Preparation and Properties of New π-Conjugated Poly(quinoxaline-5,8-diyl) and Poly(2,3-diethylquinoxaline-5,8-diyl). Enhancement of Electron-Accepting Properties of Poly(arylene)s by Introduction of Imine Nitrogen

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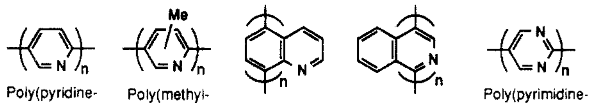
Preparation and electrical properties of poly(arylene)s having a π-conjugation system along the polymer chain are the subject of recent interest. However, in contrast to extensive studies on p-type doping of poly(arylene)s (e.g., poly(pyrrole-2,5-diyl),[1] poly(thiophene-2,5-diyl),[2,3] poly(*p*-phenylene),[3,4] and their derivatives), only a few reports have been published concerning the preparation of n-type electrically conducting poly(arylene)s.[5–8]

However, recently a dehalogenation polycondensation based on organonickel chemistry[9] has been developed[3] for the preparation of various n-type electrically conducting poly(arylene)s, and poly(pyridine-2,5-diyl) and its derivatives,[6] poly(quinolinediyl)s[7] and poly(pyrimidine-2,5-diyl),[8] have been prepared by this method.

$$n\ \text{X-Ar-X} + n\ \text{Ni(0)L}_m \longrightarrow -\!\!(\text{Ar})_n\!\!- \qquad (1)$$

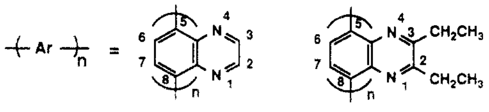


Poly(pyridine-2,5-diyl) Poly(methylpyridine-2,5-diyl) Poly(quinoline-5,8-diyl) Poly(isoquinoline-1,4-diyl) Poly(pyrimidine-2,5-diyl)

The n-type electrically conducting properties of the polymers appear to originate from π-deficient nature of the aromatic units[10] containing electron-withdrawing imine nitrogen(s). Actually, poly(pyrimidine-2,5-diyl) having two electron-withdrawing imine nitrogens in the main-chain ring shows the highest electron-accepting properties among the reported π-conjugated poly(arylene)s.[8] In order to reveal the general effect of the imine nitrogen on the electron-accepting properties of poly(arylene)s more clearly, we have prepared the following two new poly(arylene)s, poly(quinoxaline-5,8-diyl) (poly-**1**) and poly(2,3-diethylquinoxaline-5,8-diyl) (poly-**2**), with two electron-withdrawing imine nitrogens in the naphthalene-like units, and we now report the preparation and properties of the polymers. They also have been prepared by the dehalogenation polycondensation of 5,8-dibromoquinoxaline and 5,8-dibromo-2,3-diethylquinoxaline with a zero-valent nickel complex.

$$n\ \text{Br-Ar-Br} + n\ \text{Ni(0)L}_m \longrightarrow -\!\!(\text{Ar})_n\!\!- + n\ \text{NiBr}_2\text{L}_m \qquad (2)$$

Ni(0)L_m : zero-valent nickel complex (Ni(cod)_2 + bpy)



poly-**1** poly-**2**

Materials. Bis(1,5-cyclooctadiene)nickel(0) (Ni(cod)_2) was prepared as reported in the literature.[11]

5,8-Dibromoquinoxaline was prepared by modifying a method reported for the preparation of 5,8-dichloroquinoxaline.[12] An aqueous solution (40 wt %, 0.55 g) of glyoxal (3.8 mmol) was added dropwise to 3,6-dibromo-*o*-phenylenediamine[13] (1.0 g, 3.8 mmol) in 25 mL of ethanol. The reaction mixture was refluxed for 3 h. The mixture was cooled, and a pale yellow precipitate was separated by filtration. Recrystallization from acetone gave pale yellow needles (0.75 g, yield 71%). Mp: 226–228 °C (dec). Anal. Calcd for ($C_8H_4N_2Br_2$): C, 33.4; H, 1.4; N, 9.7; Br, 55.5. Found: C, 33.4; H, 1.3; N, 9.5; Br, 55.4. ^{1}H NMR ($CDCl_3$, 100 MHz): δ 8.0 (2H, s, 6,7-H), 9.0 (2H, s, 2,3-H).

Preparation of 5,8-dibromo-2,3-diethylquinoxaline was carried out analogously by using 3,4-hexanedione: yellow needles (yield 69%). Mp: 136–138 °C. Anal. Calcd for ($C_{12}H_{12}N_2Br_2$): C, 41.9; H, 3.5; N, 8.1; Br, 46.5. Found: C, 42.0; H, 3.6; N, 8.2; Br, 45.9. ^{1}H NMR ($CDCl_3$, 100 MHz): δ 1.5 (6H, t, J = 7 Hz, $-CH_3$), 3.1 (4H, q, J = 7 Hz, $-CH_2-$), 7.8 (2H, s, 6,7-H).

Polymerization. Stirring 5,8-dibromoquinoxaline (0.46 g, 1.60 mmol) with a mixture of Ni(cod)_2 (0.53 g, 1.90 mmol), 1.5-cyclooctadiene (0.35 mL), and 2,2′-bipyridine (0.30 g, 1.91 mmol) in *N,N*-dimethylformamide (25 mL) for 48 h at 60 °C afforded a precipitate of a yellow polymer. Workup of the polymer, involving removal of nickel compounds with ethylenediamine tetraacetic acid, was carried out in a manner similar to that reported previously[3,6–8] (yield 95%). Pale yellow poly-**2** was prepared analogously by using 5,8-dibromo-2,3-diethylquinoxaline (yield 98%). Poly-**1**. Anal. Calcd for $(C_8H_4N_2{\cdot}0.1H_2O)_n$: C, 73.9; H, 3.3; N, 21.6. Found: C, 73.2; H, 3.4; N, 20.9; Br, 0.4. Poly-**2**. Anal. Calcd for $(C_{12}H_{12}N_2)_n$: C, 78.2; H, 6.6; N, 15.2. Found: C, 78.1; H, 6.7; N, 14.7; Br, 0.0. The analytical data and IR absorption bands at about 3450 and 1650 cm^{-1} (Figure 1a) indicate that nonsubstituted poly-**1** contains a small amount of H_2O.

Poly-**1** is soluble in formic acid and trifluoroacetic acid and sparingly soluble in dimethyl sulfoxide. On the other hand, poly-**2** exhibits good solubility in formic acid and trifluoroacetic acid and is partially soluble in 1,1,2,2-tetrachloroethane and chloroform. The UV–visible spectra of formic acid solutions of poly-**1** and poly-**2** exhibit two π–π^* absorption peaks at 258 and 325 nm and at 260 and 333 nm, respectively. The light scattering technique applied for the formic acid solutions of these polymers indicates that poly-**1** and poly-**2** have molecular weights of 6300 (degree of polymerization (DP) = ~50) and 44 000 (DP = ~240), respectively.

Figure 1 shows IR spectra of poly-**1** and poly-**2**, which are essentially the same as those of the corresponding monomers except for the disappearance of ν(C-Br) bands of the monomers (575 and 587 cm^{-1} for 5,8-dibromoquinoxaline and 5,8-dibromo-2,3-diethylquinoxaline, respectively) in the IR spectra of poly-**1** and poly-**2**.

Figure 2 shows ^{1}H NMR spectra of poly-**1** and poly-**2** in CF_3COOD. The peaks are assigned by comparing the position of the peaks with those of quinoxaline and the corresponding monomers. As shown in Figure 2a, poly-**1** exhibits two broad peaks of 2,3-H and 6,7-H of the quinoxaline ring at 9.1 and 8.4 ppm. In Figure 2b, a broad peak at 8.3 ppm is assigned to 6,7-H protons of the quinoxaline ring, and two broad peaks at about 3.1 and 1.1 ppm are the CH_2 and CH_3 protons of the ethyl group, respectively. The peak area ratios agree with the assignment. The ^{13}C NMR spectrum of poly-**1** shows four peaks at 146 (2,3-C), 141, 139, and 137 ppm (other aromatic carbons), and the ^{13}C NMR spectrum of poly-**2** gives rise to broad peaks in a range of 145–135 ppm due to the aromatic carbons and two peaks of the ethyl group at 29 and 13 ppm. The elemental analysis, molecular weight,

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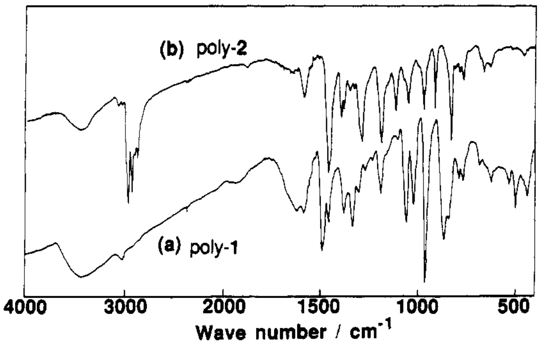


Figure 1. Infrared spectra of (a) poly(quinoxaline-5,8-diyl) (poly-1) and (b) poly(2,3-diethylquinoxaline-5,8-diyl) (poly-2).

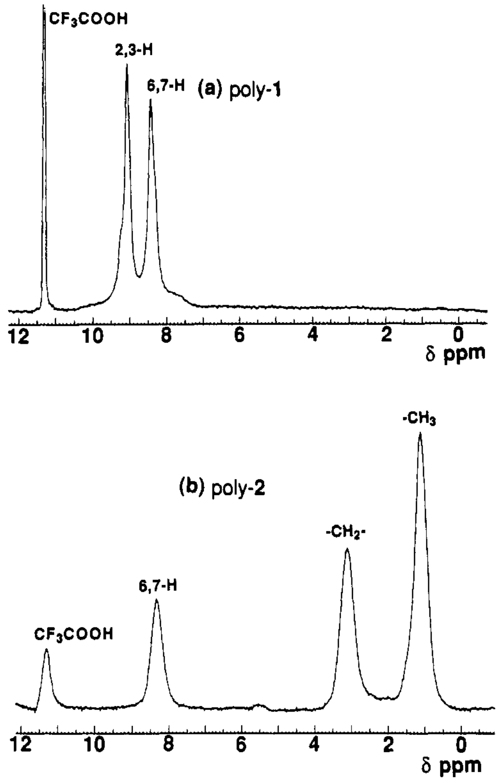
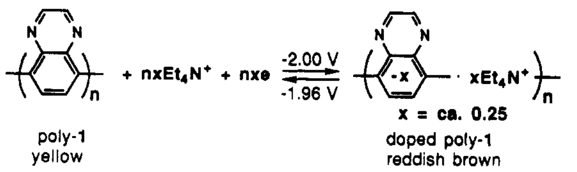


Figure 2. ^{1}H NMR spectra of (a) poly(quinoxaline-5,8-diyl) (poly-1) and (b) poly(2,3-diethylquinoxaline-5,8-diyl) (poly-2) in CF_3COOD.

and IR and NMR data agree with the structures of the polymers.

Spreading formic acid solutions of the polymers on platinum plates and evaporation of formic acid under vacuum give platinum plates coated with films of the polymers. Figure 3 depicts cyclic voltammograms (CV's) of the films of poly-1 and poly-2. As shown in Figure 3a, poly-1 gives rise to an electrochemically active cycle in the reduction region with an n-doping peak at −2.00 V *vs* Ag/Ag$^+$ and an undoping peak at −1.96 V.



(3)

The n-doping level (x) is estimated to be about 0.25 from the doping current in Figure 3a and the weight of the film of poly-1 (about 2.3×10^{-4} g cm^{-2} on a 1×1 cm area). The color of the polymer changes from yellow to reddish brown during the reduction. The polymer film is stable for repeated scanning, showing essentially the same CV and color change.

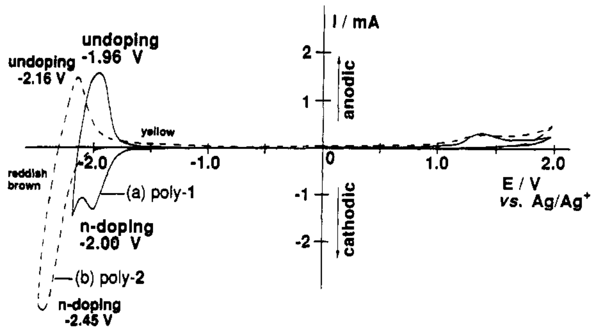


Figure 3. Cyclic voltammograms of films of (a, —) poly(quinoxaline-5,8-diyl) (poly-1 (2.3×10^{-4} g cm^{-2})) and (b, - - -) poly(2,3-diethylquinoxaline-5,8-diyl) (poly-2 (2.5×10^{-4} g cm^{-2})) on a platinum plate (1×1 cm) in an acetonitrile solution of $[(C_2H_5)_4N]ClO_4$ (0.1 M). Sweep rate = 10 mV s^{-1}.

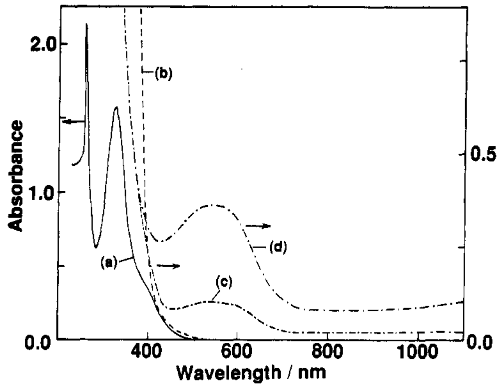


Figure 4. UV–visible absorption spectra of (a) a film of nondoped poly(quinoxaline-5,8-diyl) (poly-1) on quartz glass and (b–d) a film of electrochemically doped poly-1 on an ITO glass electrode in an acetonitrile solution of $[(C_2H_5)_4N]ClO_4$ (0.1 M). Applied voltage: (b) 0.0, (c) −1.8, and (d) −2.0 V *vs* Ag/Ag$^+$. As for (b–d), the absorption pattern in the UV region was not measured due to the absorption of the ITO glass.

The *in situ* absorption spectrum of the film of poly-1 on an indium/tin oxide (ITO)-coated glass electrode is also changed during the electrochemical n-doping. Figure 4 shows changes in the absorption spectrum of the film of poly-1 during the electrochemical n-doping. A nondoped polymer film on quartz glass gives two π-π^* absorption peaks at 260 and 330 nm and is transparent in a range of 500–1100 nm. When the polymer film is electrochemically reduced at about −2.0 V *vs* Ag/Ag$^+$, the appearance of a new broad peak in the range of 500–650 nm with tail absorption toward the near-infrared region is observed.

In spite of its facile electrochemical n-doping, the film of poly-1 is electrochemically inactive in an oxidation region, as shown in Figure 3a, except for an uncharacterized small anodic peak at about 1.35 V. A similar electrochemical inactiveness in the p-doping region has been reported for poly(pyridine-2,5-diyl)[6] and poly(quinolinediyl)s.[7] These results indicate the n-type conducting properties of poly-1.

As shown in Figure 3b, poly-2 is also electrochemically active only for the n-doping and affords a similar CV and color change. The requirement of a negatively larger potential for the reduction of poly-2 than for that of poly-1 is reasonably accounted for by the electron-donating effect of the ethyl substituent.

Table I presents a comparison of the redox potential (E^0) of the n-doping of poly(naphthalene-1,4-diyl) (P(1,4-N)),[14] poly(quinoline-5,8-diyl) (P(5,8-Q)),[7] and poly-1, all of which have similar poly(naphthalene-1,4-diyl) or its

Table I. Redox Potential for n-Doping of Poly(arylene)s

poly(arylene)	P(1,4-N)	P(5,8-Q)	poly-1
E^0/V[a]	−2.70[b]	−2.37[c]	−1.98

[a] *vs* Ag/Ag$^+$. Measured in an acetonitrile solution of $[(C_2H_5)_4N]ClO_4$ (0.1 M). The average of the peak potentials of n-doping and n-undoping is given. [b] From ref 14. [c] From ref 7.

analogous structure. As shown in Table I, the E^0 value increases on the order of P(1,4-N) < P(5,8-Q) < poly-1, and introduction of the electron-withdrawing imine nitrogen(s) in the side ring of the 1,4-naphthylene unit raises the electron-accepting property of the poly(arylene) by changing the reducing potential by about 0.35 V per each of the imine nitrogens. Polarographic reduction potentials ($E_{1/2}$) of naphthalene, quinoline, and quinoxaline are reported to be −1.98, −1.59, and −1.09 V (*vs* a mercury pool), respectively, which are measured in an *N,N*-dimethylformamide solution of tetraethylammonium iodide (0.1 M).[15] The $E_{1/2}$ values of the corresponding low-molecular-weight aromatic compounds support the electrochemical behaviors of the poly(arylene)s.

The band gap (E_g) of poly-1 is estimated as about 2.6 eV from the onset of the optical absorption band, and poly-1 has ionization potentials (I_p) of about 5.8–5.9 eV as determined by ultraviolet photoelectron spectroscopy (UPS) for its cast film. From these values, the electron affinity (E_a) of poly-1 is estimated to be about 3.2–3.3 eV. This indicates that poly-1 has large I_p and E_a values, and the E_a value is larger than those of poly(*p*-phenylene) (2.1 eV), poly(naphthalene-2,6-diyl) (2.5 eV), and poly(quinoline-2,6-diyl) (2.8 eV), all of which are calculated by a valence effective Hamiltonian method.[16] In the case of poly(*p*-phenylene), the calculated values roughly agree with the experimental estimations (I_p = 5.5 eV and E_g = 3.0–4.0 eV).[16c–e,17]

Nondoped poly-1 and poly-2 are essentially insulators with electrical conductivities (σ) of less than 10^{-10} S cm^{-1}. Sodium-doped poly-1 and poly-2, which are obtained by treatment of the polymers with sodium naphthalide in THF at room temperature,[6–8] have σ values of 1.2×10^{-3} and 8.0×10^{-4} S cm^{-1}, respectively, as measured with pellets prepared by pressing the sodium-doped powder at 200 kg cm^{-2}. However, the sodium-doped samples are sensitive to air, and exposure to air causes a rapid decrease in their electrical conductivity.

As described above, new n-type electrically conducting poly(arylene)s, poly(quinoxaline-5,8-diyl) and poly(2,3-diethylquinoxaline-5,8-diyl), are easily obtained by organometallic processes. Comparison of redox potentials for the n-doping and undoping of poly(arylene)s reveals enhancement of the electron-accepting properties of the polymers by introduction of imine nitrogen(s) in the recurring 1,4-naphthylene units.

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