# Preparation of New Main-chain Type Polyquinone and Its Properties

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New semiconducting poly(anthraquinone-1,5-diyl) with two $NO_2$ groups at 4- and 8-positions has been prepared by an Ullmann type coupling reaction using metallic copper or a zerovalent nickel complex. The polymer shows intrinsic dc conductivity of $1.4 \times 10^{-6}$ S $cm^{-1}$ at room temperature.

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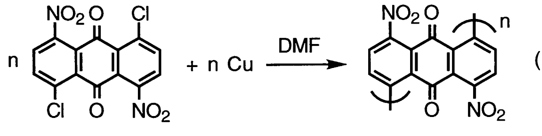
Synthesis and revealing electronic and optical properties of poly(arylene)s are the subject of recent interest.[1] Quinones belong to typical electron-accepting and redox active aromatic compounds and poly(arylene)s constituted of quinones are expected to show interesting electronic and optical properties. However, examples of poly(arylene)s with a main-chain type polyquinone structure are still limited,[2] although various polyquinones with pendandant quinone groups have been prepared.[3] Here we report preparation of a new main-chain type polyquinone constituted of anthraquinone having strongly electron-withdrawing $NO_2$ groups.

Dehalogenation polycondensation of 1,5-dichloro-4,8-dinitroanthraquinone[4] with metallic copper at 100 ℃ in DMF gives the corresponding polymer P(4,8-$NO_2$-1,5-AQ)[5] quantitatively.



(1)

Monomer-1

P(4,8-$NO_2$-1,5-AQ)
100% Yield

The IR spectrum of P(4,8-$NO_2$-1,5-AQ) (Figure 1) resembles that of the monomer, and the ν(C-Cl) absorption peak of Monomer-1 at 1125 $cm^{-1}$ is not observable in the IR spectrum of the polymer. Data from elemental analysis agree with the structure. P(4,8-$NO_2$-1,5-AQ) has a high molecular weight as judged from its [η] value of 0.7 dl $g^{-1}$ (dl = 100 $cm^3$) in *N*-methyl-2-pyrrolidone at 30 ℃; a GPC trace (eluent = DMF) gives the *M*n and *M*w values of $8.6 \times 10^3$ and $1.3 \times 10^4$ (polystyrene standard), respectively.

A similar dehalogenation polycondensation with a Ni(0) complex[2a] also gives a similar polymeric compound, however, its IR peaks are broadened and it gives a smaller [η] value of 0.10 dl $g^{-1}$.

Although a similar polycondensation using Ni(0)Lm proceeds well with various dichloroanthraquinones,[2a] the nitro group in Monomer-1 may cause some side reactions with the zerovalent nickel complex to make the IR peaks broad.

$$n\ \text{Monomer-1} + n\ \text{Ni(0)L}_m \longrightarrow \text{P(4,8-NO}_2\text{-1,5-AQ)} \quad (2)$$

A powder X-ray diffraction chart of the polymer exhibits several distinct diffractions at 2θ(CuKα) = 12.3, 16.9, and 21.0 °, supporting that the polymer has a regular structure to form the crystalline material. Observation of simple sharp signal of the C=O carbon at δ 180 ppm in the CP-MAS $^{13}C$-NMR spectrum also supports the regular structure of P(4,8-$NO_2$-1,5-AQ).

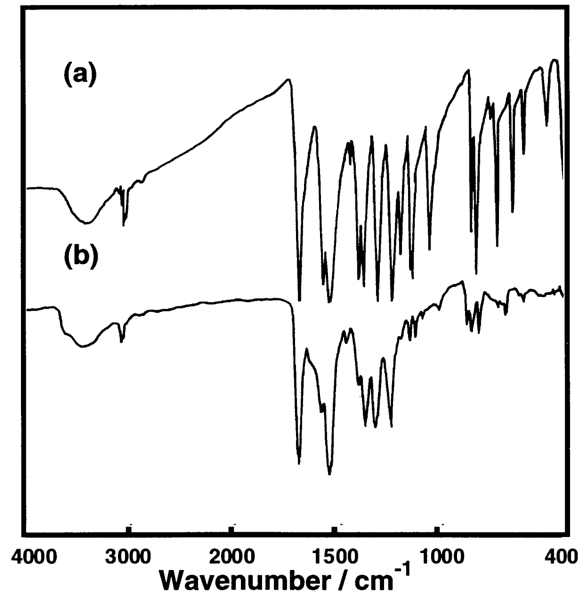


**Figure 1.** IR spectra of (a) Monomer-1 and (b) P(4,8-$NO_2$-1,5-AQ).

The polymer is soluble in various organic solvents, and its longest absorption band in the visible region shifts to a longer wavelength by increasing electron-donating ability of the solvent as shown in Figure 2. The highly electron accepting dinitro-

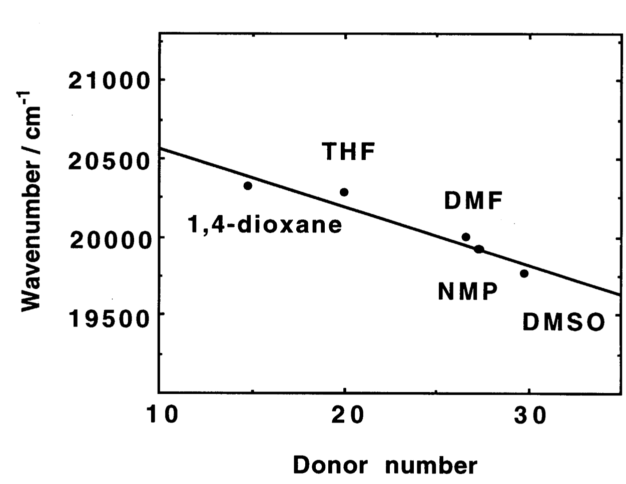


**Figure 2.** Solvatochromism of P(4,8-$NO_2$-1,5-AQ): dependence of $\nu_{max}$ on donor number of the solvent.

anthraquinone monomeric ring or the C=O group(s) may have donor-acceptor interaction with the solvents and this seems to be the origin of the solvatochromism.

One of the interesting properties of P(4,8-$NO_2$-1,5-AQ) is that the polymer has some dc conductivity ($\sigma$ = 1.4 x $10^{-6}$ S $cm^{-1}$ at room temperature; measured with compressed powder) even at the non-doped state.

Recently it has been reported that several $\pi$-conjugated polymeric compounds (e.g. poly(2,2'-bipyridine)-transition metal complexes[6] and poly(arylene)-*N*-oxides[7]) show similar intrinsic dc conductivity at the non-doped state, and their electrical conducting property has been attributed to the formation of carrier in the $\pi$-conjugated main chain by MLCT[6] or by taking of some resonance forms in the *N*-oxides.[7] Since the C=O and $NO_2$ groups attached at the aromatic rings can also form several resonance structures having positive or nagative center in the aromatic ring, similar generation of carrier(s) in the present polymer is also conceivable. This may be the reason for the intrinsic dc conductivity of the present polymer.

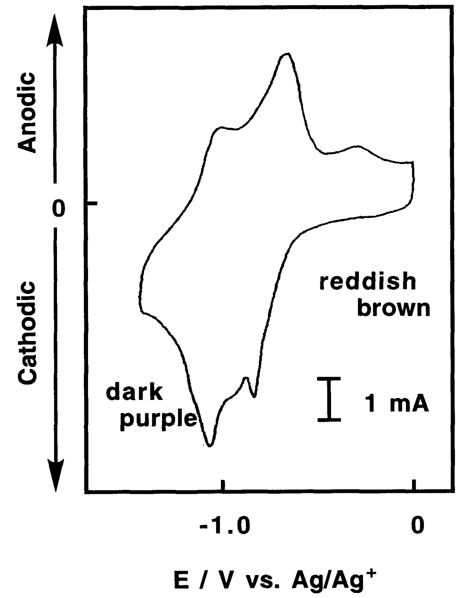


**Figure 3.** CV curve of a film of P(4,8-$NO_2$-1,5-AQ) laid (cast from DMF) on Pt plate in a $CH_3CN$ solution of $[Et_4N]BF_4$ (0.10 M) at a scanning rate of 50 mV $s^{-1}$.

Electrochemical reduction of a film of P(4,8-$NO_2$-1,5-AQ) (Figure 3) starts at about -0.6 V vs. Ag/Ag$^+$ and shows the first reduction peak at -0.8 V vs. Ag/Ag$^+$ in its cyclic voltammogram. These potentials locate at a positive side by about 0.5 V compared with those of non-substituted poly(anthraquinone-1,4-diyl)[2a] and indicate that the electrochemical reduction becomes much easier by introducing the $NO_2$ groups. To our knowledge, the reduction potential is lowest among reported reduction potentials of $\pi$-conjugated poly(arelene)s. When the CV measurement is carried out in the range of 0 to -1.5 V vs. Ag/Ag$^+$ as exhibited in Figure 3, the CV curve shows reversible redox processes. However, scanning beyond -1.5 V (e.g., to -2.0 V) vs. Ag/Ag$^+$ leads to irreversible reduction of the polymer, presumably due to occurrence of complex reaction(s) participated by the $NO_2$group.

The electrochemical reduction is accompanied with color change as depicted in Figure 3.

## References and Notes

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5 Synthetic conditions of P(4,8-$NO_2$-1,5-AQ) :Monomer-1 = 2.60 g (7.1 mmol), metallic Cu =1.80 g (28.3 mmol), DMF = 40 $cm^3$, and reaction time= 4 h. Anal. Found : C, 56.8; H, 1.5; N, = 9.6; Cl,0.6%. Calcd : C, 56.8; H, 1.4; N, = 9.5%. CP-MAS $^{13}$C-NMR : $\delta$: 128, 135, 136, 137, 144, 149, 180 ppm

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