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Preparation and Properties of New π-Conjugated Poly(benzimidazole-4,7-diyl) and Poly(2,1,3-benzothiadiazole-4,7-diyl)

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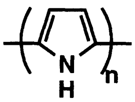
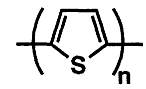
Dehalogenation polycondensation of 4,7-dibromobenzimidazole and 4,7-dibromo-2,1,3-benzothiadiazole with a zero-valent nickel complex afford poly(benzimidazole-4,7-diyl) and poly(2,1,3-benzothiadiazole-4,7-diyl), respectively. These polymers give rise to electrochemically active doping-undoping cycles in both reduction and oxidation regions, and are converted into electrically conducting materials on both n- and p-type chemical doping.

Preparation and electrical properties of π-conjugated poly(arylene)s have been widely investigated in recent years. Among the poly(arylene)s, poly(pyrrole-2,5-diyl)$^{1)}$ constituted of a typical π-electron excessive five-membered heteroaromatic ring has p-type electrically conducting properties, while poly(pyridine-2,5-diyl)$^{2)}$ and poly(pyrimidine-2,5-diyl)$^{3)}$ constituted of electron-accepting six-membered heteroaromatic rings containing imine nitrogen(s) easily accept electrons from reductants to give n-doped electrically conducting materials. In the case of poly(thiophene-2,5-diyl)$^{4)}$ constituted of moderately electron-donating thiophene ring, it can undergo both the p-doping and n-doping. In addition, it has been reported that both poly(quinoline-5,8-diyl) and poly(isoquinoline-1,4-diyl), which have π-deficient pyridine ring as the side-chain ring and the main-chain ring, respectively, also show the electron-accepting properties.$^{5)}$ These informations about the π-conjugated poly(arylene)s prompted us to design the following new π-conjugated poly(arylene)s which consist of benzazole rings such as benzimidazole ring and 2,1,3-benzothiadiazole ring (Eq. 1). Preparation of new π-conjugated polymers is considered to attribute to further understanding and application of the conductive polymers. In these cases, revealing of the conductive type (p- or n-) of these polymers are considered to be of intriguing; the five-membered rings, imidazole and thiadiazole rings, are considered to be the electron-donating rings,$^{6)}$ whereas the presence of the imine nitrogen(s) in the side chain as well as the large repeating aromatic unit may give an electron-accepting nature to the polymers.


Poly(pyrrole-2,5-diyl)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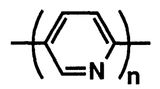
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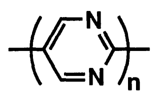
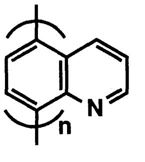
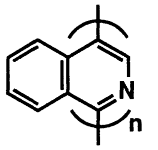
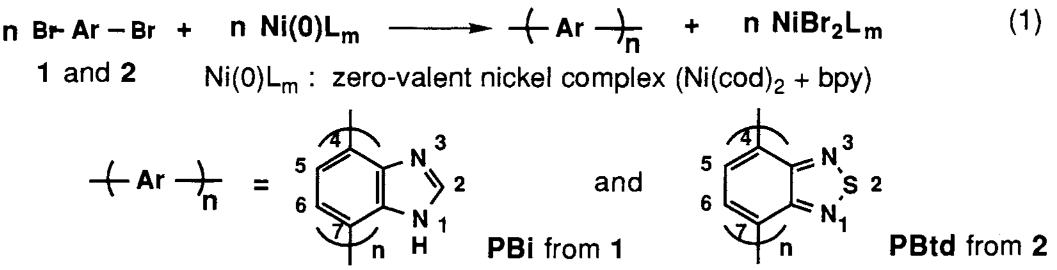

Poly(pyrimidine-2,5-diyl)


Poly(quinoline-5,8-diyl)


Poly(isoquinoline-1,4-diyl)

We now report preparation of new poly(arylene)s, poly(benzimidazole-4,7-diyl) (PBi) and poly(2,1,3-benzothiadiazole-4,7-diyl) (PBtd), by dehalogenation polycondensation of 4,7-dibromobenzimidazole **1** and 4,7-dibromo-2,1,3-benzothiadiazole **2** with a zero-valent nickel complex,$^{4d)}$ based on organonickel chemistry.$^{7)}$



$$n\ \mathrm{Br{-}Ar{-}Br} + n\ \mathrm{Ni(0)L_m} \longrightarrow -\!\!(\mathrm{Ar})\!\!-_n + n\ \mathrm{NiBr_2L_m} \qquad (1)$$

1 and **2** $\mathrm{Ni(0)L_m}$: zero-valent nickel complex ($\mathrm{Ni(cod)_2}$ + bpy)

Monomer **1** was prepared by modifying a method reported for the preparation of benzimidazole.[8]) Monomer **2** was prepared by a method reported by Pilgram et al.[9]) Stirring **1** (440 mg, 1.60 mmol) with a mixture of bis(1,5-cyclooctadiene)nickel $\mathrm{Ni(cod)_2}$ (530 mg, 1.90 mmol), 1,5-cyclooctadiene (0.35 $\mathrm{cm^3}$), and 2,2'-bipyridine (300 mg, 1.92 mmol) in N,N-dimethylformamide (25 $\mathrm{cm^3}$) for 48 h at about 60 °C afforded a precipitate of ocher yellow polymer. Work up of the polymer, involving removal of nickel compounds with an aqueous solution of ethylenediaminetetraacetic acid (with pH = about 9), was carried out in a manner similar to that reported previously.[2,3,4d,5]) Ocher yellow PBi was obtained in good yield (86%). Reddish brown PBtd (yield: 87%) was prepared analogously by using **2**.

Elemental analyses of PBi showed negligible halogen content. Anal: PBi; Found: C, 71.1; H, 4.1; N, 23.2; Br, 0.0%. Calcd for $(\mathrm{C_7H_4N_2{\cdot}0.1H_2O})_n$: C, 71.3; H, 3.6; N, 23.9%. PBtd; Found: C, 53.5; H, 2.3; N, 19.7; Br, 4.1%. Calcd for $(\mathrm{C_6H_2N_2S{\cdot}0.1H_2O})_n$: C, 53.0; H, 1.6; N, 20.6%. The analytical data and absorption bands at about 3450 and 1650 $\mathrm{cm^{-1}}$ in the IR spectra indicate contamination of the polymers with small amounts of $\mathrm{H_2O}$.

PBi was soluble in formic acid and dil HCl, and partially soluble in dimethylsulfoxide (DMSO). On the other hand, PBtd was sparingly soluble in DMSO and formic acid. UV-visible spectra of DMSO solution of PBi and PBtd showed two π-π^* absorption peaks at 295 and 340 nm, and at 320 and about 430 nm, respectively. PBi gave rise to a strong fluorescence in DMSO with a peak at 440 nm when irradiated by 340 nm light. The light scattering technique applied for a formic acid solution of PBi indicated that the polymer had molecular weight of 13000.

Figure 1 shows IR spectra of PBi and PBtd. Skeletal ring vibration (1250-1650 $\mathrm{cm^{-1}}$) and C-H out-of-plane bending vibration (700-900 $\mathrm{cm^{-1}}$) of the polymers are essentially similar to those of the corresponding monomers, whereas ν(C-Br) bands (957 $\mathrm{cm^{-1}}$ for **1** and 830 $\mathrm{cm^{-1}}$ for **2**) become negligible after the polymerization.

^{1}H NMR spectrum of PBi in DMSO-d_6 at 80 °C showed broad aromatic protons signals from 7.0 to 9.0 ppm (main signals at 7.7 and 8.3 ppm assigned to 5,6-H and 2-H protons of benzimidazole ring, respectively) and a broad signal at 12.7 ppm assigned to N-H proton.

The elemental analysis, molecular weight measurement, and IR and NMR data shown above indicate that the present preparation method affords

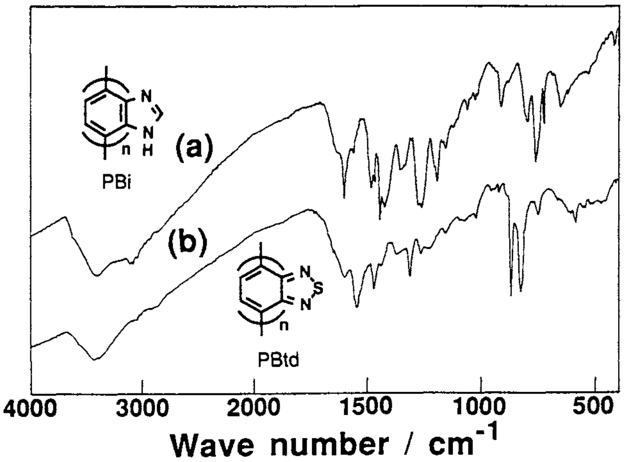


Fig. 1. Infrared spectra of (a) poly(benzimidazole-4,7-diyl) (PBi) and (b) poly(2,1,3-benzothiadiazole-4,7-diyl) (PBtd).

the proposed polymers, respectively.

Figure 2 shows cyclic voltammograms (CV) of PBi. Platinum plate coated with film of PBi was prepared by spreading the DMSO solution of PBi on platinum plate and evaporation of the solvent under vacuum. Casting formic acid solution of PBi on platinum plate, evaporation of formic acid, and washing with an aqueous NH_4OH solution gave similar PBi film. As shown in Fig. 2(a), the PBi film gives rise to an electrochemically active cycle in the reduction region, showing an n-doping peak at -1.98 V *vs.* Ag/Ag^+ and an undoping peak at -1.67 V. The n-doping level estimated from the doping current is about 0.30 per the monomer unit. Color of PBi film changed from ocher yellow to reddish brown during reduction. The polymer film was virtually stable during repeated scanning. These results suggest PBi has the n-type doping nature due to the presence of electron-withdrawing imine nitrogen in the side chain ring.

On the other hand, in an oxidation region (Fig. 2(b)), a couple of a broad anodic peak at 1.09 V assigned to p-doping and its undoping peak at -0.98 V is observed. The doping and undoping were accompanied by color change of the film between ocher yellow and dark brown. Although the n-doping and undoping (Fig. 2(a)) could be repeated without observable change of the CV curve, the redox peaks in the oxidation region (Fig. 2(b)) decreased with repeated scanning.

These results as well as the large peak separation in Fig. 2(b) suggest strong interaction between the polymer and dopant anion in the p-doped state and difficulty to remove the paired dopant anion from the polymer by applied reducing voltage. Such type of irreversibility in the electrical doping and undoping has been sometimes observed for π-conjugated polymers. Related π-conjugated polymer, poly(*p*-phenylenebenzobisthiazole-2,6-diyl), showed similar n-

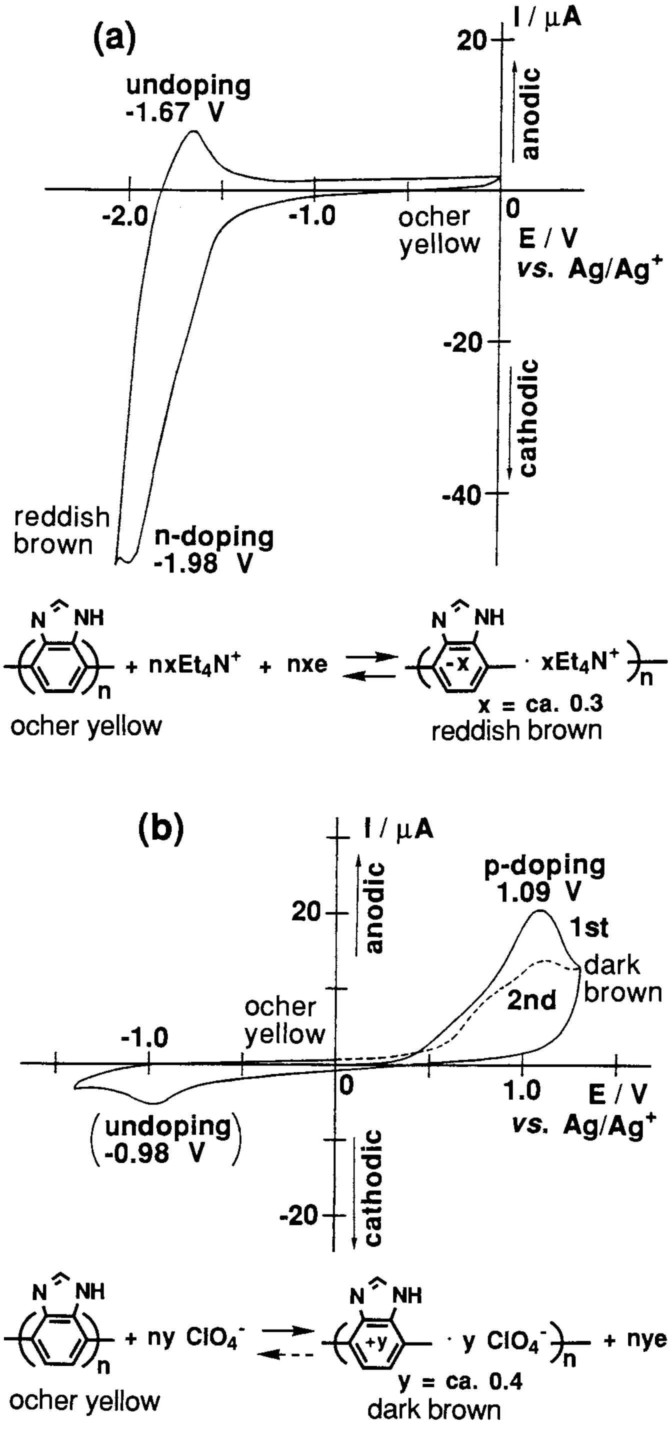


Fig. 2. Cyclic voltammograms of a film of poly(benzimidazole-4,7-diyl) (PBi) on platinum plate in an acetonitrile solution of Et_4NClO_4 (0.1 M). Sweep rate = 2 mV s^{-1}. Sweep range = (a) -2.1~0.0 V and (b) -1.4~1.4 V.

doping behavior, while oxidative processes were not electrochemically reversible as reported by DePra et al.$^{10)}$

PBtd film gave similar CV curves and color change (from reddish yellow to black at both the p- and n-doping) to those of PBi; p-doping and undoping peaks appeared at 1.35 and -1.56 V, while n-doping and undoping peaks were observed at -1.90 and -1.66 V, respectively.

These CV results of PBi and PBtd suggest that the electron-accepting nature of poly-*p*-phenylenic backbone along the polymer chains are enhanced by neighboring imine nitrogen(s), although benzazole rings have moderate electron-donating nature. According to molecular orbital calculations of related benzazole compounds and benzoxadiazole compounds, their benzene rings had electron-accepting nature due to adjacent imine nitrogens.$^{11)}$

Non-doped PBi and PBtd were essentially insulators with electrical conductivity (σ) of less than 10^{-10} S cm^{-1}. Doping of PBi and PBtd powders with sodium (treatment with sodium naphthalide in THF) or iodine (exposure to vapor of iodine) afforded electrically conducting materials with the σ values of 7.2×10^{-4}-3.5×10^{-4} S cm^{-1} and 7.1×10^{-5}-3.3×10^{-5} S cm^{-1}, respectively, as measured with pressed pellets, indicating these polymers had both the p- and n-type electrically semiconducting properties.

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