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The electrochemical properties of polyaniline derivatives: poly(4,4′-diphenylamine methylenes) and poly(4,4′-diphenylimine methines)

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Summary

The electrochemical properties of poly(4,4'-diphenylamine methylenes) and poly(4,4'-diphenylimine methines) were investigated by cyclic voltammetry. A dehydrogenation reaction occurred when poly(4,4'-diphenylamine methylenes) underwent a electrochemical reaction and transformed to poly(4,4'-diphenylimine methines). The fully oxidized poly(4,4'-diphenylimine methines) had the electrochemical band gaps of 1.60-1.72 eV, which were found to significantly smaller than those of the fully reduced poly(4,4'-diphenylamine methylenes).

Introduction

Polyaniline has probably attracted the most scientific interest among conjugated polymers for electronic, electrochemical, optical, and nonlinear optical applications in light of its relatively good environmental stability as well as the control of the electronic and optical properties by the level of oxidation and protonation(1-5). Our laboratories recently found that the various forms of polyaniline and its derivatives have interesting nonlinear optical properties(4). Cao et al. also discovered that the emeraldine base form of polyaniline with functionalized sulfonic acid was soluble in the conducting form in common organic solvents and has been used as the positive electrode for an all-plastic light-emitting diode (LED)(5).

The electrochemical properties of polyanilines have been extensively investigated because of their potential applications in rechargeable batteries(6-11). In those studies, the electrochemical redox reaction was found to strongly depend on the PH value of the electrolyte. The general mechanism of the electrochemical redox reaction of polyaniline proposed by Genies et al.(6), McManus et al.(7), and Watanabe et al.(8) is as follows: First, the polyamine form (leucoemeraldine base) is oxidized by a transfer of an electron and a radical cation at N-position is formed. By the second oxidation, a second electron is taken out from another nitrogen atom and, thus, a diradical structure is created. This diradical structure is then transformed to a diimine structure. Polyaniline derivatives such as poly(diarylamines)(9), poly(3-alkyldiphenylamine)(10), and poly(3-alkyloxydiphenylamine)(11) exhibited a similar electrochemical properties and mechanism as polyaniline. In this study, the electronic structure of polyanilines was

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elucidated by preparing poly(4,4'-diphenylamine methylenes)(**3**, in Figure 1) and poly(4,4'-diphenylimine methines)(**4**, in Figure 1) for the comparison with poly(leucoemeraldine base)(**1**, in Figure 1) and poly(pernigraniline base)(**2**, in Figure 1). The nitrogen atom of polyaniline is found here to function in an important role on the electronic, optical, and nonlinear optical properties(12, 13). The electronic structure of polyaniline is also further explored by studying the electrochemical properties of polymers **3** and **4**.

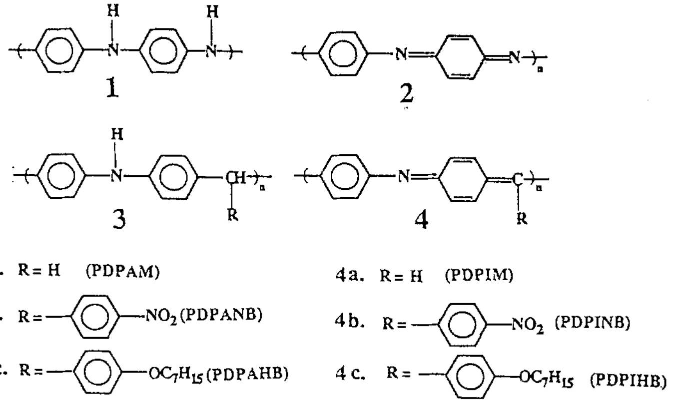

Figure 1. The chemical structures of polyanilines and derivatives.

Experimental

1. Polymer Synthesis

The synthesis of poly(4,4'-diphenylamine methylenes) and poly(4,4'-diphenylimine methines) was reported previously(12).

2. Characterization

The electrochemical properties of the polymers were studied by cyclic voltammetry. For cyclic voltammetry, an electrolyte solution of 1 M lithium chloride($LiClO_4$) in acetonitrile was used in the experiments. Platinum wire electrodes were used as both counter and working electrodes and silver/silver ion (Ag in 0.1 M $AgNO_3$ in the electrolyte solution, from Bioanalytical Systems, Inc.) was used as a reference electrode. Polymers were coated onto the working electrode by dipping the Pt wire electrode into 5-10 wt % THF or DMF solutions of polymers. The coated electrode was dried in a vacuum oven at 60°C for 2 hours. The reference electrode was calibrated at the beginning of each experiment by running cyclic voltammetry on ferrocene as the standard in an identical cell without any polymer on the working electrode. The electrochemical equipment used for the experiments was an EG&G Princeton Applied Research Model 273 Potentiostat/Galvanostat. Data were collected and analyzed using

Model 270 Electrochemical Analysis System for Model 273 from the same company. The potential values obtained versus ferrocene were converted to versus SCE by adding a constant of 0.1588 V to them. The conversion is based on the following reduction potentials from "CRC Handbook of Physics and Chemistry" (14). The gas phase Ionization Potential (IP) and Electron Affinity (EA) of the polymers were estimated using the following relations(15): $[E_{onset}]^{ox}$ = IP - 6.3 and $[E_{onset}]^{red}$ =EA - 6.3, where $[E_{onset}]^{ox}$ and $[E_{onset}]^{red}$ are the onset potentials for the oxidation and reduction of polymers versus SCE. Solid state IP and EA were obtained by subtracting 1.9 eV from the gas phase values.

Results and Discussion

Figure 2 shows the cyclic voltammograms of thin films of PDPAM and PDPIM in the potential range of -0.4 V - 1.35 V (vs. SCE) at a sweep rate of 20 mV/s. In the cyclic voltammogram labeled as **a**, an irreversible peak of electrochemical oxidation was observed at 0.62 V. This peak is assigned to the electrochemical oxidation of the amine group. The peak oxidation potential of PDPAM is 0.11 V larger than that of poly(diphenylamine) reported in previous literature (10). The substitution of one of the nitrogen atoms of polyleucoemeraldine base was found in our previous report (12) to have resulted in the decrease of π-electron delocalization. This decrease would probably account for the larger value of the oxidation potential of PDPAM than that of poly(diphenylamine) because poly(diphenylamine) has a quite similar chemical structure as polyleucoemeraldine base except for that the former has one more phenylene ring in the repeating unit. In the cyclic voltammogram labeled as **b**, a new PDPAM film was used in the electrochemical oxidation between the potential range of -0.4 - 1.35 V. Two peaks of the electrochemical oxidation were observed at 0.62 V and 1.10 V in the above potential range. The difference between the cyclic voltammograms **a** and **b** is the additional peak observed at 1.10 V. Figure 3 shows the proposed mechanism of the electrochemical oxidation of PDPAM. The oxidation reaction of PDPAM at the potential of 0.62 V takes the first electron from the amine group (eq. 1) and another electron is taken out from the polymer between the potential of 0.62-1.10 V (eq. 2). Therefore, a diradical structure is created and this is transformed to a PDPIM which has an imine bridge and a methine bridge (eq. 3). Hence, the oxidation peak of 1.10 V may be assigned to the electrochemical oxidation of PDPIM (eq. 4). This explanation can be confirmed by the cyclic voltammogram labeled as **c**, which is the electrochemical oxidation of thin film of PDPIM. A peak potential at 1.02 V was observed in the electrochemical oxidation of PDPIM. The close peak potential of the cyclic voltammograms **b** and **c** indicates that they are probably the same polymer. The electrochemical oxidation of both PDPAM and PDPIM was irreversible, which was similar to the electrochemical oxidation of polyaniline in aprotic solvents(9). The electrochemical oxidation of PDPANB, and PDPAHB also experienced a similar dehydrogenation reaction as that of PDPAM.

Figures 4 and 5 show the cyclic voltammograms of thin films of the electrochemical oxidation and reduction of polymers **4**. The electrochemical properties of the polymers **3** and **4** are summarized in Table 1. The onset potential of the electrochemical oxidation between polymers **3** and **4** did not show a significant difference. However, the onset of the electrochemical reduction of polymers **3** and **4** exhibited a major difference. The peak potential of the electrochemical reduction of thin films of polymers **4** was in the range of -1.58 - -1.31 V; meanwhile, that of polymers **3** did not have a reduction peak in the range between -0.4 V to -2.5 V (vs. SCE). Hence, the difference between polymers **3** and **4** is the larger electron affinity of polymers **4**. The electrochemical band gaps of polymers **3** and **4** were calculated from the difference between the ionization potentials and electron affinities. Experimental results indicated that the band gaps of polymers **4** in the range of 1.60-1.72 eV had much smaller band gaps than those of **3** (3.65 eV) due to the conjugated chemical structures of polymers **4**. The observed electrochemical band gaps of polymers **4** are in a sufficient correlation with those determined from the optical absorption spectra, which were in the range of 1.46-1.65 eV (12).

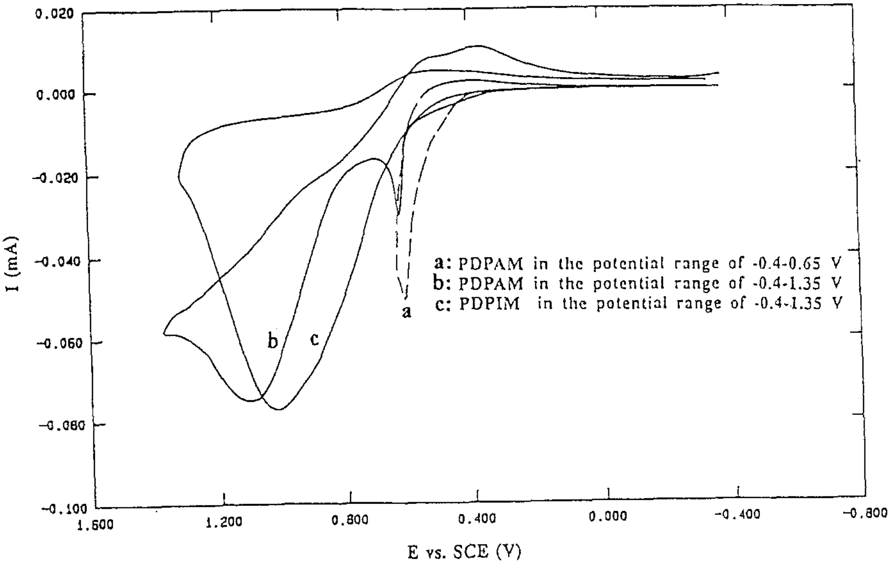

Figure 2. Cyclic voltammograms of PDPAM, and PDPIM in 1 M $LiClO_4$ in acetonitrile at a sweep rate of 20 mV/s.

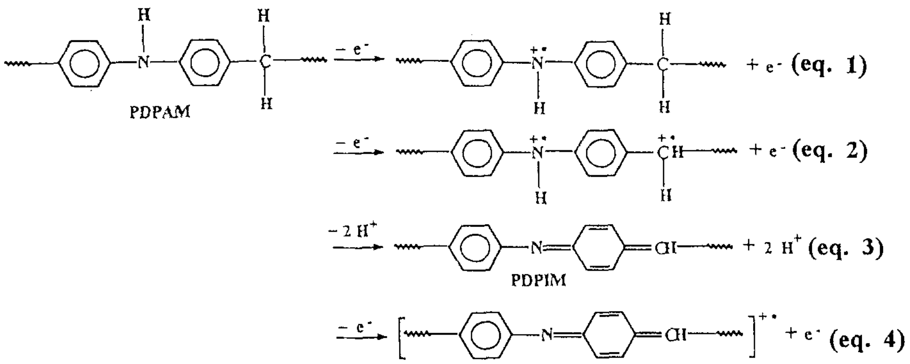

Figure 3. The proposed mechanism of the electrochemical oxidation of PDPAM.

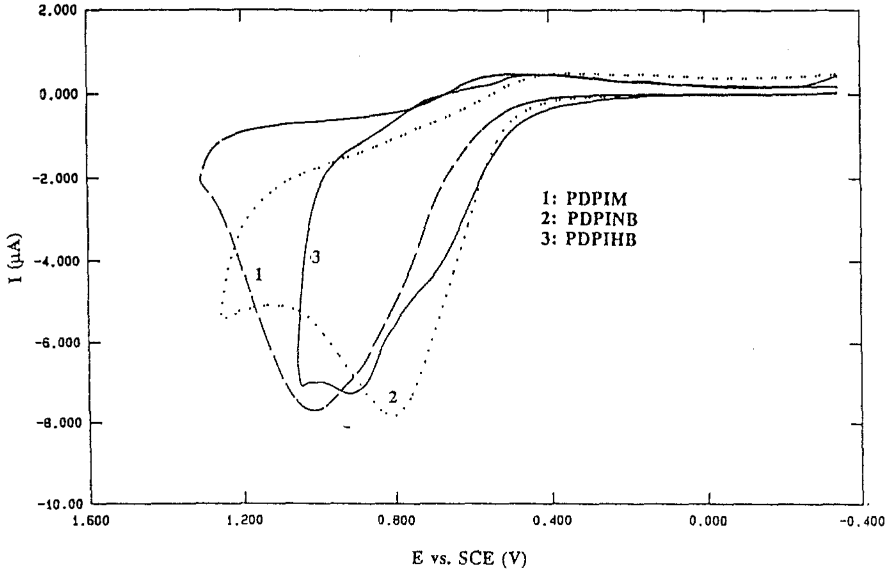

Figure 4. Cyclic voltammograms of PDPIM, PDPINB, and PDPIHB in 1 M $LiClO_4$ in acetonitrile at a sweep rate of 20 mV/s.

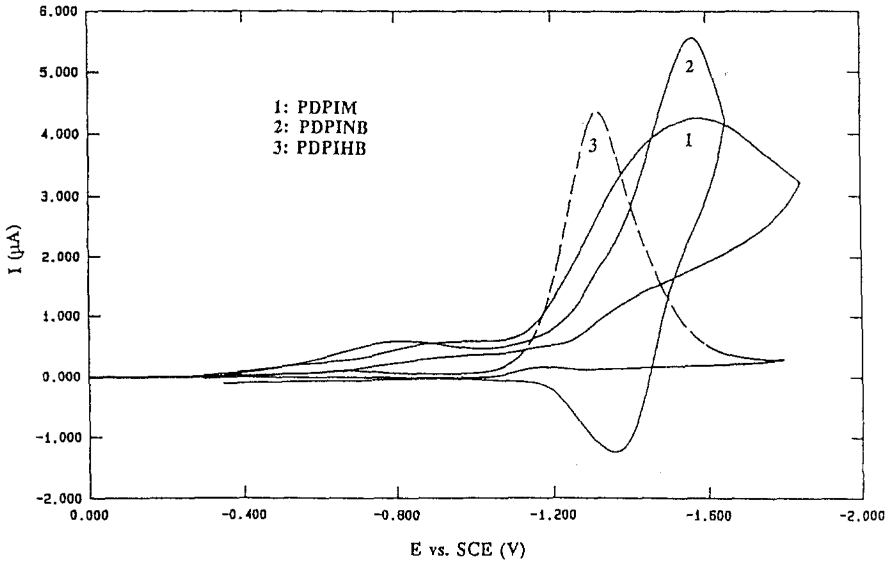

Figure 5. Cyclic voltammograms of PDPIM, PDPINB, and PDPIHB in 1 M $LiClO_4$ in acetonitrile at a sweep rate of 20 mV/s.

Table 1. Oxidation and reduction potentials of poly(4,4'-diphenylamine methylenes) and poly(4,4'-diphenylimine methines)

	Oxidation (vs. SCE)			Reduction (vs. SCE)				
Polymer	E_p (V)	E_{onset} (V)	IP (eV)	E_p (V)	E_{onset} (V)	EA (eV)	$E_g{}^a$ (eV)	$E_g{}^b$ (eV)
PDPAM	0.62, 1.10	0.56	4.96	—	—	—	—	3.65
PDPANB	0.74, 0.91	0.56	4.96	—	—	—	—	3.65
PDPAHB	0.70, 0.86	0.60	5.00	—	—	—	—	3.65
PDPIM	1.02	0.58	4.98	-1.53	-1.14	3.26	1.72	1.65
PDPINB	0.81	0.51	4.91	-1.56	-1.18	3.22	1.69	1.49
PDPIHB	0.91	0.51	4.91	-1.31	-1.09	3.31	1.60	1.46

a:electrochemical band gap E_g= IP-EA.

b:optical band gap determined from the threshold of an optical absorption spectrum of a polymer thin film(12).

Conclusions

The electrochemical properties of poly(4,4'-diphenylamine methylenes) and poly(4,4'-diphenylimine methines) were investigated in this study. Experimental results indicated that the fully reduced form poly(4,4'-diphenylamine methylenes) could be transformed to the fully oxidized form poly(4,4'-diphenylimine methines) by electrochemical reaction. The band gaps of poly(4,4'-diphenylimine methines) were found to be significantly smaller than poly(4,4'-diphenylamine methylenes). This result would suggest that the conjugated structure of the fully oxidized form resulted in a smaller bandgap than the fully reduced form.

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