Macromolecules **1994,** *27,* 756–761

Electrochemical and Chemical Preparation of Linear π-Conjugated Poly(quinoline-2,6-diyl) Using Nickel Complexes and Electrochemical Properties of the Polymer

Nobuo Saito, Takaki Kanbara, Yoshiyuki Nakamura, and Takakazu Yamamoto*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

Kenji Kubota

Faculty of Engineering, Gumma University, Tenjincho, Kiryu 376, Japan

Received July 13, 1993; Revised Manuscript Received November 1, 1993[⊗]

ABSTRACT: Dehalogenation polycondensations of 2,6-dichloroquinoline with electrochemically generated zerovalent nickel complex and isolated zerovalent nickel complex afford π-conjugated poly(quinoline-2,6-diyl) (P(2,6-Q)) in high yields. Comparison of the polymerizations using various dihaloquinolines and dihaloisoquinolines as the monomer reveals that the electrochemical polymerization is more sensitive to the position of halogen in the monomer than the chemical polymerization and proceeds most smoothly for 2,6-dihaloquinoline. The electrochemically and chemically prepared P(2,6-Q)'s have molecular weights of 26 000 and 15 000, respectively, as determined by a light scattering method, which also reveals that P(2,6-Q)'s have a linear rodlike stiff structure with ρ_v values of 0.21 and 0.20, respectively, and a large specific refractive index increment ($\Delta n/\Delta c$ = 0.57 cm^3 g^{-1}) in formic acid. The electrochemical method gives the polymer as a thin film on the electrode. The cyclic voltammogram of the film of P(2,6-Q) shows a reversible electrochemical n-type doping–undoping cycle at considerably higher potential (*ca.* −2.1 V *vs* Ag/Ag$^+$) than that of isomeric poly(quinoline-5,8-diyl), with a reversible color change of the film between yellow (undoped) and dark blue (doped); n-doping with sodium naphthalide also gives an electrically conducting dark blue adduct. UV–visible as well as cyclic voltammetric data suggest that P(2,6-Q) has a longer effective π-conjugation system along the polymer chain than other isomeric poly(quinolinediyl)s and poly(isoquinolinediyl)s due to its less sterically hindered structure to form the π-conjugation system. The electron affinity of P(2,6-Q) is estimated as 3.3 eV.

Introduction

The synthesis and electrical properties of π-conjugated poly(arylene)s have become an active area of recent polymer science, and numerous reports have been published on p-type electrically conducting poly(arylene)s such as poly(thiophene-2,5-diyl)[1] and poly(pyrrole-2,5-diyl).[2] However, studies on n-type electrically conducting poly(arylene)s are still limited. Recently, we reported preparation of poly(pyridine-2,5-diyl),[3] poly(quinoline-5,8-diyl) and poly(isoquinoline-1,4-diyl),[4] and poly(pyrimidine-2,5-diyl)[5] constituted of electron-withdrawing aromatic rings with imine nitrogen(s) and that these polymers exhibited n-type electrically conducting properties. Preparation of these polymers was mainly carried out by dehalogenation polycondensation of dihaloaromatic compound X–Ar–X with zerovalent nickel (Ni(0)) complex (eq 1).[1b,3–6]

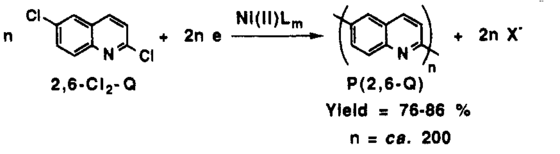
$$n\ \mathrm{X{-}Ar{-}X} + n\ \mathrm{Ni(0)L}_m \longrightarrow \mathrm{-\!\!\left(Ar\right)\!\!-}_n + \mathrm{NiX_2L}_m \qquad (1)$$

On the other hand, it is known that electrochemical reduction of divalent nickel (Ni(II)) complex generates Ni(0) complex (eq 2), and this Ni(0) complex is useful for dehalogenation polycondensation of dihalogenated arylenes such as 1,4-dibromobenzene,[7] 2,7-dibromo-9,10-dihydrophenanthrene,[8] 2,5-dibromopyridine,[9] and 3,6-dibromo-*N*-ethylcarbazole.[10]

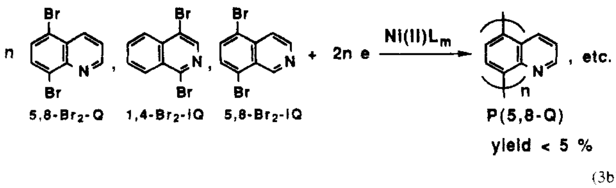
$$\mathrm{Ni(II)L}_m + 2\mathrm{e} \longrightarrow \mathrm{Ni(0)L}_m \qquad (2)$$

These polymerization methods using isolated Ni(0) complex and electrochemically generated Ni(0) complex afford poly(arylene)s with a well-defined linkage between the monomer units. In addition, the electrochemical polymerization usually gives the polymer as a thin film on the electrode,[7–10] which is suitable for revealing electrochemical properties of the obtained polymer.

In the course of our studies on π-conjugated poly(quinolinediyl)s and poly(isoquinolinediyl)s,[4] we have found that the electrochemical polymerization using Ni(II) complex is more sensitive to the position of halogen than the chemical polymerization and proceeds most smoothly for 2,6-dihaloquinoline among various dihaloquinolines (eq 3a). The highest yield attained by using 2,6-dihaloquinoline is presumably due to the less sterically hindered structure of the obtained polymer, P(2,6-Q), compared with the other π-conjugated poly(quinolinediyl)s like poly(quinoline-5,8-diyl) (P(5,8-Q)) (eq 3b).



(3a)



(3b)

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1993.

0024-9297/94/2227-0756$04.50/0

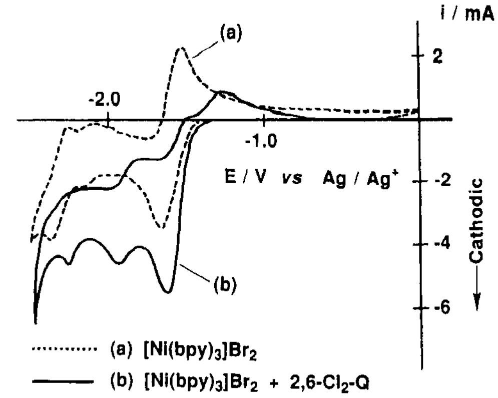
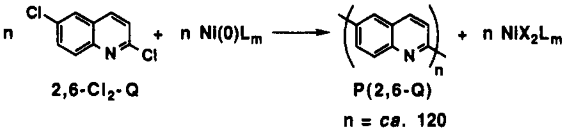


Figure 1. Cyclic voltammograms of (a) 5×10^{-3} M [Ni(bpy)$_3$]Br$_2$ and (b) a mixture of 5×10^{-3} M [Ni(bpy)$_3$]Br$_2$ and 1×10^{-2} M 2,6-Cl$_2$-Q in an acetonitrile solution of [Et$_4$N][ClO$_4$] (0.1 M). Sweep rate = 50 mV s^{-1}.

P(2,6-Q) has been also prepared by the method using isolated Ni(0) complex in a high yield (eq 4).

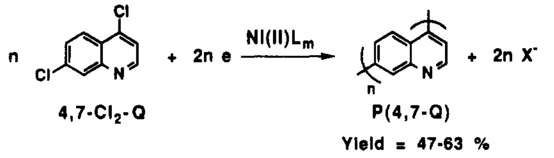


(4)

Stille has prepared P(2,6-Q) derivatives by the Friedlander reaction;[11] however, preparation of nonsubstituted P(2,6-Q) by this method is difficult due to the occurrence of side reactions.[12] Chiang *et al.* prepared nonsubstituted quinoline oligomers by dehydrogenative oligomerization of tetrahydroquinoline.[13] However, nonsubstituted P(2,6-Q) with high molecular weight has not been prepared yet.

Both the electrochemically and chemically prepared P(2,6-Q)'s exhibit interesting optical and electrochemical properties fairly different from those of previously reported P(5,8-Q)[4] (*cf.* eq 3b) presumably because of the presence of a more highly extended π-conjugation in P(2,6-Q) than in P(5,8-Q) due to the less hindered structure of P(2,6-Q). We now report the electrochemical and chemical preparation of P(2,6-Q)'s and properties of the polymers.

Electrochemical polymerization of 4,7-dichloroquinoline also proceeds smoothly to give nonconjugated poly(quinoline-4,7-diyl) (P(4,7-Q)), which has already been prepared chemically,[4] in good yield (47–63%) (eq 5), and we outline the electrochemical preparation of P(4,7-Q).



(5)

Results and Discussion

Electrochemical Preparation of Poly(quinoline-2,6-diyl) (P(2,6-Q)). Electrochemical Redox Reaction of Ni(II) Complex and Polymerization. Figure 1 shows cyclic voltammograms (CV) of (a) tris(2,2′-bipyridine)nickel(II) bromide ([Ni(bpy)$_3$]Br$_2$) (broken line) and (b) a mixture of [Ni(bpy)$_3$]Br$_2$ and 2,6-dichloroquinoline (2,6-Cl$_2$-Q) (solid line) in an acetonitrile solution of tetraethylammonium perchlorate ([Et$_4$N][ClO$_4$]). As shown in Figure 1a, Ni(II) complex is reduced to Ni(0) complex at −1.7 V *vs* Ag/Ag$^+$ and the generated Ni(0) complex is reoxidized at −1.5 V, and this redox reaction is reversible.

Table 1. Electrochemical Polymerization of Dihaloquinolines and Dihaloisoquinolines[a]

run	monomer[b]	monomer/ mM	Ni complex[c]/mM	temp/ °C	time/ h	yield[d]/ %
1	2,6-Cl$_2$-Q	40	40	60	48	86
2	2,6-Cl$_2$-Q	40	20	60	48	76
3	2,6-Cl$_2$-Q	40	10	60	48	0
4	4,7-Cl$_2$-Q	40	40	60	22	47
5	4,7-Cl$_2$-Q	40	40	90	24	53
6	4,7-Cl$_2$-Q	40	40	120	24	63
7	5,8-Br$_2$-Q	20	20	120	16	3
8	1,4-Br$_2$-iQ	40	40	120	44	1
9	1,4-Br$_2$-iQ	40	60	60	96	2
10	5,8-Br$_2$-iQ	40	40	120	18	3
11	5,8-Br$_2$-iQ	40	60	60	72	3

[a] Solvent = *N,N*-dimethylformamide (DMF); electrolyte = [Et$_4$N][ClO$_4$] (0.25 M). [b] 2,6-Cl$_2$-Q = 2,6-dichloroquinoline; 4,7-Cl$_2$-Q = 4,7-dichloroquinoline; 5,8-Br$_2$-Q = 5,8-dibromoquinoline; 1,4-Br$_2$-iQ = 1,4-dibromoisoquinoline; 5,8-Br$_2$-iQ = 5,8-dibromoisoquinoline. [c] Ni complex = [Ni(bpy)$_3$]Br$_2$. [d] Based on polymer weight.

In the presence of 2,6-Cl$_2$-Q (Figure 1b), the reductive peak current at −1.7 V is enhanced, whereas the reoxidation peak current at −1.5 V is markedly decreased. This is reasonably accounted for by conversion of the generated Ni(0) species to Ni(II) species by oxidative insertion of 2,6-Cl$_2$-Q to form a Cl–Ar–Ni(II)–Cl complex. A new reduction peak at −1.9 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$_2$-Q resembles that of a mixture of [Ni(bpy)$_3$]Br$_2$ and 2,5-dibromopyridine.[14] Repeated scanning gives a yellow film on the electrode surface, whereas the electrochemical polymerization is mainly carried out at −1.7 V *vs* Ag/Ag$^+$, which corresponds to the reduction potential of the Ni(II) species.

Table 1 summarizes the results of the polymerization. As shown in Table 1, the electrochemical polymerization of 2,6-Cl$_2$-Q proceeds smoothly at 60 °C by using [Ni(bpy)$_3$]Br$_2$ as the Ni(II) species in an equimolar or half-molar amount to 2,6-Cl$_2$-Q (runs 1 and 2). The yield of polymerization in the presence of an equimolar amount of [Ni(bpy)$_3$]Br$_2$ is 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) is passed. The obtained P(2,6-Q) in 76% yield in the presence of the half-molar amount of [Ni(bpy)$_3$]Br$_2$ (run 2) indicates that the Ni(II) species is recycled and works as a catalyst to some extent. However, use of a smaller amount of [Ni(bpy)$_3$]Br$_2$ (run 3) does not lead to the deposition of P(2,6-Q) although precipitation of a gray material in the solution suggests the formation of oligomeric materials.

At the beginning of the electrochemical polymerization, the surface of the platinum electrode becomes dark green and the electrode is gradually covered with brown polymer film. At the early stage of the polymerization, after passing 6 C of charge per cm^2, P(2,6-Q) is deposited as spots on the surface of the electrode. However, after prolonged electrochemical polymerization (*e.g.*, after passing 12 C of charge per cm^2), all of the surface of the electrode is covered with P(2,6-Q) film. Figure 2 shows the scanning electron micrograph of the surface of P(2,6-Q) film obtained on the platinum electrode after passing 12 C of charge per cm^2.

The electrochemical polymerization at −1.7 V *vs* Ag/Ag$^+$ gives P(2,6-Q) in a nondoped neutral insulating state as judged from its doping voltage (*ca.* −2.1 V *vs* Ag/Ag$^+$; *vide infra*), and consequently formation of only a thin electrode-blocking film may be expected. However, in the actual polymerization, the film on the electrode continues

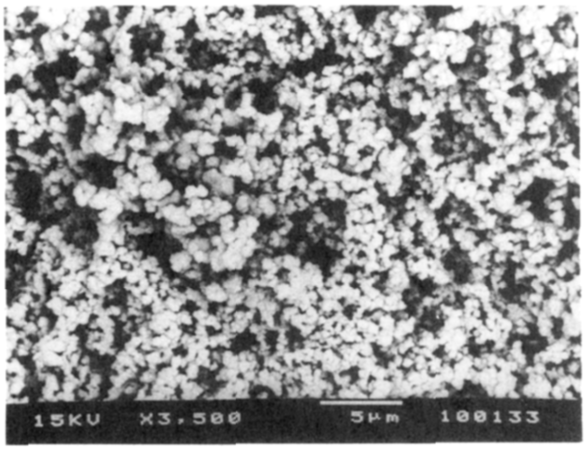


Figure 2. Scanning electron micrograph of the surface of P(2,6-Q) films obtained on a platinum electrode after passing 12 C of charge per cm^2.

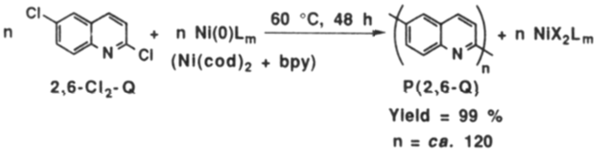
growing and becomes granular. If P(2,6-Q) has head-to-head junctions, the chelating 2,2′-biquinoline part of P(2,6-Q) appears to be able to coordinate to Ni(II) species in the polymerization system, and the smooth growth of the polymer may be related to Ni-mediated electron transfer. A CV curve of the electrochemically formed P(2,6-Q) film in an acetonitrile solution of $[Et_4N][ClO_4]$ (0.1 M) shows a redox cycle at *ca.* −1.7 V *vs* Ag/Ag^+, which is assignable to redox of Ni(II) species coordinated to the nitrogen of the π-conjugated polymers.[15] Elemental analysis of the unwashed polymer film indicates that *ca.* 15 wt % of ash remains after burning the sample. Enhancement of the electrical conductivity of chelating poly(2,2′-bipyridine-5,5′-diyl) by coordination to a transition metal has been reported,[15] and the Ni(II) species are removed during the workup of P(2,6-Q) as revealed by its elemental analysis (*cf.* Experimental Section).

The content of Cl in the polymer is 0%, revealing that chain growth by coupling proceeds by removing Cl at the 2- and 6-positions.

Electrochemical Polymerization of Other Monomers. In contrast to the occurrence of the facile electrochemical polymerization of 2,6-Cl_2-Q, similar electrochemical polymerization of 5,8-dibromoquinoline, 1,4-dibromoisoquinoline, and 5,8-dibromoisoquinoline gives the corresponding polymers only in low yields (<5%, eq 3b, runs 7–11 in Table 1). The low yields may be ascribed to steric repulsion between the monomer units in the polymer chains which have *ortho*-substituted structures at both of the two bonds between the monomer units. Electrochemical polymerization of 1,4-dibromoisoquinoline on a platinum electrode by using bis(triphenylphosphine)nickel(II) bromide ($NiBr_2(PPh_3)_2$) deposits a film which contains PPh_3 in a high proportion, and removing PPh_3 from the film is difficult.

Polymerization of 4,7-dichloroquinoline (4,7-Cl_2-Q) gives P(4,7-Q), which has one *ortho*-substituted and one non-*ortho*-nonsubstituted structure at the bonds between the monomer units, and the electrochemical polymerization proceeds well with 4,7-Cl_2-Q (eq 5, runs 4–6 in Table 1) although it gives somewhat lower yields and requires a higher temperature compared with the electrochemical polymerization of 2,6-Cl_2-Q.

Chemical Preparation of P(2,6-Q). Dehalogenation polycondensation of 2,6-Cl_2-Q by using Ni(0) complex (a mixture of bis(1,5-cyclooctadiene)nickel ($Ni(cod)_2$) and 2,2′-bipyridine (bpy)) gives P(2,6-Q) quantitatively (eq 6).



(6)

The high yield and somewhat larger degree of polymerization (n = *ca.* 120) than that (n = 85) of previously reported P(5,8-Q) prepared analogously[4] are compatible with the favored formation of π-conjugated poly(quinolinediyl) linked at the 2,6-positions. The chemically prepared P(2,6-Q) shows no halogen content, and $[\eta] = 0.44$ dL g^{-1} in formic acid at 29 °C.

Attempts to polymerize 2,6-Cl_2-Q by using Mg as the dehalogenation material in the presence of nickel complex catalyst[3a,16] have not been successful due to the low reactivity of 2,6-Cl_2-Q against Mg (*cf.* Experimental Section). Stirring a mixture of 2,6-Cl_2-Q and Mg in the presence of a catalytic amount of $NiCl_2$(diphenylphosphinoethane) ($NiCl_2$(dppe)) in THF under reflux did not give the polymer either.

Characterization and Properties of P(2,6-Q). Both the electrochemically and chemically prepared P(2,6-Q)'s are soluble in formic acid, hydrochloric acid, and trifluoroacetic acid; however, they are insoluble in other organic solvents tested (*e.g.*, chloroform, THF, DMF, DMA, NMP, and DMSO). Since evaporation of formic acid from the formic acid solution of P(2,6-Q) gives pure P(2,6-Q) as proved by IR spectroscopy, formic acid is considered to have no strong interaction with P(2,6-Q) and essentially serves as solvent. On the other hand, P(2,6-Q) seems to be dissolved in hydrochloric acid by forming its salt with HCl.

Electrochemically and chemically prepared P(2,6-Q)'s have weight-average molecular weights (M_w) of 26 000 and 15 000, respectively, as determined by light scattering. The degrees of depolarization (ρ_v)[17] of the electrochemically and chemically prepared P(2,6-Q)'s measured by light scattering in formic acid are 0.21 and 0.20, respectively. The ρ_v values of 0.21 and 0.20 suggest that P(2,6-Q)'s have a rodlike linear stiff structure having a π-conjugation system with mobile electrons along the polymer chains. Polymer showing such a large ρ_v value in spite of its considerably long polymer chain has no precedent, although the ρ_v values of P(2,6-Q)'s are not so large as that ($\rho_v = 0.33$) of poly(pyridine-2,5-diyl) with M_w of 3800.[3] The large ρ_v value suggests that aggregation of P(2,6-Q) does not take place in the solution, at least in the dilute solution used for the light scattering measurement. A decrease in the ρ_v value due to such an aggregation has been proposed for poly(isoquinoline-1,4-diyl) in $CHCl_3$.[4]

P(2,6-Q)'s exhibit a large specific refractive index increment of $\Delta n/\Delta c = 0.57$ cm^3 g^{-1}, and the large value compared with that of usual non-π-conjugated polymers ($\Delta n/\Delta c = 0.1$–0.2 cm^3 g^{-1}) is related to the presence of delocalized π-electrons along the polymer chain.

Figure 3 shows IR spectra of electrochemically and chemically prepared P(2,6-Q)'s. The electrochemically prepared P(2,6-Q) and chemically prepared P(2,6-Q) show essentially the same IR spectrum. The IR spectrum of P(2,6-Q) shows a strong absorption band at 826 cm^{-1} assignable to a C–H out-of-plane vibration. Strong absorption bands at 1583 and 1475 cm^{-1} are assigned to the skeletal vibration of the quinoline ring. The IR spectra of P(2,6-Q) are very similar to that of 2,6-Cl_2-Q except for a ν(C–Cl) band at 1090 cm^{-1}. The ^1H-NMR spectra of electrochemically and chemically prepared P(2,6-Q)'s in trifluoroacetic acid-*d* show peaks in the range δ 8–10 due

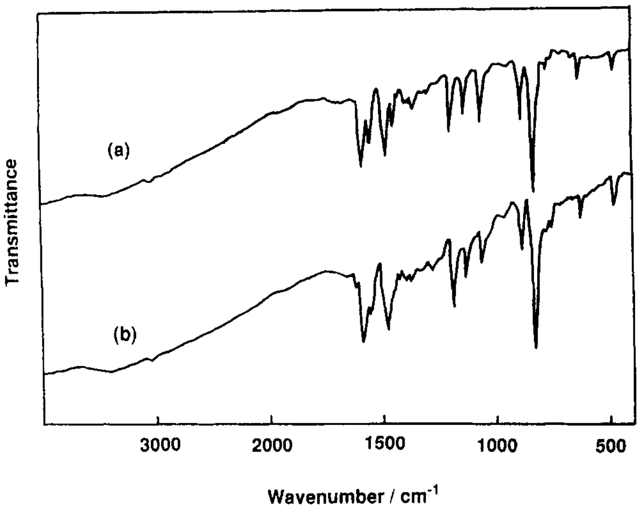


Figure 3. IR spectra of (a) chemically prepared P(2,6-Q) and (b) electrochemically prepared P(2,6-Q).

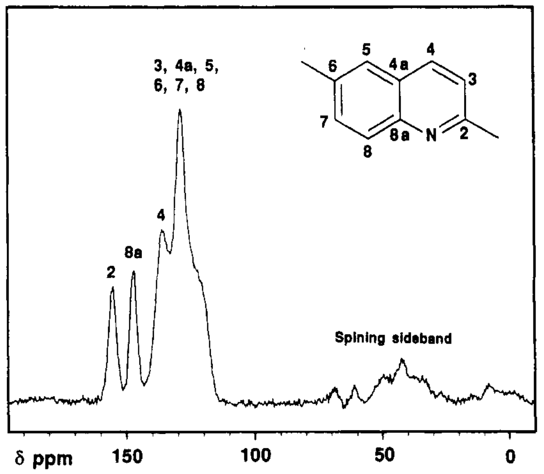


Figure 4. ^{13}C CP/MAS spectrum of chemically prepared P(2,6-Q).

to the aromatic protons of the quinoline ring. Figure 4 shows the ^{13}C CP/MAS NMR spectrum of chemically prepared P(2,6-Q) in the solid state. The peaks of the carbon groups have been assigned on the basis of solution ^{13}C-NMR spectral data of quinoline and 2,6-dichloroquinoline. The peaks at δ 155, 147, and 136 are assigned to the 2-C, 8a-C, and 4-C carbons of the quinoline ring, respectively, and the peak at δ 129 is assigned to an overlapped peak of the 3-C, 4a-C, 5-C, 6-C, 7-C, and 8-C carbons.

The UV-visible spectrum of electrochemically prepared P(2,6-Q) measured in formic acid shows π–π^* absorption peaks at 288 and 403 nm. The absorption peaks of P(2,6-Q) are shifted to longer wavelength compared with those (λ_{max} = 258, 322, and 343 nm) of P(5,8-Q),[4] suggesting that P(2,6-Q) has a longer effective π-conjugation system than P(5,8-Q), presumably due to a better coplanarity of the polymer because of the smaller steric repulsion between the monomer units; not only the non-*ortho*-substituted structure but also the absence of *o*-H at the nitrogen of the quinoline ring are expected to give the longer effective π-conjugation system in P(2,6-Q). The formic acid solution and the cast film of chemically prepared P(2,6-Q) give a broad fluorescence peak at 550 and 580 nm, when irradiated by 435- and 415-nm light, respectively, and these values are shifted to longer wavelength compared with that of P(5,8-Q) (fluorescence peak at 503 nm when irradiated by 340-nm light in formic acid).

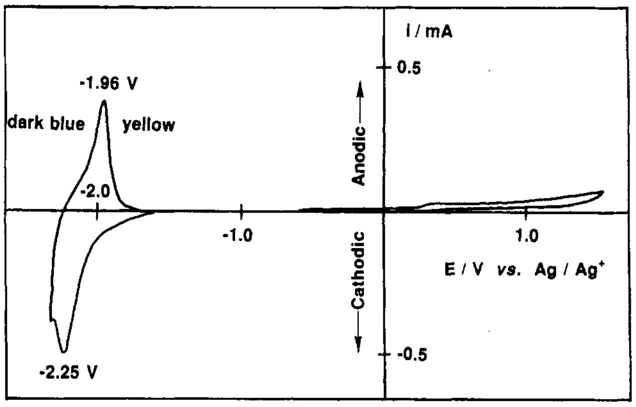
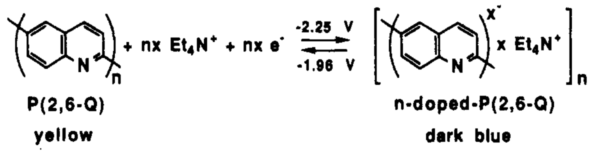


Figure 5. Cyclic voltammogram of electrochemically prepared P(2,6-Q) film in an acetonitrile solution of [Et$_4$N][ClO$_4$] (0.1 M). Sweep rate = 5 mV s^{-1}.

The TGA curve of the chemically prepared P(2,6-Q) reveals a very high thermal stability with only 30% weight loss at 900 °C under nitrogen, and this weight loss is comparable to those of substituted polyquinolines prepared by the acid-catalyzed Friedlander reaction.[18] The small difference between the found value and the calculated value in elemental analysis may arise from the high thermal stability of the polymer. Powder X-ray diffraction patterns of both the electrochemically and chemically prepared P(2,6-Q)'s show broad diffraction peaks at 2θ(Cu Kα) = 15.3, 18.0, 24.5, 27.2, and 44.3°. The broadening of the peaks suggests the presence of both the head-to-head and head-to-tail structures in the polymer.

The electrochemically prepared P(4,7-Q) exhibits essentially the same ^{1}H-NMR and IR spectra of those of chemically prepared P(4,7-Q).[4]

Electrical and Electrochemical Properties of P(2,6-Q). Figure 5 shows a CV curve of P(2,6-Q) film electrochemically deposited on the platinum electrode. As shown in Figure 5, P(2,6-Q) film gives rise to an electrochemically active cycle in the reduction region with an n-doping peak at −2.25 V *vs* Ag/Ag$^+$ and an undoping peak at −1.96 V (eq 7).



(7)

The P(2,6-Q) film is electrochemically inert in the oxidation region, and only a weak electric current due to electrochemical decomposition of solvent is observed.

The polymer film is stable during repeated scanning, showing essentially the same CV. These doping and undoping processes are accompanied by a reversible color change. The color of the P(2,6-Q) film changes from yellow to dark blue during doping. 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 evaporating the solvent under vacuum, and the polymer film shows the same CV curve and color change as those described above.

The redox potential value of P(2,6-Q) is shifted to the positive side by *ca.* 0.4 V from that of poly(naphthalene-2,6-diyl) ($E°$ = −2.5 V *vs* Ag/Ag$^+$),[19] consistent with the general trend that the introduction of electron-withdrawing imine nitrogen enhances the electron-accepting properties of the poly(arylene).[3b,6,20] It is noted that the redox potential value of P(2,6-Q) is higher than that of P(5,8-Q) ($E°$ = −2.37 V)[4] by 0.26 V. In the case of P(5,8-Q), it has

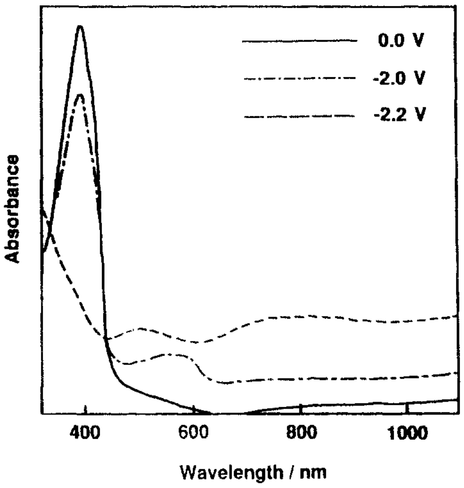


Figure 6. Change of the UV-visible spectrum of chemically prepared P(2,6-Q) film on an ITO electrode during electrochemical doping in an acetonitrile solution of $[Et_4N][ClO_4]$ (0.1 M).

a poly(*p*-phenylene) backbone along the polymer chain and a pyridine ring as a side chain, and consequently the effect of the electron-withdrawing imine nitrogen is considered indirect. On the other hand, in the case of P(2,6-Q), the entire quinoline ring seems to participate directly in the π-conjugation along the polymer chain to enhance the electron-accepting properties of the polymer, and the more effective π-conjugation will also assist the enhancement of the electron-accepting properties.

The change of the UV-visible absorption spectrum of the chemically prepared P(2,6-Q) on an indium-tin oxide (ITO) electrode during the electrochemical n-doping processes is shown in Figure 6. At 0.0 V *vs* Ag/Ag^+, the neutral nondoped P(2,6-Q) gives rise to an absorption peak at 403 nm. At -2.0 V, the π-π^* transition peak decreases and a new absorption peak appears at 580 nm. When P(2,6-Q) film is highly doped with Et_4N^+ at -2.2 V, the π-π^* transition peak at 403 nm further decreases and broad peaks at *ca.* 500 and 800 nm appear. The color of the heavily doped film is dark blue. The electrochemically prepared P(2,6-Q) film shows essentially the same change in the UV-visible spectrum during the n-doping. This change of the UV-visible spectrum of P(2,6-Q) during the cation doping is similar to those of poly(thiophene-2,5-diyl)[21] and poly(pyrrole-2,5-diyl)[22] during anion doping and that of poly(2,5-thienylenevinylene)[23] during cation doping. Formation of electronic states like polaron and bipolaron are suggested in the electrochemical cation doping of P(2,6-Q); the absorption peak at 580 nm at the intermediate reduction potential may be ascribed to polaron whereas as those at 500 and 800 nm at higher reduction potential may be ascribed to bipolaron.

The band gap (E_g) of P(2,6-Q) is estimated as 2.5 eV from the onset of the optical absorption band, and the polymer has ionization potentials (IP) of *ca.* 5.8 eV as determined by ultraviolet photoelectron spectroscopy (UPS) for its cast film. From these values, the electron affinity (EA) of the polymer is estimated as 3.3 eV. This indicates that P(2,6-Q) has large IP and EA values, and the EA value of the polymer is larger than that of poly(*p*-phenylene) (2.1 eV) and poly(naphthalene-2,6-diyl) (2.5 eV),[24] which are calculated by the valence effective Hamiltonian (VEH) method. Brêdas *et al.* have reported that the E_g, IP, and EA values of P(2,6-Q), which are calculated by the VEH method, are 3.2, 6.0, and 2.8 eV, respectively.[25] These estimated values essentially agree with the results described above and explain the facile n-type doping properties of P(2,6-Q).

The electrical conductivity (σ) of pristine chemically prepared P(2,6-Q) film is less than 10^{-7} S cm^{-1}. Sodium doping of chemically prepared P(2,6-Q) film affords semiconducting material with an electrical conductivity of 2.6×10^{-2} S cm^{-1}, supporting the n-type doping property of P(2,6-Q). The σ value of the Na-doped P(2,6-Q) is higher than that of the Na-doped P(5,8-Q) ($\sigma = 3.5 \times 10^{-4}$ S cm^{-1}),[4] suggesting that the polymer has a longer effective π-conjugation system than the isomeric poly(quinolinediyl)s.

Conclusion

P(2,6-Q) is obtained in high yield by electrochemical and chemical dehalogenation polycondensation of 2,6-dichloroquinoline using Ni complexes. The polymer has a well-defined linkage between the monomer units. The electrochemically prepared polymer is obtained as a thin film on the electrode. The polymer film is electrochemically active and shows an n-type doping-undoping cycle at -2.11 V *vs* Ag/Ag^+. The UV-visible spectrum and CV data indicate that P(2,6-Q) has a longer effective π-conjugation system along the polymer chain than other isomeric poly(quinolinediyl)s and poly(isoquinolinediyl)s, presumably due to its less sterically hindered structure to form the π-conjugation. The color of the polymer film changes from yellow to dark blue during n-type doping. The electrical conductivity of sodium-doped polymer film is 2.6×10^{-2} S cm^{-1}.

Experimental Section

Materials. 2,6-Dichloroquinoline was synthesized by chlorination of 6-chloroquinoline[26] according to a method reported by Bobranski.[27] 5,8-Dibromoquinoline, 1,4-dibromoisoquinoline, and 5,8-dibromoisoquinoline were prepared by methods reported by de la Mare and co-workers,[28] Sanders and co-workers,[29] and Gordon and Pearson,[30] respectively. Commercially available 4,7-dichloroquinoline was used after recrystallization. $Ni(cod)_2$,[31] $[Ni(bpy)_3]Br_2$,[32] $NiBr_2(PPh_3)_2$,[33] and $NiCl_2(dppe)$[34] were prepared as reported in the literature. *N,N*-Dimethylformamide (DMF) and acetonitrile were dried by CaH_2, distilled, and stored under nitrogen. $[Ni(bpy)_3]Br_2$ and $[Et_4N][ClO_4]$ were dried before use.

Polymerization. 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, and an Ag/0.1 M $AgNO_3$ electrode was used as a reference electrode. In a typical experiment (run 1 in Table 1), 2,6-Cl_2-Q (105 mg, 0.53 mmol) and $[Ni(bpy)_3]Br_2$ (416 mg, 0.61 mmol) were added to a DMF (12 cm^3) 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 aqueous ammonia and an aqueous solution of ethylenediaminetetraacetic acid to remove nickel compounds, then treated with methanol and toluene to remove low molecular weight products, and dried; yield = 86%. 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.

The polymerization of other monomers listed in Table 1 was carried out analogously. Chemical polymerization of 2,6-Cl_2-Q using $Ni(cod)_2$ was carried out in a manner similar to that reported previously.[1b,3-5] Under a nitrogen atmosphere, 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 DMF (30 cm^3) for 48 h at 60 °C yielded a precipitate of the polymer. The polymer was treated with a series of washing solutions and solvents in a manner similar to that applied for the isolation of the electrochemically prepared P(2,6-Q). The polymer was obtained as a yellow powder in 99% yield. 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.

Attempted reaction of 2,6-Cl_2-Q (71 mg, 0.36 mmol) with Mg grains (9.6 mg, 0.40 mmol), which were activated by vigorous stirring under argon overnight, in THF (3 mL) under reflux did not cause any apparent decrease of the Mg grains even after 20 h. A catalytic amount of NiCl$_2$(dppe) was added to the reaction mixture, and the mixture was stirred for 15 h under reflux; however, formation of P(2,6-Q) was not observed.

Measurements. IR spectra were recorded on a JASCO IR-810 spectrometer with KBr pellets. UV–visible spectra, fluorescence spectra, and TGA curves were recorded on a JASCO Ubest-35 spectrometer, a Hitachi F-4010 fluorescence spectrophotometer, and a Shimadzu DT-30 thermoanalyzer, respectively. ^{1}H-NMR and ^{13}C CP/MAS NMR spectra were taken with a JEOL JNM-GX-500 spectrometer. X-ray diffraction and ultraviolet photoelectron spectroscopy (UPS) measurements were carried out with a Rigaku Geigerflex RAD-B system and a Rikenkagaku AC-1 system, respectively.

The intrinsic viscosity of P(2,6-Q) in formic acid was determined with a Ubbelohde viscometer in thermostated water, which give a linear relation between η_{sp}/c (dL g^{-1}) and the concentration c (g dL^{-1}, c = 0.012–0.062 g dL^{-1}) at 29 °C: $\eta_{sp}/c = 0.44 + 2.52c$.

Cyclic voltammetry and the change of the absorption spectrum during electrochemical doping were measured in an acetonitrile solution containing 0.1 M [Et$_4$N][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-Q) were cast from a formic acid solution of the polymer onto glass plates. The P(2,6-Q) films on the glass plates were doped by sodium naphthalide in THF at room temperature and dried under vacuum. The electrical conductivities of the sodium-doped samples were measured by a four-probe method in the chamber filled with argon.

Acknowledgment. We are very grateful to Tetsuji Inoue of TDK Corp. for UPS measurements.

References and Notes

(1) (a) Yamamoto, T.; Sanechika, K.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1497; *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 8; *Polym. Prepr. Jpn.* **1979**, *28*, 966. (b) Yamamoto, T.; Morita, A.; Miyazaki, Y.; Maruyama, T.; Wakayama, H.; Zhou, Z.-H.; Nakamura, Y.; Kanbara, T.; Sasaki, S.; Kubota, K. *Macromolecules* **1992**, *25*, 1214. (c) Yamamoto, T.; Morita, A.; Maruyama, T.; Zhou, Z.-H.; Kanbara, T.; Sanechika, K. *Polym. J.* **1990**, *22*, 187. (d) Kobayashi, M.; Chen, J.; Chung, T.-C.; Moraes, F.; Heeger, A. J.; Wudl, F. *Synth. Met.* **1984**, *9*, 77. (e) Kaneto, K.; Kohno, Y.; Yoshino, K.; Inuishi, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 382.

(2) (a) Diaz, A. F.; Kanazawa, K. K.; Gardini, G. P. *J. Chem. Soc., Chem. Commun.* **1979**, 635. (b) Diaz, A. F.; Castillo, J. I. *J. Chem. Soc., Chem. Commun.* **1980**, 397. (c) Bull, R. A.; Fan, F.-R. F.; Bard, A. J. *J. Electrochem. Soc.* **1981**, *129*, 1009.

(3) (a) Yamamoto, T.; Hayashi, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2091. (b) Yamamoto, T.; Ito, T.; Sanechika, K.; Hishinuma, M. *Synth. Met.* **1988**, *25*, 103. (c) Yamamoto, T.; Ito, T.; Kubota, K. *Chem. Lett.* **1988**, 153. (d) Yamamoto, T.; Maruyama, T.; Kubota, K. *Chem. Lett.* **1989**, 1951.

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

(5) Kanbara, T.; Kushida, T.; Saito, N.; Kuwajima, I.; Kubota, K.; Yamamoto, T. *Chem. Lett.* **1992**, 583.

(6) Yamamoto, T. *Prog. Polym. Sci.* **1992**, *17*, 1153.

(7) Fauvarque, J.-F.; Digua, A.; Petit, M.-A.; Savard, J. *Makromol. Chem.* **1985**, *186*, 2415.

(8) Saito, N.; Kanbara, T.; Sato, T.; Yamamoto, T. *Polym. Bull.* **1993**, *30*, 285.

(9) Schiavon, G.; Zottti, G.; Bontempelli, G.; Coco, F. L. *Synth. Met.* **1988**, *25*, 365.

(10) Siove, A.; Ades, D.; Chevrot, C.; Froyer, G. *Makromol. Chem.* **1989**, *190*, 1361.

(11) Stille, J. K. *Macromolecules* **1981**, *14*, 870.

(12) Imai, Y.; Johnson, E. F.; Katto, T.; Kurihara, M.; Stille, J. K. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 2233.

(13) Chiang, L. Y.; Swirczewski, J. W.; Kastrup, R.; Hsu, C. S.; Upasani, R. B. *J. Am. Chem. Soc.* **1991**, *113*, 6574.

(14) Schiavon, G.; Zotti, G. *J. Electroanal. Chem.* **1988**, *242*, 131.

(15) Yamamoto, T.; Yoneda, Y.; Maruyama, T. *J. Chem. Soc., Chem. Commun.* **1992**, 1652.

(16) Yamamoto, T.; Yamamoto, A. *Chem. Lett.* **1977**, 353.

(17) Kubota, K.; Urabe, H.; Tominaga, Y.; Fujime, S. *Macromolecules* **1984**, *17*, 2096.

(18) Sybert, P. D.; Beever, W. H.; Stille, J. K. *Macromolecules* **1981**, *14*, 493.

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

(20) Kanbara, T.; Yamamoto, T. *Macromolecules* **1993**, *26*, 3464.

(21) Sato, M.; Tanaka, S.; Kaeriyama, K. *Synth. Met.* **1986**, *14*, 279.

(22) Brédas, J. L.; Scott, J. C.; Yakushi, K.; Street, G. B. *Phys. Rev.* **1984**, *B30*, 1023.

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

(24) (a) Thémans, B.; André, J. M.; Brédas, J. L. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 121. (b) Brédas, J. L.; Silbey, R.; Boudreaux, D. S.; Chance, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 6555.

(25) Thémans, B.; André, J. M.; Brédas, J. L. *Solid State Commun.* **1984**, *50* (12), 1047.

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

(27) Bobranski, B. *Ber.* **1938**, *71*, 578.

(28) de la Mare, P. B. P.; Kiamud-din, M.; Ridd, J. H. *J. Chem. Soc.* **1960**, 561.

(29) Sanders, G. M.; Dijk, M.; Hertog, H. J. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 298.

(30) Gordon, M.; Pearson, D. E. *J. Org. Chem.* **1964**, *29*, 329.

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

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

(33) Yamamoto, K. *Bull. Chem. Soc. Jpn.* **1954**, *29*, 501.

(34) Booth, G.; Chatt, J. *J. Chem. Soc.* **1965**, 3239.