Poly(1,5-naphthyridine-2,6-diyl) Having a Highly Extended and Electron-Withdrawing π-Conjugation System. Preparation, Optical Properties, and Electrochemical Redox Reaction

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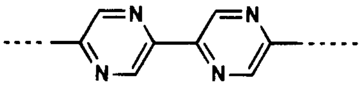
ABSTRACT: Dehalogenation polycondensations of 2,6-dichloro-1,5-naphthyridine with isolated zerovalent nickel complex and electrochemically generated zerovalent nickel complex afford π-conjugated poly(1,5-naphthyridine-2,6-diyl) (P(2,6-N)) in high yields. The electrochemical polymerization gives the polymer as a thin film on the electrode. UV–visible data indicate that P(2,6-N) has, among poly(naphthalene)-like π-conjugated polymers, the longest effective π-conjugation system along the polymer chain due to its less sterically hindered structure to form the π-conjugation system. Electrochemical reduction of P(2,6-N) takes place at $E^\circ = -1.79$ V *vs* Ag/Ag$^+$, the value revealing that P(2,6-N) belongs to the most easily reducible π-conjugated conducting polymers reflecting a very strong π-electron-deficient nature of the 1,5-naphthyridine ring. As for poly(naphthalene-2,6-diyl)-type polymers, introduction of every imine nitrogen leads to a shift of the reducing potential to the positive side by 0.3–0.4 V. Chemically reduced (or n-doped) P(2,6-N) with sodium naphthalide gives a dark blue adduct, which exhibits electrical conductivity of 1.8×10^{-2} S cm^{-1}. The electrochemical reduction of a cast P(2,6-N) film causes a color change with the appearance of a new broad adsorption band in a near-infrared region.

Introduction

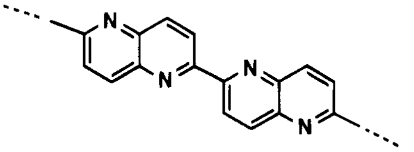
Since it was reported that π-conjugated poly(heterocycle)s[1] such as poly(thiophene-2,5-diyl),[2] poly(pyrrole-2,5-diyl),[3] poly(pyridine-2,5-diyl),[4] and their derivatives had electrical conducting properties as well as chemical and thermal stability, π-conjugated poly(heterocycles)s have been the subject of many papers,[1] although the chemical structure of poly(pyrrole-2,5-diyl) is still controversial.[5]

As for electronic and optical properties of poly(arylene)s including poly(heterocycles)s, the following are recognized: (a) ease of reduction and oxidation of poly(arylene)s reflects that of recurring arylene units; i.e. poly(heterocycle)s constituted of π-electron excessive[6a] five-membered heterocycles (e.g., thiophene and pyrrole) can be easily oxidized (or p-doped) whereas poly(heterocycle)s constituted of π-deficient[6a] heterocycles containing electron-withdrawing imine nitrogen(s)[6b-e] (e.g., pyridine,[4] quinoline,[7] and pyrimidine[2e]) are easily reduced (or n-doped); and (b) the presence or absence of steric repulsion around the bond connecting the arylene units is crucial for formation of an extensively π-conjugated system; for example, the presence of steric repulsion between the *o*-hydrogens (*o*-H's) of the *p*-phenylene units in poly(*p*-phenylene) leads to twisting of the phenylene rings around the bond and thus prevents formation of the coplanar extensively π-conjugated system of poly(*p*-phenylene).

On the basis of these results, it may be expected that poly(heterocycle)s having the electron-withdrawing imine nitrogens at the *o*-positions, e.g.,



poly(pyrazine-2,5-diyl)



poly(1,5-naphthyridine-2,6-diyl)
P(2,6-N)

will form more extensively π-conjugated systems with higher electron-accepting properties due to a minor steric repulsion between the imine N and the *o*-H and they will exhibit interesting optical and electrical properties which are not observed with other poly(arylene)s.

Poly(heterocycle)s have been prepared by various methods including chemical oxidation polymerization, electrochemical oxidation polymerization, organometallic dehalogenation polycondensation, and electrochemical dehalogenation polymerization mediated by organonickel complexes.[1-4] However, among the methods, chemical and electrochemical oxidation polymerization using the logical monomers (e.g., pyrazine and 1,5-naphthyridine for the above shown polymers) is not suited to the preparation of the polymers constituted of π-electron-deficient units, because the oxidation polymerization proceeds more easily with π-electron-excessive monomers like pyrrole whereas getting polymers from π-electron-deficient monomers by the method is difficult. On the contrary, the organometallic dehalogenation polycondensation and electrochemical deha-

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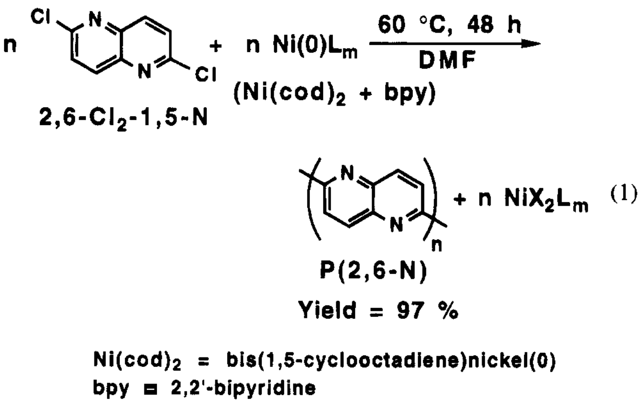
logenation polymerization of the corresponding dihalo monomers are suited to the preparation of poly(heterocycle)s constituted of π-electron-deficient heterocycles.[4,7]

Our preliminary investigation indicates that preparation of poly(pyrazine-2,5-diyl) from its logical monomers, 2,5-dichloropyrazine and 2,5-dibromopyrazine, by the organometallic dehalogenation polycondensation does not proceed well, whereas similar polycondensation of 2,6-dichloro-1,5-naphthyridine[8] gives the above shown poly(1,5-naphthyridine-2,6-diyl) (P(2,6-N)) in a high yield. We here report the preparation of P(2,6-N) by the method and its doping and optical properties, which are considered to reflect the presence of the expected extensively π-conjugated system along the polymer chain. π-Conjugated poly(arylene)s with high electron-accepting ability are important compounds for making electric devices which require n-type conducting organic materials, and obtaining the poly(arylene)s with a higher degree of π-conjugation is expected to contribute to comprehension of electric and optical properties of π-conjugated polymers.

Results and Discussion

Preparation. Chemical Polymerization. Dehalogenation polycondensation of 2,6-Cl_2-1,5-N by using a Ni(0) complex (a mixture of bis(1,5-cyclooctanediene)-nickel (Ni(cod)$_2$) and 2,2′-bipyridine (bpy)) gives P(2,6-N) in a high yield (97%) (eq 1). The reaction conditions



(use of bpy as neutral ligand L at 60 °C) which were used for the preparation of poly(pyridine-2,5-diyl)[4] and poly(quinoline-2,6-diyl)[7] are also suitable to the preparation of P(2,6-N). Repeated preparations give essentially the same results. The chemical polymerization is assumed to proceed through oxidative addition, disproportionation, and reductive elimination, as discussed below.

Data from the elemental analysis (*cf.* Experimental Section) agree with the structure of P(2,6-N), although the elemental analytical data and its IR bands at about 3400 and 1650 cm^{-1} indicate that P(2,6-N) contains a small amount of water.

The chemically prepared P(2,6-N) is partially soluble in formic acid; however, it is insoluble in other organic solvents tested (*e.g.*, chloroform, THF, DMF, DMA, NMP, DMSO). The lower solubility of P(2,6-N) than poly(quinoline-2,6-diyl) (P(2,6-Q)),[7] which is soluble in formic acid, presumably arises from the high symmetric structure of P(2,6-N). Drying up the formic acid solution containing the soluble part of P(2,6-N) under vacuum recovers original P(2,6-N), as judged from IR spectroscopy, indicating that formic acid essentially serves as solvent. The lower solubility of P(2,6-N) and tail absorption of the formic acid solution of P(2,6-N) at the positions of Ar$^+$ and He–Ne lasers prevented the molecular weight from being determined by a light-scattering method. However, if we assume that the both end units have chlorine, the number average molecular weight is calculated as 24 000 from its chlorine content (0.3%, *cf.* Experimental Section). Since some of the polymer molecules seem to contain H-terminated end units,[4d] the value thus calculated is taken as the upper limit of the molecular weight.

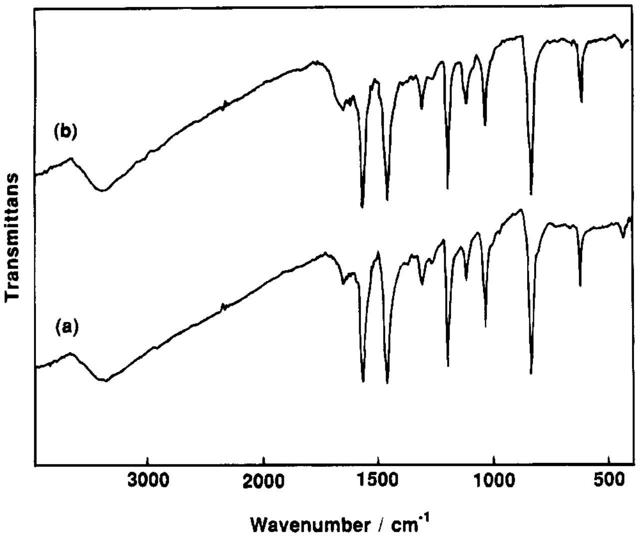


Figure 1. IR spectra of (a) chemically prepared P(2,6-N) and (b) electrochemically prepared P(2,6-N). The signal at about 2350 cm^{-1} is due to CO_2 in air.

Figure 1a shows the IR spectrum of the chemically prepared P(2,6-N). The IR spectrum of P(2,6-N) shows a strong absorption band at 841 cm^{-1} assignable to a C–H out-of-plane vibration. Two strong absorption bands at 1573 and 1466 cm^{-1} are assigned to the ring vibrations of the 1,5-naphthyridine unit. The IR spectrum is very similar to that of 2,6-Cl_2-1,5-N except for a ν(C–Cl) band at 880 cm^{-1}, which is not observed in the IR spectrum of P(2,6-N). Weak aliphatic ν(C–H) absorption bands at 2860 and 2920 cm^{-1} are assigned to occluded DMF; DMF shows the ν(C–H) absorption bands at the same positions.[9] Elongation of drying time (under vacuum) made the absorption bands weaker; however, complete removal of DMF was not possible.

Figure 2 shows the ^{13}C CP/MAS NMR spectrum of chemically prepared P(2,6-N) in the solid state. The peaks of the carbon groups have been assigned on the basis of reported[8] ^{13}C-NMR data of 2,6-Cl_2-1,5-N in $CDCl_3$; the peaks at δ 155, 143, 138, and 122 ppm are assigned to the 4a-C, 2-C, 4-C, and 3-C carbons, respectively, as depicted in Figure 2.

P(2,6-N) has high thermal stability, showing a residual weight of 93 and 55% at 450 and 900 °C, respectively, under nitrogen. The powder X-ray diffraction pattern of P(2,6-N) shows broad diffraction peaks at 2θ (Cu Kα) = 14.5, 18.0, 25.0, and 44.7°. The diffraction pattern of P(2,6-N) is very similar to that of P(2,6-Q),[7] and these two polymers are considered to have almost the same *ab* two-dimensional packing structure (*c* axis is the direction of the polymer chain).

Electrochemical Polymerization. The polymerization can be also achieved by the electrochemically generated Ni(0) species. Figure 3a (dashed line) shows a cyclic voltammogram (CV) of [Ni(bpy)$_3$]Br$_2$ in an acetonitrile solution of [Et$_4$N][ClO$_4$]. As shown in Figure 3a, the Ni(II) complex is reduced to the Ni(0) complex at −1.7 V *vs* Ag/Ag$^+$ and the generated Ni(0) complex is re-oxidized at −1.5 V, and this redox reaction is

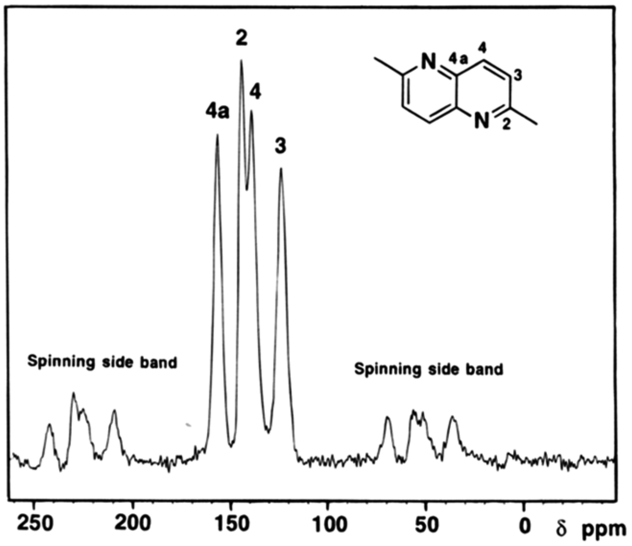


Figure 2. ^{13}C CP/MAS NMR spectrum of chemically prepared P(2,6-N).

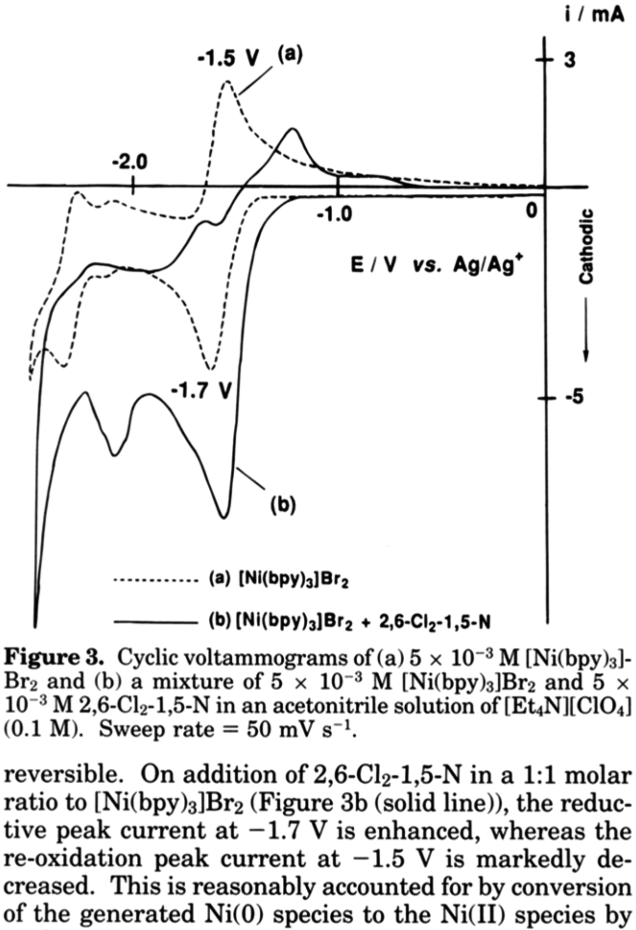


Figure 3. Cyclic voltammograms of (a) 5×10^{-3} M $[Ni(bpy)_3]Br_2$ and (b) a mixture of 5×10^{-3} M $[Ni(bpy)_3]Br_2$ and 5×10^{-3} M 2,6-Cl_2-1,5-N in an acetonitrile solution of $[Et_4N][ClO_4]$ (0.1 M). Sweep rate = 50 mV s^{-1}.

reversible. On addition of 2,6-Cl_2-1,5-N in a 1:1 molar ratio to $[Ni(bpy)_3]Br_2$ (Figure 3b (solid line)), the reductive peak current at −1.7 V is enhanced, whereas the re-oxidation peak current at −1.5 V is markedly decreased. This is reasonably accounted for by conversion of the generated Ni(0) species to the Ni(II) species by oxidative insertion of 2,6-Cl_2-1,5-N to form a Cl−Ar−Ni^{II}−Cl (Ar: arylene) type complex. A new reduction peak at −2.1 V is assigned to reduction of the Cl−Ar−Ni^{II}−Cl species or its disproportionation product like Cl−Ar−Ni^{II}−Ar−Cl complex. The CV curve of the mixture of $[Ni(bpy)_3]Br_2$ and 2,6-Cl_2-1,5-N resembles that of a mixture of $[Ni(bpy)_3]Br_2$ and 2,6-dichloroquinoline.[7] After 10 scans, the electric current due to a couple of n-dopings and n-undopings of P(2,6-N) (*vide infra*) becomes major, as depicted in Figure 4.

Preparative electrochemical polymerization on a platinum plate (2 cm^2) is carried out at a fixed potential, −1.7 V *vs* Ag/Ag$^+$, where the reduction of $[Ni(bpy)_3]Br_2$ occurs. The initial electric current of 20 mA cm^{-2} gradually decreases to 1 mA cm^{-2} after 15 h and zero after 48 h. At the beginning of the polymerization, the surface of the electrode becomes dark green and the electrode is gradually covered with brown polymer film. With prolonged electrochemical polymerization (e.g., after passing 12 C of charge/1 cm^2), all of the electrode is covered with P(2,6-N) film. Figure 5 shows the scanning electron micrograph of the surface of P(2,6-N) film obtained on the platinum electrode after passing 12 C of charge/1 cm^2. The smooth growth of the polymer film indicates that the film is conductive under the electrochemical polymerization conditions. The yield of electrochemical polymerization of 2,6-Cl_2-1,5-N is 97% after passing 210 C of charge. The passed charge corresponds to 4.5 F/mol of 2,6-Cl_2-1,5-N. The yield of electrochemical polymerization is somewhat higher than that of the similar electrochemical polymerization of 2,6-dichloroquinoline (86% after passing of 280 C of charge).[7]

A reaction mechanism[4d,7] involving the following elementary reactions reasonably accounts for the electrochemical polymerization. The mechanism involves

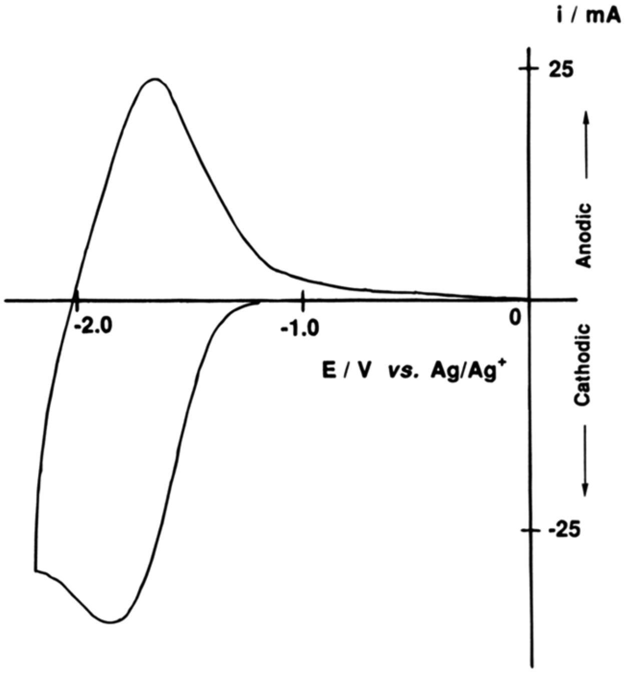


Figure 4. Cyclic voltammogram of a mixture of 5×10^{-3} M $[Ni(bpy)_3]Br_2$ and 5×10^{-3} M 2,6-Cl_2-1,5-N in an acetonitrile solution, after 10 scans.

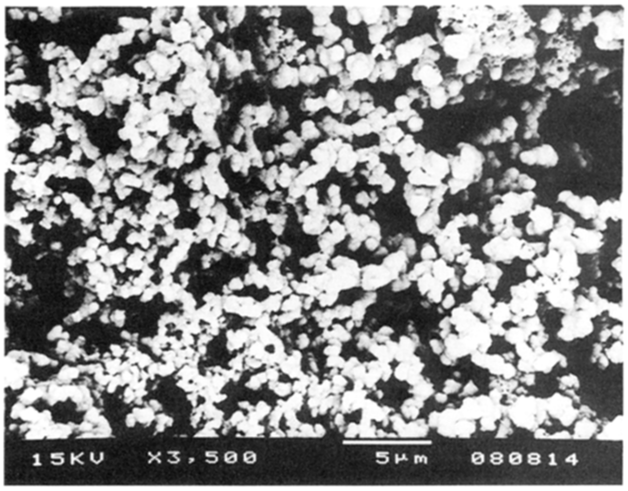
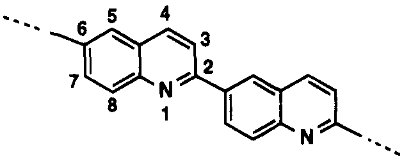


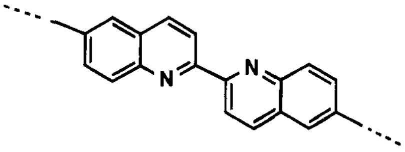
Figure 5. Scanning electron micrograph of the surface of P(2,6-N) films obtained on a platinum electrode after passing 12 C of charge/1 cm^2.

Chart 1. H–T Structure of P(2,6-Q) (Electrochemically Prepared)



λ_{max} = 403 nm

Chart 2. H–H Unit of P(2,2′-bQ)



reduction of Ni(II) complex to Ni(0) complex (eq 2),

$$\mathrm{Ni^{II}L}_m + 2e \rightarrow \mathrm{Ni^{0}L}_m \qquad (2)$$

$$\mathrm{Ni^{0}L}_m + \mathrm{X{-}Ar{-}X} \xrightarrow[\text{addition}]{\text{oxidative}} \mathrm{L}_m\mathrm{Ni(ArX)X} \qquad (3)$$

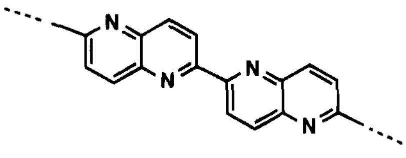
$$2\mathrm{L}_m\mathrm{Ni(ArX)X} \xrightarrow[\text{disproportionation}]{\text{bimolecular}} \mathrm{L}_m\mathrm{Ni(ArX)_2} + \mathrm{L}_m\mathrm{NiX_2} \qquad (4)$$

$$\mathrm{L}_m\mathrm{Ni(ArX)_2} \xrightarrow[\text{elimination}]{\text{reductive}} \mathrm{X{-}Ar{-}Ar{-}X} + \mathrm{L}_m\mathrm{Ni} \qquad (5)$$

oxidative addition of aryl halide (eq 3), disproportionation of the complex thus formed (eq 4), and reductive elimination (eq 5). The propagation process involving coupling between $X(Ar)_xX$ and $X(Ar)_yX$ to give $X(Ar)_{x+y}X$ is also accounted for by a similar reaction mechanism.

The IR spectrum of the electrochemically prepared P(2,6-N)(Figure 1b) is identical to that of the chemically prpared P(2,6-N). The properties (e.g., solubility and thermal stability) of electrochemically prepared P(2,6-N) are very similar to those of the chemically prepared P(2,6-N).

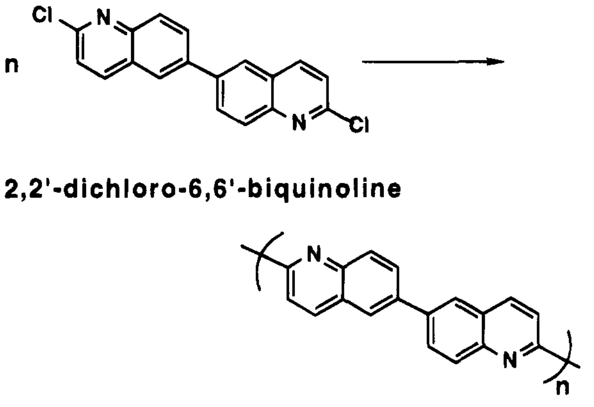
Optical and Doping Properties. Optical Properties. The UV–visible spectra of electrochemically and chemically prepared P(2,6-N)'s measured in formic acid show π–π^* absorption peaks at 438 and 439 nm, respectively.



λ_{max} = 438 or 439 nm

On the other hand, poly(quinoline-2,6-diyl) (P(2,6-Q)), which is prepared by a similar electrochemical polymerization from 2,6-dichloroquinoline by using $[Ni(bpy)_3]Br_2$, exhibits the π–π^* absorption at a somewhat shorter wavelength, λ_{max} = 403 nm,[7] than P(2,6-N) (Chart 1). Monomeric quinoline shows the π–π^* absorption at 300 nm, appearing at almost the same position as the λ_{max} of 1,5-naphthyridine (302 nm), and the difference in the λ_{max} position between P(2,6-Q) and P(2,6-N) seems to be attributable to the difference in the *o*-H repulsion.

In order to reveal the effect of *o*-H more clearly, we have prepared poly(6,6′-biquinoline-2,2′-diyl) (P(2,2′-bQ)) from 2,2′-dichloro-6,6′-biquinoline by an analogous method, and P(2,2′-bQ) thus prepared gives rise to the



2,2′-dichloro-6,6′-biquinoline

(6)

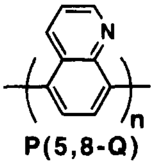
P(2,2′-bQ)

λ_{max} = 431 nm

absorption peak at 431 nm. The appearance of the absorption peak of P(2,2′-bQ) at a position different from that of the electrochemically prepared P(2,6-Q) suggests that the electrochemically prepared P(2,6-Q) contains a large proportion of head-to-tail (H–T) units, as depicted above (Chart 1).

If the electrochemically prepared P(2,6-Q) is mainly constituted by the H–T unit, most of the bonding between the quinoline rings is to receive the *o*-H repulsion to cause the twisting of most of the quinoline rings around the bonding. On the other hand, half of the bondings in P(2,2′-bQ) are expressed as a bonding similar to that in the above depicted P(2,6-N) (Chart 2). The two quinoline rings in P(2,2′-bQ) are thus expected to take a coplanar conformation to make formation of a full π-conjugation system between the two rings possible.

The appearance of the π–π^* absorption band of P(2,6-N) at almost the same position (λ_{max} = 438 or 439 nm) as that of P(2,2′-bQ) (λ_{max} = 431 nm) indicates the importance of the formation of the full π-conjugation system between the two naphthalene-like units, and further expansion of the π-conjugation system gives only a minor effect on the position of the π–π^* transition. In the case of poly(pyridine-2,5-diyl), it is reported that the position of the π–π^* transition is virtually unvaried with the change of its molecular weight in a range of 1200 (degree of polymerization (DP) = 16) through 3800 (DP = 49).[4d] As for poly(quinoline)s, connection of the quinoline ring at the 5,8-positions leads to formation of much more sterically hindered poly(quinoline-5,8-diyl),[10]



λ_{max} = 343 nm

P(5,8-Q)

and it shows the π–π^* absorption peak at 343 nm, a considerably shorter wavelength than the λ_{max} of P(2,6-Q).

In contrast to the electrochemically prepared P(2,6-Q), chemically prepared P(2,6-Q) from 2,6-dichloroquinoline using the Ni(0) complex exhibits the absorption band at almost the same position as observed with P(2,2′-bQ), suggesting chemically prepared P(2,6-Q) is mainly constituted of head-to-head (H−H) units presumably due to preferential formation of the H−H type dimer at the first step in the chemical polymerization because of a different in chemical reactivity (regioselectivity) between the C−Cl bonds at the 2- and 6-positions; similar preferential formation of the H−H type π-conjugated poly(3-alkylthiophene-2,5-diyl) by the chemical polymerization using the Ni complex has been reported.[2e,f,11]

Figure 6 depicts ^{1}H-NMR spectra of P(2,2′-bQ), chemically prepared P(2,6-Q) and electrochemically prepared P(2,6-Q). As shown in Figure 6a, P(2,2′-bQ) gives rise to a simple ^{1}H-NMR spectrum in accord with the symmetrical microstructure; the simple ^{1}H-NMR pattern further suggests all of the units in the polymer take the same conformation, presumably an *s*-trans conformation (cf. Chart 2) concerning the bond connecting the two quinoline units depicted in Figure 6a. Assignment of the signals has been made by comparing the ^{1}H-NMR data with those of quinoline derivatives like 2,2′-dichloro-6,6′-biquinoline (eq 6), and the signal area ratio agrees well with the structure of the polymer. The chemically prepared P(2,6-Q) gives rise to a ^{1}H-NMR spectrum (Figure 6b) similar to that of P(2,2′-bQ), whereas the ^{1}H-NMR spectrum (Figure 6c) of the electrochemically prepared P(2,6-Q) shows a complicated absorption pattern. These ^{1}H-NMR results agree with the above described assumption that the chemically prepared P(2,6-Q) is mostly constituted of the H−H unit whereas the electrochemically prepared P(2,6-Q) does not have such a regulated structure. The presence of an electrochemical field near the electrode and/or the difference in the active Ni species may be responsible for obtaining P(2,6-Q) with a microstructure considerably different from that of the chemically prepared P(2,6-Q). IR spectra of P(2,2′-bQ) and chemically prepared P(2,6-Q) are essentially identical to each other, whereas that of the electrochemically prepared P(2,6-Q) shows some difference in a ring vibration region.[12] The band gap of P(2,6-N) estimated from the edge (470 nm) of the adsorption spectrum is 2.63 eV.

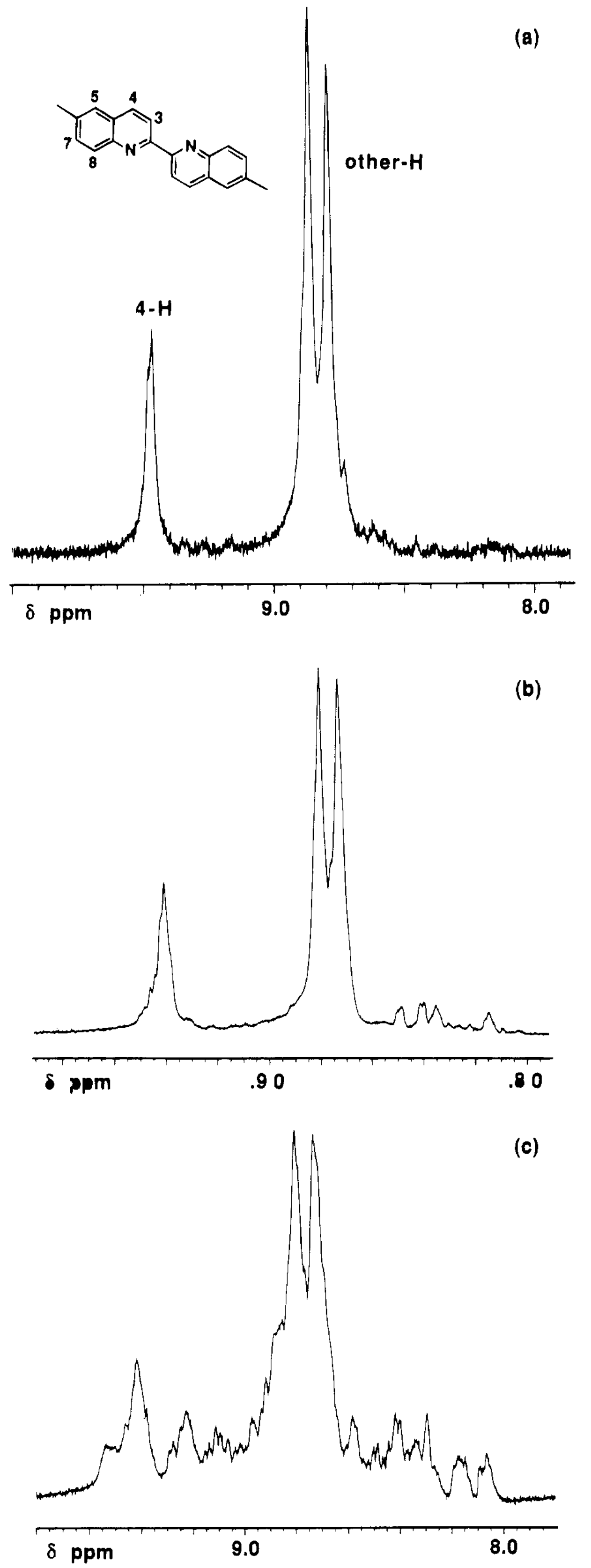
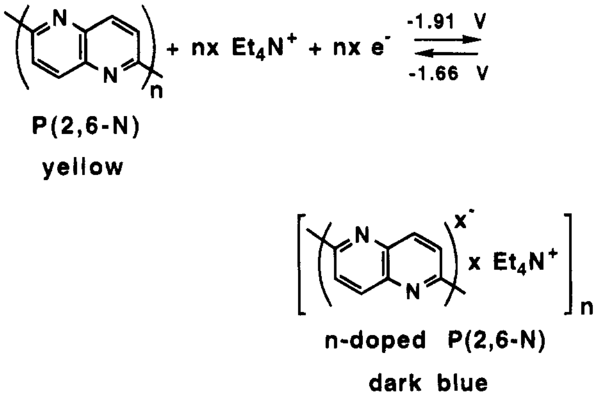


Figure 6. ^{1}H-NMR spectra of (a) P(2,2′-bQ), (b) chemically prepared P(2,6-Q) with Ni(0) complex, and (c) electrochemically prepared P(2,6-Q) at 500 MHz in CF_3COOD.

Electrical and Electrochemical Properties of P(2,6-N). Figure 7 shows a CV curve of P(2,6-N) film electrochemically deposited on a platinum electrode. As shown in Figure 7, reduction or n-doping of P(2,6-N) film starts about −1.4 V *vs* Ag/Ag$^+$ and an n-doping cathodic peak E_{pc} appears at −1.91 V *vs* Ag/Ag$^+$ (eq 7). The n-doping is accompanied by a color change from yellow to dark blue, and a reverse color change takes place at the n-undoping process with an n-undoping anodic peak E_{pa} at −1.66 V *vs* Ag/Ag$^+$. In contrast to the easy n-doping, P(2,6-N) film is electrochemically inactive in an anodic sweep range (0−1.5 V *vs* Ag/Ag$^+$), and only a weak electric current due to electrochemical decomposition of solvent at high voltage is observed. These electrochemical behaviors of P(2,6-N) are consistent



(7)

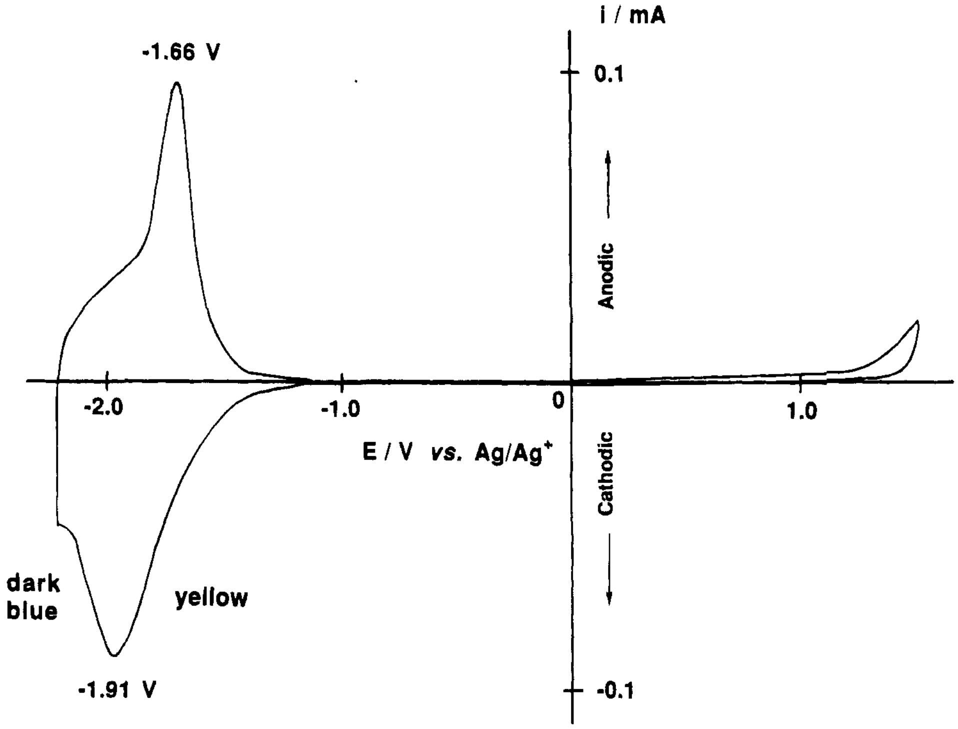
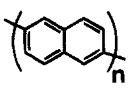
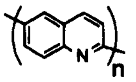
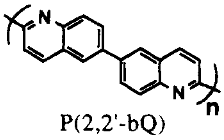
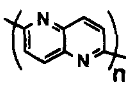


Figure 7. Cyclic voltammogram of electrochemically prepared P(2,6-N) film in an acetonitrile solution of $[Et_4N][ClO_4]$ (0.1 M). Sweep rate = 10 mV s^{-1}.

Table 1. Redox Potential for n-Doping of Poly(arylene)s

poly(arylene)[a]	E° / V[b]
 P(2,6-Na)[c]	-2.50
 P(2,6-Q)[d]	-2.11
 P(2,2'-bQ)	-2.06
 P(2,6-N)	-1.79

[a] P(2,6-Na) = poly(naphthalene-2,6-diyl), P(2,6-Q) = poly(quinoline-2,6-diyl), P(2,2'-bQ) = poly(2,2'-biquinoline-6,6'-diyl), P(2,6-N) = poly(1,5-naphthyridine-2,6-diyl). [b] *vs* Ag/Ag⁺. [c] From ref 13. [d] From ref 7.

with the strong π-electron-deficient properties of the 1,5-naphthyridine ring. As for naphthalene-type aromatic compounds, the value of electron affinity increases linearly with the number of imine nitrogen(s) in the compound.[6b–d] The polymer film is stable during repeated scanning, showing essentially the same CV.

The average value of E_{pc} and E_{pa}, -1.79 V *vs* Ag/Ag⁺, is taken as the $E°$ value of the redox reaction. Table 1 shows the comparison of the $E°$ value of the n-doping of poly(naphthalene-2,6-diyl) (P(2,6-Na)),[13] P(2,6-Q),[7] P(2,2'-bQ), and P(2,6-N), all of which have a similar 2,6-naphthylene-like structure. As shown in Table 1, the $E°$ value increases in the order P(2,6-Na) < P(2,6-Q) < P(2,6-N), indicating introduction of the electron-withdrawing imine nitrogen(s) in the polymer chain increases the electron-accepting property of the poly(arylene).[2e,7,14] The $E°$ value increases by about 0.3–0.4 V for introducing every imine nitrogen in the naphthalene-like unit. A small difference in the $E°$ between P(2,6-Q) and P(2,2'-bQ) may be ascribed to the taking of the coplanar binaphthalene-like structure in P(2,2'-bQ).

A platinum electrode coated with a film of chemically prepared P(2,6-Q) can also be prepared by spreading the formic acid solution of the polymer on the electrode and evaporation of the solvent under vacuum, and the polymer film shows the same CV curve and color change as described above.

Figure 8 shows the change of the UV–visible absorption spectrum of a film of the chemically prepared P(2,6-N) on an indium–tin oxide (ITO) glass electrode during the electrochemical n-doping processes. At 0 V *vs* Ag/Ag⁺, the P(2,6-N) film gives rise to an absorption peak of nondoped P(2,6-N). At -1.7 V, the π–π* transition peak of nondoped P(2,6-N) decreases and new absorption peaks appear at 520 and 700 nm. When P(2,6-N) film is highly doped with Et_4N^+ at -2.1 V, the π–π* transition peak of original P(2,6-N) further decreases and two peaks at about 450 nm and a very broad absorption toward the near-infrared appear. The color of heavily n-doped film is dark blue (eq 7). This change of the UV–visible spectrum of P(2,6-N) during the cation doping is similar to those of P(2,6-Q)[7] and poly(2,5-thienylene vinylene).[15] Formation of polaron and/or bipolaron seems to be responsible for the two new absorption bands.

Electrical conductivity (σ) of pristine chemically prepared P(2,6-N) film is less than 10^{-7} S cm^{-1}. Sodium doping of chemically prepared P(2,6-N) film with sodium naphthalide affords a dark blue n-doped polymer, which has a σ value of 1.8×10^{-2} S cm^{-1}. The σ value of the Na-doped P(2,6-N) is almost the same as that of the Na-doped P(2,6-Q) ($\sigma = 2.6 \times 10^{-2}$ S cm^{-1}).[7] The n-doped

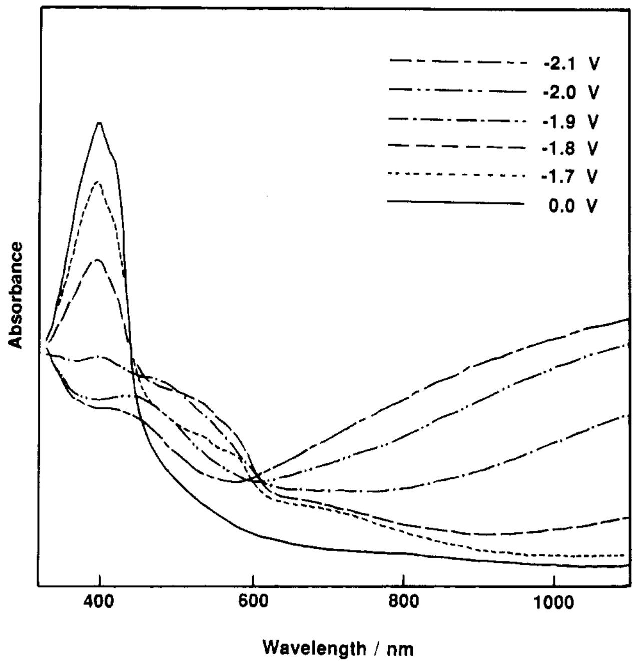


Figure 8. Charge of UV–visible spectrum of chemically prepared P(2,6-N) film on an ITO glass electrode during electrochemical n-doping in an acetonitrile solution of $[Et_4N][ClO_4]$ (0.1 M). Potential: *v* Ag/Ag^+.

state of the polymer is stable under nitrogen, argon, and vacuum. However, exposure of the dark blue Na-doped P(2,6-N) to air causes a slow color change to the original yellow color of P(2,6-N), revealing that the n-doped state is sensitive to oxygen and/or moisture in air.

Conclusion and Scope

P(2,6-N) is obtained in high yields by chemical and electrochemical dehalogenation polycondensation of 2,6-dichloro-1,5-naphthyridine using Ni complexes. The electrochemically prepared polymer is obtained as a thin film on the electrode. The UV–visible spectra indicate that P(2,6-N) has a long effective π-conjugation system along the polymer chain due to its less sterically hindered structure to form the π-conjugation system. The polymer film is electrochemically active and shows an n-type doping–undoping cycle at $E° = 1.79$ V *vs* Ag/Ag^+ with reversible color change between yellow and dark blue. Chemical doping with sodium naphthalide gives similar dark blue n-doped P(2,6-N), which shows semiconductivity. Obtaining π-conjugated polymers like P(2,6-N) is expected to contribute to design electronic and optical devices which require electron-conducting n-type organic materials. For example, preparation of a light-emitting diode with similar electron-withdrawing n-type poly(2,3-diphenylquinoxaline-5,8-diyl) has been reported.[14c]

Experimental Section

Materials. Bis(1,5-cyclooctadiene)nickel, $Ni(cod)_2$,[16] and tris(2,2′-bipyridine)nickel(II) bromide, $[Ni(bpy)_3]Br_2$,[17] were prepared as reported in the literature. *N,N*-dimethylformamide (DMF), acetonitrile, and tetrahydrofuran (THF) were dried, distilled, and stored under nitrogen. $[Ni(bpy)_3]Br_2$ and tetraethylammonium perchlorate $[Et_4N][ClO_4]$ were dried before use.

Synthesis of Monomers. 2,6-Dichloro-1,5-naphthyridine. 2,6-Dichloro-1,5-naphthyridine ($2,6\text{-}Cl_2\text{-}1,5\text{-}N$) was synthesized by chlorination of 1,5-naphthyridine[18] according to a method reported by Newkome.[8]

2,2′-Dichloro-6,6′-biquinoline. 6-Chloroquinoline *N*-oxide was synthesized from 6-chloroquinoline[19] according to a method reported in the literature.[8] 6,6′-Biquinoline di-*N*-oxide was synthesized by a C–C coupling reaction of 6-chloroquinoline *N*-oxide by using $Ni(cod)_2$ complex (1 mol/mol of the oxide) at 60 °C for 24 h in DMF (yield = 66%). 2,2′-Dichloro-6,6′-biquinoline was synthesized by chlorination of 6,6′-biquinoline di-*N*-oxide according to a method reported by Bobranski.[20] ^1H NMR ($CDCl_3$, δ, TMS): 7.46 (d, J = 8.59 Hz, 1H, 3-H), 8.13 (s, 3H, 5-H, 7-H, and 8-H), 8.21 (d, J. = 8.59 Hz, 1H, 4-H). Anal. Calcd for $C_{18}H_{10}N_2Cl_2$: C, 66.5; H, 3.1; N, 8.6; Cl, 21.8. Found: C, 66.2; H, 2.7; N, 8.2; Cl, 21.9.

Polymerization. Chemical polymerization of $2,6\text{-}Cl_2\text{-}1,5\text{-}N$ using $Ni(cod)_2$ was carried out in a manner similar to that reported previously.[4a] Under a nitrogen atmosphere, stirring $2,6\text{-}Cl_2\text{-}1,5\text{-}N$ (105 mg, 0.53 mmol) with a mixture of $Ni(cod)_2$ (180 mg, 0.65 mmol), 1,5–cyclooctadiene (0.14 mL), and 2,2′-bipyridine (112 mg, 0.72 mmol) in DMF (12 mL) for 48 h at 60 °C yielded a precipitate of the polymer. The polymer was stirred with an aqueous ammonia solution and an aqueous solution of ethylenediaminetetraacetic acid to remove nickel compounds, then washed wtih stirring in methanol and toluene to remove low molecular weight compounds, and dried. The polymer was obtained as a yellow powder. Anal. Calcd for $(C_8H_4N_2{\cdot}0.5H_2O)_n$: C, 70.1; H, 3.7; N, 20.4. Calcd for $(C_8H_4N_2{\cdot}0.4H_2O{\cdot}0.07DMF)_n$: C, 70.3; H, 3.8; N, 2.06. Found: C, 69.8; H, 3.3; N, 20.1; Cl, 0.3.

Electrochemical polymerization was carried out in a nitrogen-filled H-shaped three-electrode cell with cathodic and anodic compartments separated by a sintered glass disk. Platinum plates (2 cm^2) were used as working and counter electrodes, respectively, and an Ag/0.1 M $AgNO_3$ electrode was used as a reference electrode. In a typical experiment, $2,6\text{-}Cl_2\text{-}1,5\text{-}N$ (97 mg 0.48 mmol) and $[Ni(bpy)_3]Br_2$ (372 mg, 0.54 mmol) were added to a DMF (12 mL) solution of $[Et_4N]ClO_4$ (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 treated with a series of washing solutions and solvents in a manner similar to that applied to the isolation of the chemically prepared P(2,6-N). Anal. Calcd for $(C_8H_4N_2{\cdot}0.6H_2O)_n$: C, 69.2; H, 3.8; N, 20.2. Calcd for $(C_8H_4N_2{\cdot}0.5H_2O{\cdot}0.1DMF)_n$: C, 69.0; H, 4.0; N, 20.4. Found: C, 69.3; H, 3.2; N, 20.1; Cl, 0.0.

Electrochemical polymerization of 2,2′-dichloro-6,6′-biquinoline was carried out analogously. P(2,2′-bQ) was obtained as a yellow powder in 92% yield. Anal. Calcd for $(C_9H_5N)_n$: C, 85.0; H, 4.0; N, 11.0. Found: C, 83.2; H, 3.7; N, 10.8; Cl, 0.0. Chemical polymerization of 2,2′-dichloro-6,6′-biquinoline also gave P(2,2′-bQ), showing an IR spectrum identical to that of the electrochemically prepared P(2,2′-bQ).

Measurements. IR spectra were recorded on a JASCO IR-810 spectrometer with KBr pellets. ^{13}C-NMR spectra were taken using a JEOL JNM-GX-500 spectrometer. UV–visible spectra and TGA curves were recorded on a JASCO Ubest-35 spectrometer and a Shimadzu thermoanalyzer DT-30, respectively. X-ray diffraction was obtained with a Rigaku Geigerflux RAD-B system.

Cyclic voltammograms and change of absorption spectrum during electrochemical doping were measured in an acetonitrile solution containing 0.1 M $[Et_4N][ClO_4]$. Electrolysis and cyclic voltammetry were carried out with a Hokuto Denko HA-501 galvanostat/potentiostat and a Hokuto Denko HB-104 function generator.

Films of P(2,6-N) were obtained by casting from a formic acid solution containing the soluble part of the polymer onto a glass plate. The P(2,6-N) film on the glass plate was doped by sodium naphthalide in THF at room temperature and dried under vacuum. The electrical conductivity of the Na-doped sample was measured by a four-probe method in the chamber filled with argon.

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References and Notes

(1) (a) Skotheim, T. A., Ed. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986; Vols. I and II. (b) MacDi-

armid, A. G.; Heeger, A. J. *NRL Memo. Rep.* (Proceedings of the Molecular Electron Devices Workshop) **1981**, AD-A 05816, 208. (c) Salaneck, W. R.; Clark, D. L.; Samuelsen, E. J. E. *Science and Applications of Conducting Polymers*; Adam Hilger: New York, 1990. (d) Andre, J.-M.; Delhalle, J.; Bredas, J.-L. *Quantum Chemistry Aided Design of Organic Polymers*; World Scientific: London, 1991.

(2) (a) Yamamoto, T.; Sanechika, K.; Yamamoto, A. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 9. (b) Sanechika, K.; Yamamoto, T.; Yamamoto, A. *Polym. Prepr. Jpn.* **1979**, *28*, 966. (c) Jpn. Pat. Doc. 81-47421, Tokyo Institute of Technology, invs.; Yamamoto, T.; Sanechika, K.; Yamamoto, A. *Chem. Abstr.* **1981**, *95*, 98612k; Appl. No. 79-124813. (d) Tourillon, G.; Garnier, F. *J. Electrochem. Soc.* **1983**, *130*, 2042. (e) Yamamoto, T. *Prog. Polym. Sci.* **1992**, *17*, 1153. (f) Yamamoto, T.; Sanechika, K. *Chem. Ind. (London)* **1982**, 301.

(3) Kanazawa, K. K.; Diaz, A. F.; Geiss, R. H.; Gill, W. G.; Kwak, J. F.; Logan, J. A.; Robolt, J. F.; Street, G. B. *J. Chem. Soc., Chem. Commun.* **1979**, 854.

(4) (a) Yamamoto, T.; Hayashi, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2091. (b) Yamamoto, T.; Ito, T.; Kubota, K. *Chem. Lett.* **1988**, 153. (c) Schiavon, G.; Zotti, G. *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *242*, 131. (d) Yamamoto, T.; Maruyama, T.; Zhou, Z.-H.; Ito, T.; Fukuda, T.; Yoneda, Y.; Begum, F.; Ikeda, T.; Sasaki, S.; Takezoe, H.; Fukuda, A.; Kubota, K. *J. Am. Chem. Soc.* **1994**, *116*, 4832.

(5) Yamamoto, T.; Zhou, Z.-H.; Ando, I.; Kikuchi, M. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 833.

(6) (a) Newkome, G. R.; Paudler, W. W. *Contemporary Heterocyclic Chemistry*; John Wiley: New York, 1982. (b) Dillow, G. W.; Kebarle, P. *Can. J. Chem.* **1989**, *67*, 1628. (c) Tabner, B. J.; Yandle, J. R. *J. Chem. Soc.* **1968**, 381. (d) Nenner, I.; Schulz, G. J. *J. Chem. Phys.* **1975**, *62*, 1747. (e) Wiberg, K. B.; Leuis, T. P. *J. Am. Chem. Soc.* **1970**, *92*, 7154.

(7) Saito, N.; Kanbara, T.; Nakamura, Y.; Yamamoto, T.; Kubota, K. *Macromolecules* **1994**, *27*, 756.

(8) Newkome, G. R.; Garbis, S. J. *J. Heterocycl. Chem.* **1978**, *15*, 685.

(9) Pouchert, C. J. *The Aldrich Library of Infrared Spectra*, 2nd ed.; Aldrich: Milwaukee, WI, 1975; p 392.

(10) Kanbara, T.; Saito, N.; Yamamoto, T.; Kubota, K. *Macromolecules* **1991**, *24*, 5883.

(11) Miyazaki, Y.; Yamamoto, T. *Synth. Met.* **1994**, *64*, 69.

(12) An IR absorption peak of P(2,2′-bQ) and chemically prepared P(2,6-Q) at 1547 cm^{-1} is split into two signals (with separation of about 10 cm^{-1}) in the IR spectra of the electrochemically prepared P(2,6-Q). In addition, two sharp peaks of P(2,2′-bQ) and chemically prepared P(2,6-Q) at 1443 and 1475 cm^{-1} (peak strength ratio of about 1:2) are broadened in the IR spectrum of the electrochemically prepared P(2,6-Q) to give an unsharpened peak at 1475 cm^{-1}.

(13) Tomat, R.; Zecchin, S.; Schiavon, G.; Zotti, G. *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *252*, 215.

(14) (a) Yamamoto, T.; Ito, T.; Sanechika, K.; Hishinuma, M. *Synth. Met.* **1988**, *25*, 103. (b) Kanbara, T.; Yamamoto, T. *Macromolecules* **1993**, *26*, 3464. (c) Yamamoto, T.; Inoue, T.; Kanbara, T. *Jpn. J. Appl. Phys.* **1994**, *33*, L25.

(15) Onoda, M.; Morita, S.; Iwasa, T.; Nakayama, H.; Yoshino, K. *Jpn. J. Appl. Phys.* **1992**, *31*, 1107.

(16) Wilke, G. *Angew. Chem.* **1960**, *72*, 581.

(17) Jeager, F. M.; van Dijk, J. A. *Z. Anorg. Chem.* **1936**, *227*, 273.

(18) Hamada, Y.; Takeuchi, I. *Chem. Pharm. Bull.* **1971**, *19*, 1857.

(19) Fitton, A. O.; Smalley, R. K. *Practical Heterocyclic Chemistry*; Academic Press: New York, 1968; p 82.

(20) Bobranski, B. *Chem. Ber.* **1938**, *71*, 578.

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