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Preparation of New π-Conjugated Poly(2,3-diphenylquinoxaline-5,8-diyl) and Poly(2,3-di(*p*-tolyl)-quinoxaline-5,8-diyl). Electrochemical Activity and Light-emitting Diode

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Reactions of 5,8-dibromo-2,3-diphenylquinoxaline and 5,8-dibromo-2,3-di(*p*-tolyl)-quinoxaline with a zero-valent nickel complex afford poly(2,3-diphenylquinoxaline-5,8-diyl) (**poly-1**) and poly(2,3-di(*p*-tolyl)quinoxaline-5,8-diyl), respectively. These polymers show good electrochemical activity for n-type doping and strong fluorescence in solutions as well as in cast films. A light-emitting diode consisted of MgAg/**poly-1**/ITO electric junction is driven at about 2 V and has a peak emission wavelength of 490 nm.

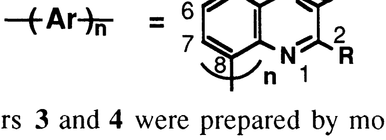
Preparation and application of π-conjugated poly(arylene)s are the subject of recent interest.$^{1)}$ Among the application, light-emitting diodes (LED's) using fluorescent π-conjugated poly(arylene)s such as poly(*p*-phenylene), poly(thiophene-2,5-diyl), poly(*p*-phenylenevinylene), and their derivatives are now actively investigated because of their potential usefulness in making large-area displays.$^{2)}$ Many π-conjugated poly(arylene)s exhibit good processability, and their electronic and optical properties (e.g., energy gap Eg corresponding to the emission color) can be controlled by choosing the recurring arylene units as well as introducing substituents such as alkyl and alkoxy groups$^{2c\text{-}h)}$ to the arylene unit.

Recently, poly(quinoxaline-5,8-diyl) and its diethyl homologue (R = H, C_2H_5 in Eq.1) have been prepared$^{3)}$ by dehalogenation polycondensation based on organonickel chemistry,$^{4)}$ and these polymers show good n-type electrically conducting properties because of π-deficient nature of the recurring arylene units with two imine nitrogens in the side-chain ring. However, the polymers exhibited only weak fluorescence.

We now report modification of poly(quinoxaline-5,8-diyl) by introducing phenyl and tolyl groups to the side ring and that the introduction of the aryl group in the side chain gives a strong fluorescent properties to the polymers in solutions as well as in cast films and the polymers are useful materials to make LED. The new polymers have been also prepared by using the organometallic method shown below.

$$\underset{\textbf{3 or 4}}{\text{n Br-Ar-Br}} + \text{n Ni(0)L}_m \longrightarrow \text{—(Ar)}_n\text{—} + \text{n NiBr}_2\text{L}_m \qquad (1)$$

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



poly-1 : R = Ph (from **3**)
poly-2 : R = *p*-tolyl (from **4**)

Monomers **3** and **4** were prepared by modifying a method by Bird et al.$^{5)}$ Stirring **3** (0.70 g, 1.59 mmol) with a mixture of bis(1,5-cyclooctadiene)nickel Ni(cod)$_2$ (0.53 g, 1.90 mmol), 1,5-cyclooctadiene (0.35

cm^3), and 2,2'-bipyridine (bpy, 0.30 g, 1.91 mmol) in N,N-dimethylformamide (25 cm^3) for 24 h at 40 °C afforded a precipitate of a light yellow **poly-1**. Work up of the polymer, involving removal of nickel compounds with ethylenediaminetetraacetic acid, was carried out in a manner similar to that reported previously (yield: 95%).[1b,3,4] Light yellow **poly-2** was prepared analogously by using **4** (yield: 99%). Anal.: **poly-1**; Found: C, 84.7; H, 4.4; N, 9.7; Br, 0.0%. Calcd for $(C_{20}H_{12}N_2)_n$: C, 85.7; H, 4.3; N, 10.0%. **poly-2**; Found: C, 85.4; H, 5.1; N,8.9; Br, 0.3%. Calcd for $(C_{22}H_{16}N_2)_n$: C, 85.7; H, 5.2; N, 9.1%.

Poly-1 is soluble in CF_3COOH and partially soluble in $CHCl_3$; about 35 wt% of original **poly-1** is extracted from the source polymer by Soxhlet extraction with $CHCl_3$. **Poly-2** is soluble in CF_3COOH and formic acid, and partially soluble in $CHCl_3$ and *o*-xylene. The light scattering technique applied for the CF_3COOH solutions of **poly-1** and **poly-2** indicates **poly-1** and **poly-2** have weight-average molecular weight (M_w) of 6.1 x 10^4 and 2.4 x 10^4, respectively, whereas the number-average molecular weight (M_n) and M_w of $CHCl_3$-extractable parts of **poly-1** are 14500 and 15500, respectively, as determined by GPC using polystyrene standard. The $CHCl_3$ solutions of the $CHCl_3$-extractable parts of **poly-1** and **poly-2** show strong fluorescence with a peak at 480 nm, when irradiated by 380 nm light, respectively, whereas the CF_3COOH solutions of **poly-1** and **poly-2** give rise to rather weak fluorescence.

Figure 1 shows ^{1}H-NMR spectra of **poly-1** and **poly-2** in CF_3COOD. **Poly-1** exhibits a peak of the 6,7-H protons of the quinoxaline ring at δ 8.8 ppm and two peaks of aromatic protons of phenyl group at δ 7.3 and 7.1 ppm. In Fig. 1(b), a peak at δ 8.7 ppm is assigned to 6,7-H protons of the quinoxaline ring, two peaks at δ 7.0 and 6.8 ppm to aromatic protons of *p*-tolyl group, and a peak at δ 2.2 ppm to the CH_3 protons of *p*-tolyl group.

Figure 2 depicts cyclic voltammogram (CV) of the cast film of $CHCl_3$-extractable parts of **poly-1**. The polymer gives rise to an electrochemically active cycle in the reduction region, showing an n-doping peak at -2.02 V *vs.* Ag/Ag^+ and an undoping peak at -1.82 V. The n-doping and undoping potentials are almost same as those of poly(quinoxaline-5,8-diyl) (-2.00 V/-1.96 V *vs.* Ag/Ag^+).[3] The color of the polymer film changes from light yellow to dark purple by the reduction. The polymer film is stable during repeated scanning and shows essentially the same CV curve after 50 cycles. The peak current for the n-doping and undoping (i_{pc} and i_{pa}) is proportional to sweep rates (v) over 5 to 100 mV s^{-1}. On the other hand, **poly-1** is less stable in the oxidation (p-doping) region, and only irreversible anodic current is observed.

Changes in absorption spectrum of the cast film of $CHCl_3$-extractable parts of **poly-1** on indium-tin oxide (ITO) glass electrode during n-doping are shown in Fig. 3. At 0.0 V *vs.* Ag/Ag^+, the neutral state of the polymer gives rise to π-π* absorption peaks at 370 and 420 nm. When the polymer film is electrochemically reduced to -2.0 V, the π-π*

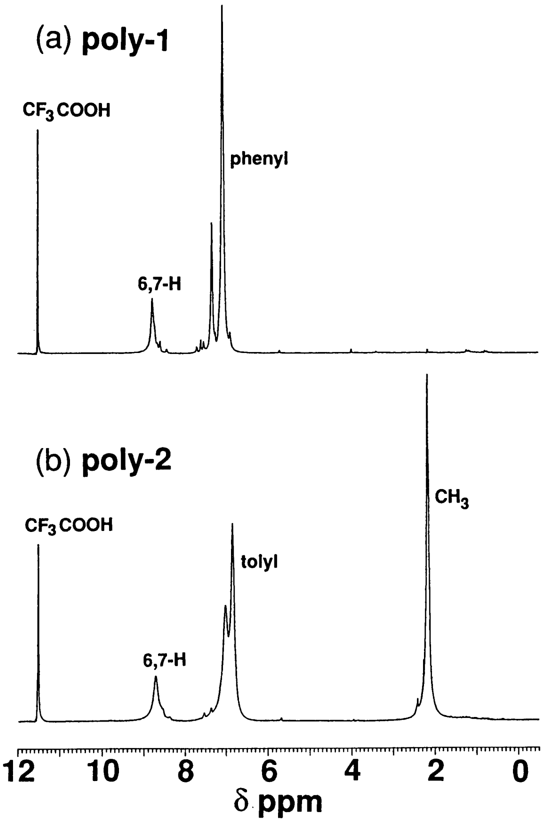


Fig. 1. ^{1}H NMR spectra of **poly-1** and **poly-2** in CF_3COOD.

absorption peaks are decreased, and appearance of a new broad absorption band in a range of 450-700 nm with tail absorption toward near infrared region is observed. The change in the absorption spectrum of the polymer film by the electrochemical doping (electrochromism) is stable during repeated measurement.

Cast film of **poly-2** from a formic acid solution also gives a similar reversible CV curve (an n-doping peak at -1.95 V *vs.* Ag/Ag$^+$ and an undoping peak at -1.82 V) and electrochromic phenomena (π-π* absorption peak at neutral state: 395 nm; a new broad absorption band at doping at -2.0 V: 450-700 nm) only for the n-doping.

Non-doped **poly-1** and **poly-2** are essentially insulators with electrical conductivity (σ) of less than 10^{-10} S cm^{-1}. Sodium-doping of cast films of **poly-1** and **poly-2** with sodium naphthalide in THF at room temperature give semiconducting films with σ values of 1.2 x 10^{-4} and 1.1 x 10^{-4} S cm^{-1}, respectively. However, the sodium-doped samples are sensitive to air, and exposure of the sample to air causes a rapid decrease in their electrical conductivity.

LED consisted of ITO/**poly-1**/MgAg electric junction was prepared by spin-casting of $CHCl_3$-extractable parts of **poly-1** (typical thickness of 50-100 nm) and vacuum deposition of MgAg on the film of **poly-1**. The forward bias current is obtained when ITO electrode is biased positively and MgAg electrode negatively under vacuum (about 10^{-1} Pa) or N_2 atmosphere at room temperature, and the current almost exponentially increases with increase in potential under forward bias conditions. However, application of reverse bias causes flow of considerably lower electric current and the diode exhibits good rectification of the electric current with a rectification ratio of about 20 at ±5.0 V.

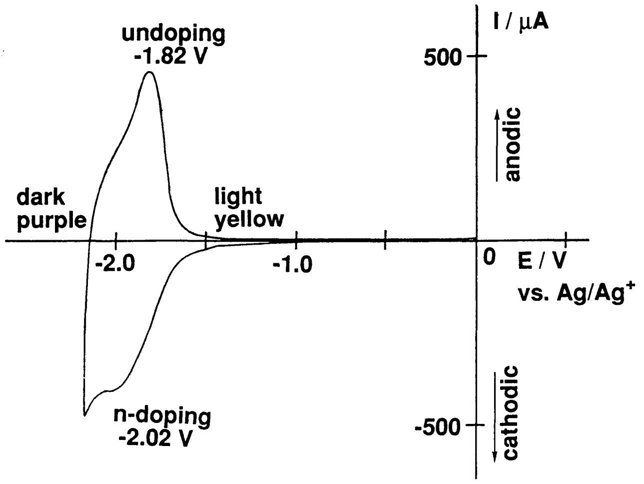


Fig. 2. Cyclic voltammogram of a film of **poly-1** on platinum plate in an acetonitrile solution of $[Et_4N]ClO_4$ (0.1 M). Sweep rate = 10 mV s^{-1}.

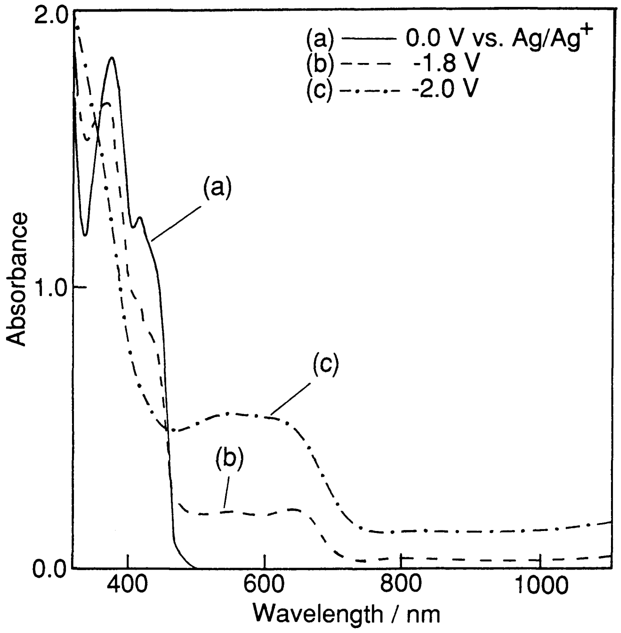


Fig. 3. Changes in absorption spectrum of a film of **poly-1** on ITO-glass electrode during electrochemical n-doping in an acetonitrile solution of $[Et_4N]ClO_4$ (0.1 M).

The emission of blue-green light starts at an applied voltage of about 2 V under the forward bias conditions, and the emission intensity almost proportionally increases with increase in injected current. Figure 4 shows photoluminescence (PL) spectrum of the spin-cast film of $CHCl_3$-extractable parts of **poly-1** and electroluminescence (EL) spectrum of the LED at driven voltage of 11 V under the forward bias conditions.

The EL spectrum shows a peak at 490 nm with a shoulder at about 400 nm, and the spectrum essentially coincides with the PL spectrum of **poly-1**, indicating the emission occurs at the polymer film. The peak of PL and EL of **poly-1** corresponds to the photon energy of about 2.5 eV, which roughly coincides with E_g value of **poly-1** estimated from the edge of the absorption spectrum, suggesting that the emission is originated from a recombination of electrons in the valence band and holes in the conduction band. Similar correlation between PL and EL as well as that between the peak position and Eg have been reported for fluorescent π-conjugated poly(arylene)s.[2] The present LED has a emission intensity of 1.0 cd m^{-2} at 14 V.

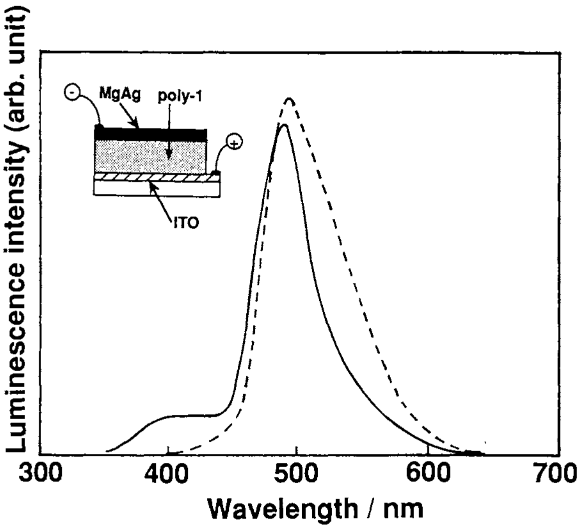


Fig. 4. Photoluminescence spectrum of spin-cast film of **poly-1** (----) and electroluminescence spectrum of ITO/**poly-1**/MgAg LED at 11 V (——).

Poly-2 also indicates similar PL and EL with a peak at about 500 nm. On the other hand, as described above similar poly(quinoxaline-5,8-diyl) type polymers (R = H, C_2H_5 in Eq.1) without the aromatic R group show considerably weaker PL and EL. Moreover, 2,3-diphenylquinoxaline and the monomer **3** also give considerably weaker PL, indicating that both the introduction of the aromatic R substituent to the quinoxaline ring and expansion of the π-conjugation system through the 5,8-linkage between the quinoxaline units are important for PL and EL.

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