CHAPTER IV
MANUSCRIPT

Synthesis and Characterization of Poly(2,5-dimethoxyaniline) for Use as Electrochromic Smart Materials

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Abstract

Colors of electrochromic smart materials are reversible when burst of charges are applied. These materials are widely used in displays, automotive industry, smart windows, and architecture. Poly (2,5–dimethoxyaniline) or PDMA possesses excellent properties: light weight, high electrical conductivity, environmental stability, simple doping and de-doping chemistry, and relatively inexpensive monomer. Due to their properties, PDMA is a candidate as electrochromic materials. The polymer was synthesized via the electrochemical polymerization method by using an oxalic acid as the supporting electrolyte. This work aims to investigate the effects of electric field strength and electrolyte type on electrochromic properties, electrical properties, and the response time. PDMA was submerged into HCl and H_2SO_4 electrolytes, and then submitted to various voltages of 0.8, 1.0, 1.2, 1.4 and 1.6 V. The transient color changes were observed in both electrolytes and the time for material undergoing the changes were recorded. It was observed that the response time was reduced as applied voltage increased for both HCl and H_2SO_4 electrolytes.

Keywords: Electrochromic polymer, Poly (2, 5–dimethoxyaniline), Electrochemical polymerization

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1. Introduction

Presently, the conductive polymers have received attentions due to their unique characteristics between metals or semiconductors; electric, electronic, magnetic and optical properties; and mechanical properties. These polymers have conjugated double bonds along the backbones [1, 2]. Each bond contains a strong sigma (σ) bond and a weaker pi (π) bond, so the conjugation can occur along the polymer backbone. Hence the conductive polymers possess good electrical conductivity properties [3].

However, the electrical conductivity of pure conductive polymers is rather low, thus a doping process is necessary to achieve a higher conductivity [4]. The applications of conductive polymers are organic light-emitting diodes, super capacitors, biosensors, organic solar cells, actuators, flexible transparent displays, electrochromism, electromagnetic shielding, and possibly replacement for the popular transparent conductor indium tin oxide [5].

The most interesting conductive polymers belong to the chromogenic polymers which can change colors when they are stimulated by heat, biochemical reaction, electric field, ultraviolet (UV) light, pressure, ion concentration, and magnetic field. An electrochromic polymer is one type of the chromogenic polymers which can change their colors under applied electric field [6]. This polymer is the most suitable for the chromogenic technology for energy control and saving in buildings. The mechanism occurs via the oxidation–reduction reaction. It results from the energy difference between the π-bonding orbital (conduction band) and the π^*-antibonding orbital (valence band) that lies within the visible region. Upon oxidation, the intensity of the π-to-π^* transition decreases, and the two row energy transitions emerge to produce a second color [7]. These materials are widely used in displays, automotive industry, smart windows, and architecture.

In this work, PDMA will be synthesized with an oxalic acid via the electrochemical polymerization. Then PDMA were characterized by the cyclic voltammetry (CV), FTIR, the thermalgravimetry analysis (TGA), the conductivity measurement, and the UV-VIS absorption spectroscopy to study the effects of electric field strength and types of electrolyte on the electrochromic properties in the response time.

2. Experimental

2.1 Materials

2,5 – Dimethoxyaniline (Sigma Aldrich, AR grade, 98%) was used as the monomer. Oxalic acid (Ajax Finechem, AR grade) was used as the supporting electrolyte to synthesize the polymer. Hydrochloric acid (RCI Lab Scan, AR grade, 37%) and Sulfuric acid (Lab Scan, AR grade, 98%) were used as the electrolytes to investigate the electrochromic properties.

2.2 Synthesis of Poly(2,5-dimethoxyaniline) (PDMA)

Poly (2,5 – dimethoxyaniline) was deposited as the conducting film on an indium tin oxide (ITO) coated glass by the electrochemical polymerization (ECP) of 2,5 – dimethoxyaniline (DMA) at a room temperature [8, 9]. The oxalic acid was used as the supporting electrolyte. A 0.125 mol of DMA was added to 0.1 M of oxalic acid. The electrochemical polymerization proceeded at 1.2 volt in a cuvette of 1 cm path length assembled as an electrochemical cell with PDMA film coated on the ITO glass as the working electrode, another ITO glass as the counter electrode, and 0.1 M oxalic acid as the supporting electrolyte. Before each experiment, the ITO electrodes were cleaned with acetone and distilled water.

2.3 Characterization and Testing of PDMA

A Fourier Transform Infrared spectrometer or FT-IR (Bruker, Equinox 55/FRA 106/S) was used to characterize for the polymer functional groups in the absorption mode with 32 scans and a resolution of ± 2 cm^{-1}, in a wavenumber range of 4000 – 400 cm^{-1}. Optical grade KBr (Carlo Erba Reagent) was used as the background material.

A thermogravimetric analyzer (Perkin Elmer, TGA7) was used to study the thermal stability and determine the decomposition temperature of poly (2,5-dimethoxyaniline). The experiment was carried out by weighting a powder sample of 5 – 10 mg and placed it in a platinum pan then heated it under nitrogen flow with the heating rate 10 °C/min from 50 – 800 °C.

Two point probe coupled with an electrometer (Keithley, model 6517A) was used to measure electrical conductivity under atmosphere condition. A voltage was applied between probes numbered 1 and 2 and the resultant current was measured across the probes numbered 1 and 2. The specific conductivity, σ (S/cm) was obtained by measuring the resistance (R), and using the following relation

$$\sigma = (1/KRt), \tag{1}$$

where t is the film thickness, and K is the geometric correction factor or the ratio of the probe width divided by the probe length. A geometric correlation factor was calibrated by using standard silicon wafer sheets with known specific resistivity values. This measurement was repeated at least three times.

2.4 Cyclic Voltammetry (CV) of PDMA

Multi-Channel Potentiostat (VMP, Bio Logic Science Instrument) was used to determine electrochemical properties of PDMA through the cyclic voltammetry [5,6]. Measurements were carried in a cuvette of a 1 cm path length, assembled with a three electrodes cell consisting of a Ag/AgCl electrode and two pieces of the ITO glass used as the reference electrode, the working electrode, and the counter electrode, respectively. The experiment was separated in two parts:

In the first part, the CV voltammetry was used to study the synthesis performance of PDMA between –0.5 to +0.5 V for 50 cycles with a sweep rate 20 mV/s in a solution of 0.1 M of oxalic acid and 0.125 mol of DMA. The electrochromic device was compiled with the following configuration:

$$\text{ITO} \parallel \text{DMA} - \text{C2O4H2}\cdot\text{2H2O} \parallel \text{ITO} \qquad (2)$$

In the second part, the potential was used to study the life time of the electrochemical properties, between -0.5 to +0.5 V for 100 cycles with a sweep rate 20 mV/s in 0.001 M HCl electrolyte and 0.001 M H_2SO_4 electrolyte, respectively. The electrochromic device was compiled with the following configuration:

$$\text{ITO} \parallel \text{HCl} \parallel \text{PDMA/ ITO} \quad \text{and} \quad \text{ITO} \parallel \text{H2SO4} \parallel \text{PDMA/ ITO} \qquad (3)$$

After 100 cycles, the PDMA films in both electrolytes were characterized for the % transmittance by the UV spectrophotometer in the wavelength range 300 – 900 nm, the scan speed was 240 mm/min, a slit width of 1.0 nm, using a deuterium, and a tungsten lamp as the light source.

2.5 UV-VIS Absorption Spectrophotometer of PDMA

A UV-VIS absorption spectrophotometer (Shimadzu, UV-1800) was used to investigate the electrochromic properties, and to identify properties of the conducting polymer related to the electronic structure and the optical behavior upon the doping and the dedoping processes. Measurements were carried out in a cuvette cell of 1 cm path length, assembled as an electrochemical cell with the PDMA film coated ITO glass as the working electrode, another ITO glass as the counter electrode, and with 0.001 M HCl and 0.001 M H_2SO_4 as supporting electrolyte. The wavelength range was 300 – 900 nm, the scan speed was 240 mm/min, a slit width of 1.0 nm, using a deuterium, and a tungsten lamp as the light source. The experiment was separated into two parts:

1. Comparison of the response times between 0.001 M HCl electrolyte and 0.001 M H_2SO_4 electrolyte for each potential.
2. Comparison the response times at 1.2 V at different concentrations: 0.001, 0.01 M and 0.1 M for each electrolyte.

3. Results and Discussion

3.1 Characterization of PDMA

The FT-IR spectra of dope – Poly (2, 5 – dimethoxyaniline) display the characteristics of the oxalic acid group. The board band at 835 cm^{-1} can be assigned to the O–C=O in-plane deformation. Figure 1 show the absorption bands at 1208 and 1182 cm^{-1} which are assigned to the C–O stretching. The bands at 1673 and 3363 cm^{-1} represent the C=O oxalate ion and the O–H stretching, respectively. These results confirm the successful polymerization of the doped-PDMA [10].

The thermal behavior of the PDMA was investigated by using the TGA technique. The TGA thermogram of D-PDMA shows a two-stage weight loss. The first one is the decomposition of D-PDMA chain at around 118.7 °C, and the second refer to the complete degradation of D-PDMA at around 346.2 °C [11].

The two points probe coupled with an electrometer was used to measure electrical conductivity under an atmospheric condition. The specific conductivity of PDMA is $(3.556 \pm 0.022) \times 10^{-4}$ S/cm [11].

3.2 Cyclic Voltammetry of PDMA

3.2.1 The First Part:

The CV curves were corded during the electropolymerization of PDMA. It can be seen that DMA monomer was electroactive. Figure 2 shows the cycle of CV curve revealing two redox peaks corresponding to the transition from. The first redox is the transition between leucoemeraldine and emeraldine (A/A', +0.15 / -0.02 V), and the second redox is the transition between emeraldine and pernigraniline (B/B'. + 0.28 / +0.18 V) during to the growth of the film in the oxalic acid [12, 13, 14, 15].

Upon subsequent cycles, there were gradual increases in the current intensity representing the broad anodic and cathodic peaks corresponding to the oxidation and the reduction of PDMA, indicating that the films were formed on the surface of ITO more easily [16].

3.2.2 The Second Part

The potentials were used to study the life time of electrochemical properties. It can be seen that after 100 cycles (1 cycle times = the fully oxidized and the fully reduced state), the % transmittance of PDMA film on ITO glass in 0.001 M HCl and 0.001 M H_2SO_4 electrolytes are nearly the same as for the first cycle. They change only 1.43% in HCl and 2.43% in H_2SO_4, as shown in Figures 3a and 3b, respectively. The results indicate that this PDMA film in both electrolyte still have good efficiency, even though they have been used for 100 cycles.

3.3 UV-VIS Absorption Spectrophotometer of PDMA

The UV-VIS absorption spectrophotometer (Shimadzu, UV-1800) was used to investigate the reversible color changes of PDMA as shown in Figure 4 and to observe the transient color change and the response times in the HCl and H_2SO_4 electrolytes. The absorption spectra of PDMA film on the ITO electrode recorded at different potential times in both electrolytes show three peaks at 370 nm, 470 nm and 720 nm, which correspond to yellow, green, and blue color, respectively. The first band at 370 nm corresponds to the fully reduced state of PDMA, called "Leucoemeraldine" (yellow color). This band disappears upon the oxidation reaction. A decreasing intensity of this band is observed when the potential is shifted to a higher value or an extended time. The second band at 470 nm represents the intermediate state, called "Emeraldine" (green color). After a long time, it transforms in to a fully oxidized state at 720 nm corresponding to "Pernigraniline" (blue color), as shown in Figure 5.

3.3.1 The First Part: Comparison of the response times between 0.001 M HCl electrolyte and 0.001 M H_2SO_4 electrolyte at each applied voltage

3.3.1.1 The oxidation reaction

Table 1 shows the response time of the PDMA film in the oxidation reaction with a fixed voltage with various response times in the 0.001 M HCl electrolyte and the 0.001 M H_2SO_4 electrolyte. For both electrolytes at 0.2 V to 0.6 V, the colors of the PDMA films do not change. This results from the fact that potentials in this range do not sufficient energy to remove protons from PDMA films.

For the potential voltages in the range of 0.8 V to 1.6 V, the colors of the PDMA films change from yellow color to blue color. It shows that the response time of each electrolyte decreases with increasing positive potentials.

At the low voltage (0.8 V), the 0.001 M HCl electrolyte shows a shorter response time than that of 0.001 M H_2SO_4 electrolyte as a result of the large value of HCl dissociation in water: the deprotonation of PDMA films in the HCl electrolyte is easier than in the H_2SO_4 electrolyte. At high voltages (over 1.0 V), in 0.001 M HCl electrolyte, PDMA film shows longer response times than 0.001 M H_2SO_4 electrolyte due to the electronegativity value of the HCl electrolyte was lower than that of the H_2SO_4 electrolyte (EN of Cl = 3.16, EN of O = 3.16).

The UV spectra of PDMA film were measured at 0.2 to 1.6 V every 6 minute time intervals in the 0.001 M HCl electrolyte and the 0.001 M H_2SO_4 electrolyte.

The spectra at 0.2 V to 0.6 V in the 0.001 M HCl electrolyte and 0.001 M H_2SO_4 electrolyte show the initial peak at around 480 nm (yellow color). With increasing potential time, their colors do not change, as shown in Figure 6.

The spectra at 0.8 V to 1.6 V in the 0.001 M HCl electrolyte and the 0.001 M H_2SO_4 electrolyte show the highest intensity occurring at around 480 nm which can be referred to a yellow color as can be clearly seen in the first spectra. The intensity of this peak gradually decreases with increasing potential time. At the same time, the presence of another peak at around 680 nm, which can be referred to blue color, occurs as shown in Figure7.

3.3.1.2 The reduction reaction

Table 2 shows the response times of the PDMA film in the reduction reaction when the voltage are fixed and the response time are varied in the 0.001 M HCl electrolyte and in the 0.001 M H_2SO_4 electrolyte. For both electrolytes at 0.2 V to 0.6 V, the colors of PDMA films do not change. This results from the fact that the potentials in this range do not enough energy to remove protons from PDMA films.

For the potential voltages in the range of 0.8 V to 1.6 V, the colors of the PDMA films change from blue to yellow color. It shows that the response time of each electrolyte decreases with increasing negative potential. As a result of at high potential, electron can move easier.

At the low voltage (0.8 V), the 0.001 M HCl electrolyte shows a shorter respond time than that of 0.001 M H_2SO_4 electrolyte as a result of the large value of HCl dissociation in water; the protonation PDMA films in HCl electrolyte is easier than that of H_2SO_4 electrolyte. Over 1.0 V, in the 0.001 M HCl electrolyte, PDMA shows longer response times than those of the 0.001 M H_2SO_4 electrolyte due to the higher voltage; the H_2SO_4 electrolyte protonates two hydrogen ions ($2H^+$), whereas the HCl electrolyte gives only one hydrogen ion (H^+).

The UV spectra of PDMA film were measured at 0.2 to 1.6 V every 6 minute time intervals in the 0.001 M HCl electrolyte and in the 0.001 M H_2SO_4 electrolyte.

The spectra at 0.2 V to 0.6 V in the 0.001 M HCl electrolyte and the 0.001 M H_2SO_4 electrolyte show the initial peak occurring at around 700 nm (blue color). With increasing negative potential time, their colors do not change, as shown in Figure 8.

The spectra at 0.8 V to 1.6 V in the 0.001 M HCl electrolyte and the 0.001 M H_2SO_4 electrolyte show the highest intensity occurring at around 700 nm which can be referred to a blue color as can be clearly seen in the first spectra. The intensity of this peak gradually decreases with increasing negative potential time. At the same time, the presence of other peak at around 480 nm, which can be referred to yellow color, occurs as shown in Figure 9.

3.3.2 The Second Part: Comparison the response times in the different concentrations 0.001 M, 0.01 M and 0.1 M of each electrolyte

3.3.2.1 The oxidation reaction

Table 3 shows the response times of the PDMA film in the oxidation reaction when the voltage is fixed at 1.2 V and the response time is varied in the various concentrations of 0.001 M, 0.01 M and 0.1 M of the HCl electrolyte and the H_2SO_4 electrolyte, respectively. For both electrolytes at 0.01 M and 0.1 M, the colors of PDMA films do not change due to the high protons in the electrolytes, hence PDMA films do not deprotonate protons in both electrolytes, while at 0.001 M, the colors of the PDMA films change from yellow to blue color because of less protons in the electrolytes.

The UV spectra of PDMA film were measured at 1.2 V in the concentrations of 0.001 M, 0.01 M and 0.1 M for the HCl electrolyte and the H_2SO_4 electrolyte.

The spectra in the concentrations of 0.01 M and 0.1 M in both electrolytes show the initial peak occurring at around 480 nm (yellow color). With increasing positive potential time, their colors do not change.

Whereas the spectra in the concentrations of 0.01 M show the first spectra occurring at around 380 and 480 nm, which can be referred to yellow, the peaks gradually decrease with increasing positive potential time. At the same time, the presence of anoother peak at around 680 nm can be referred to blue color.

3.3.2.2 The reduction reaction

Table 4 shows the response time of the PDMA film in the reduction reaction when the voltage is fixed at 1.2 V and the response time is varied in the different concentrations of 0.001 M, 0.01 M and 0.1 M in the HCl electrolyte and the H_2SO_4 electrolyte, respectively. For both electrolytes, the higher concentrations give the lower respond times due to the high protons; hence PDMA film protonation occurs rapidly. The colors of the PDMA films change from blue to yellow color

The UV spectra of PDMA film were measured at 1.2 V in the concentrations of 0.001 M, 0.01 M and 0.1 M for the HCl electrolyte and the H_2SO_4 electrolyte. With increasing negative potential time, their colors change from the highest intensity peak at around 700 nm, which can be referred to blue color, to the another peak at around 480 nm which can be referred to yellow color.

4. Conclusions

Poly (2,5-dimethoxyaniline) was successfully synthesized and coated on the Indium tin oxide electrode glass from the aqueous oxalic acid solution by using the electropolymerization technique.

The PDMA films have three absorption peaks in the redox process; they are leucoemeraldine (yellow color), emeraldine (green color), and pernigraniline (blue color) depending on the reaction state upon applying the electrical potential. With applied positive potential, the oxidation state occurs. The films change their color from yellow to blue. With applied negative potential, the reduction state occurs. The color of the films turns back from blue to yellow.

The response time and the color intensity of the PDMA films can be controlled by the electrical potential (a high voltage corresponds with a short response time), the type of electrolyte (the H_2SO_4 electrolyte corresponds with a shorter response time), and the concentration of the electrolytes.

Using HCl as the electrolyte, the films have shorter response times than those of H_2SO_4 at 0.8 V, while shorter response times can be obtained when applying the potential greater than 1.0 V, using H_2SO_4 as the electrolyte. The complete redox reaction occurs by using the electrolyte concentration lower than 0.001 M.

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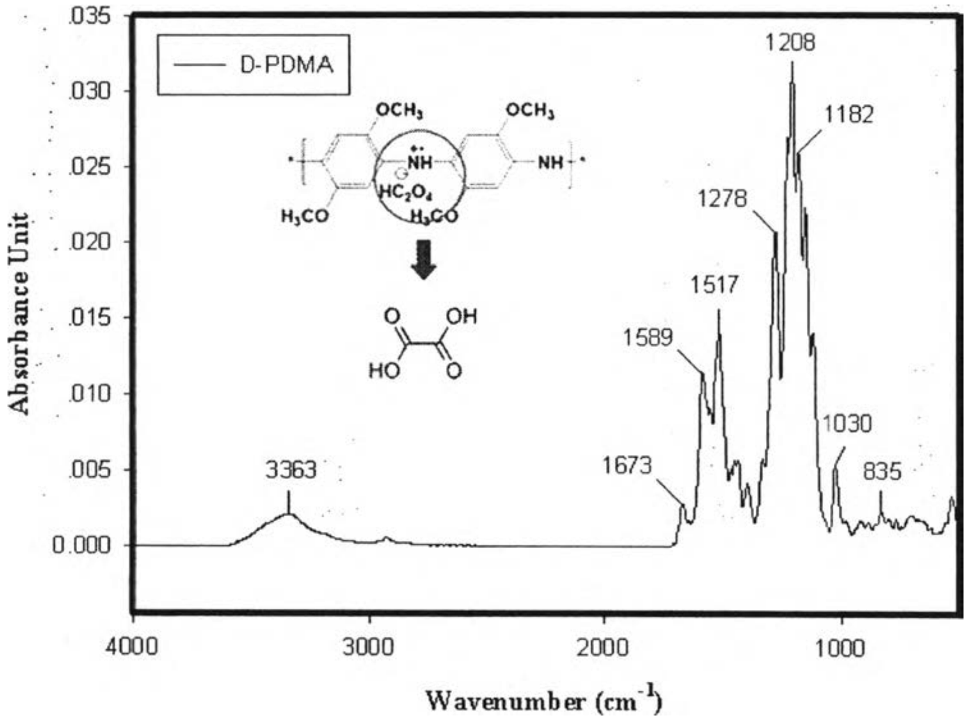

Figure 1. The FT-IR spectra of dope- Poly(2,5-dimethoxyaniline) (D-PDMA).

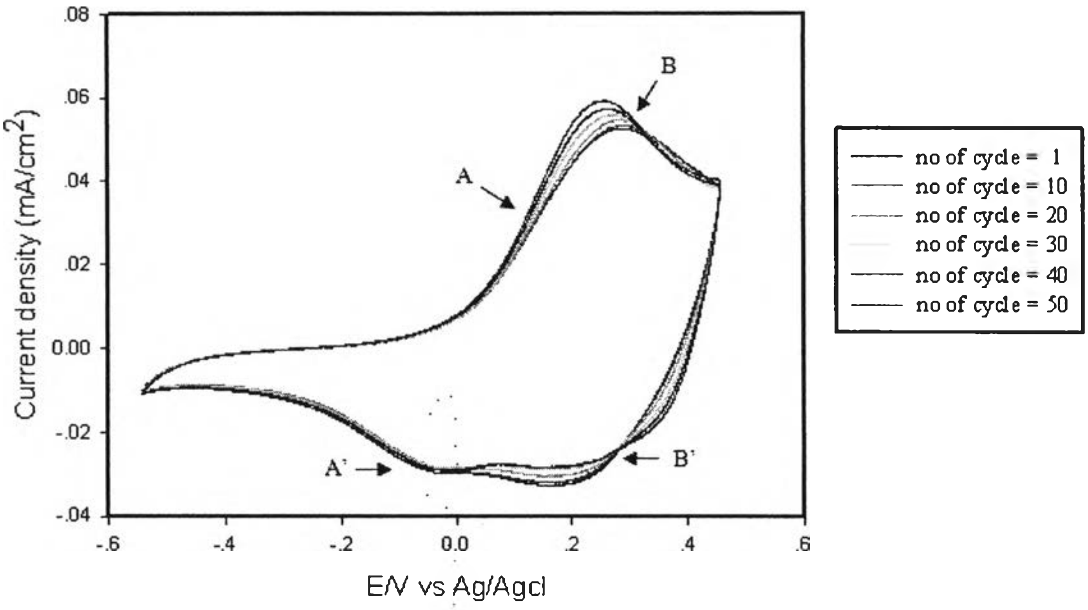

Figure 2. Cyclic voltammogram of the PDMA film grown on the ITO electrode in the 0.1 M of oxalic acid aqueous electrolyte, [DMA] = 0.125 mol at the potential range of -0.5 to +0.5 V, and a scan rate of 20 mV/s for 1 – 50 cycles.

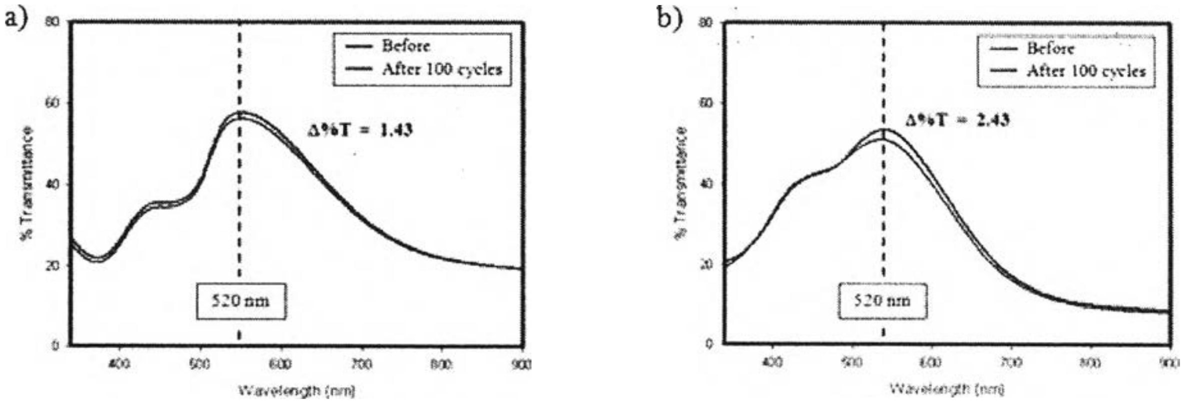

Figure 3. The % transmittance of PDMA film coated on the ITO electrode before and after 100 cycles in a) 0.001 M HCl electrolyte b) 0.001 M H_2SO_4 electrolyte.

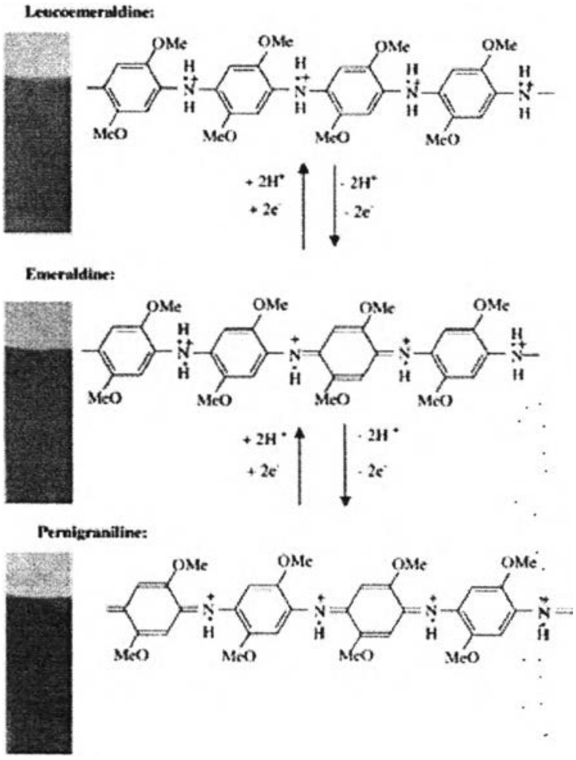

Figure 4. Scheme for the PDMA redox process and the samples.

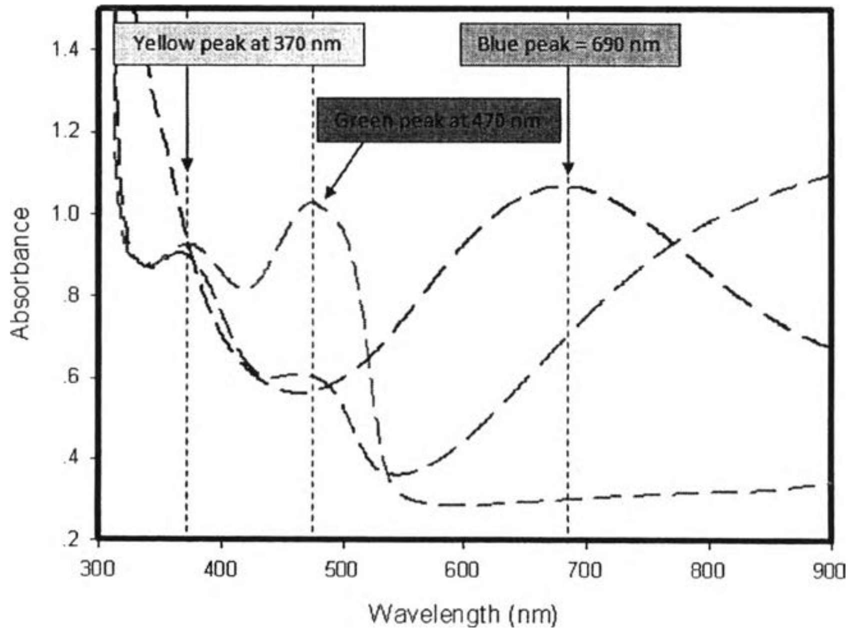

Figure 5. UV-VIS spectra of the PDMA film coated on the ITO electrode obtained at different times and potentials.

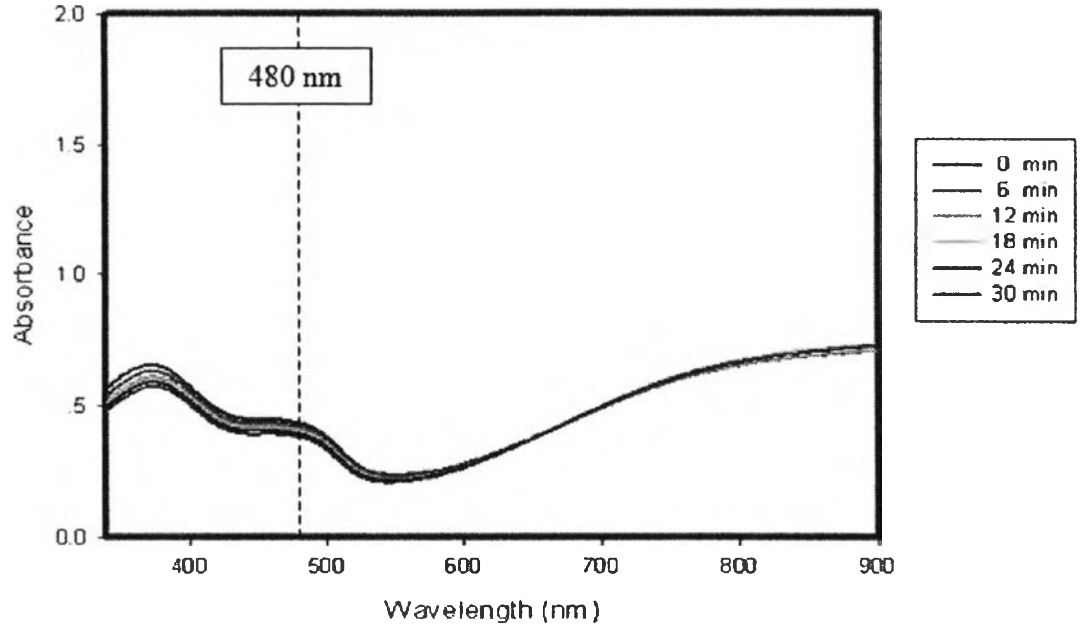

Figure 6. In situ spectra of PDMA film coated on the ITO electrode during the oxidation reaction in the 0.001 M HCl electrolyte at 0.2 V at 6 minute intervals.

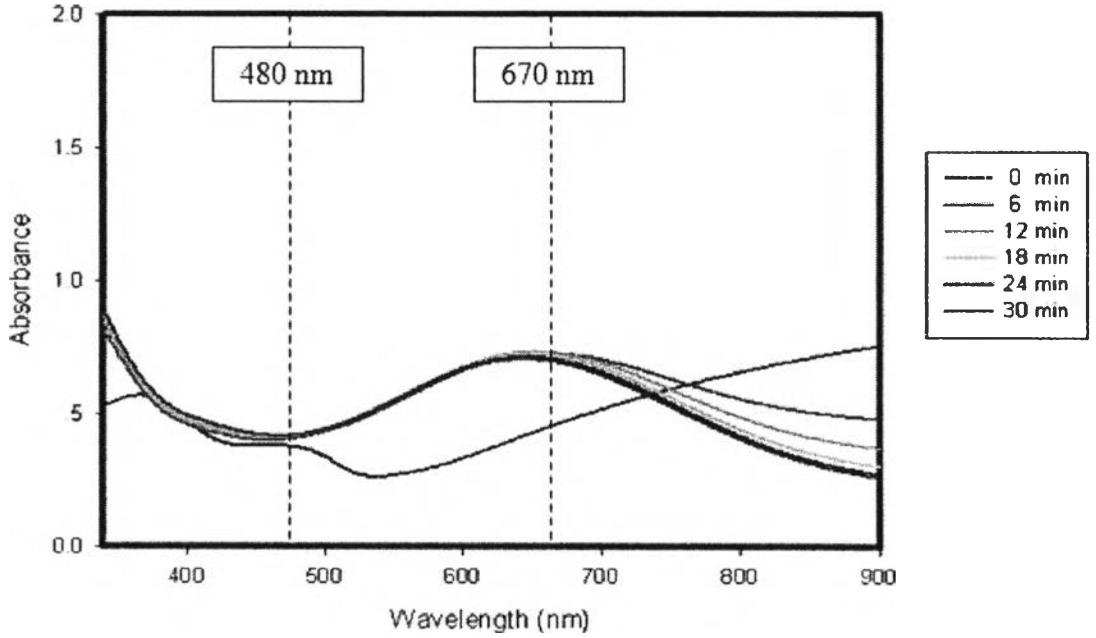

Figure 7. In situ spectra of PDMA film coated on the ITO electrode during the oxidation reaction in the 0.001 M HCl electrolyte at 1.6 V at 6 minute intervals.

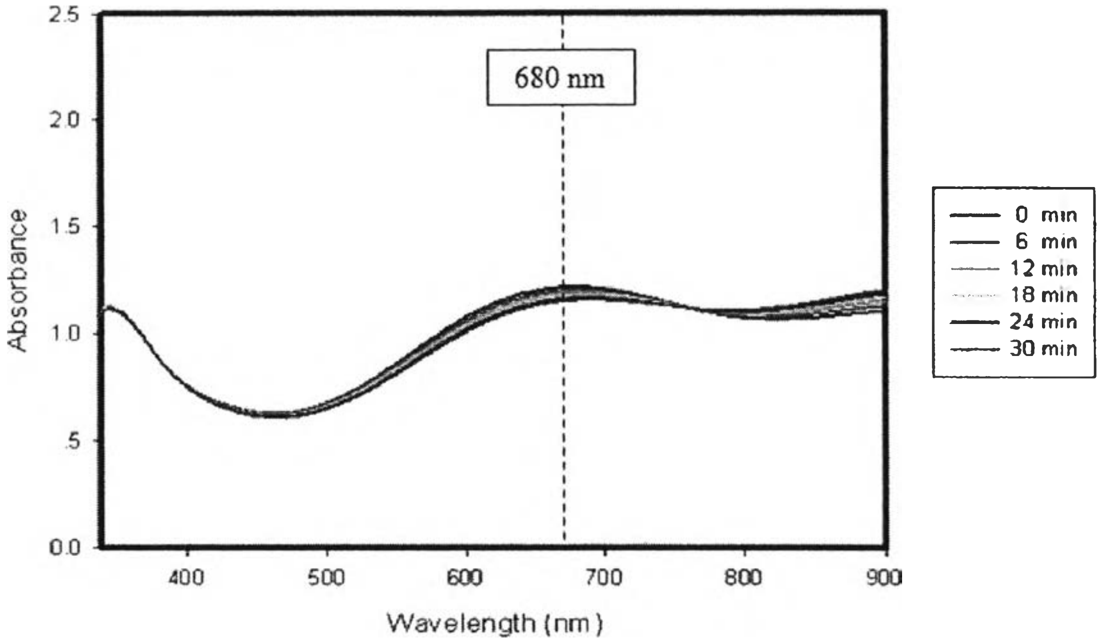

Figure 8. In situ spectra of PDMA film coated on the ITO electrode during the reduction reaction in the 0.001 M HCl electrolyte at 0.2 V at 6 minute intervals.

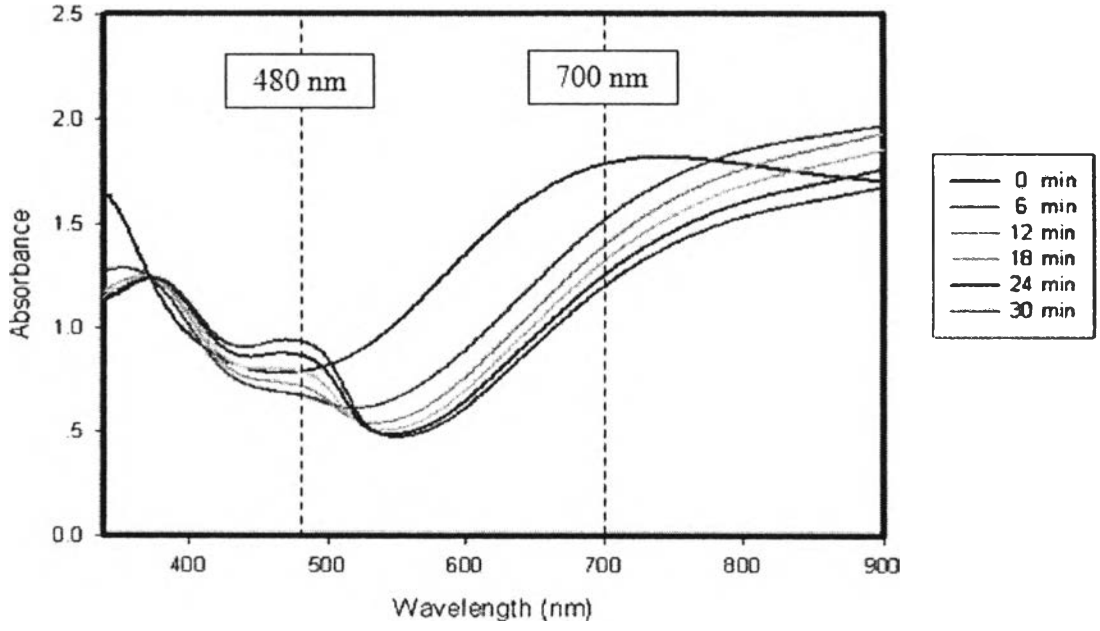

Figure 9. In situ spectra of PDMA film coated on the ITO electrode during the reduction reaction in the 0.001 M HCl electrolyte at 1.6 V at 6 minute intervals.

Table 1. The response times of PDMA in the oxidation reaction at various potentials in the 0.001 M HCl and the 0.001 M H_2SO_4 electrolytes

Electrolyte Volt	Oxidation (Positive Potential)	
	0.001 M HCl	**H_2SO_4**
0.2 V	No change in color (Yellow color)	No change in color
0.4 V	No change in color (Yellow color)	No change in color
0.6 V	No change in color (Yellow color)	No change in color
0.8 V	34 minute (Yellow to Blue color)	40 minute
1.0 V	22 minute (Yellow to Blue color)	18 minute
1.2 V	14 minute (Yellow to Blue color)	8 minute
1.4 V	6 minute (Yellow to Blue color)	4 minute
1.6 V	2 minute (Yellow to Blue color)	1 minute

Table 2. The response times of PDMA in the reduction reaction at various potentials in the 0.001 M HCl and the 0.001 M H_2SO_4 electrolytes

Electrolyte Volt	Reduction (Negative Potential)	
	0.001 M HCl	**0.001 M H_2SO_4**
0.2 V	No change in color (Blue color)	No change in color (Blue color)
0.4 V	No change in color (Blue color)	No change in color (Blue color)
0.6 V	No change in color (Blue color)	No change in color (Blue color)
0.8 V	12 minute (Blue to Yellow color)	No change in color (Blue color)
1.0 V	10 minute (Blue to Yellow color)	6 minute (Blue to Yellow color)
1.2 V	6 minute (Blue to Yellow color)	6 minute (Blue to Yellow color)
1.4 V	4 minute (Blue to Yellow color)	4 minute (Blue to Yellow color)
1.6 V	2 minute (Blue to Yellow color)	1 minute (Blue to Yellow color)

Table 3. The response times of PDMA in the oxidation reaction at 1.2 V at various concentrations in the HCl and H_2SO_4 as electrolytes

Electrolyte Concentration	Oxidation (Positive Potential)	
	HCl	**H_2SO_4**
0.001 M	14 minute (Yellow to Blue color)	8 minute (Yellow to Blue color)
0.01 M	No change in color (Yellow color)	No change in color (Yellow color)
0.1 M	No change in color (Yellow color)	No change in color (Yellow color)

Table 4. The response times of PDMA in the reduction reaction at 1.2 V in various concentrations in the HCl and H_2SO_4 electrolytes

Electrolyte Concentration	Reduction (Negative Potential)	
	HCl	H_2SO_4
0.001 M	6 minute (Blue to Yellow color)	6 minute (Blue to Yellow color)
0.01 M	1 minute (Blue to Yellow color)	1 minute (Blue to Yellow color)
0.1 M	0.2 minute (Blue to Yellow color)	0.2 minute (Blue to Yellow color)

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