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Chemical and electrochemical preparation of poly(9,10-dihydrophenanthrene-2,7-diyl) using nickel complexes and electrochemical properties of the polymer

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Summary

Dehalogenation polycondensations of 2,7-dibromo-9,10-dihydrophenanthrene with isolated zero-valent nickel complex and electrochemically generated zero-valent nickel complex afford π-conjugated poly(9,10-dihydrophenanthrene-2,7-diyl). The electrochemically synthesized polymer is obtained as a thin film on electrode, and shows a reversible electrochemically doping-undoping cycle in an oxidation region. The polymer has essentially the same π-conjugation system as that of poly(*p*-phenylene).

Introduction

Preparation and electrical properties of poly(arylene)s having π-conjugation system along the polymer chain are the subject of recent interest. Poly(*p*-phenylene) (PPP) is one of the typical π-conjugated poly(arylene)s (1), and has high crystallinity (2) and electric conductivity (3). Since PPP shows insoluble and infusible properties which limit its application, several substituent groups such as alkyl and phenyl groups are introduced to increase the solubility of the polymer (4).
Recently, preparation of several π-conjugated poly(arylene)s such as PPP, poly(thiophene-2,5-diyl), poly(pyridine-2,5-diyl), poly(quinolinediyl)s and their related polymers by dehalogenation polycondensation of corresponding dihalogenated aromatic compounds with zero-valent nickel (Ni(0)) complex has been reported (5).

$$\mathrm{n\ X\text{-}Ar\text{-}X\ +\ n\ Ni(0)L_m\ \rightarrow\ \text{-}\!\left(Ar\right)\!\text{-}_n\ +\ n\ NiX_2L_m} \qquad (1)$$

Since the Ni(0) complex can be generated by electrochemical reduction of divalent nickel (Ni(II)) complex (6), the polymerization can also be carried out using the electrochemically generated Ni(0) complex (7).

$$\mathrm{Ni(II)L_m\ +\ 2e\ \rightarrow\ Ni(0)L_m} \qquad (2)$$

These methods afford π-conjugated polymers with well-defined linkage between the monomer units. In adition, the latter electrochemical polymerization usually gives the polymer as a thin film, which is more suitable to practical uses than powder, on the electrode.
In the course of our investigation on the preparation of poly(arylene)s, we have found that dehalogenation polycondensation of 2,7-dibromo-9,10-dihydrophenanthrene (2,7-Br_2-9,10-H_2Phen) with isolated Ni(0) complex and electrochemically generated Ni(0) complex gives a new unique PPP derivative, poly(9,10-dihydrophenanthrene-2,7-diyl) (PH_2Phen), in good yields (Eqs. (3) and (4)).
PH_2Phen is expected to have higher solubility than PPP due to the presence of methylene groups between the two phenylene units. PH_2Phen is considered to show electrically conducting property and electrochromism like those of PPP.

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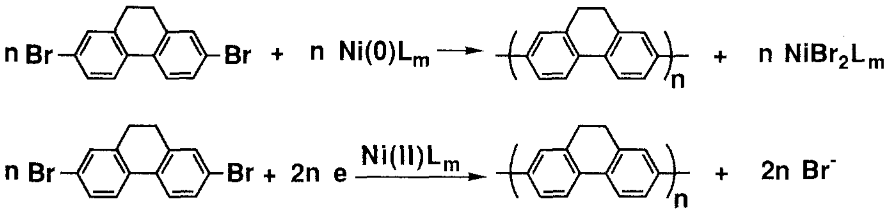


(3)

(4)

2,7-Br$_2$-9,10-H$_2$Phen

PH$_2$Phen

We now report results of preparation of PH$_2$Phen and chemical and electrochemical properties of the polymer.

Experimental

Materials

2,7-Br$_2$-9,10-H$_2$Phen was prepared by bromination of 9,10-dihydrophenanthrene (8). Bis(1,5-cyclooctadiene)nickel, Ni(cod)$_2$ (9), and tris(2,2'-bipyridine)nickel(II) bromide, [Ni(bpy)$_3$]Br$_2$ (10), were prepared as reported in literature, respectively.

Chemical Polymerization

Preparation of PH$_2$Phen with Ni(cod)$_2$ was carried out in a manner similar to that reported previously (5). Stirring 2,7-Br$_2$-9,10-H$_2$Phen (632 mg, 1.87 mmol) with a mixture of Ni(cod)$_2$ (639 mg, 2.32 mmol), 1,5-cyclooctadiene (0.8 cm^3), and 2,2'-bipyridine (362 mg, 2.32 mmol) in N,N-dimethylformamide (DMF) (25 cm^3) for 24 h at about 60 °C yielded a precipitate of the polymer. Work up of the polymer, involving removal of nickel compounds with ethylenediaminetetraacetic acid, afforded a reddish yellow powder of PH$_2$Phen. Elemental analysis: Found C, 89.2; H, 5.6; Br, 1.3 %. Calcd for $(C_{14}H_{10})_n$: C, 94.3; H, 5.7 %. A part of the difference between the calculated and found values seems to be attributable to high thermal stability of the polymer (*cf.* TGA data in Results and Discussion).

Electrochemical Polymerization

The electrochemical polymerization was carried out in a nitrogen-filled three-electrode cell with two compartments separated by a sintered glass disk. Platinum plates (1 X 2 cm) were used as a working electrode and a counter electrode, respectively, and Ag/0.1 M AgNO$_3$ electrode was used as a reference electrode. In a typical experiment, 0.48 mmol of [Ni(bpy)$_3$]Br$_2$ and 0.48 mmol of 2,7-Br$_2$-9,10-H$_2$Phen were added to a DMF (12 cm^3) solution of tetraethylammonium perchlorate (Et$_4$NClO$_4$, 0.25 M). The working electrode was polarized at a potential of -1.7 V *vs.* Ag/Ag$^+$ at 60 °C. After finishing the electrochemical polymerization (after passing total electric charge of about 70 C), the reddish yellow polymer film formed on the working electrode surface was washed with an aqueous ammonia, an aqueous solution of ethylenediaminetetraacetic acid, hot water and methanol in this order, and dried under vacuum. Elemental analysis: Found C, 87.6; H, 4.8; N, 1.1; Br, 5.2 %. Calcd for $(C_{14}H_{10})_n$: C, 94.3; H, 5.7 %.

Polymer Characterization

IR spectra, UV-visible spectra, TGA curves, and X-ray diffraction patterns were recorded on a JASCO IR-810 spectrometer, a JASCO Ubest-35 spectrometer, a Shimadzu thermoanalyzer DT-30, and a Rigaku Geigerflex RAD-B System, respectively. Elemental analysis was carried out with a Yanagimoto CHN Autocorder Type MT-2 and a Mitamura Riken Kogyo Micro Elementary Analyzer. Cyclic voltammetry and electrolysis were carried out with a Hokuto Denko galvanostat/potentiostat HA-501 and a Hokuto Denko HB-104 function generator. The electrical conductivity (σ) was measured using a two-probe method with a Takeda Riken TR-8651 electrometer. GPC analysis of a CHCl$_3$-soluble part of PH$_2$Phen was carried out with Shimadzu LC-6A liquid chromatography system using CHCl$_3$ as the eluent.

Results and Discussion

Chemically prepared PH_2Phen was obtained in good yield (96 %). Elemental analysis of the polymer shows only a low halogen content of chemically prepared PH_2Phen (Br, 1.3 %). The low bromine content indicates that the dehalogenation polycondensation is proceeding.

Figure 1 shows cyclic voltammograms (CV) of $[Ni(bpy)_3]Br_2$ with and without 2,7-Br_2-9,10-H_2Phen. In the absence of 2,7-Br_2-9,10-H_2Phen, a redox couple of Ni(0)/Ni(II) was clearly observed at about -1.6 V *vs.* Ag/Ag^+ (curve (a)); a cathode peak potential for the reduction of Ni(II) to Ni(0) = -1.61 V and an anode peak potential for reoxidation of Ni(0) to Ni(II) = -1.55 V. The reoxidative peak current markedly decreases in the presence of 2,7-Br_2-9,10-H_2Phen (curve (b)), indicating the occurrence of oxidative addition of 2,7-Br_2-9,10-H_2Phen to the electrochemically generated Ni(0) complex to form a Br-Ni^{II}-Ar-Br complex. In the repeated scanning, the working electrode surface was covered with a smooth yellow film. According to the results of the CV, the electrochemical polymerization was carried out at a working potential corresponding to the reduction of the Ni(II) species (i.e. -1.7 V *vs.* Ag/Ag^+).

Electrochemically prepared PH_2Phen was obtained as a film on the electrode. The nitrogen content (*cf.* Experimental) and an absorption band at about 1680 cm^{-1} in the IR spectrum (Fig. 2(b)) indicate contamination of the polymer film with DMF, which is difficult to remove completely.

Chemically and electrochemically prepared PH_2Phen is scarcely (about 5 % of the prepared polymer) soluble in $CHCl_3$ and partialy (about half of the prepared polymer) soluble in N-methyl-2-pyrrolidone (NMP) at room temperature. The solubilities of chemically prepared PH_2Phen in $CHCl_3$ and NMP are 0.5 mg/ml and 3.1 mg/ml, respectively. The $CHCl_3$-soluble part has number-average molecular weight (M_n) of about 900 (*vs.* polystyrene) as determined by GPC. The very poor solubility of PPP is increased by the bridging ethylene unit in PH_2Phen, although the enhancement of the solubility is not sufficient.

UV-visible spectra of the chemically and electrochemically prepared PH_2Phen show π-π^* absorption peaks at 361 nm and 356 nm in NMP, respectively. The absorption peaks are almost

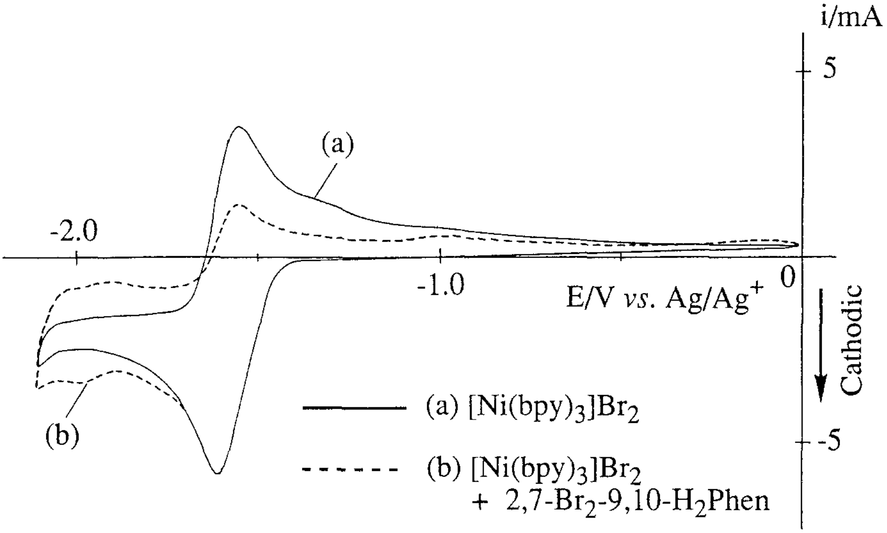


Figure 1: Cyclic voltammograms recorded with a platinum electrode in an acetonitrile solution of Et_4NClO_4 (0.1 M) containing (solid line) 5 X 10^{-3} M $[Ni(bpy)_3]Br_2$ or (broken line) 5 X 10^{-3} M $[Ni(bpy)_3]Br_2$ and 10 X 10^{-3} M 2,7-Br_2-9,10-H_2Phen. Sweep rate = 50 mV s^{-1}. At 25 °C.

same as that of PPP (11) measured by a reflection method with powdery PPP, indicating that conjugation length of PH_2Phen is essentially the same as that of PPP.

Figure 2 shows IR spectra of 2,7-Br_2-9,10-H_2Phen and chemically and electrochemically prepared PH_2Phen. The IR spectra of PH_2Phen are similar to that of 2,7-Br_2-9,10-H_2Phen except for a ν (C-Br) band (1080 cm^{-1}), which is almost negligible in the spectra of PH_2Phen. Powder X-ray diffraction patterns of both the chemically and electrochemically prepared PH_2Phen give rise to diffraction peaks at essentially the same positions (2θ ($CuK\alpha$) = 19.6°, 22.8°, 28.0°, and 43.3°) as those observed for PPP (12), although the diffraction peaks are considerably broadened.

TGA curve of chemically prepared PH_2Phen indicates initiation of the weight lose at 300 °C and 80 % residual weight at 900 °C under nitrogen, revealing very high heat-resistance of PH_2Phen.

Figure 3 shows CV of a film of PH_2Phen obtained by electrochemical polymerization. As shown in Fig. 3(a), the PH_2Phen film gives rise to an electrochemically active cycle in the oxidation region, showing a p-type doping peak at 1.05 V *vs*. Ag/Ag^+ and an undoping peak at 0.67 V. Color of PH_2Phen changes from yellow to dark blue during oxidation. The redox potentials as well as the color change are essentially the same as those of PPP (1(a), (g)). The polymer film electrode is stable during repeated scanning.

When the CV measurement was carried out to a higher swiching potential (1.5 V), flow of only irreversible current was observed without the corresponding undoping peak (Fig. 3(b)). This

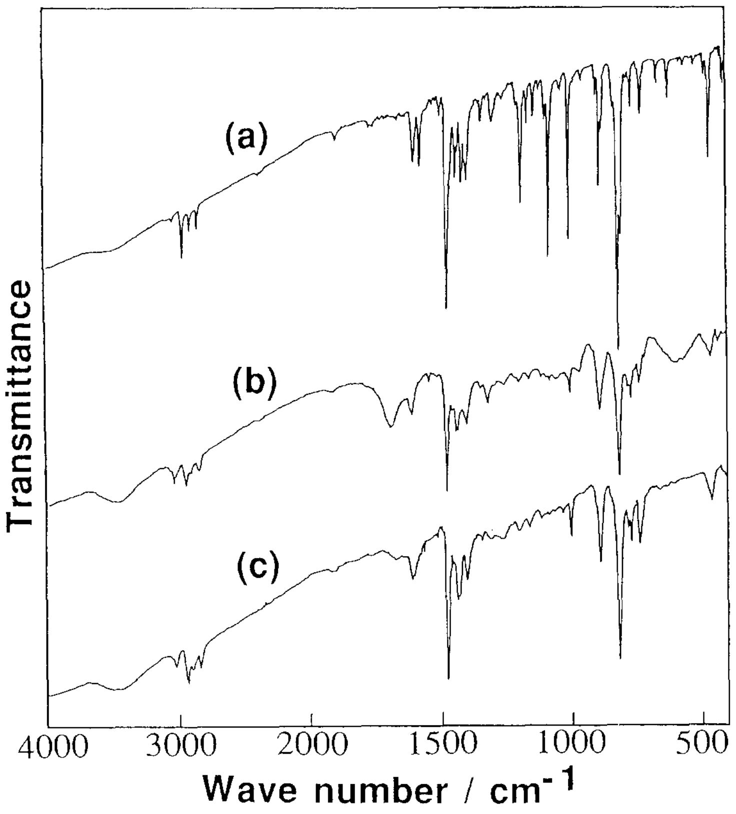
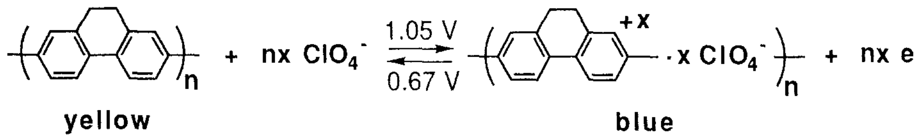


Figure 2: Infrared spectra of (a) 2,7-Br_2-9,10-H_2Phen, (b) electrochemically prepared PH_2Phen, and (c) chemically prepared PH_2Phen.



(5)

phenomenon is called "overoxidation degradation" and has been found in some kinds of π-conjugated poly(arylene)s (13).

Platinum plate coated with film of chemically prepared PH_2Phen can also be prepared by spreading the NMP solution of the polymer on platinum plate and evaporation of the solvent under vacuum. The polymer film electrode shows similar voltammogram and color change as described above.

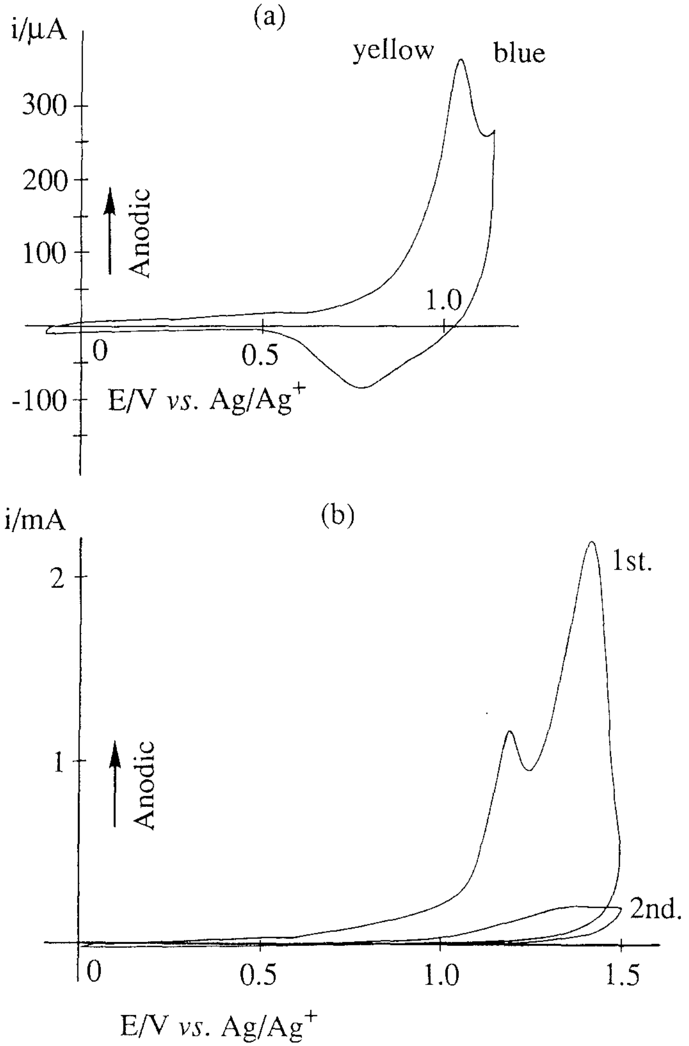


Figure 3: Cyclic voltammograms of a film of PH_2Phen on platinum electrode (1 X 1 cm) in an acetonitrile solution of Et_4NClO_4 (0.1 M). Sweep rate = 10 mV s^{-1}. Sweep range: (a) 0-1.2 V and (b) 0-1.5 V. At 25 °C.

Electrical conductivity (σ) of pristine chemically prepared PH_2Phen is less than 10^{-9} S cm^{-1} as measured with pressed polymer pellet. Exposure of the polymer pellet to a vapor of iodine gives iodine-doped sample, however, the σ value of the iodine-doped polymer is in the range of 10^{-6} S cm^{-1}. Iodine is a weak oxidizing doping agent and σ values of iodine-doped PPP remain in the almost insulating region (1,14). Absorbed iodine seems not to be strong enough to convert PH_2Phen into the electrically conducting cation-radical. Other stronger doping agents (e.g. $SbCl_5$, AsF_5) seem to be necessitated to obtain material with higher conductivity.

References

1. (a) T. A. Skotheim, ed., *"Handbook of Conjugated Polymers"*, Vol. 1 and 2, Marcel Dekker, New York (1986); (b) H. Kuzmany, M. Mehring, and S. Roth. ed., *"Electronic Properties of Conjugated Polymers"*, Springer (1987); (c) T. Yamamoto, Y. Hayashi, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **51**, 2091 (1978); (d) N. Toshima, K. Tanaka, A. Koshirai, and H. Hirai, *Bull. Chem. Soc. Jpn.*, **61**, 2551 (1988); (e) E. Tsuchida, K. Yamamoto, T. Asada, and H. Nishide, *Chem. Lett.*,1541 (1978); (f) P. Kovacic and A. Kyriakis, *Tetrahedron Lett.*, **1962**, 476; (g) T. Yamamoto, H. Wakayama, T. Fukuda, and T. Kanbara, *J. Phys. Chem.*, in press.
2. (a) P. Kovacic, M. B. Feldman, J. P. Kovacic, and J. B. Lando, *J. Appl. Polym. Sci.* **12**, 1735 (1968); (b) T. Yamamoto, A. Morita, Y. Miyazaki, T. Maruyama, H. Wakayama, T. Kanbara, S. Sasaki, and K. Kubota, *Macromolecules*, **25**, 1214 (1992)
3. D. M. Ivory, G. G. Miller, J. M. Sowa, L. W. Schacklette, R. R. Chance, and R. H. Baughman, *J. Chem. Phys.* **71**, 1506 (1979).
4. V. Percec, S. Okita, and R. Weiss, *Macromolecules*, **25**, 1816 (1992).
5. (a) T. Yamamoto, A. Morita, Y. Miyazaki, T. Maruyama, H. Wakayama, T. Kanbara, S. Sasaki, and K. Kubota, *Macromolecules*, **25**, 1214 (1992); (b) T. Yamamoto, A. Morita, T. Maruyama, Z.-H. Zhou, T. Kanbara, and K. Sanechika, *Polym. J.*, **22**, 187 (1990); (c) T. Yamamoto, T. Ito, K. Sanechika, and M. Hishinuma, *Synth. Met.*, **25**, 103 (1988); (d) *Chem. Ind. (London)*, **1988**, 337; (e) T. Kanbara, N. Saito, T. Yamamoto, and K. Kubota, *Macromolecules*, **24**, 5883 (1991); (f) M. Ueda, Y. Miyaji, T. Ito, Y. Oba, and T. Sone, *Macromolecules*, **24**, 2694 (1991). These polymerization is based on organonickel C-C coupling reactions (e.g., T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Am. Chem. Soc.*, **93**, 3350 (1971); T. Yamamoto, S. Wakabayashi, and K. Osakada, *Organometallics*, **428**, 223 (1992); M. F. Semmelhack and L. S. Ryono, *J. Am. Chem. Soc.*, **97**, 3873 (1975)).
6. (a) G. Bontempelli, F. Magno, B. Corain, and G. Schiavon, *J. Electroanal. Chem.*, **103**, 243 (1979); (b) G. Bontempelli, F. Magno, S. Daniele, and G. Schiavon, *ibid.*, **159**, 117 (1983).
7. (a) J.-F. Fauvarque, M.-A. Petit, F. Pfluger, A. Jutand, C. Chevrot, and M. Troupel, *Makromol. Chem., Rapid Commun.*, **4**, 455 (1983); (b) G. Schiavon, G. Zotti, and G. Bontempelli, *J. Electroanal. Chem.*, **161**, 323 (1984); (c) G. Schiavon, G. Zotti, G. Bontempelli, and F. L. Coco, *ibid.*, **242**, 131 (1988).
8. D. E. Pearson, U. S. Patent 3988369 (1976)
9. G. Wilke, *Angew. Chem.*, **72**, 581 (1960).
10. (a) F. M. Jeager and J. A. van Dijk, *Z. Anorg. Chem.*, **227**, 273 (1936); (b) T. Yamamoto, A. Morita, Y. Miyazaki, T. Maruyama, H. Wakayama, T. Kanbara, S. Sasaki, and K. Kubota, *Macromolecules*, **25**, 1214 (1992)
11. P. Kovacic, L. Hsu, *J. Polym. Sci.* Part A-1, **4**, 5 (1966).
12. S. Sasaki, T. Yamamoto, T. Kanbara, A. Morita, and T. Yamamoto, *J. Poly. Sci., Polym. Phys. Ed.*, **30**, 293 (1992).
13. (a) D. E. Stilwell and S.-M. Park, *J. Electrochem. Soc.*, **136**, 688 (1989); (b) B. Krische and M. Zagorska, *Synth. Met.*, **28**, C257 and C263 (1989); (c) H. Harada, T. Fuchigami, and T. Nonaka, *J. Electroanal. Chem.*, **303**, 139 (1991).
14. M. Sato and K. Kaeriyama, *Makromol. Chem.*, **184**, 2241 (1983).

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