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# Synthesis of Poly (2,5-dimethoxyaniline) and Electrochromic Properties

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Poly(2,5-dimethoxyaniline) (PDMA) was synthesized using electrochemical polymerization of DMA in oxalic acid. The PDMA film coated onto ITO glass was studied for its chemical structure, morphology, electro-deposition, and electro-activity by FT-IR, TGA, SEM, cyclic voltammetry, and UV-Vis spectrophotometry. The PDMA film showed reversible color changes from yellow to blue representing the transition between the fully reduced state to the fully oxidized state upon switching the potentials. The response time of the PDMA film in term of color change was investigated under various applied potentials and different types of acid electrolyte (HCl and $H_2SO_4$). The fast response time of less than 2 sec was observed at the applied potential of 1.6 V. In comparison with HCl, the use of $H_2SO_4$ as an electrolyte resulted in the fastest response time. Thus, the PDMA is a potential candidate in electrochromic devices due to its reversible color change and fast response time.

**Keywords:** *electrochromic polymer, Poly(2,5–dimethoxyaniline), electrochemical polymerization, response time*

## 1. Introduction

In recent years, there has been much interest in the development of electrochromic devices (ECDs) based on light modulation effect. They can be used in a wide variety of applications such as smart windows, electromagnetic shutters, nonemissive displays, and rear-view mirrors[1-5]. An electrochromic device is an electrochemical cell that is composed of optically transparent electrodes coated with electrochromic materials and separated by a suitable solid or liquid electrolyte. Electrochromic materials change their color in a persistent but reversible manner by an electrochemically induced redox reaction under the applied potential[6]. Two types of electrochromic materials are currently used in electrochromic devices: inorganic and organic compounds[7,8]. However, inorganic materials are generally expensive to process which limits the commercial and industrial applications. Therefore, the use of organic materials, particularly conducting polymers, has received more attention because of their fast response, low cost, good processibility, and color tailor ability[9].

Polyaniline, discovered in 1982 by Letheby[10], is one of the most studied conducting polymers and has been used in many applications due to their environmental stability, low cost of fabrication, and unusual electrical and optical properties[11-15]. In addition, polyaniline exhibits electrochromic effects, from pale yellow to green to blue-velvet[16-18]. However, the main disadvantages of polyaniline are its insolubility in common organic solvents and its infusibility[19]. Previous studies revealed that introducing mono alkyl or alkoxy substituents on the *ortho* position of the phenyl ring resulted in an increase of solubility, and at the same time, a decrease in conductivity[20-25]. However, the presence of 2,5-dialkoxy substituted on the phenyl rings resulted in an enhanced conductivity[12]. Recently, 2,5-dimethoxyaniline (DMA) has been reported to produce soluble poly(2,5-dimethoxyaniline) (PDMA) with a conductivity similar to polyamine[26-33]. Zotti and coworkers reported the first electrosynthesis of PDMA in 1.0 M $NaHSO_4$ and found that the properties of PDMA were of great value for using as an electrochromic material in electrochromic devices[26]. Generally, the properties of polymers depend on the synthesis conditions, *e. g.* the type of acids used as a supporting electrolyte, monomer concentration, applied potential, solvent, and pH. The influence of anions of strong acids (HCl, $H_2SO_4$, $HClO_4$, and $CCl_3COOH$) on the formation and electroactivity of PDMA was studied by Palys and coworker[28]. Moreover, the performances of PDMA film, such as optical contrast, stability, and switching time, were improved by blending PDMA with other polymers such as poly(styrene sulfonic acid)[31], poly (3-trimethoxysilanyl-propyl-N-aniline)[32], and waterborne polyurethane[33].

Herein, we reported the electrodeposition of PDMA on an indium tin oxide (ITO) glass electrode from an oxalic acid medium. The electroactivity of the prepared PDMA film was studied by cyclic voltammetry and in situ UV-VIS spectrophotometry. The effects of acid electrolyte type and the applied potential on the response time of the PDMA films were investigated and reported here.

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## 2. Experiment

### *2.1. Materials*

2,5-Dimethoxyaniline (DMA, 98%) was obtained from Aldrich Chemical Co. and used without further purification. The AR grade chemicals, oxalic acid (Ajax Finechem), hydrochloric acid (RCI Lab Scan), and sulfuric acid (Lab Scan), were used as received.

### *2.2. Synthetic of poly(2,5-dimethoxyaniline)*

Poly(2,5-dimethoxyaniline) (PDMA) film was deposited on the ITO (indium tin oxide) coated glass by the potentiostatically electrochemical polymerization of DMA at room temperature according to the published procedure[34-36]. Prior to each experiment, the ITO coated glass electrode was cleaned with acetone and distilled water.

The electrolyte solution used to obtain PDMA (0.125 M) was prepared by dissolving DMA in 1.0 M oxalic acid. Electrochemical polymerizations were performed using a DC power supply (Goldsun DC supply, GPS-3003B). The ITO glasses were used as the working and the reference electrodes. The PDMA film was formed on ITO glass plate by applying a constant potential of 1.2 V at 10 minutes.

#### 2.2.1. Electrochemical measurement

Cyclic voltametric studies were performed with a multi-channel potentiostat (VMP, Bio Logic Science Instrument) using a cuvette cell with a 1 cm path length. A three-electrode cell assembly was used with Ag/AgCl as a counter electrode and two ITO glasses as the reference and the working electrodes. Cyclic voltammetry was carried out by scanning the potential from –0.5 to +0.5 V for 50 cycles with a sweep rate of 20 mV/s in a 0.125 M DMA electrolyte solution.

#### 2.2.2. Characterization

A Fourier transform infrared spectrometer (FT-IR; Thermo Nicolet, Nexus670) was used to investigate the chemical structure of PDMA in the absorption mode with 64 scans, a wavenumber range of 4000-400 cm$^{-1}$, and using KBr as the background material. The thermal stability and decomposition temperature of PDMA were investigated using a thermogravimetric analyzer (TGA; Perkin Elmer, TGA7). The sample was weighed (5-10 mg) and then placed it in an alumina pan and heated under nitrogen atmosphere with a heating rate of 10 °C/min from 50-800 °C. The morphology of PDMA film was examined by a field-emission scanning electron microscopy (FE-SEM; Hitachi S4800).

#### 2.2.3. Spectroelectrochemical measurement

UV-VIS spectra of PDMA films were recorded on a UV-VIS-spectrophotometer (Shimadzu, UV-1800). Measurements were carried out in a cuvette of 1 cm path length with 0.001 M HCl and 0.001 M $H_2SO_4$ as the supporting electrolytes. The wavelength was in the range 300 to 900 nm with the scan speed of 240 nm/min and the slit width of 1.0 nm.

## 3. Results and Discussion

### *3.1. Electrochemical polymerization of poly(2,5-dimethoxyaniline)*

The electrodeposition of PDMA on an ITO glass electrode was carried out from the electrolyte solution containing 0.125 M DMA and 1.0 M oxalic acid. The use of dibasic oxalic acid rather than mineral acids such as HCl and $H_2SO_4$ showed higher adhesion of polyaniline on substrate[35,37]. The polymers were deposited on the ITO glass electrode by scanning the potentials between –0.5 to +0.5 eV *versus* Ag/AgCl reference electrode.

The mechanism of electrochemical polymerization of PDMA consists of three steps as illustrated in Figure 1[38]. The first step is the formation of DMA cation radicals by anionic oxidation on the electrode surface. The next step is the coupling of DMA cation radicals followed by the elimination of two protons and rearomatization leading to the formation of dimer or oligomer. The dimer or oligomer is further oxidized on the anode together with the monomer. The chain propagation is achieved by coupling radical cations of the oligomer with DMA radical cation. Finally, the counter anion originatings from the acid dopes the polymer. The positively charged structure can react with the negatively charged oxalate counter ion to form doped-PDMA whose structure was examined using FTIR. The FTIR spectra showed the absorption bands at 1208 and 1182 cm$^{-1}$ which were assigned to the C–O stretching. The bands at 1673 and 3363 cm$^{-1}$ represented the C=O oxalate ion and the O–H stretching, respectively[39]. Furthermore, there were three steps in the PMDA decomposition. The initial weight loss at ~ 120 °C was the degradation temperature of water or moisture molecules. The weight loss at~280 °C was the decomposition of the dopant anion (oxalate anion). Finally, the decomposition temperature of PDMA backbone was at~400 °C[40,41]. These results confirm the successful polymerization of the doped-PDMA.

Cyclic voltammograms of ITO/PDMA electrode in the potential range of –0.5 to +0.5 V are shown in Figure 2. According to previous studies, two sets of redox peaks are usually observed for PMDA[28-30,42,43]. The first redox peak corresponds to the transition from totally reduced leucoemeraldine form to emeraldine (polaron cation radical) form, and the second redox peak is the transition from emeraldine form to fully oxidized pernigraniline (bipolaron) form, as illustrated in Figure 3. As can be seen in Figure 2, in oxalic acid solution, a broad oxidation peak is observed in the potential range 0.20 to 0.25V, and two reduction peaks are observed in the range +0.18 to +0.28 V and at –0.02 V. In this study, it is difficult to separate two oxidation transitions of PDMA film from the broad oxidation peak. This result can be explained by the anion effect. Palys and coworkers studied the electroactivity of PDMA in various strong acid solutions ($HClO_4$, $H_2SO_4$, HCl, and $CCl_3COOH$) and reported that the shapes of PDMA cyclic voltammograms strongly depended on the type of anion[28]. Therefore, the larger anion inhibits polymer oxidation resulting in the broad oxidation peak.

On sequential cycles to 50 cycles, the current intensity gradually increased indicating that the PDMA films were

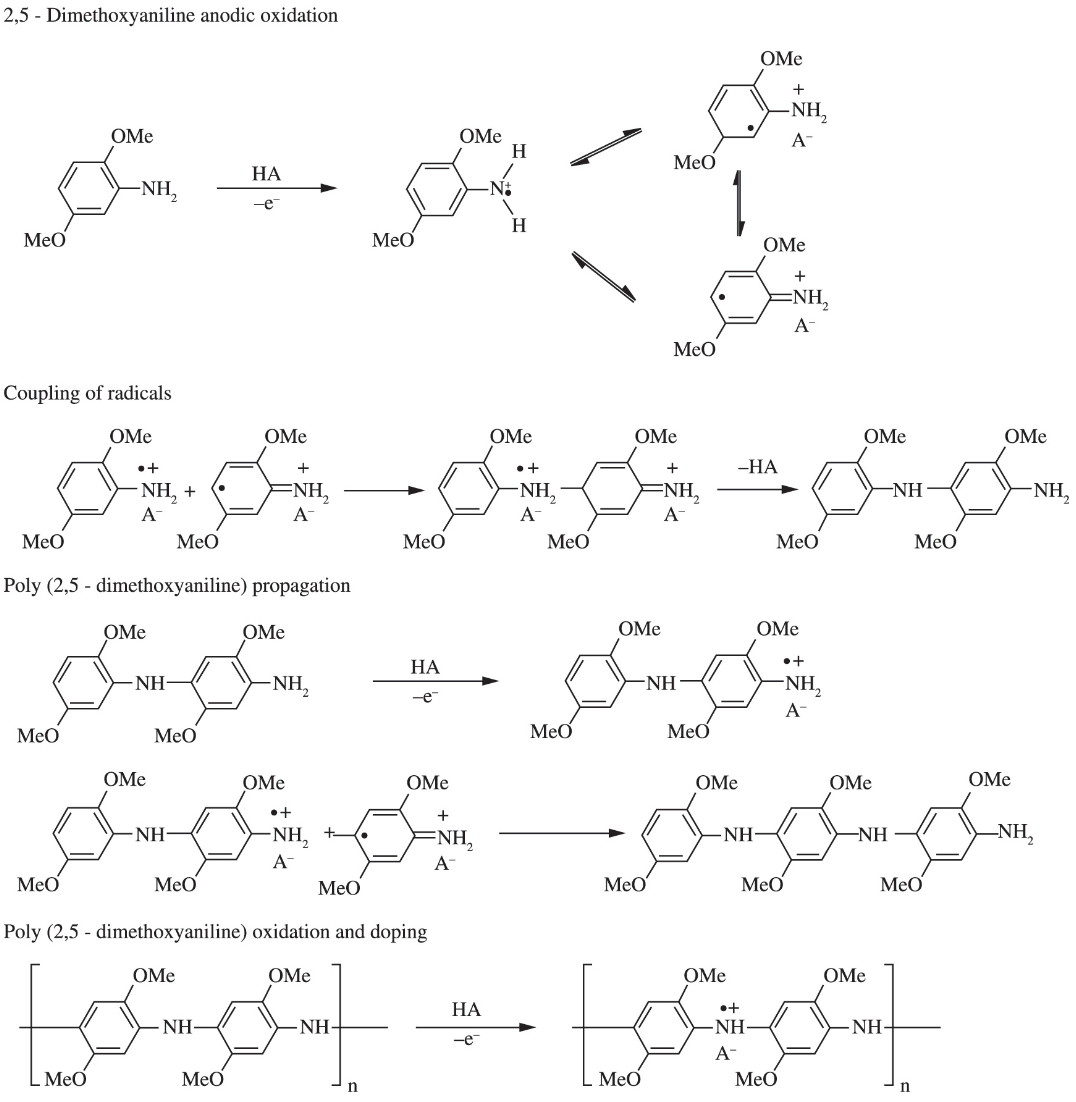


**Figure 1.** 2,5-Dimethoxyaniline to poly(2,5-dimethoxyaniline) electrochemical polymerization mechanism[38].

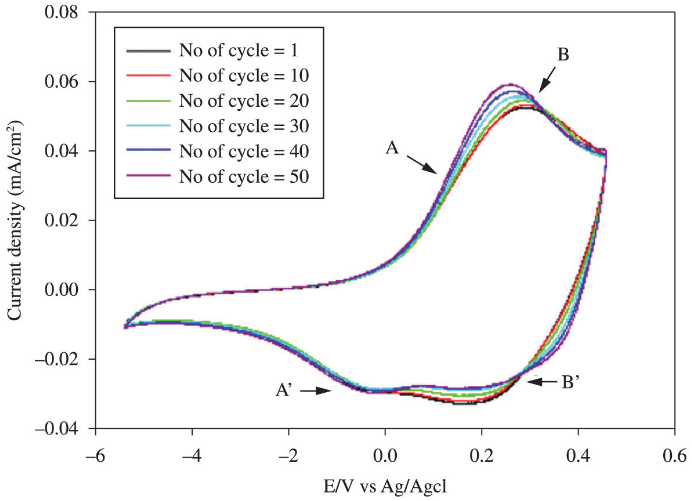


**Figure 2.** Cyclic voltammograms of the PDMA films coated on the ITO glass electrode during the repetitive cycling (10-50 cycles) between –0.5-+0.5 V; scan rate = 20 mV/S; 0.125 M of DMA electrolyte solution.

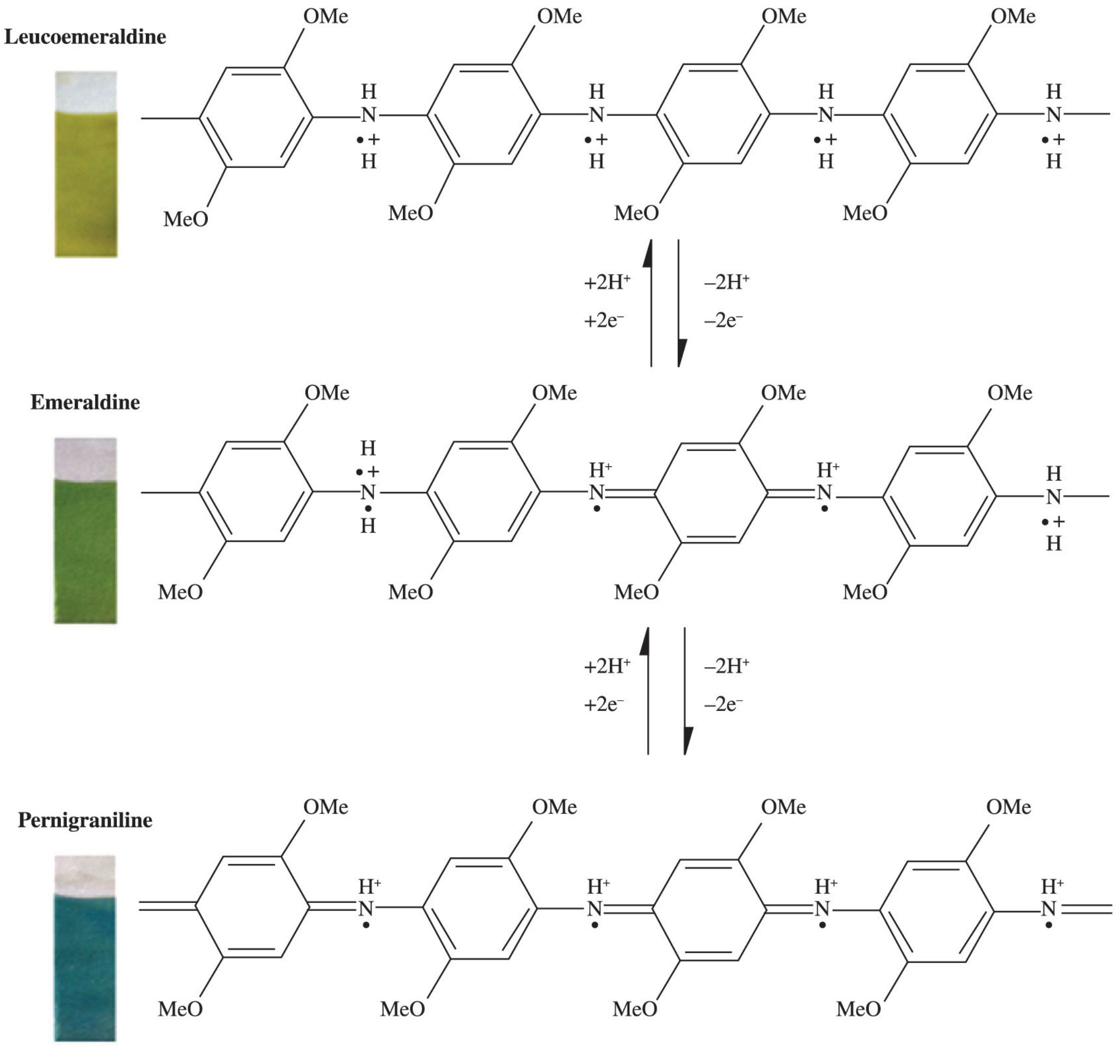


**Figure 3.** Various forms of poly(2,5-dimethoxyaniline).

formed on the ITO surface[4,44]. The increase of a peak current with the number of potential scans is the characteristic of the formation of a conductive and electroactive polymer on a conductive substrate surface[4]. The onset of oxidation potential gradually decreasing under repeated cycles is attributed to the formation of thicker layer of PDMA on the ITO electrode. Hence, the polymer is more easily oxidized. The increase in potential scans also results in the more anodic oxidation peak and the more cathodic reduction peak. These observations can be explained by heterogeneous transfer kinetics with a decrease in conductivity, counter-ion mobility, and the conjugate length[4,45,46].

The morphology of PDMA film synthesized on ITO glass is a porous structure as shown in Figure 4 In the previous work, Suephatthima et al. studied the effect of electrolytes namely oxalic acid, hydrochloric acid, and nitric acid on the morphology of PDMA. The morphology appeared as a highly porous microfiber structure, disordered microfiber, and ordered tiny-granular aggregate for the PDMA films synthesized using oxalic acid, nitric acid, and hydrochloric acid, respectively. The PDMA film synthesized by using oxalic acid was a less compact structure because it was the largest doping acid size ($C_2O_4^{2-}$) leading to a larger space within PDMA chain[41].

## *3.2. Spectroelectrochemistry of poly(2,5-dimethxyaniline) film*

The UV-VIS spectra of PDMA film recorded at different applied potentials (0.3 V, 0.5 V, and 1.0 V) in 0.001 M HCl as supporting electrolyte show three absorption bands at 370, 470 and 690 nm, as depicted in Figure 5. The peak at 370 nm corresponds to the full reduced leucoemeraldine state of PDMA (yellow). Upon partial oxidation, this peak changes to a peak at 470 nm which is an intermediate state between leucoemeraldine form containing benzenoid rings and emeraldine form containing conjugated quinoid rings in the backbone of the PDMA (green)[30]. For the complete oxidation, the fully oxidized pernigraniline form (blue) occurs at 690 nm whereas the peak at 470 nm disappears.

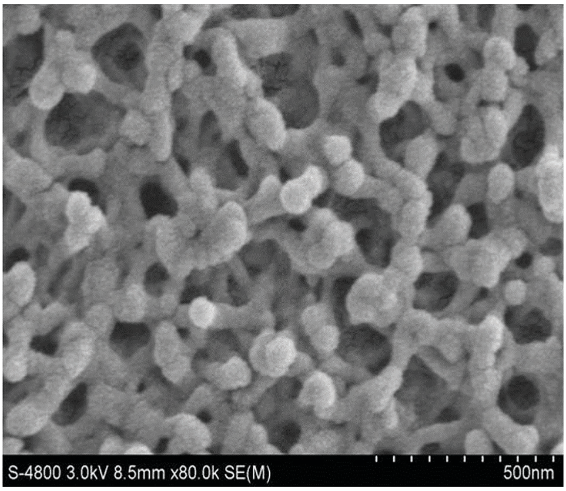


**Figure 4.** Morphology of poly(2,5-dimethoxyaniline).

### 3.3. Response and reversibility of poly(2,5-dimethoxyaniline) film

The response and reversibility of the PDMA film can be determined by a response time which is the time that the polymer takes in response to the potential pulse to go from the color of fully oxidized/reduced state to the color of fully reduced/oxidized state. In this study, the effect of electrolyte types (0.001 M HCl and 0.001 M $H_2SO_4$) on the response time of the synthesized PDMA films coated on the ITO glass electrode was investigated using UV-VIS spectrophotometry. Table 1 shows the response times of the PDMA films obtained from the oxidation (positive potential) and the reduction processes (negative potential) under the specific applied potential (0.2 to 1.6 eV). For the oxidation reaction, the color changes from yellow to blue and *vice versa* for the reduction reaction.

It can be seen from the data in Table 1 that, at the potentials between 0.2 to 0.6 V, no color change of the

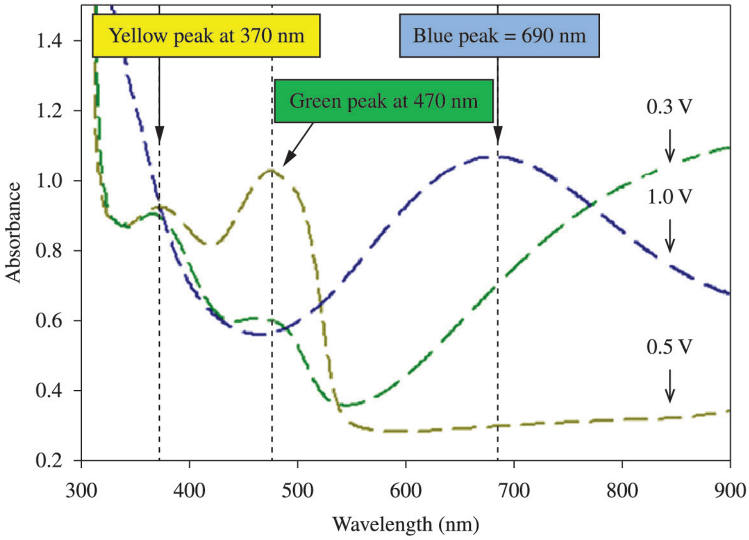


**Figure 5.** UV-VIS Spectra of the PDMA film coated on the ITO glass electrode recorded at different applied potentials.

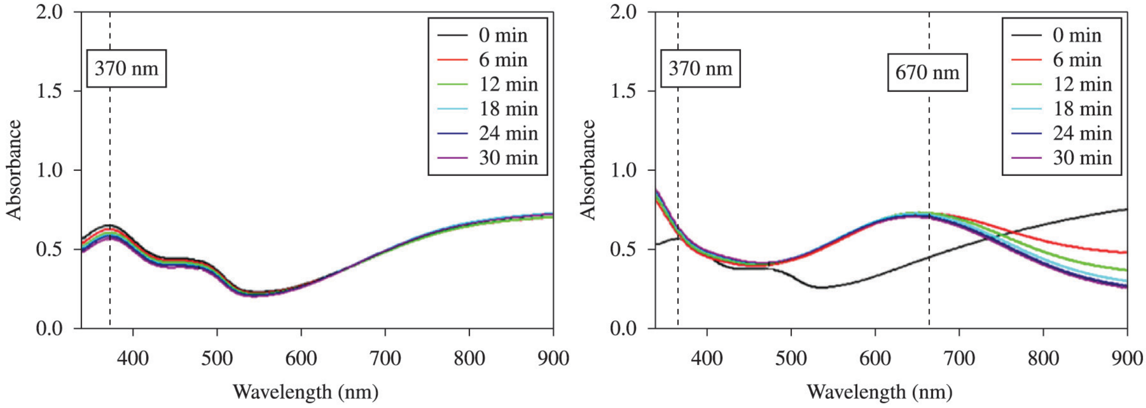
**Table 1.** The response times of PDMA in the oxidation and reduction processes at different applied potentials using 0.001 M HCl and 0.001 M $H_2SO_4$ as acid electrolytes.

| Voltage | Oxidation (Positive Potential) | | Reduction (Negative Potential) | |
|---|---|---|---|---|
| | HCl | $H_2SO_4$ | HCl | $H_2SO_4$ |
| 0.2-0.6 V | No change in color (Yellow) | No change in color (Yellow) | No change in color (Blue) | No change in color (Blue ) |
| 0.8 V | 34 sec (Yellow to Blue) | 40 sec (Yellow to Blue) | 12 sec (Blue to Yellow) | No change in color (Blue) |
| 1.0 V | 22 sec (Yellow to Blue) | 18 sec (Yellow to Blue) | 10 sec (Blue to Yellow) | 6 sec (Blue to Yellow) |
| 1.2 V | 14 sec (Yellow to Blue) | 8 sec (Yellow to Blue) | 6 sec (Blue to Yellow) | 6 sec (Blue to Yellow) |
| 1.4 V | 6 sec (Yellow to Blue) | 4 sec (Yellow to Blue) | 4 sec (Blue to Yellow) | 4 sec (Blue to Yellow) |
| 1.6 V | 2 sec (Yellow to Blue) | 1 sec (Yellow to Blue) | 2 sec (Blue to Yellow) | 1 sec (Blue to Yellow) |

PDMA film is observed due to the insufficient redox energy for the dopants to induce charge transport in polymer[47]. At the potential of 0.8 V, the response time of PDMA in HCl electrolyte (34 s) under the oxidation process is faster than that of in $H_2SO_4$ electrolyte (40 s). This can be explained by the effect of the doping acid size; *i.e.* if the doping acid size is large, the diffusion of doping acid into the polymer matrix will be hindered[48]. On increasing the potential from 1.0 to 1.6 V, the response times of the PDMA films in both acid electrolytes decrease due to the increase of the conductivity upon increasing the applied potential[49]. The response time for the reduction process is generally faster than that of for the oxidation process. The faster response time in the reduction process in comparison with the oxidation process was also observed for polyaniline. The protonation of PDMA film can easily occur due to the higher amount of protons in the electrolyte solution[8].

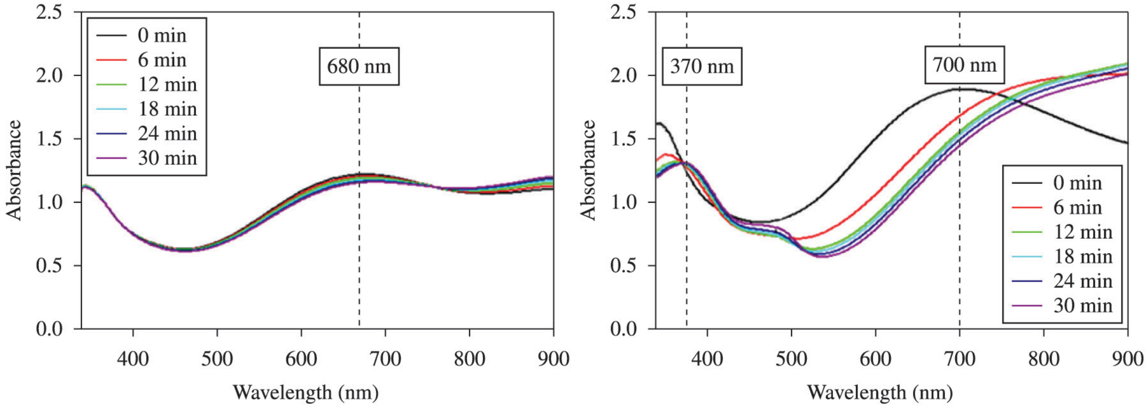
In comparison with HCl, the response time in $H_2SO_4$ was faster. This can be explained by the extent of doping the polymer[50]. Due to the diprotic nature of $H_2SO_4$, the concentration of $H^+$ ions in the matrix was higher resulting in increasing extent of doping via a protonation/deprotonation mechanism. The $H^+$ ions were required for the formation of quinoid rings and anions initiate the formation of polarons and bipolarons as the conducting states. Therefore, the response time in $H_2SO_4$ was faster due to the higher conductivity.

Figures 6a and 6b show the UV-VIS spectra of the PDMA films obtained from the oxidation reactions at the applied potentials of 0.2 and 1.6 V, respectively. The spectra were recorded from 0 to 30 sec with a 6 sec interval. At 0.2 V, the peak at 370 nm representing the leucoemeraldine structure remains unchanged upon increasing the reaction time because these potentials are not effectively for the dopants to induce charge transfer in polymer. However, at 1.6 V, on increasing the reaction time, the peak corresponding to the leucoemeraldine form gradually decreases with a simultaneous increase of the peak at 670 nm which belongs to the fully oxidized pernigraniline form. For the reduction process, the UV-VIS spectra are shown in Figure 7. Due to the low applied potential of –0.2 V, the initial peak at 680 nm remains the same with the increase in the reaction



(a) (b)

**Figure 6.** In-situ spectra of PDMA film coated on the ITO glass electrode during the oxidation reaction in the 0.001 M HCl electrolyte at 6 sec intervals: (a) at 0.2 V and (b) at 1.6 V.



(a) (b)

**Figure 7.** In-situ spectra of PDMA film coated on the ITO glass electrode during the reduction reaction in the 0.001 M HCl electrolyte at 6 sec intervals: (a) at 0.2 V and (b) at 1.6 V.

time, as shown in Figure 7a. At –1.6 V, the transformation of the fully oxidized pernigraniline form to the fully reduced leucoemeraldine form can be observed, as shown by the presence of the new peak at 370 nm in Figure 7b.

Huang et al. studied the electrochromic properties of PDMA synthesized by the electrochemical polymerization under using $H_2SO_4$ as an electrolyte. They reported the time necessary for coloration of PDMA, under the oxidation reaction at electrical potential 0.4 V, was 9 sec which was faster than that of the present work (no color change at 0.4 V) due to the difference of strong acid electrolyte for synthesis. $H_2SO_4$ is evidently stronger than oxalic acid it is easy to produce electrons and deprotonation of PDMA under the oxidation reaction. The response time for coloration of PDMA under $H_2SO_4$ is faster than that of oxalic acid[30]. However, using oxalic acid as an electrolyte for the synthesis of PDMA brings about higher adhesion of film on substrate than using $H_2SO_4$ as the electrolyte[35,37]. In summary, the PDMA film can be switched successfully from yellow to blue and blue to yellow through applying negative and positive potentials via the redox switching.

## 4. Conclusion

The synthesis of poly(2,5-dimethoxyaniline) (PDMA) coated on an ITO glass electrode by the electrochemical polymerization method from an oxalic acid solution under a constant applied potential of 1.2 V was investigated and reported here. The PDMA films exhibited multiple colored states depending on the redox state upon switching potentials. The response time of the PDMA film could be controlled by the applied potential and the type of electrolyte. The minimum response time of less than 2 sec was observed at the applied potential of 1.6 V in $H_2SO_4$ electrolyte . The response time of the PDMA film in HCl electrolyte was longer than that of the $H_2SO_4$ electrolyte.

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