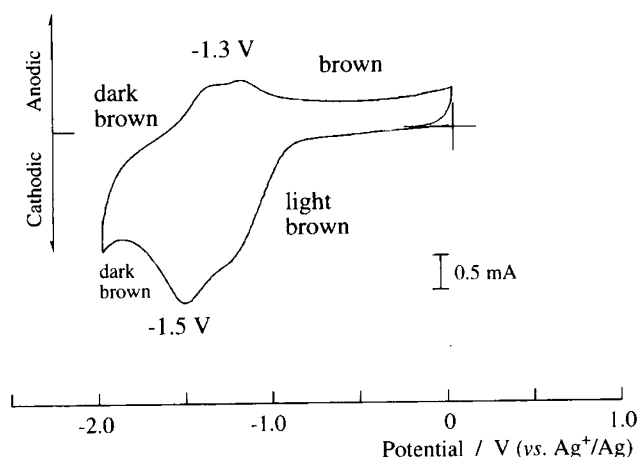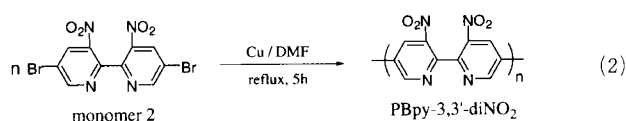
Figure 2. Cyclic Voltammogram of PPy-3-NO$_2$ film placed on a Pt plate in CH$_3$CN solution of [NH$_4$][BF$_4$] (0.1 M) (sweep rate=50 mV s^{-1}).

N-dimethyl-2-imidazolidinone (DMI) and in acidic solvents (nitric acid, formic acid, and sulfuric acid). GPC analysis gave a number average molecular weight (M_n) of 9300 and weight average molecular weight (M_w) of 24000. The polymer gave intrinsic viscosity, [η], of 0.53 dL g^{-1} in DMF.

Polycondensation of Monomer 2 expressed by eq 2 proceeded in DMF under reflux. Polymerization was com-

pleted in 5 h. IR spectrum of PBpy-3,3′-diNO$_2$ was almost identical to that of PPy-3-NO$_2$. Compared with PPy-3-NO$_2$, PBpy-3,3′-diNO$_2$ exhibited somewhat poor solubility in organic and acidic solvents (nitric acid, formic acid, and sulfuric acid), probably due to increase in crystallinity because of its regular structure. GPC analysis (soluble part in DMF) gave M_n of 4100 and M_w of 7600.

UV-vis spectra of PPy-3-NO$_2$ and PBpy-3,3′-diNO$_2$ gave an absorption peak at 400 nm (ε =8300 M^{-1}cm^{-1} for PPy-3-NO$_2$) in HCOOH, respectively. The peak position of the polymer was somewhat longer wavelength than for PPy and PBpy (λ_{max}=about 370 nm in HCOOH).[2] Previously reported polypyridine derivatives, poly(3-methylpyridine-2,5-diyl) and poly(3,3′-dimethyl-2,2′-bipyridine-5,5′-diyl), gave an absorption band at shorter wavelength (λ_{max}=about 320 nm) compared to PPy and PBpy due to steric effect of methyl group at the 3-position.[2] The introduction of nitro group thus leads to bathochromic shift of the absorption band of polypyridines in spite of the large steric effect of the nitro group, possibly a consequence of the extended π-conjugation from the pyridine ring to the nitro group.[12,13] PBpy-3,3′-diNO$_2$ gave an absorption peak at 430 nm in DMF, which may originate from the improved coplanarity induced by the absence of hydrogen at the protonated imine nitrogen in the adjacent ring. In film, the peak position of PBpy-3,3′-diNO$_2$, somewhat shifted to a longer wavelength (λ_{max}=450 nm).

Figure 2 shows a cyclic voltammogram of a cast film of PPy-3-NO$_2$ on a Pt plate in an CH$_3$CN solution of [NEt$_4$]

[BF$_4$] (0.1 M). As shown in Figure 2, a reduction (or n-doping) peak of the polymer appeared at -1.5 V vs. Ag$^+$/ Ag. The corresponding oxidation (or n-undoping) peak appeared at -1.3 V vs. Ag$^+$/Ag. PBpy-3,3′-diNO$_2$ gave analogous cyclic voltammographic results. The electrochemical reduction seems to be expressed by eq 3. Electrochemical reduction potential of PPy is about -2.2 V vs. Ag$^+$/Ag.[2] The electrochemical reduction potential of
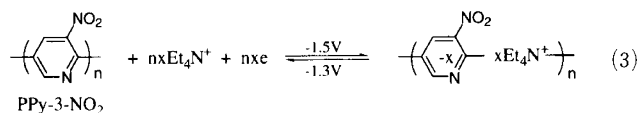
PPy-3-NO$_2$ was located on the positive side by about 0.8 V compared with that of PPy. The present results indicate that the introduction of nitro group enhances electron-withdrawing properties of recurring pyridine units and electrochemical reduction of PPy-3-NO$_2$ proceeds much more easily than PPy. The electrochemical reduction potential of 3-nitropyridine is -1.36 V vs. Ag$^+$/Ag.[14,15] Overlapping of reduction regions of PPy-3-NO$_2$ with its nitro group indicates the possibility of reduction of nitro group followed by delocalization of the electron to the pyridine ring and main chain.[16,17]

Even before doping (oxidation or reduction), PPy-3-NO$_2$ exhibits dc conductivity of 3.3×10^{-9} S cm^{-1} as measured with a compressed powder. Several π-conjugated polymers with the NO$_2$ group show certain electrical conductivity even without doping.[13,18] Treatment of a PPy-3-NO$_2$ powder with sodium naphthalenide in THF afforded an n-doped (or Na-doped) polymer, which had a dc conductivity of 5.1×10^{-3} S cm^{-1} as measured with a compressed powder. Although the n-doped polymer was sensitive to air and moisture, treatment of the n-doped polymer with H$_2$O recovered the original PPy-3-NO$_2$, as proved by IR spectroscopy. n-Doping with Na is thus considered to occur at the π-conjugated main chain, and reduction of the NO$_2$ group is unlikely.

REFERENCES

1. T. A. Skotheim, R. L. Elsenbaumen, and J. R. Reynolds, Ed., "Handbook of Conducting Polymers, 2nd ed," Marcel Dekker, New York, N.Y., 1997; H. S. Nalwa, Ed., "Handbook of Organic Conductive Molecules and Polymers," John Wiley, New York, N.Y., 1997.
2. T. Yamamoto, T. Maruyama, Z. -H. Zhou, T. Ito, T. Fukuda, Y. Yoneda, F. Begum, T. Ikeda, S. Sasaki, H. Takezoe, A. Fukuda, and K. Kubota, *J. Am. Chem. Soc.*, **116**, 4832 (1994).
3. S. S. Zhu and T. M. Swager, *Adv. Mater.*, **8**, 497 (1996).
4. N. Saito and T. Yamamoto, *Macromolecules*, **28**, 4260 (1995).
5. D. D. Gebler, Y. Z. Wang, J. W. Blatchford, S. W. Jessen, L. -B. Lin, T. L. Gustafson, H. L. Wang, T. M. Swager, A. G. MacDiarmid, and A. J. Epstein, *J. Appl. Phys.*, **78**, 4264 (1995); S. Dailey, M. Halim, E. Rebourt, L. E. Horsburgh, I. D. W. Samuel, and A. P. Monkman, *J. Phys. : Condens. Matter*, **10**, 5171 (1998).
6. P. E. Fanta, *Chem. Rev.*, **38**, 139 (1946).
7. G. R. Newkome and W. W. Pandler, "Contemporary Heterocyclic Chemistry," John Wiley, New York, N.Y., 1982.
8. J. M. Bakke and E. Ranes, *Synthesis*, 281 (1997).
9. A. R. A. Palmans, J. A. J. M. Vekemans, and E. W. Meijer,

Recl. Trav. Chim. Pays-Bas, **114**, 277 (1995).

10. T. Batkowski, *Rocz. Chem.*, **41**, 729 (1967).

11. P. H. Gore and G. K. Hughes, *J. Chem. Soc.*, 1615 (1959); T. Yamamoto and Y. Kurata, *Can. J. Chem.*, **61**, 86 (1983).

12. T. Yamamoto and H. Etori, *Macromolecules*, **28**, 3371 (1995).

13. Y. Muramatsu and T. Yamamoto, *Chem. Lett.*, 581 (1997).

14. T. Batkowski, M. Kalinowski, and P. Tomasik, *Annali di Chimica*, **63**, 121 (1973).

15. W. Drzeniek and P. Tomasik, *Ann. Chim.*, **63**, 135 (1973).

16. M. M. Baizer, Ed., "Organic Electrochemistry," Marcel Dekker, New York, N.Y., 1973.

17. M. E. Peover and J. S. Powell, *J. Electroanal. Chem.*, **20**, 427 (1969).

18. T. Yamamoto, Y. Muramatsu, T. Shimizu, and W. Yamada, *Macromol. Rapid Commun.*, **19**, 263 (1998).