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Chemical and Electrochemical Preparation of Poly(quinoline-2,6-diyl), Poly(quinoxaline-2,6-diyl), and Poly(1,5-naphthyridine-2,6-diyl) by Using Nickel Complexes. Importance of the 2,6-Bonding for Linear Structure, Highly Extended π-Conjugation, and Strong Electron-accepting Properties

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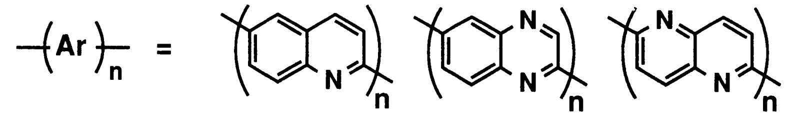
Chemical and electrochemical dehalogenation polycondensations of 2,6-dichloroquinoline, 2,6-dibromoquinoxaline, and 2,6-dichloro-1,5-naphthyridine using nickel complexes afford poly(quinoline-2,6-diyl), poly(quinoxaline-2,6-diyl) and poly(1,5-naphthyridine-2,6-diyl), respectively. These polymers take linear structures, and have more extensively delocalized π-conjugation system as well as higher electron-accepting properties than their isomeric poly(quinoline-5,8-diyl) and poly(quinoxaline-5,8-diyl) as revealed by their λ_{max} positions and reducing potentials.

Recently, preparation of poly(arylene)s constituted of electron-accepting heterocyclic aromatic units, such as poly(pyridine-2,5-diyl),1) poly(2,2'-bipyridine-5,5'-diyl),1c,d) poly(quinolinediyl)s,2) poly(quinoxaline-5,8-diyl) (P(5,8-Qx)),3) and poly(pyrimidine-2,5-diyl),4) by dehalogenation polycondensation of corresponding dihalogenated aromatic compounds with zero-valent nickel (Ni(0)) complex has been reported. These polymers exhibit n-type electrically conducting properties originating from π-deficient nature of the aromatic units containing electron-withdrawing imine nitrogen(s). On the other hand, electrochemical reduction of divalent nickel (Ni(II)) complex generates Ni(0) complex and this Ni(0) complex is useful for dehalogenation polycondensation of dihalogenated aromatic compounds.5) These two polymerization methods afford various π-conjugated polymers with well defined linkage which can not be attained by other polymerization methods, and the polymers thus obtained are suitable for comparison of chemical and physical properties of isomeric poly(arylene)s with different π-conjugation systems.

We now report preparation of new π-conjugated poly(arylene)s, poly(quinoline-2,6-diyl) (P(2,6-Q)), poly(quinoxaline-2,6-diyl) (P(2,6-Qx)), and poly(1,5-naphthyridine-2,6-diyl) (P(2,6-N)), by chemical and electrochemical dehalogenation polycondensation of 2,6-dichloroquinoline (2,6-Cl_2-Q), 2,6-dibromoquinoxaline (2,6-Br_2-Qx), and 2,6-dichloro-1,5-naphthyridine (2,6-Cl_2-1,5-N) by using nickel complexes. These polymers have similar 2,6-naphthylene-like units with imine nitrogen(s) and have more extended π-conjugation system as well as higher electron-accepting properties than their isomeric poly(quinoline-5,8-diyl) (P(5,8-Q)) and P(5,8-Qx), revealing that the 2,6-naphthylene-like bonding between the monomer units is especially suitable for the extensive π-conjugation.

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

$$\mathrm{n\ X\text{-}Ar\text{-}X\ +\ 2n\ e \xrightarrow{Ni(II)L_m} \left(Ar\right)_n\ +\ 2n\ X^-} \qquad (2)$$



P(2,6-Q) P(2,6-Qx) P(2,6-N)

2,6-Cl_2-Q,$^{6)}$ 2,6-Br_2-Qx,$^{7)}$ and 2,6-Cl_2-1,5-N$^{8)}$ were synthesized according to methods in literatures. Chemical polymerization of 2,6-Cl_2-Q using bis(1,5-cyclooctadiene)nickel (Ni(cod)$_2$) was carried out by stirring 2,6-Cl_2-Q (315 mg, 1.59 mmol) with a mixture of Ni(cod)$_2$ (530 mg, 1.93 mmol), 1,5-cyclooctadiene (0.35 cm^3), and 2,2'-bipyridine (300 mg, 1.92 mmol) in N,N-dimethylformamide (DMF) (30 cm^3) for 48 h at 60 °C. Work up of the polymer was carried out in a manner similar to that reported previously.$^{1\text{-}4)}$ Yellow P(2,6-Q) was obtained in high yield (99%). Anal. Found: C, 84.7; H, 3.9; N, 10.2; Cl, 0.0%. Calcd for $(C_9H_5N)_n$: C, 85.0; H, 4.0; N, 11.0%.

Electrochemical polymerization was carried out in an H-shaped three-electrode cell using platinum plates as working and counter electrode, and Ag / 0.1 M $AgNO_3$ electrode as a reference electrode. 2,6-Cl_2-Q (105 mg, 0.53 mmol) and tris(2,2'-bipyridine)nickel(II) bromide ([Ni(bpy)$_3$]Br_2) (416 mg, 0.61 mmol) were added to a DMF (12 cm^3) solution of tetraethylammonium perchlorate ([Et_4N][ClO_4]) (0.25 M). The working electrode was polarized at a potential of -1.7 V *vs.* Ag/Ag^+ for 48 h at 60 °C. The polymer film formed on the working electrode surface was washed with a series of solutions and solvents in a manner similar to that applied for the isolation of the chemically prepared polymer. The yield of polymerization was 86% after 280 C of charge per 2 cm^2 of the platinum electrode (5.4 F per mol of 2,6-Cl_2-Q) was passed. Anal. Found: C, 84.1; H, 4.0; N, 11.0; Cl, 0.0%. Calcd for $(C_9H_5N)_n$: C, 85.0; H, 4.0; N, 11.0%.

Chemical and electrochemical polymerizations of 2,6-Br_2-Qx and 2,6-Cl_2-1,5-N were carried out in a manner similar to the chemical and electrochemical polymerizations of 2,6-Cl_2-Q; yields = 88% and 40% for P(2,6-Qx), and 97% and 66% for P(2,6-N), respectively.

Chemically and electrochemically prepared P(2,6-Q)'s and P(2,6-Qx)'s are soluble in fromic acid, hydrochloric acid, and trifluoroacetic acid, however, P(2,6-N)'s are only partially soluble in these solvents. Weight-average molecular weights (M_w) of chemically and electrochemically prepared P(2,6-Q)'s determined by light scattering method are 15000 and 26000, respectively, and M_w of chemically prepared P(2,6-Qx) is 10000. The degree of depolarization (ρ_v)$^{9)}$ of the chemically and electrochemically prepared P(2,6-Q)'s in formic acid are 0.20 and 0.21, respectively, as measured by the light scattering method. The ρ_v values indicates that P(2,6-Q)'s have a rod-like linear stiff structure. Although a very large ρ_v value (ρ_v = 0.33) has been reported for poly(pyridine-2,5-diyl) with M_w of 3800,$^{1)}$ such a large ρ_v value of about 0.2 for the polymer with fairly large M_w of 26000 has no precedent.

The chemically and electrochemically prepared polymers show almost the same IR spectrum to each other for P(2,6-Q), P(2,6-Qx), and P(2,6-N). The IR spectra of polymers are essentially similar to those of corresponding monomers except for negligibly weak ν(C-halogen) band in the polymers. Solid state ^{13}C-NMR spectra of chemically prepared P(2,6-Q), P(2,6-Qx), and P(2,6-N) show peaks in a range of δ 110-160 ppm.

Figure 1 exhibits cyclic voltammograms (CV's) of P(2,6-Q), P(2,6-Qx), and P(2,6-N) films on the platinum electrode. The electrochemically active cycle observed in a range of -1.5–-2.5 V is assigned to n-doping and undoping of the polymers and the n-doping and undoping reaction can be expresed by the equation (3).

Table 1 shows the comparison of the n-doping potential (E°) and λ_{max} value of P(2,6-Q), P(2,6-Qx), and P(2,6-N) with those of their following isomeric polymers, P(5,8-Q) and P(5,8-Qx). As shown in Table 1, the E° value of P(2,6-Q) is higher than that of P(5,8-Q) by 0.26 V and this shift to the higher E° value is, at least partly, explained by more direct effect of the electron withdrawing imine nitrogen of P(2,6-Q) on the π-conjugation system compared with the imine nitrogen of P(5,8-Q), which exists in the side chain and will not give such a direct effect on the π-conjugation system.

The appearance of the π-π* absorption band of P(2,6-Q) at considerably longer wavelength compared with that of P(5,8-Q) strongly suggests that P(2,6-Q) has much more highly extended π-conjugation system than P(5,8-Q), presumably due to ease in formation of a coplanar structure along the polymer chain because of its *o*-nonsubstituted structure and lack of H at the *o*-N position. On the other hand, P(5,8-Q) has not only an *o*-substituted structure at both the bondings between the monomer units but also *o*-H's at both the bondings, thus making the formation of such a coplanar structure difficult.

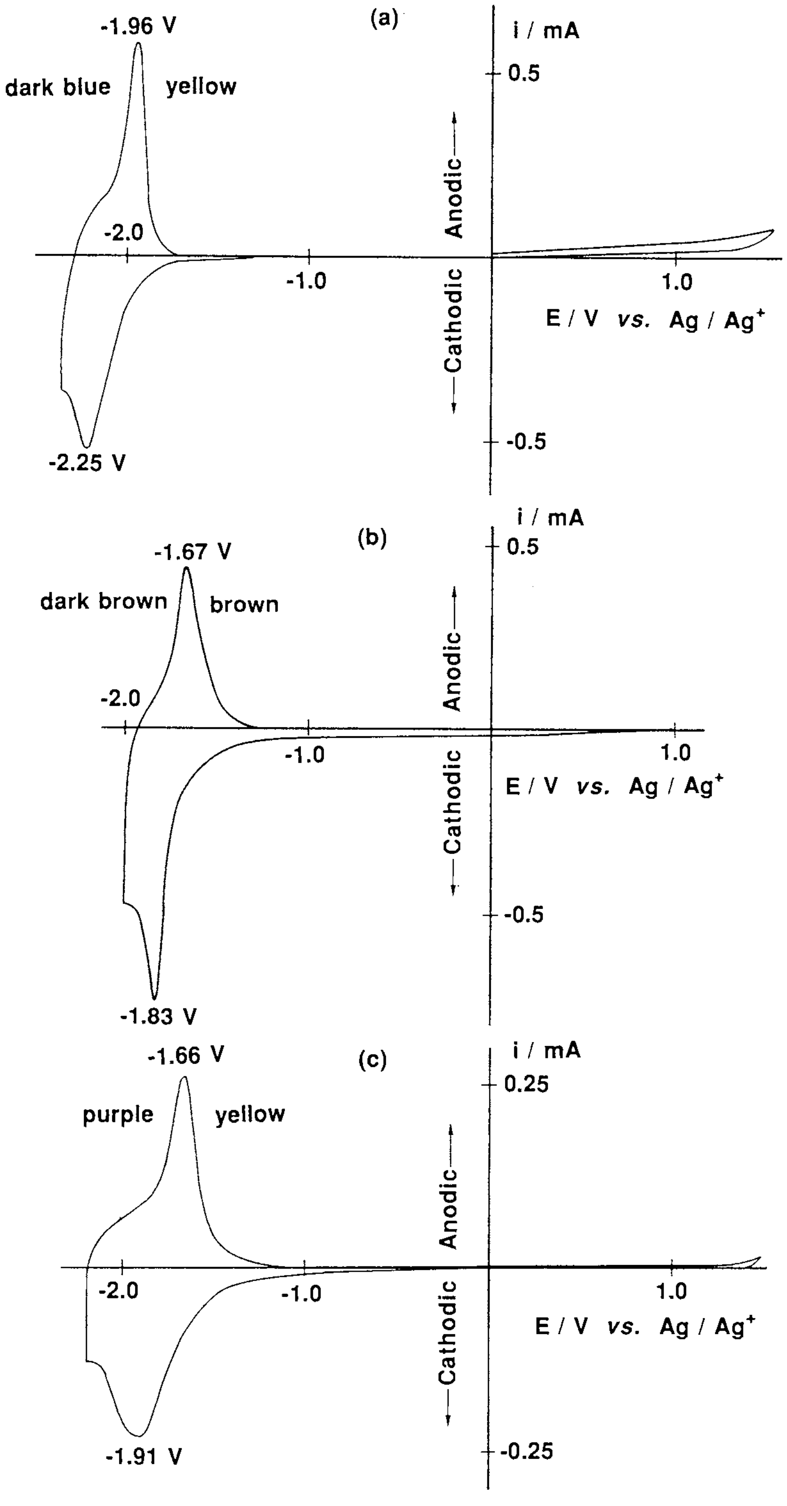
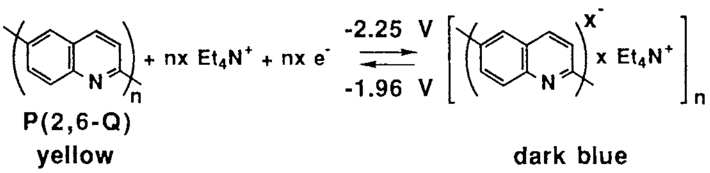


Fig. 1. Cyclic voltammograms of films of (a) P(2,6-Q), (b) P(2,6-Qx), and (c) P(2,6-N) on platinum plates in an acetonitrile solution of $[Et_4N][ClO_4]$ (0.1 M). Sweep rate (a) 5 mV s^{-1} and (b), (c) 10 mV s^{-1}. Color change during doping and undoping is shown in the figure.

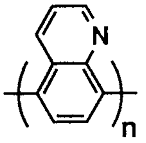
Table 1. Comparison of n-doping potential (E°) and λ_{max} value of polymers

polymer	E° / V[a]	λ_{max} / nm[b]
P(2,6-Q)	-2.11	436
P(5,8-Q)	-2.37	343
P(2,6-Qx)	-1.75	415
P(2,6-N)	-1.79	439
P(5,8-Qx)	-1.98	325

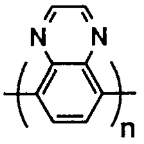
a) *vs*. Ag/Ag$^+$. b) In formic acid.



(3)



P(5,8-Q)[2)]



P(5,8-Qx)[3)]

Comparison of E° and λ_{max} values of P(2,6-Qx) with those of P(5,8-Qx) also supports such view (Table 1). On the other hand, P(2,6-N) gives the E° and λ_{max} values essentially the same as those of P(2,6-Qx), revealing that the positions of the two imine nitrogens have only minor effects on the degree of electron accepting properties and π-conjugation.

Electrical conductivity (σ) of non-doped chemically prepared P(2,6-Q), P(2,6-Qx), and P(2,6-N) are less than 10^{-7} S cm^{-1}. Sodium doping of films of chemically prepared P(2,6-Q), P(2,6-Qx), and P(2,6-N) affords semiconducting materials with the σ values of 2.6×10^{-2} S cm^{-1}, 3.0×10^{-4} S cm^{-1}, and 1.8×10^{-2} S cm^{-1}, respectively, which support the n-type doping properties of the polymers.

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