Comparison of Optical Properties and Doping Behavior of –[(p-C_6H_4)$_m$NH]$_n$– ($m = 1$–4) Type Polymers

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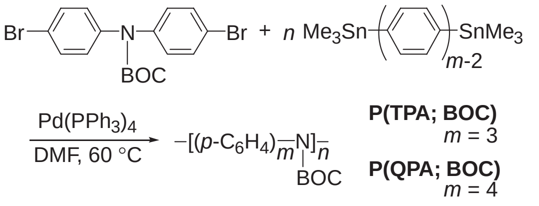
Poly(p-oligophenylene amine)s, –[(p-C_6H_4)$_m$NH]$_n$– ($m = 2$–4), receive electrochemical and chemical oxidation similar to polyaniline ($m = 1$). In the electrochemical oxidation (or p-doping) in aqueous media and acetonitrile, the oxidation of the polymer with $m = 3$ occurs at higher potentials by about 1.0 and 0.6 V, respectively, compared with that of polyaniline.

Polyaniline **PAn** and poly(p-phenylene) **PPP** are typical electro-functional polymers,[1] and numerous papers have been published on their chemical properties. –[(p-C_6H_4)$_m$NH]$_n$– ($m = 2, 3, 4$, etc.) type polymers are considered to be intermediate polymers between **PAn** and **PPP**, and comparison of their chemical properties with those of **PAn** and **PPP** is considered to be interesting. However, studies carried out on such a line have been limited, and optical and electrochemical properties of –[(p-C_6H_4)$_2$NH]$_n$–, **P(DPA)**, in a non-aqueous solution have been reported.[2] Herein, we report the comparison of optical and doping properties of –[(p-C_6H_4)$_m$NH]$_n$– ($m = 2$, 3, and 4) with those of **PAn** and **PPP**.

P(TPA) ($m = 3$) and **P(QPA)** ($m = 4$) were prepared via BOC (t-butoxycarbonyl)-protected polymers:



(1)

$$\textbf{P(TPA; BOC)}, \textbf{P(QPA; BOC)} \xrightarrow{200\ ^\circ\text{C}} \textbf{P(TPA)}, \textbf{P(QPA)} \quad (2)$$

The Pd-catalyzed polycondensation[1d,3] between the dibromo[4] and distannyl[5,6] compounds gave **P(TPA; BOC)**[7] and **P(QPA; BOC)**[8] in 93 and 87% yields, respectively. The BOC-protected polymers were soluble in organic solvents and films of the polymers were obtained by casting chloroform solutions of the polymers. Deprotection of the BOC group proceeded cleanly by thermal treatment of the BOC-polymers at 200 °C for 30 min under vacuum as revealed by IR spectroscopy,[9] and good films of **P(TPA)** and **P(QPA)** suited for optical and electrochemical studies were obtained by the thermal treatment of films of the BOC-polymers. The deprotected **P(TPA)** and **P(QPA)** were insoluble in organic solvents. **P(TPA)** and **P(QPA)** are considered as intermediate polymers between **PAn** and **PPP**.

By using films of **P(TPA)** and **P(QPA)**, as well as by using cast films of **PAn**[10] and previously reported **P(DPA)** ($m = 2$)[2,11] and a vacuum deposited film of **PPP**,[12] oxidation reactions of –[(p-C_6H_4)$_m$NH]$_n$– ($m = 1$–4) and **PPP** have been compared. The UV–vis absorption peak of the films of **PAn**, **P(DPA)**, **P(TPA)**, and **P(QPA)** shifted to a longer wavelength with the number of the p-phenylene unit, m, and the polymer films gave UV–vis absorption peaks at 335,[1,4] 368, 375, and 375 nm, respectively. The films of **P(TPA)** and **P(QPA)** showed photoluminescence peaks at 431 and 469 nm, respectively.

Figure 1 shows cyclic voltammograms (CV's) of the films of **P(DPA)** and **P(TPA)** measured in a 10 wt % aqueous solution of sulfuric acid. For comparison, a CV chart of **PAn** measured in an analogous aqueous solution of sulfuric acid (2 M)[10] is also shown.

As seen from Figure 1, the oxidation (or p-doping) of the polymer requires a higher potential when the number m in the polymer increases; a shift of 1.0 V is observed between $m = 1$ and $m = 3$. The film of **P(QPA)** showed a shoulder oxidation peak at about 1.3 V vs AgCl/Ag, near the oxidation peak of **P(TPA)**. The electrochemical oxidation of **P(DPA)** is accompanied with color change from yellow (original color of **P(DPA)**) to blue, as indicated in Figure 1. The UV–vis spectrum of the oxidized blue **P(DPA)** film exhibits broad absorption of light in a range from 400 nm to a near infrared region. The color change (electrochromism) was reversible, similar to **PAn** which exhibits electrochromism between yellow and blue. The electrochemical oxidation process of **PAn** in acidic aqueous media has

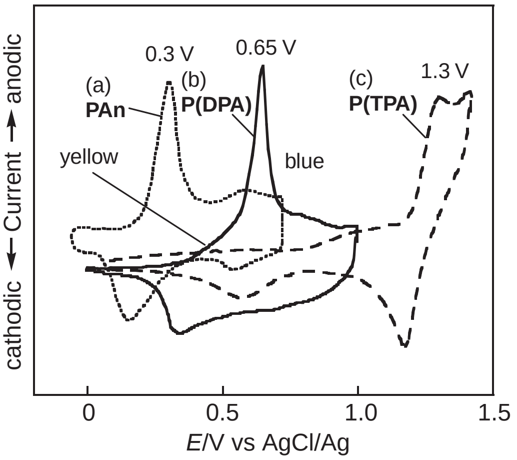
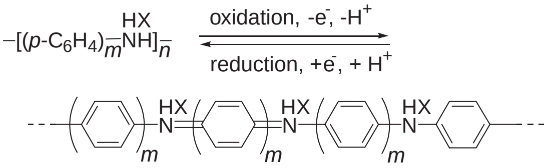


Figure 1. CV charts for films of **PAn** (dotted line),[10] **P(DPA)** (solid line), and **P(TPA)** (broken line) on a Pt electrode, measured in an aqueous solution of sulfuric acid. Sweep rate = 100 mV s^{-1}. The reported data of **PAn** was obtained in a 2 M aqueous solution of sulfuric acid.[10] Color of the **P(DPA)** film before and after oxidation is also shown.

been explained by the formation of a polyemeraldine salt or a polypernigraniline salt,[1,10] and the electrochemical oxidation of **P(DPA)**, **P(TPA)**, and **P(QPA)** may also be explained by formation of a similar salt, e.g.,



$$-[(p\text{-}C_6H_4)_m\overset{HX}{N}H]_n- \underset{\text{reduction, }+e^-,\ +H^+}{\overset{\text{oxidation, }-e^-,\ -H^+}{\rightleftarrows}} \quad (3)$$

Polyemeraldine type salt(HX = H_2SO_4)

The IR spectrum of electrochemically doped **P(DPA)** showed a broad absorption peak at 1100 cm^{-1}, which was characteristic of salts of sulfuric acid, and showed electrical conductivity of 0.13 S cm^{-1} and activation energy of 19.5 kJ mol^{-1} for the electrical conduction. The p-doping potential of **P(DPA)** was lowered to 0.51 V vs AgCl/Ag by increasing the concentration of sulfuric acid to 50 wt %.[11]

When the electrochemical oxidation was carried out in nonaqueous solutions, comparison of the data obtained with neutral **PAn**, **P(DPA)**, **P(TPA)**, **P(QPA)**, and **PPP** becomes possible. Figure 2 exhibits CV charts of the polymer films.

Reported CV charts of **PAn** and **P(DPA)**[2] are shown in Figure 2, and the position of peak oxidation potential (E_{pa}) of **PPP**[12] is shown by a bar. As seen from Figure 2, the peak oxidation potential shifts systematically to a higher potential in going from **PAn** to **P(QPA)**. The electrochemical oxidation may be explained by an equation similar to eq 3 and without HX or by p-doping mainly occurred at the *p*-oligophenylene unit. The absence or presence of the acid is considered to affect the E_{pa} difference between **PAn** and **P(TPA)**. **P(TPA)** and **P(QPA)** underwent oxidation on exposure to a vapor of iodine, similar to oxidation of **PAn**[13] and **P(DPA)**[2] by dihalogen, however, **PPP** was unreactive toward iodine. The original non-doped **P(TPA)** and **P(QPA)** showed only a very weak ESR signal. On exposure to a vapor of iodine, the ESR signal became stronger, and the spin concentration reached about 8×10^{21} per mol of the repeating monomeric unit after exposure to the vapor of iodine at room temperature for 15 h (in the case of **P(TPA)**) and 40 h (in the case of **P(QPA)**), respectively.

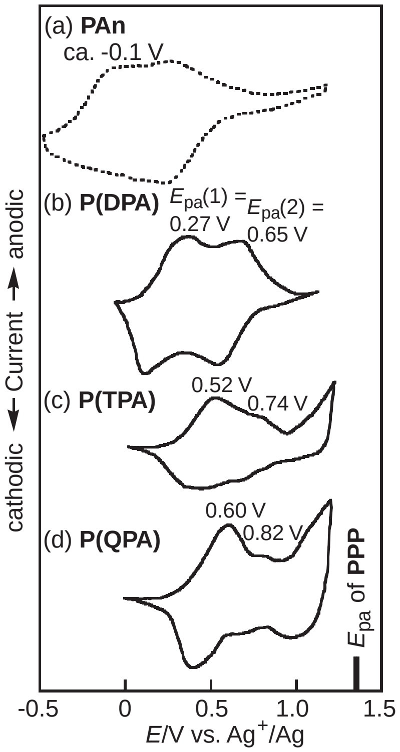


Figure 2. Comparison of CV data of films of **PAn**,[2] **P(DPA)**,[2] **P(TPA)**, **P(QPA)**, and **PPP**[12] measured in an acetonitrile solution of 0.10 M $[NEt_4]BF_4$. Sweep rate = 20 mV s^{-1}.

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8 ^1H NMR ($CDCl_3$): δ 7.74–7.12 (16H), 1.46 (9H). M_n = 9200. M_w = 11600.

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11 0.58, 0.54, and 0.52 V vs AgCl/Ag at 20, 30, and 40 wt % of sulfuric acid, respectively. The sample obtained by oxidation in the 50 wt % aqueous solution of sulfuric acid showed electrical conductivity of 1.0 S cm^{-1} and 7.1 kJ mol^{-1} activation energy for the electric conduction.

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