



## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Electrochromism

Electrochromism is the reversible and visible change in transmittance and or reflectance that is associated with an electrochemically induced oxidation–reduction reaction. This results from the generation of different visible regions of the electrochromic absorption bands upon switching between the redox states (Sonmez, 2005).

Conductive polymers generally show an optical absorption band in the visible region due to the extended delocalization of  $\pi$  electron along the polymer backbone. Upon doping, charge carriers are created on the conjugated polymer backbone, namely the polaron and the bipolaron which make the change in the absorption spectra (Fesser *et al.*, 1983). By adjusting the electronic character of the  $\pi$  system along the neutral polymer backbone, the  $\pi$ – $\pi^*$  transition can be adjusted across the electromagnetic spectrum (Sonmez *et al.*, 2003). Conducting polymers possessing gap energy ( $E_g > 3$  eV.) are optically colorless or lightly colored when undoped and highly colored in the doped state, exhibiting a pronounced optical contrast and a reasonable switching coloration time. Like other kinds of materials, the electrochromism of conducting polymers is strongly related to the synthesis conditions, i.e. it is affected by structure, stoichiometry, bonding, and defects content in the films. In terms of opto-electrochemical devices, it becomes desirable to find new materials with tailored optical properties. Among the different strategies to obtain tailored polymers with more ordered structures with few conjugation interrupting defects, such as  $sp^3$ -hybridized carbons or twists and kinks in the polymer chain, template synthesis is a very promising and powerful tool (Neves *et al.*, 2004). However, most of the electroactive polymers are limited with two colors, where only few show multiple color states (Sotzing *et al.*, 1997). Although there are some reports on multichromic materials (Argun *et al.*, 2004 and Reddinger *et al.*, 1996), it is still important to achieve materials that display distinctive color changes covering the entire visible region upon applying potential. The multichromic

materials can be achieved via a blending and a copolymerization. The copolymerization and blending can combine the characteristic of both polymers that can improve the properties of the device such as electrochromic activity, thermal stability, and electrochromic properties.

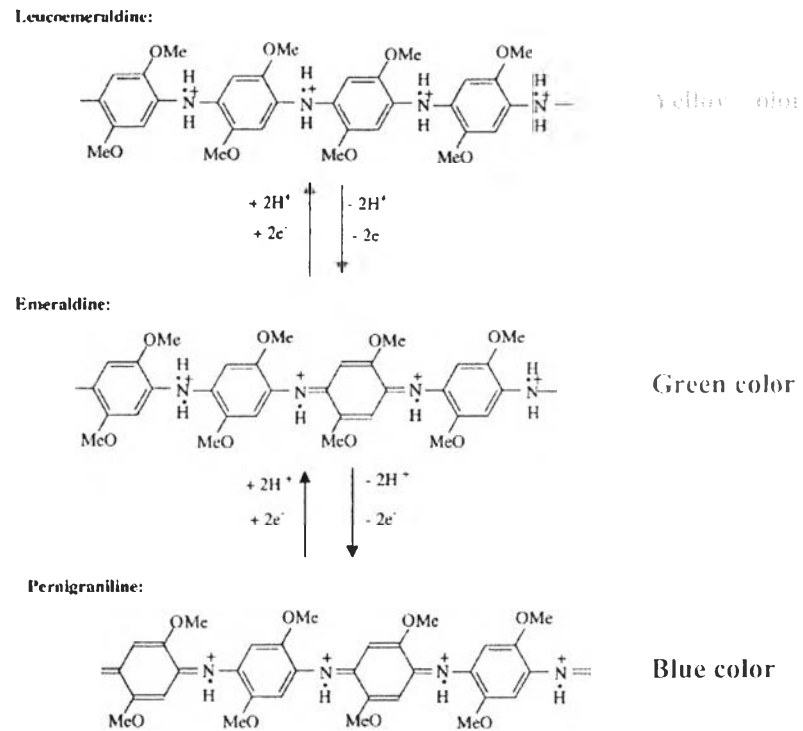
The high performance electrochromic polymer should comprise of the merits such as multicolor, high optical contrast, high thermal stability, stable on many redox cycles, high conductivity, and less switching time.

The **doping** of conductive polymers could be done in two approaches: the chemical or electrochemical doping.

- **Chemical** doping : There are an oxidant (eg. iodine or bromine) and a reductant (eg. alkaline metal)
- **Electrochemical** doping : Electrons are transferred between the electrode and electrolyte or species in solution.

Both kinds of doping are subjected to an increase in the charge carrier (electrons and holes) in the system, since the conduction of material comes from electron shifting from the valence band to the conduction band.

The example for the color changing of an electrochromic polymer is in the Figure 2.1.

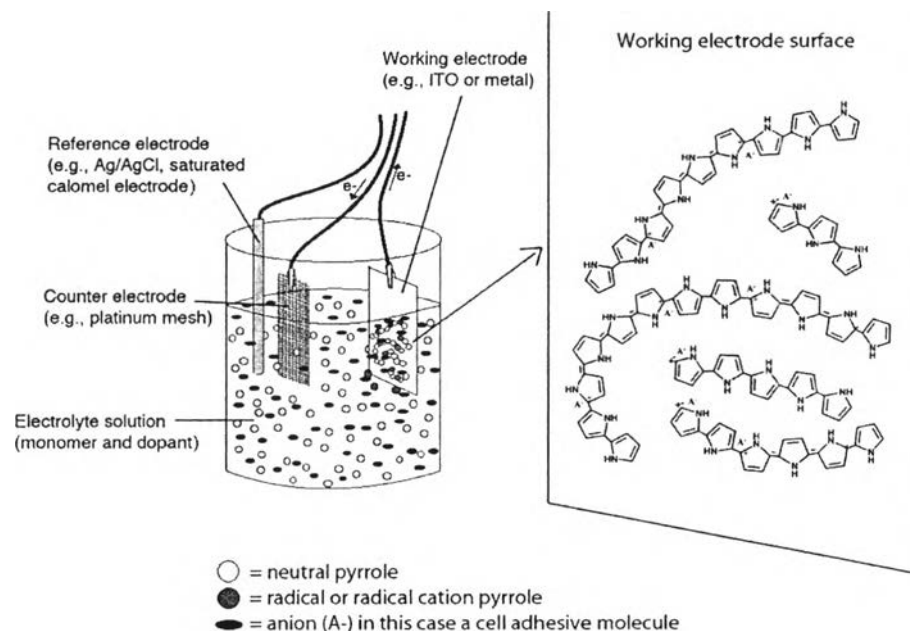


**Figure 2.1** The structures of poly(2,5-dimethoxy aniline) under applied potential (Huang *et al.*, 2002).

Poly (2,5-dimethoxy aniline), PDMA, generally shows reversible color changes from yellow (leucoemeraldine) to green (emeraldine) and to blue (pernigraniline) representing the transition between reduced to oxidized state upon switching the potentials (Huang *et al.*, 2002).

## 2.2 Electropolymerization

Conjugated polymer can be synthesized by either the chemical or electrochemical polymerization. Compared with the chemical route, the electrochemical polymerization produces a conjugated polymer film on a conductive substrate directly (Wang *et al.*, 2011).



**Figure 2.2** Electrochemical polymerization of polypyrrole (PPy).

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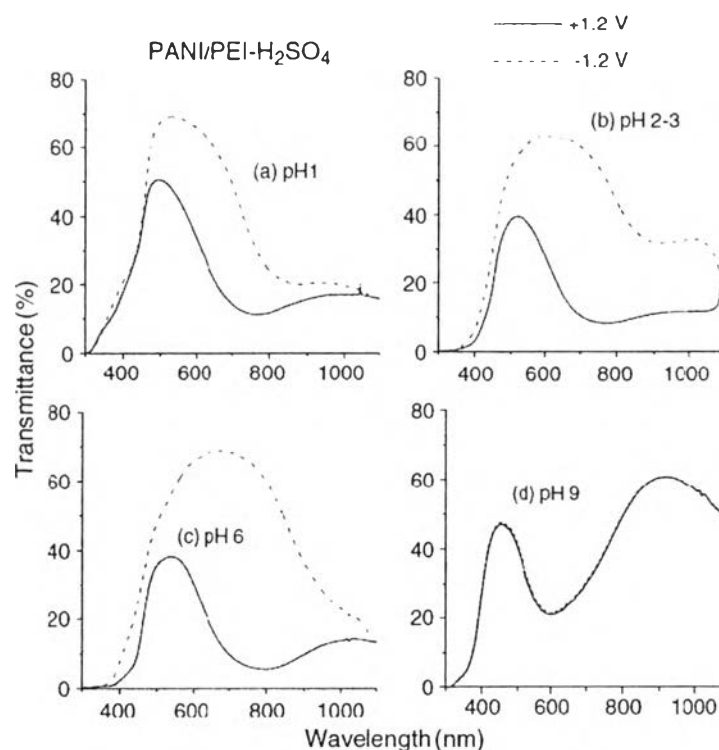
### 2.3 Electrolytes

The electropolymerization of polyaniline was prepared in various types and concentration of the electrolyte as follows:

- $\text{H}_2\text{SO}_4$  in aqueous solution (Huang *et al.*, 2002 and Kang *et al.*, 2009)
- $\text{LiClO}_4$  in acetonitrile (Randriamahazaka *et al.*, 2005 and Paoli *et al.*, 2001)
- $\text{HClO}_4$  in aqueous solution (Widera *et al.*, 1997)
- $\text{HCl}$  in aqueous solution (Ansari *et al.*, 2006)
- $\text{HCl}$  and  $\text{CaCl}_2$  in aqueous solution (Bessière *et al.*, 2004)

In 2007, Hu and coworkers reported the effect of pH of the poly(ethylenimine)- $\text{H}_2\text{SO}_4$  electrolyte on the electrochromic property of polyaniline (PANI). When a PANI based ECD was polarized under a positive potential of +1.2 V bias PANI, the device reached a blue color because PANI suffered from an oxidation

process from leucoemeraldine into emeraldine base. As a negative potential of -1.2 V was applied to the device, it became a transparent yellow and PANI was reduced from emeraldine base into leucoemeraldine.

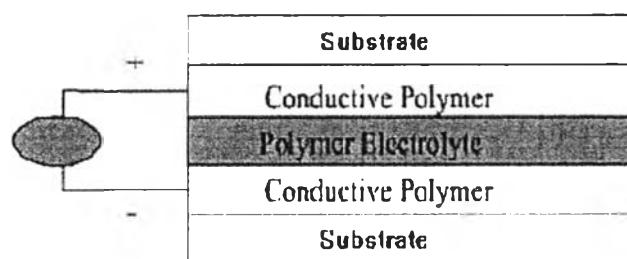


**Figure 2.3** Optical transmittance spectra of four ITO/PANI/PEI-H<sub>2</sub>SO<sub>4</sub>/ITO ECDs under applied potentials of +1.2 V and 1.2 V. The pH value of the polyelectrolytes is equal to: (a) 1, (b) 2–3, (c) 6 and (d) 9 (Hu *et al.*, 2007).

The Optical transmittance spectra shows that for all ECDs with pH value lower than 7, the electrochromic property is noticeable.

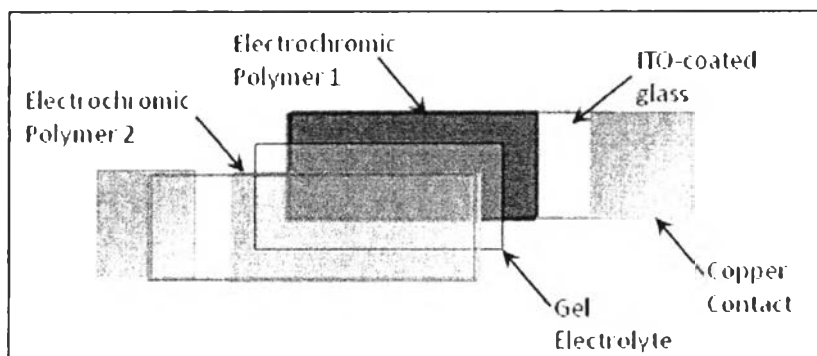
## 2.4 Electrochromic Device

Generally speaking, the electrochromic device has a multilayered structure as shown in Figure 2.4. It has two electrodes, one working, one counter, and one ion conductive layer in between. Normally the device performs the color change during operation of the device.



**Figure 2.4** Multi-layers structure of ECD.

(<http://www.mse.ntu.edu.sg/Research/Areas/Pages/Electrochromicdevice.aspx>)



**Figure 2.5** Structure of EC device.

(<https://ww2.chemistry.gatech.edu/reynolds/research/electrochromics>)

An electrochromic device construction is a sandwich matrix based on phenothiazine derivatives (PDs) material (Tu *et al.*, 2010), as shown in Figure 2.5. PDs were dissolved in THF and a propylene carbonate solution of a P(MMA-Vac)/LiClO<sub>4</sub> polymer electrolyte as the ionic conductive layer and as the film forming agent. A piece of common paper (15mm - 20 mm) was dipped into the mix agent to be used as the electrochromic material interlayer between the ITO glasses.

Up to now, most of the studies devoted to the realization of flexible electrochromic displays have been oriented towards the use of the inorganic electrochromic WO<sub>3</sub> (Antinucci *et al.*, 1994 and Lechner *et al.*, 1998). Though the synthesis of this compound on glass substrates is now well understood and well controlled, the deposition of WO<sub>3</sub> thin films on plastic substrates still raises great

difficulties. For the plastic temperature-sensitive substrate supporting the device, annealing steps must be avoided. Hence  $\text{WO}_3$  thin films in plastic devices usually do not reach good electrochromic properties as in solid ones. Moreover, the presently best  $\text{WO}_3$ -based systems have been realized by the magnetron sputtering (Brigouleix *et al.*, 2001), which represents a quite expensive route of synthesis. Unlike inorganic semiconductors, organic semiconductors can be deposited easily in a thin film using inexpensive techniques and they can be applied to flexible support systems (Wittman *et al.*, 1997).

The research attention of ECD has been focused on flexible substrates because of their advantages over glass substrates and the potential application in the field of flexible paper-like displays. In Table 2.1, the differences between plastic and glass substrates are summarized.

**Table 2.1** Comparison of glass and plastic substrates (Ma *et al.*, 2008)

	Density (g/cm <sup>3</sup> )	Thickness	Flexibility	Easy patterning	Mechanical stability	Cost	ITO coating
Glass	~3	~1 mm	No	No	No	High	Easy
Plastic	~1.4	~100 $\mu\text{m}$	Yes	Yes	Yes	Low	Difficult

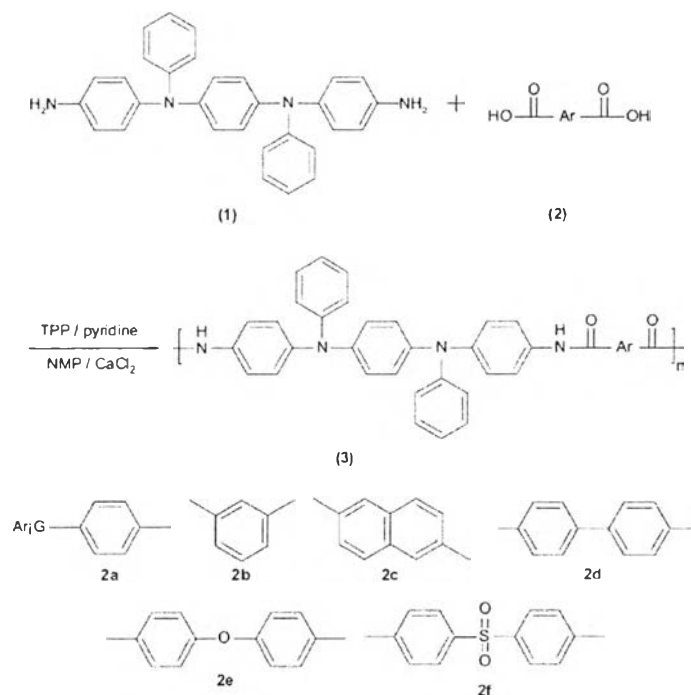
A plastic substrate has less weight and volume, is more flexible, and easier to pattern. The only problem is that it is more difficult to get a high quality ITO coating on a plastic substrate.

## 2.5 Electrochromic Polymers of the Previous Work

The previous work of the electrochromic polymers have been carried out with several types of conductive polymers such as polyamide, carbazole – containing polymer, polyphenothiazine derivatives, polythiophene, and polyaniline (Mortimer, 1997)

### 2.5.1 Polyamide

Various derivatives of polyamide are electrochromic materials. For example, N,N,N',N'- tetraphenyl-1,4-phenylenediamine moiety on novel aromatic polyamides and their electrochromic properties were investigated (Liou and Fang, 2007).



**Figure 2.6** The reactions forming polyamide: (1) diamine; (2a) terephthalic acid, (2b) isophthalic acid; (2c) 2,6-naphthalenedicarboxylic acid, (2d) 4,4'-biphenyldicarboxylic acid; (2e) 4,4'-oxydibenzoic acid, (2f) 4,4'-sulfonyldibenzoic acid; and (3) triphenylamine-containing polyamide (Liou and Fang, 2007).

The results showed that the planarity of backbone affected the gap between HOMO – LUMO. When the planarity was disturbed, the HOMO value decreased and then the energy gap increased. Moreover, wholly aromatic polyamides were characterized as highly thermally stable polymers with a favorable balance of physical and chemical properties. However, the rigidity of the backbone and the strong hydrogen bonding resulted in a high melting or glass-transition temperatures ( $T_g$ ) and limited solubility in most organic solvents. These properties make them generally intractable or difficult to process, thus restricting their applications.

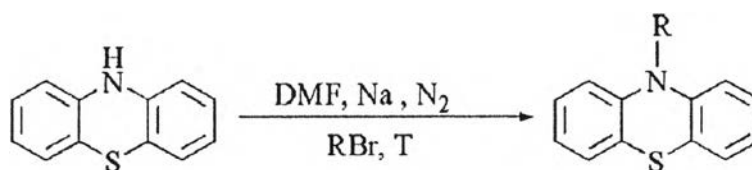


### 2.5.2 Carbazole – containing polymer

Wang and coworkers (2011) studied the copolymerization and the electrochromic properties of copolymer based on 4,4'-di(N-carbazoyl ) biphenyl and 2,2' bithiophene. The advantages of carbazoyl – containing polymer form the stable polarons, high charge carrier mobility, the photochemical stability, and the electrochromic properties (Kimoto *et al.*, 2005, Oral *et al.*, 2009 and Koyuncu *et al.*, 2009). The results revealed that the P(CPB – co –BT) showed high thermal stability. The color change of the copolymer was from orange to yellow when neutral and blue color while oxidized.









### 2.5.3 Polyphenothiazine derivatives

Tu and coworkers (2010) studied the effect of pendant groups on the phenothiazine derivatives. A series of N-substituted phenothiazine derivatives (PDs) were synthesized and their corresponding ECDs were assembled. Phenothiazine and PDs showed two of the three complementary colors (red, green, and blue, RGB) in the reduced state and the oxidized state, respectively. They found that the pendant functional groups (R) did not have an effect on the color of the phenothiazine derivatives as shown in the Table 2.2. As compared with the prior ECMs, PDs had many crucial figures of merit such as stability, lifetime, response speed, coloration efficiency, low cost starting materials, short synthetic routes, and environment friendly. They are potential commercial materials towards use in electrochromic devices and displays.



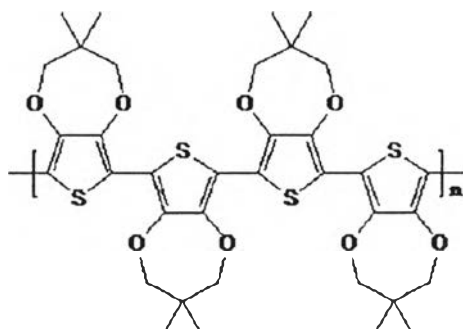
**Figure 2.7** Synthetic route of phenothiazine derivatives (Tu *et al.*, 2010).

**Table 2.2** Phenothiazine and its derivatives [temperature, melt point (Mp), electrochromic color and yield] (Tu *et al.*, 2010)

Compound	R	Formula	T (°C)	Mp (°C)/form	Electrochromic color
1	H	C <sub>12</sub> H <sub>9</sub> NS	-	183	Green
2a		C <sub>16</sub> H <sub>17</sub> NS	40	Viscous liquid	Red
2b		C <sub>18</sub> H <sub>21</sub> NS	40	Viscous liquid	Red
2c		C <sub>20</sub> H <sub>25</sub> NS	40	Viscous liquid	Red
2d		C <sub>24</sub> H <sub>33</sub> NS	80	Viscous liquid	Red
2e		C <sub>15</sub> H <sub>14</sub> NS	40	Viscous liquid	Red
2f		C <sub>19</sub> H <sub>16</sub> NS	40	103	Red
2g		C <sub>21</sub> H <sub>18</sub> NS	80	98	Red
2h		C <sub>18</sub> H <sub>11</sub> N <sub>2</sub> O <sub>4</sub> S	110	83	Red

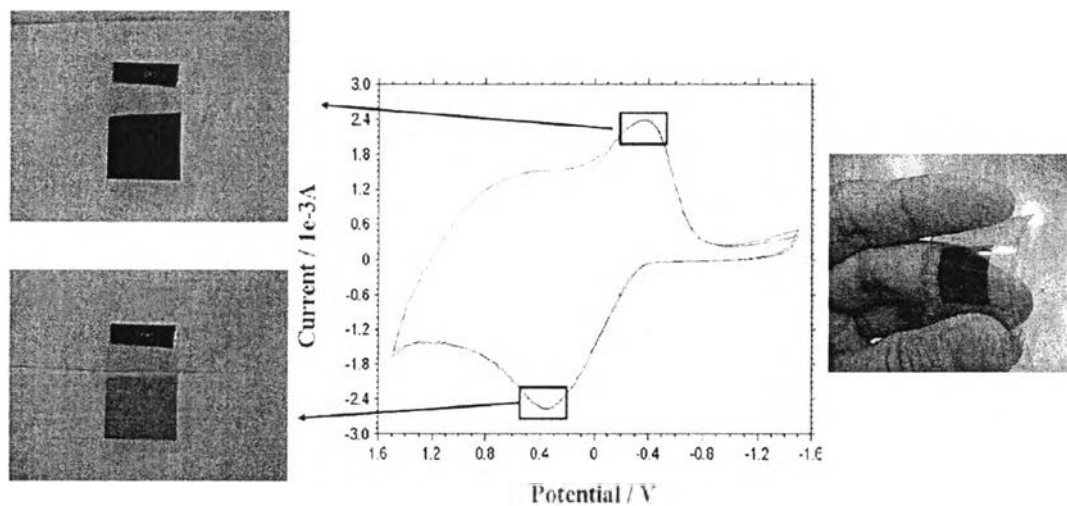
#### 2.5.4 Polythiophene

Ma and coworkers (2008) studied the design, fabrication, and characterization of a flexible electrochromic device based on indium tin oxide (ITO) coated polyethylene terephthalate (PET) plastic. The working electrochromic material film was poly (3,4-(2,2-dimethylpropylenedioxy) thiophene) (PProDOT-Me<sub>2</sub>).



**Figure 2.8** Structure of PProDOT-Me<sub>2</sub> (Ma *et al.*, 2008).

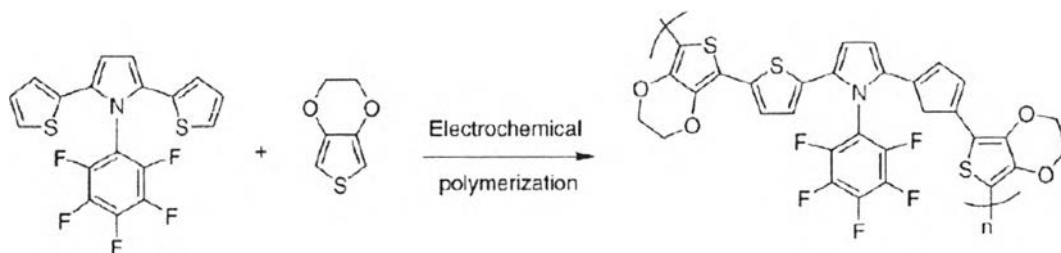
The device exhibited a tunable light transmittance between transparent and deep blue color, with a maximum contrast ratio at 580 nm wavelength.



**Figure 2.9** CV curve of EC film deposited on ITO/PET substrate (Ma *et al.*, 2008).

Other important properties, such as switching speed, life time, and coloration efficiency have been improved. Similar to the glass based ECD, the developed plastic lens exhibited an adjustable transmittance of light, fast response time (about 0.5 s), low driving potential (1.2 V), good repeatability and long lifetime (over 40,000 cycles of switch). Meanwhile it offered several advantages over a glass substrate including greater flexibility, less weight and volume, and easier patterning. This flexible plastic based ECD could be widely used in manufacturing smart sunglasses, automobile windows, and paper-like flexible display.

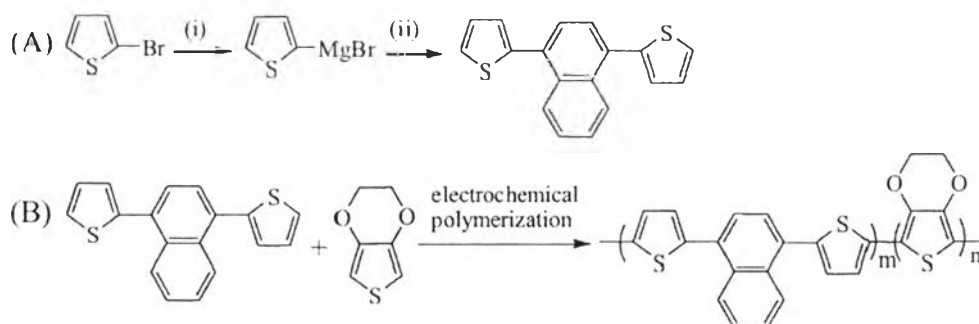
Moreover, in 2007, Carmurlu and coworkers studied the electrochemical copolymerization of 1-(perfluorophenyl)-2,5-di(thiophen-2-yl)-1H-pyrrole and 3,4-ethylenedioxythiophene to fulfill a strategy in achieving desired multichromic properties.



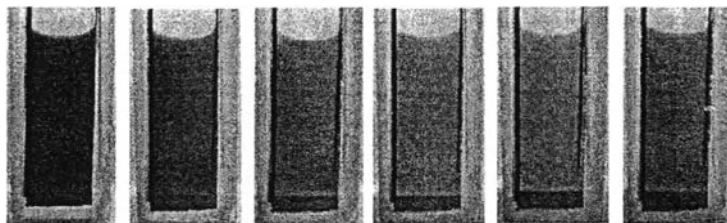
**Figure 2.10** Schematical representation for the electrochemical polymerization of FFTPpy with EDOT (Carmurlu *et al.*, 2007).

The resultant polymer displayed distinct color changes between red–violet, amber, green and blue colors with good switching times and optical contrast. Hence, it was possible to achieve colors from maroon, red–violet, and eggplant to indigo depending on the applied potential.

It has been known that the introduction of aromatic bridge in the bithiophene polymer main chains could result in changing the HOMO–LUMO band gap relative to those of the homopolymers. The polymers having the structure like thiophene-arylene-thiophene usually present reasonable electrochromic properties, which render possible to build the electrochromic devices. Recently, Wang and coworkers (2011) synthesized 1,4-bis(2-thienyl)-naphthalene (BTN) monomer via the coupling reaction according to Figure 2.11A. Electrochemical copolymerization of BTN with EDOT was carried out in 0.2M NaClO<sub>4</sub>/ACN solution (Figure 2.11B).



**Figure 2.11** Synthetic routes of: (A) monomer; and (B) copolymer. Reagents: (i) Mg, Et<sub>2</sub>O; (ii) 1,4-dibromonaphthalene, NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, THF (Wang *et al.*, 2011).



**Figure 2.12** Multichromic behavior of P(BTN-co-EDOT) film at 0.4V (purplishred), 0 V (brownishred), 0.2V(orangeyellow), 0.4V(yellowishgreen), 0.6V(green) and 1.3V (blue) (Wang *et al.*, 2011).

The effect of copolymerization between BTN and EDOT led to an obvious decrease in the  $E_g$  comparing with that of PBTN, which indicated that the introduction of EDOT units into PBTN could reduce the  $E_g$  of the copolymer.

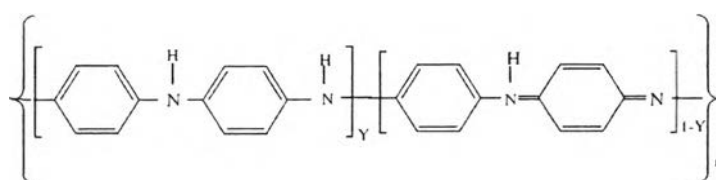
Polythiophene has the high conductivity and high thermal stability (Somboonsub *et al.*, 2010) while polyaniline exhibits the high environmental stability and low cost (Randriamahazaka *et al.*, 2005).

Initially, aniline–thiophene copolymers have attracted attention because of the apparently higher stability of the oxidized form of the copolymer and the highly reversible switching of the conductivity up to rather high electrode potentials.

### 2.5.5 Polyaniline

Bessiere and coworkers (2004) studied and optimized the flexible electrochromic device based on polyaniline. The synthesis of polyaniline (PANI) thin films was made onto commercially available 5 cm x 5 cm polyethylene terephthalate (PET)/indium tin oxide (ITO) substrates. Complete flexible cells could then be built by using a transparent gel electrolyte and a simple PET/ITO counter-electrode. Branched poly(ethyleneimine) (BPEI)- $H_3PO_4$  and poly(methylmethacrylate) (PMMA) -PC- $LiClO_4$  were both tested as electrolytes, but only the latter led to a non-degrading system when the device underwent several switching potential steps. This flexible, middle-scale and inexpensive device was capable of obtaining a 18% transmission contrast at 780 nm within 3 min.

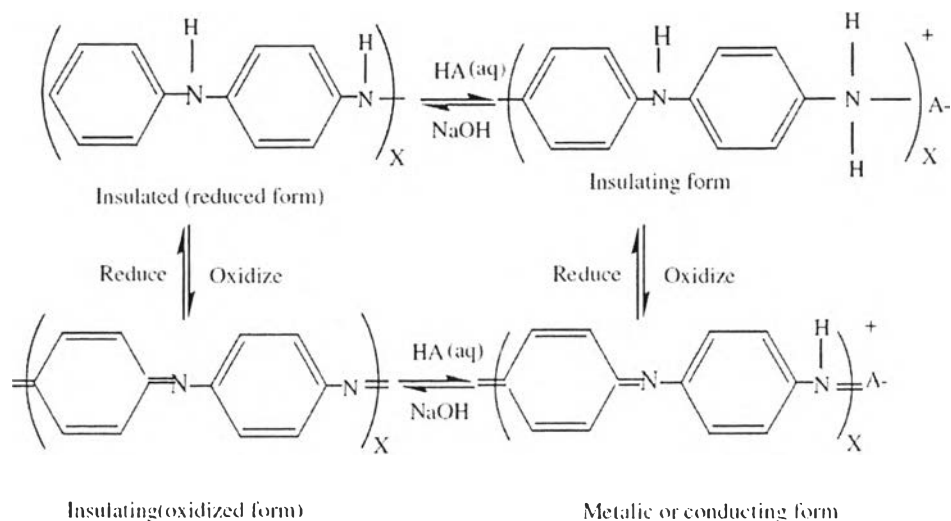
On the basis of conductivity, and stability of the product, HCl and H<sub>2</sub>SO<sub>4</sub> are the best dopants for the protonation of PANI. The electrochemical polymerization of aniline is believed to proceed via the cation radical. It has been found that the growth mechanism of PANI is autocatalytic. The oxidation process is accompanied by the insertion of anion to maintain the charge neutrality. Polyaniline has been reported to have the following idealized structure (Figure 2.13)



**Figure 2.13** The general structure of PANI conducting polymers (Ansari and Keivani, 2006).

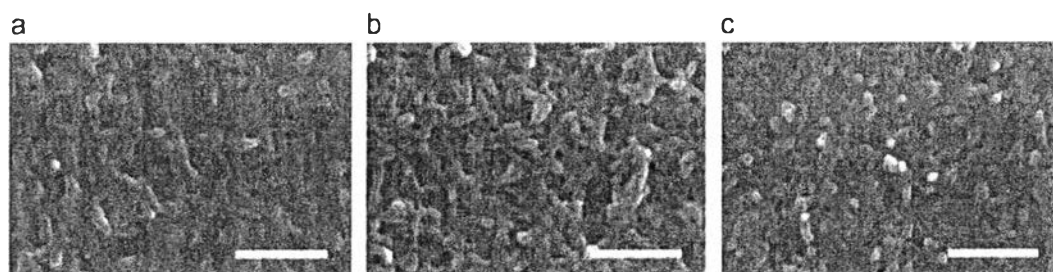
The structure containing  $Y$  reduced (benzenoid diamine) and  $(1-Y)$  oxidized repeat groups (quinoid diamine) where the oxidation state can be defined by the value of  $(1-Y)$ .  $Y$  can be varied continuously from one (the completely reduced material), to zero (the completely oxidized polymer). The completely reduced material ( $Y = 1$ ) is called leucoemeraldine, and the completely oxidized form ( $Y = 0$ ) is termed pernigraniline.

Intermediate oxidation states where  $Y = 0.5$  are the emeraldine oxidation state. The value  $y = 0.5$  of polyaniline corresponds to the case where 50 % of the nitrogen atoms are protonated. Each oxidation state can exist in the form of its base or its protonated form (salt) by treatment of the base with an acid (Figure 2.14). These forms may be interconverted by a chemical and/or electrochemical oxidation or reduction (Ansari and Keivani, 2006).



**Figure 2.14** Four redox forms of polyaniline (Ansari and Keivani, 2006).

In 2009, Kang and coworkers worked in an electrochromic device of PEDOT–PANI hybrid system for a fast response and a high optical contrast. Three electrodes were used for the electro polymerization of conducting monomers: ITO glass as a working, fluorine doped tin oxide glass as a counter, and saturated calomel electrode (SCE) as a reference. In order to produce the PANI electrode, aniline monomer was electrochemically polymerized on ITO glass in a deposition solution consisting of 0.5 M aniline monomer and 1 M H<sub>2</sub>SO<sub>4</sub> in deionized water under the condition of 0.75V for various intervals (50, 60, and 90 s).



**Figure 2.15** SEM images for the surface of PANI electrodes with different electro-polymerization times: (a) 50 s, 60 s (b), and (c) 90 s. Each scale bar corresponds to 500nm (magnification, 70 K) (Kang *et al.*, 2009).

Figure 2.15 shows the surface morphology of PANI electrodes. Based on the formation mechanism of the interconnected and branched nanofiber networks of PANI film which could be explained as follows:

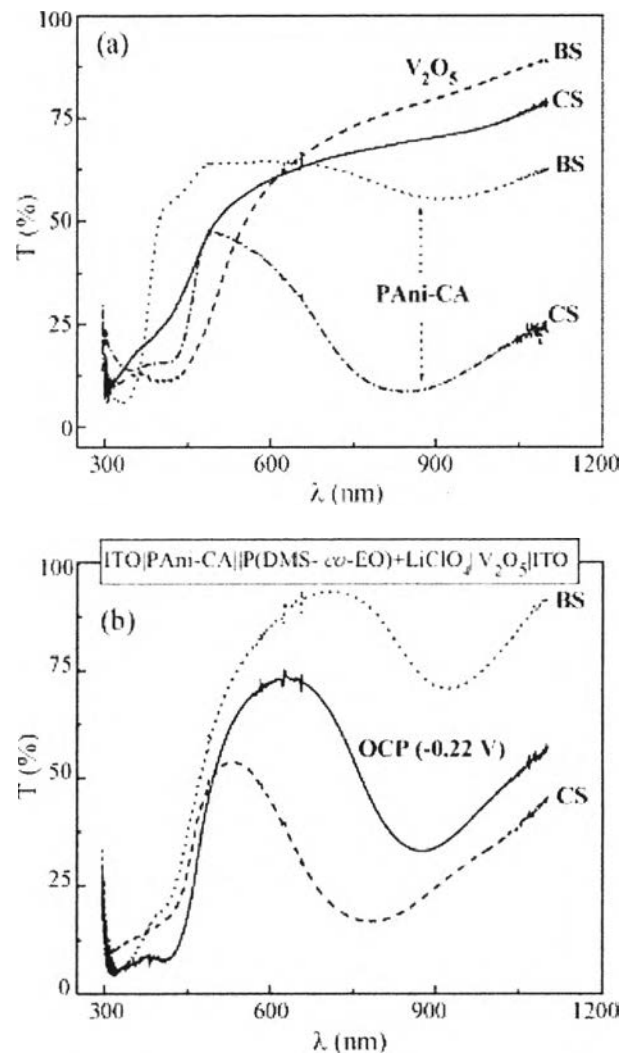
After an electrochemical deposition for 60 s (Figure 2.15a), a large number of granular PANI particles were deposited on the substrate, which could serve as nucleation sites to grow PANI nanofibers. Also, it can be seen that some short-branched PANI fibers begin to form on the granular layer. In the advanced stage (Figure 2.15b), the PANI fibers further grow on the surface of the granular layer and eventually form a loosely bound open structure, resulting in high porosity and surface area. Finally in Figure 2.15c, as the deposition time increases, aggregated PANI fibers as well as gel-like PANI nanoparticles are formed, leading to a dense structure.

In general, if the surface of film is porous, the lithium intercalation / deintercalation process becomes easier, resulting in a fast response time. But the optical contrast could be poor. On the other hand, if it is too dense, the lithium diffusion onto the films becomes much more difficult. It is therefore very important to control the film thickness and surface morphology properly.

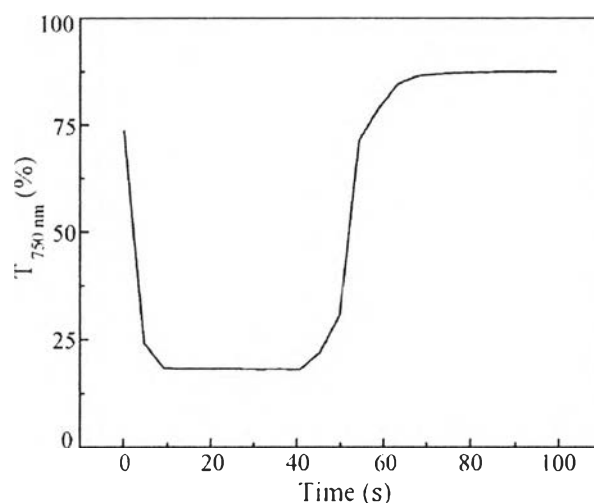
Neves and coworkers (2004) attempted to enhance the optical characteristics of an electrochromic device by using the template synthesis method to prepare the electrode materials. A polyaniline-cellulose acetate composite (PANI-CA) was used as the primary electrochromic layer and vanadium oxide was the secondary electrode. A complex of poly(dimethylsiloxane-co-ethylene oxide), P(DMS-co-EO), and  $\text{LiClO}_4$  was used as electrolyte in this device. Their attention is focused on the influence of template synthesis used to obtain PANI composite film on the electrochromic properties.

Figure 2.16b shows the spectra of the colored and bleached forms of the entire device, in which a surprisingly higher optical contrast is observed ( $\Delta T_{750\text{nm}}=78\%$ ). This value is higher than the optical response observed for each component separately. As the vanadium pentoxide electrochromic response is weak (Figure 2.16a), this material acts mainly as an ion storage electrode in the electrochromic device, improving the charge transfer process and enhancing the device performance.





**Figure 2.16** Optical transmittance changes of: (a) components; and (b) electrochromic device under constant polarization at -2.25 V (Bleached States=BS) and 1.50 V (Colored States=CS). PANi-CA electrode vs.  $V_2O_5$  electrode (Neves *et al.*, 2004).

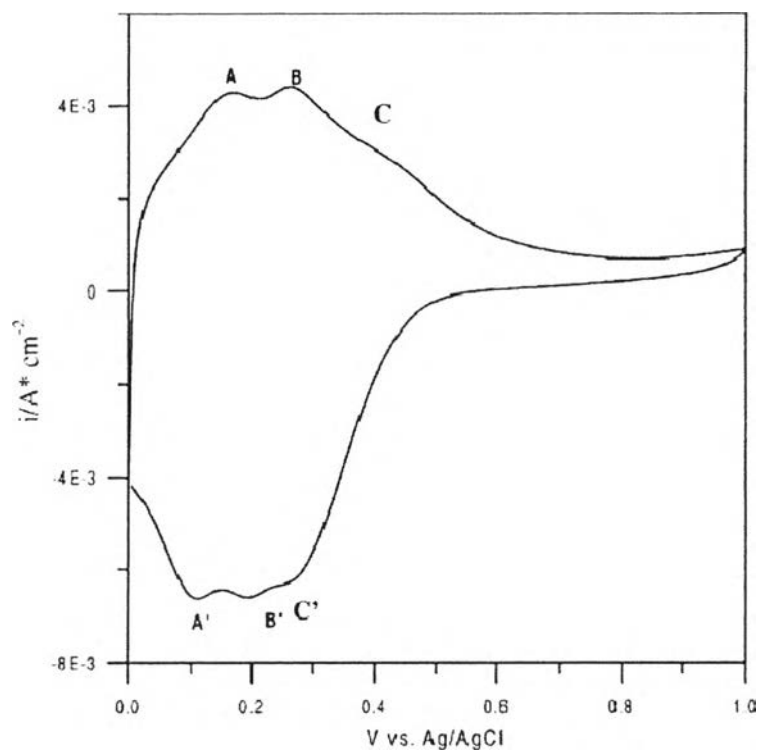


**Figure 2.17** Optical response of the device during a double potential step chronoamperometry (Bleaching potentials =  $-2.25$  V and coloring potentials =  $+1.5$  V). PANI -CA electrode vs.  $V_2O_5$  electrode (Neves *et al.*, 2004).

Figure 2.17 shows the optical response time of PANI-CA based electrochromic device submitted to a double potential step (spectrochronoamperometric experiments). For the coloring and bleaching processes, the optical response times are 4.0 s and 7.5 s, respectively. The long response time observed can be associated to the low ionic diffusion occurring at the gel polymer electrolyte, since ion transport is the rate-limiting step.

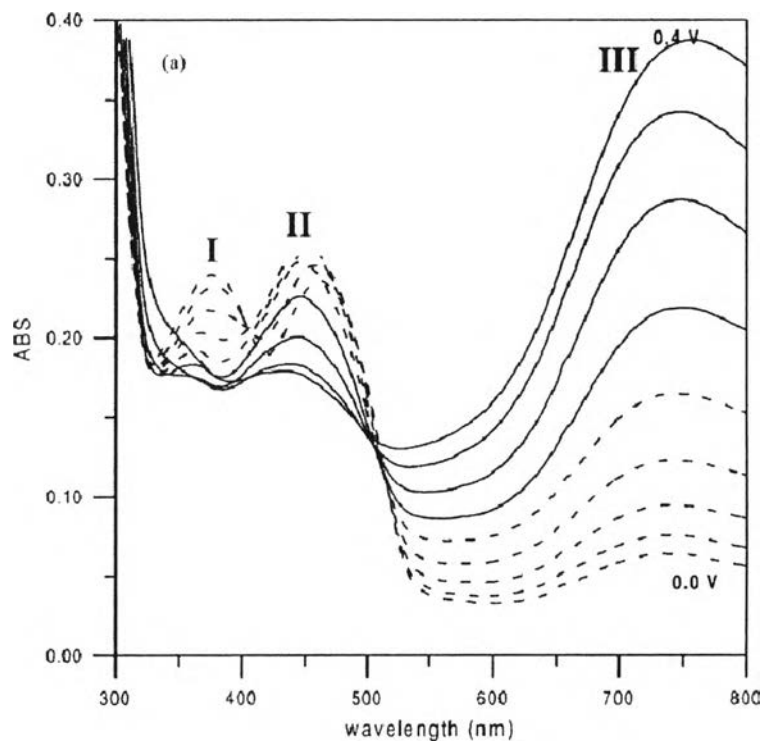
Poly (2,5-dimethoxy aniline) is one of the polyaniline derivatives which has a conductivity value the same as polyaniline but it is faster in response and better in solubility (Huang *et al.*, 2002).

In 2002, Huang and coworkers investigated the properties of poly (2,5-dimethoxy aniline). The PDMA film was synthesized via the electropolymerization of 0.01 M 2,5-dimethoxy aniline monomer in a 0.5 M  $H_2SO_4$  solution. The cyclic voltammogram of PDMA-modified Pt electrode is shown in Figure 2.18.



**Figure 2.18** Cyclic voltammogram of PDMA-modified Pt electrode in 0.01 M 2,5-dimethoxy aniline monomer in 0.5 M  $\text{H}_2\text{SO}_4$  solution (Huang *et al.*, 2002).

The first two redox peaks at 0.17 V/0.11 V and 0.27 V/0.20 V are attributed to the conversion of yellow (leucoemeraldine) to green (emeraldine) and to blue (pernigraniline), respectively. The electrochromic property was studied via UV-Visible absorption spectra as shown in the Figure 2.19.



**Figure 2.19** UV-VIS spectra of PDMA coated ITO electrode obtained at different electrode potentials (Huang *et al.*, 2002).

The band at  $\lambda_{\text{max}} = 375$  nm (band I) corresponds to the reduced state (leucoemeraldine). This band disappears upon an oxidation. The band II at  $\lambda_{\text{max}} = 460$  nm corresponds to the partial oxidation of PDMA or the intermediate state between the leucoemeraldine form and the emeraldine form.

The electrochromic properties of polyaniline and poly (2,5-dimethoxy aniline) of previous studies are reported in Table 2.3.

**Table 2.3** The electrochromic properties of PDMA and PANI of the previous studies

References	Optical contrast ( $\Delta T\%$ )	Reduction time (sec)	Oxidation time (sec)	Response time (sec)
PDMA deposited potentiostatically (0.4 V) as film on ITO coated glass plate (with a specific surface conductivity of ca. $10 \Omega\text{cm}^{-2}$ ). (Huang <i>et al.</i> , 2002)	23%	4	16	20
PDMA–PSS composite films deposited on ITO coated glass plate (sheet conductivity $\leq 15 \Omega/\text{sq}$ ), by cyclic voltammetry. (Li <i>et al.</i> , 2006)	69%	10.2	20	30.2
PANI produced inside the pores of cellulose acetate membranes by potentiodynamical synthesis. (Neves <i>et al.</i> , 2004)	78%	7.5	4	11.5
PES ITO PANI-CSA  PEO-PC-LiClO <sub>4</sub>   PEDOTPSS ITO PES (Huang <i>et al.</i> , 2006)	42.1%	11.1	8.9	20
PES ITO PANI-PSS  PEO-PC-LiClO <sub>4</sub>   PEDOT-PSS ITO PES (Huang <i>et al.</i> , 2006)	40.2%	9.7	8.8	18.5
Poly(o-methoxy aniline) deposited onto ITO–PET by spin coating. The cathodic coloration electrode PET–ITO   PEDT. (Paoli <i>et al.</i> , 2001)	75%	-	10	-

PANI electrode polymerized for 60s and used PEDOT as the cathode coloration. (Kang <i>et al.</i> , 2009)	66%	-	-	0.16
PDMA single electrode polymerized for 6 minutes in oxalic acid at 1.5 V with testing potential 3.5 V.	73%	9	12	21