N-Oxidation of π-Conjugated Poly(heterocycle)s Containing Nitrogen and Electrically Conducting Properties of the N-Oxidized Products

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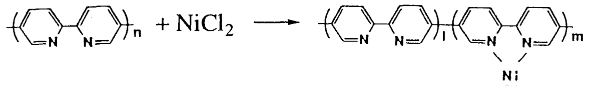
Oxidation of poly(quinoline-2,6-diyl) and its analogue with H_2O_2 gives N-oxidized products, which show dc conductivity of 2.3-3.2 x 10^{-6} S cm^{-1} without doping.

Electrically conducting polymer materials based on π-conjugated poly(heterocycle)s are the subject of recent many papers.[1] However, the electrically conducting polymer materials are usually obtained by doping and have ionic structures with counter ions such as I^-, ClO_4^-, and Na^+, which may give wrong effect in use of the materials in electric devices. On these bases, obtaining electrically conducting materials without the dopant is desired.

Recently, it has been reported that Ni(II) and Ru(II) complexes of poly(2,2'-bipyridine-5,5'-diyl) PBpy, e.g.,

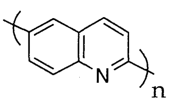


(1)

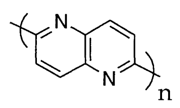
PBpy

PBpy-Ni complex

have dc conductivity (σ) of 10^{-7} - 10^{-5} S cm^{-1},[2] although PBpy itself has a σ value of below 10^{-14} S cm^{-1} and the Ni-complex has a neutral structure like Ni(bpy) halides.[3] Transition metal complexes of the following P(2,6-Q)[4] and P(2,6-N)[4] also show rise of the σ-value by similar complex formation.[5] The rise of the electrical conductivity by the complex formation may originate from generation of carrier in the polymer chain due to special electronic state(s) of the complex (e.g., MLCT electronic state).



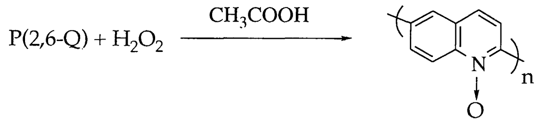
P(2,6-Q)



P(2,6-N)

These results prompted us to examine possibility for obtaining conducting polymers without the dopant by modification of nitrogen in π-conjugated poly(heterocycle)s, and we report here that oxidation of nitrogen in π-conjugated poly(heterocycle)s actually gives conducting polymers without the dopant.

Treatment of powdery P(2,6-Q) (100 mg) with a mixture of acetic acid (20 cm^3) and 30% H_2O_2 aqueous solution (8 cm^3) at 60 °C under stirring gave a yellow powder, which was treated with aqueous solution of NaOH and dil HCl(aq) and dried under vacuum to obtain P(2,6-Q-N-ox).[6]



(2)

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

IR spectrum of P(2,6-Q-N-ox) (Figure 1) exhibits ν(N-O) band[7] at about 1300 cm^{-1}. As shown in Figure 2, UV-visible spectrum of P(2,6-Q-N-ox) reveals shift of π-π* band of P(2,6-Q) at 437 nm to 407 nm in formic acid. The molecular model of P(2,6-Q-N-ox) shows the presence of steric repulsion between the NO group and o-hydrogen of the quinoline unit, which will leads to twisting of the bond between the monomer units to cause the shift of the π-π* absorption band to shorter wavelength. P(2,6-Q-N-ox) is partly soluble in an aqueous solution of NaOH and the IR spectrum of the soluble part is identical to that of original P(2,6-Q-N-ox). P(2,6-Q-N-ox) has dc conductivity of 2.3 x 10^{-6} S cm^{-1} (measured with compressed powder), which is raised by an order of 10^4 from the σ-value (4.0 x 10^{-10} S cm^{-1}) of P(2,6-Q). The conductivity of P(2,6-Q-N-ox) did not show time dependence indicating that the electrical conduction is not due to ionic conduction. Similar N-oxidation of P(2,6-N) also gives analogous polymer with two N-oxides in the repeating unit and it shows a σ value of 3.2 x 10^{-6} S cm^{-1} (measured with compressed powder), which is also raised from the σ value (1.1 x 10^{-9} S cm^{-1}) of P(2,6-N). Cyclic voltammogram of a film of P(2,6-Q-N-ox) laid on a Pt plate indicates that the polymer is inert against oxidation similarly to a film of P(2,6-Q);[4] on the other hand its reduction proceeds at about -2.1 V *vs* Ag/Ag^+.

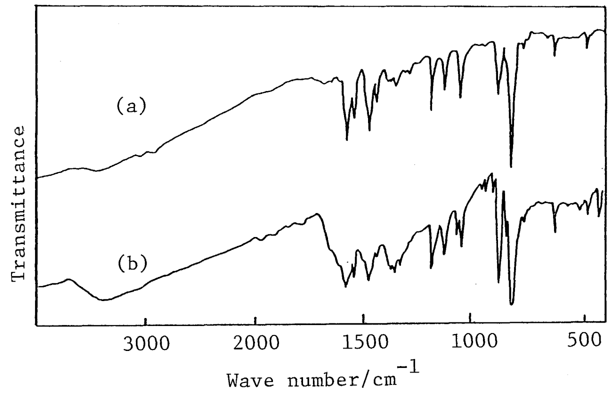


Figure 1. IR spectra of (a) P(2,6-Q) and (b) P(2,6-Q-N-ox).

As described above, N-oxidized poly(heterocycle)s show some dc conductivity and suggests possibility for obtaining conducting polymers without the dopant by modification of nitrogen or introduction of a polar group in the π-conjugated poly(heterocycle)s. Since π-conjugated heterocycles with the N-O group take various resonance structures including ones having electrically positive and negative centers in the π-conjugated system, respectively, generation of charged carrier(s) in the π-conjugated polymers is conceivable.

Although the electrical conductivity of P(2,6-Q-N-ox) is not high, the σ value may be sufficient to remove static electricity and to be used for such purposes.

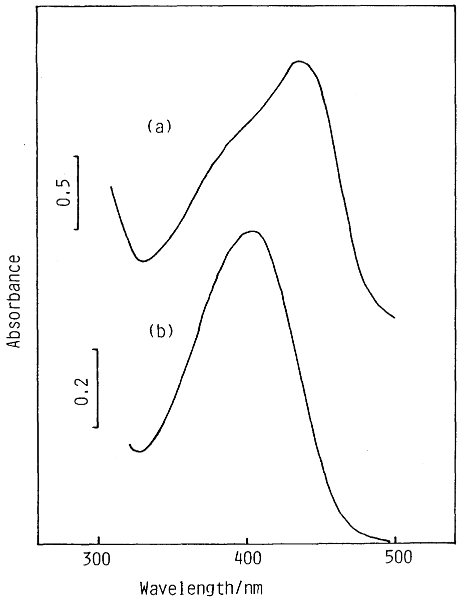


Figure 2. UV-visible spectra of (a) P(2,6-Q) and (b) P(2,6-Q-N-ox) in formic acid.

References and Notes

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3 T. Yamamoto, T. Kohara, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **54**, 2010 (1981).

4 N. Saito and T. Yamamoto, *Macromolecules*, **28**, 4260 (1995) and references therein.

5 Unpublished data. The σ value is raised by a factor of about 10^2 by the complex formation with Pd and Pt.

6 Anal. Found: C, 71.0; H, 3.7; N, 9.2%. Calcd. for $(C_9H_5NO \cdot 0.49H_2O)_n$:$_7$ C, 71.1; H, 4.0; N, 9.2%. Quinoline and its oxide[7] take water of crystallization. Since the UV-visible spectrum shows the large difference shown in Figure 2 after the N-oxidation, most part of the nitrogen in P(2,6-Q) is considered to undergo the N-oxidation. Jpn. Pat. Applied.

7 C. J. Pouchart, "The Aldrich Library of Infrared Spectra," Aldrich Chemical Co., Milwaukee (1975) 1240E.