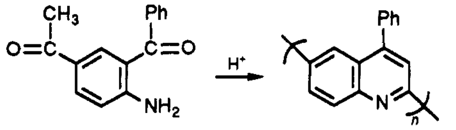
Communications to the Editor

Preparation and Properties of Poly(quinolinediyl)s and Poly(isoquinoline-1,4-diyl) with New π-Conjugation Systems

Reactions of 5,8-dibromoquinoline, 4,7-dichloroquinoline, and 1,4-dibromoisoquinoline with a zero-valent nickel complex afford poly(quinoline-5,8-diyl), poly(quinoline-4,7-diyl), and poly(isoquinoline-1,4-diyl), respectively. These polymers have well-defined linkages between monomer units and show electrical conducting properties on *n*-type doping.

Preparation and electrical properties of poly(arylene)s having π-conjugation system along the polymer chain are the subject of recent interest. However, most of reported poly(arylene)s such as poly(pyrrole-2,5-diyl)[1] and poly(thiophene-2,5-diyl)[2] show *p*-type electrically conducting properties, and preparation of n-type electrically conducting poly(arylene)s has been limited.[3,4]

Stille reported preparation of poly(4-phenylquinoline-2,6-diyl) by an acid-catalyzed Friedlander reaction.[5]

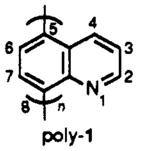


(1)

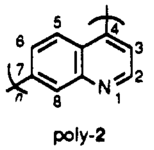
This polymer as well as its 4- and 2-substituted derivatives showed n-type electrically conducting properties (σ_{max} = 50 S cm^{-1}) on doping with Na$^+$, $(C_2H_5)_4N^+$, and $(n\text{-}C_4H_9)_4N^+$.[3] However, poly(quinolinediyl)s with an isomeric linkage between the monomer units have not been reported, although it is considered to be of interest to compare chemical and physical properties of poly(quinolinediyl)s with different types of linkages between the monomer units and different π-conjugation systems.

Recently, a new method for the preparation of poly(arylene)s such as poly(pyridine-2,5-diyl),[4] poly(thiophene-2,5-diyl)[6], and poly(*p*-phenylene)[6] by dehalogenation polycondensation of corresponding dihalogenated aromatic compounds with zero-valent nickel complexes has been reported. This method affords the poly(arylene)s with an exactly defined linkage between the monomer units and is suitable to the molecular design of the π-conjugated poly(arylene)s with desired recurring monomer units. We now report the preparation of new poly(arylene)s, poly(quinoline-5,8-diyl) (**poly-1**), poly(quinoline-4,7-diyl) (**poly-2**), and poly(isoquinoline-1,4-diyl) (**poly-3**), having new π-conjugation systems along the polymer chain by using the zero-valent nickel complexes, typically a mixture of bis(1,5-cyclooctadiene)nickel(0), Ni(cod)$_2$, and 2,2′-bipyridine, bpy.

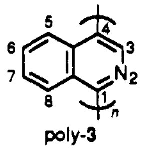
$$n\mathrm{XArX} + n\mathrm{Ni^0L}_m \longrightarrow \left[\mathrm{Ar}\right]_n + n\mathrm{NiX_2L}_m \qquad (2)$$



poly-1



poly-2



poly-3

Ni^{0}L$_m$: zero-valent nickel complex (Ni(cod)$_2$ + bpy)

Materials. 5,8-Dibromoquinoline and 1,4-dibromoisoquinoline were prepared by methods reported by de la Mare et al.[7] and Sanders et al.,[8] respectively. Commercially available 4,7-dichloroquinoline was used after recrystallization.

Polymerization. Stirring 5,8-dibromoquinoline (536 mg, 1.87 mmol) with a mixture of bis(1,5-cyclooctadiene)nickel (639 mg, 2.32 mmol), 1,5-cyclooctadiene (0.8 cm^3), and 2,2′-bipyridine (362 mg, 2.32 mmol) in *N,N*-dimethylformamide (25 cm^3) for 24 h at about 60 °C afforded a precipitate of a reddish yellow polymer. Workup of the polymer, involving removal of nickel compounds with ethylenediaminetetraacetic acid, was carried out in a manner similar to that reported previously.[4,6] Reddish yellow **poly-1** was obtained in high yield (92%). Pale yellow **poly-2** (yield 99%) and **poly-3** (yield 95%) were prepared analogously by using 4,7-dichloroquinoline and 1,4-dibromoisoquinoline, respectively. Elemental analysis of these polymers was reasonable for the polymers and showed almost negligible halogen content (<0.03%). Anal. Calcd for $(C_9H_5N)_n$: C, 85.0; H, 4.0; N, 11.0. Found for **poly-1**: C, 84.3; H, 4.0; N, 10.9; Br, 0.0. Found for **poly-2**: C, 83.5; H, 4.2; N, 10.9; Cl, 0.0. Found for **poly-3**: C, 83.5; H, 4.0; N, 10.6; Br, 0.0. A part of the difference between the calculated and found values seems to be attributable to the difficulty in achieving a complete combustion when performing the elemental analysis of the polymer.

Poly-1 is soluble in formic acid and sparingly soluble in chloroform, whereas **poly-2** and **poly-3** are soluble in formic acid and chloroform. The UV–visible spectrum of a formic acid solution of **poly-1** shows triple π–π* absorption peaks at 258, 322, and 343 nm, while, in the case of **poly-2** and **poly-3**, two π–π* absorption peaks are observed at 280 and 342 nm and at 258 and 370 nm, respectively.

Table I summarizes the molecular weight and degree of depolarization,[9] ρ_V, of the polymers measured by GPC analysis and the light scattering method.[9] The M_w (weight-average molecular weight) and ρ_V values determined in HCOOH and CHCl$_3$ reveal the following:

(1) **Poly-1** has a degree of polymerization (DP) of about 85 and gives a very large ρ_V value in HCOOH; the very large and theoreticaly almost limiting ρ_V value can be taken as an indication of taking a rodlike linear structure of the polymer in HCOOH.[4,9]

(2) **Poly-2** and **poly-3** have lower molecular weights of 1700–2000 corresponding to DP of 14–16 as determined by the light scattering method in HCOOH. The ρ_V value of **poly-2** is almost zero, indicating that **poly-2** takes a random-coil structure in HCOOH due to its obvious nonlinear structure. **Poly-3** in HCOOH gives a ρ_V value of 0.1, the value being comparable to that observed for non-π-conjugated linear polymers like aromatic polyamides.[10] The ρ_V value of 0.1 suggests that **poly-3** also takes a linear structure, but anisotropy of the polarizability of **poly-3**, which determines the ρ_V value,[9] is not as large as those of poly(pyridine-2,5-diyl)[4] and **poly-1**, presumably due to the relatively large π-conjugation system of the recurring monomer unit compared with poly(pyridine-2,5-diyl) and a consideraby lower molecular weight than that of **poly-1**.

0024-9297/91/2224-5883$02.50/0

Table I
Molecular Weight and Degree of Depolarization of Poly(quinolinediyl)s and Poly(isoquinoline-1,4-diyl)

	GPC[a]		light scattering method			
			in HCOOH		in $CHCl_3$	
polymer	M_n	M_w	M_w	ρ_V[b]	M_w	ρ_V[b]
poly-1			11 000	>0.3		
poly-2	7 900	11 900	1 700	<0.01	70 000	<0.003
poly-3	2 600	5 200	2 000	0.10	75 000	<0.005

[a] In $CHCl_3$ (polystyrene standards). [b] Degree of depolarization.[9]

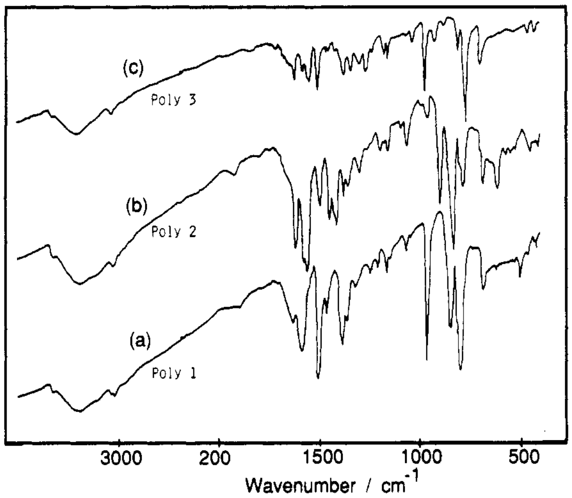


Figure 1. Infrared spectra of (a) poly(quinoline-5,8-diyl) (poly-1), (b) poly(quinoline-4,7-diyl) (poly-2), and (c) poly(isoquinoline-1,4-diyl) (poly-3).

(3) In $CHCl_3$, the light scattering method gives a much higher molecular weight than that in HCOOH. We tentatively assume that this unusual observation originates from aggregation of poly-2 and poly-3 in $CHCl_3$. The assumption of the aggregation is supported by the ρ_V value of almost zero for poly-3 in $CHCl_3$. For example, if the poly-3 molecules aggregate with the isoquinoline planes facing each other, an intermolecular movement of electron perpendicular to the polymer chain may occur to afford a lower degree of anisotropy of the polarizability for the aggregated mass.

The aggregation in a flow $CHCl_3$ solution may not be strong, and this soft aggregation may explain that the M_w values of poly-2 and poly-3 determined by GPC are between the M_w values determined by the light scattering method in HCOOH and $CHCl_3$.

Figure 1 shows IR spectra of poly-1–poly-3. Comparison of skeletal in-plane ring vibration (1650–1350 cm^{-1}) and C–H out-of-plane bending (1000–650 cm^{-1}) of the polymers shows clear contrast between the polymers. The IR spectra are reasonable for their expected structures (eq 2).

Figure 2 shows ^1H NMR spectra of poly-2 and poly-3 in $CDCl_3$. Assignment of the peaks has been carried out by comparison of the positions of the peaks with those of quinoline, isoquinoline, and the corresponding dihalogenated aromatic compounds. As shown in Figure 2a, two broad peaks at δ 9.3–9.0 and 8.8–8.3 are assigned to the 2 H and 8 H protons of the quinoline ring, respectively, and broad peaks at δ 8.2–7.3 are assigned to the other three protons. On the other hand, in Figure 2b, the broad peak at δ 9.2–8.9 is assigned to the 3 H proton of the isoquinoline unit, and a broad peak assigned to the other aromatic protons is observed at δ 8.2–7.3. The peak area ratios agree well with the proposed assignment for poly-2 and poly-3. In the case of poly-1 in $CDCl_3$, a broad peak at δ 9.0–8.8 assignable to the 2 H proton and a broad peak at δ 8.0–7.3 assignable to the other aromatic protons are observable. However, the low solubility of poly-1 prevented us from obtaining a reasonably sharp spectrum. ^{13}C NMR spectra of poly-2 and poly-3 show resonances in a range of 160–120 ppm due to the aromatic carbons of the quinoline and isoquinoline ring, respectively.

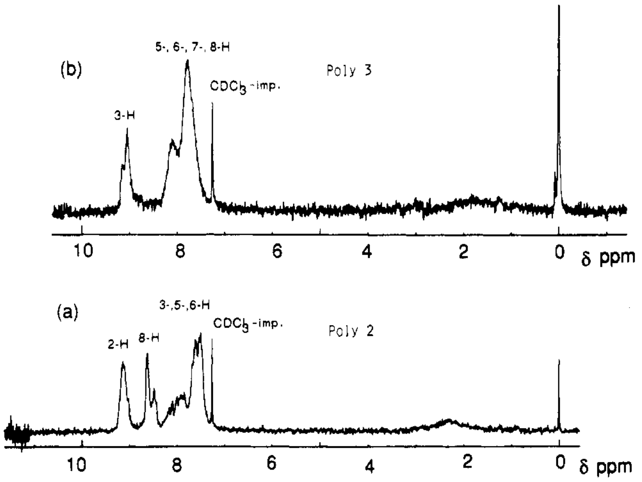


Figure 2. ^1H NMR spectra of (a) poly(quinoline-4,7-diyl) (poly-2) and (b) poly(isoquinoline-1,4-diyl) (poly-3) in $CDCl_3$.

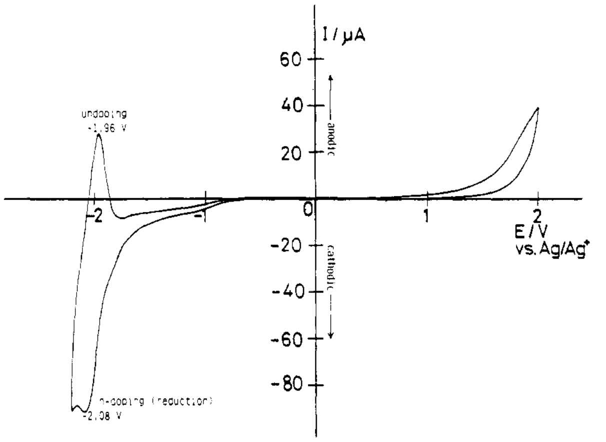
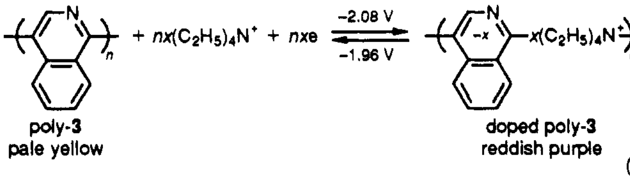


Figure 3. Cyclic voltammogram of a film of poly(isoquinoline-1,4-diyl) (poly-3) on a platinum plate in an acetonitrile solution of $[(C_2H_5)_4N]ClO_4$ (0.1 M).

The elemental analysis, molecular weight determination, light scattering properties, and IR and NMR data shown above clearly indicate that the present preparation method affords the proposed poly(quinolinediyl)s and poly(isoquinolinediyl) with new π-conjugation systems.

Spreading the formic acid solution of these polymers on a platinum plate and ensuing evaporation of formic acid under air afforded a platinum plate coated with films of poly-1–poly-3.

Figure 3 shows a cyclic voltammogram (CV) of poly-3. As shown in Figure 3, the poly-3 film gives rise to an electrochemically active cycle in the reduction region, showing an n-doping peak at −2.08 V vs Ag/Ag$^+$ and an undoping peak at −1.96 V.



poly-3
pale yellow

doped poly-3
reddish purple

(3)

Table II
Electrical and Electrochemical Properties of Poly(quinolinediyl)s and Poly(isoquinoline-1,4-diyl)

polymer	$E_{red}{}^a$/V	$E_{ox}{}^a$/V	σ^b/S cm^{-1}
poly-1	−2.46	−2.29	3.5×10^{-4}
poly-2	(−2.23)^c	(−2.06)^c	3.8×10^{-9}
poly-3	−2.08	−1.96	1.8×10^{-3}

[a] Versus Ag/Ag$^+$ in an acetonitrile solution of 0.1 M tetraethylammonium perchlorate. [b] Doped by treatment with $NaC_{10}H_8$. [c] Observed only at the first cycle.

However, the poly-3 film was electrochemically inert in an oxidation region, and only electric current due to electrical decomposition of solvent was observed. The polymer film electrode is stable during repeated scanning, showing essentially the same CV. The color of poly-3 changes from pale yellow to reddish purple during reduction. These CV results and color change resemble those of poly(pyridine-2,5-diyl),[4] which gives *n*-doping and undoping peaks at −2.24 and −1.98 V vs Ag/Ag$^+$, respectively. Poly-1 was also electrochemically active only for the *n*-doping, and a similar voltammogram and color changes were obtained. These results reveal that the introduction of electron-withdrawing imine nitrogen not only in the main-chain ring (poly-**3**) but also in the side-chain ring (poly-1) renders the electron-accepting properties to the poly(arylene). In contrast to poly-1 and poly-**3**, nonconjugated poly-**2** was essentially electrochemically inert except for the flow of an uncharacterized current only at the first cycle (Table II).

Table II summarizes electrochemical and electrical properties of these polymers. Electrical conductivity (σ) was measured with pellets prepared by pressing powdery Na$^+$-doped samples, which were obtained by treatment of the polymers with sodium naphthalide in THF at room temperature followed by filtration under argon and drying under vacuum. As shown in Table II, poly-1 and poly-3 show an *n*-type electrically conducting property with the σ value of 10^{-4}–10^{-3} S cm^{-1}, whereas the nonconjugated poly-2 shows a much lower electrical conductivity.

According to valence effective Hamiltonian (VEH) calculations of poly(quinoline-2,6-diyl),[11] the polymer has a large ionization potential and a large electron affinity. This basic electronic structure of poly(quinoline-2,6-diyl) agrees well with the facile *n*-type doping and difficult *p*-type doping of the polymer prepared by Stille (cf. eq 1). In organic chemistry, it is also recognized that the imine-containing aromatic ring such as pyridine, quinoline, and isoquinoline has a π-deficient character.[12] Poly(pyridine-2,5-diyl),[4] poly-1, poly-3, and previously reported poly(quinoline-2,6-diyl) derivatives[5] are examples of the π-conjugated polymers constituted of the π-deficient aromatic units, and the present results clearly indicate that the π-conjugated polymers constituted of such π-deficient aromatic units in general show the *n*-type electrically conducting properties. Poly-1 and poly-**3**, regardless of whether the π-conjugation system is built through the benzene ring or the pyridine ring, essentially show the same *n*-type electrically conducting properties.

References and Notes

(1) (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.
(2) (a) Yamamoto, T.; Sanechika, K.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1497 and 1503; *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 9. (b) Kobayashi, M.; Chen, J.; Chung, T.-C.; Moraes, F.; Heeger, A. J.; Wudl, F. *Synth. Met.* **1984**, *9*, 77. Kaneto, K.; Kohno, Y.; Yoshino, K.; Inuishi, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 382.
(3) (a) Tunney, S. E.; Suengag, J.; Stille, J. K. *Macromolecules* **1983**, *16*, 1398. (b) Denisevich, P.; Papir, Y. S.; Kurkov, V. P.; Current, S. P.; Schroeder, A. H.; Suzuki, S. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chim.*) **1983**, *24*, 330.
(4) (a) Yamamoto, T.; Ito, T.; Kubota, K. *Chem. Lett.* **1988**, 153. (b) Yamamoto, T.; Ito, T.; Sanechika, K.; Kubota, K.; Hisinuma, M. *Chem. Ind.* (*London*) **1988**, 337. (c) Yamamoto, T.; Ito, T.; Sanachika, K.; Hishinuma, M. *Synth. Met.* **1988**, *25*, 103.
(5) Stille, J. K. *Macromolecules* **1981**, *14*, 870.
(6) Yamamoto, T.; Morita, A.; Maruyama, T.; Zhou, Z.-h.; Kanbara, T.; Sanechika, K. *Polym. J.* **1990**, *22*, 187.
(7) de la Mare, P. B. P.; Kiamud-din, M.; Ridd, J. H. *J. Chem. Soc.* **1960**, 561.
(8) Sanders, G. M.; Dijk, M.; Hertog, H. J. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 298.
(9) (a) Kubota, K.; Chu, B. *Biopolymers* **1983**, *22*, 1461. (b) Saito, N. *Kobunshi Butsurigaku*; Shyokabo: Tokyo, 1976; p 181.
(10) Zero, K.; Aharoni, S. M. *Macromolecules* **1987**, *20*, 1957.
(11) Themans, B.; Andre, J. M.; Bredas, J. L. *Solid State Commun.* **1984**, *50*, 1047.
(12) Newkome, G. R.; Paudler, W. W. *Contemporary Heterocyclic Chemistry*; John Wiley: New York, 1982.

Takaki Kanbara, Nobuo Saito, and Takakazu Yamamoto*

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

Kenji Kubota

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

Received April 19, 1991
Revised Manuscript Received August 8, 1991