

CHAPTER II

LITERATURE REVIEW

2.1 Conductive Polymers

Conductive Polymers, e.g. polyacetylene (PA), polyaniline (PAni), polypyrrole (PPy), polythiophene (PTh), poly (phenylene vinylene) (PPV), and their derivatives as shown in Figure 2.1, can conduct the electricity or act as electrical semiconductors (Bai *et al.*, 2007). These polymers have conjugated double bonds along the backbone. Each bond contains a strong sigma (σ) bond and a weaker pi (π) bond; hence polymers have the electrical conductivity property. However, the conductivity of pure conductive polymers is rather low, thus a doping process is necessary to achieve highly conductivity (Kumar and Sharma, 1998). They undergo either the p and/or n redox doping by the chemical and/or electrochemical processes during which the number of electrons on the polymer backbone changes (Skotheim, 1986; Kanatzidis 1990). The intrinsically conducting polymers, without a presence of any conductive filler, generally are comprised simply of C, H and simple heteroatoms such as N and S. The myriad properties of conductive polymers emanate uniquely from the π – conjugation (Chandrasekhar, 1999).

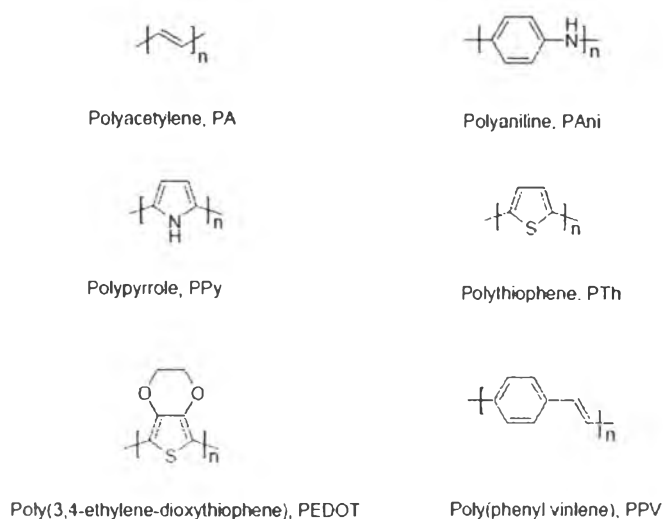


Figure 2.1 The chemical structure of conductive polymers (Bai *et al.*, 2007).

These polymers are widely used in many applications because of their advantages: light weight, less expensive, high sensitive and short response time at room temperature, easy to synthesize, and their molecular chain structure can be modified conveniently by a copolymerization and structure derivations (Bai *et al.*, 2007). The interesting applications of these polymers are light-emitting diodes, electrochromic windows, energy storage, sensor and actuation devices (Skotheim *et al.*, 1998).

Conducting polymers have been recognized as electrochromic materials since their electronic properties have been studied systematically. Polyaniline was the first conductive polymer reported for its electrochromism by Goppelsröder in 1876 and explained by the Spectral band mode (Brédas *et al.*, 1984). Conducting polymers are highly optical in color in the dope state and lightly optical color or colorless in the de-dope state. These properties provide a pronounced optical contrast and a reasonable switching coloration time (Neves *et al.*, 2004)

2.2 The Synthetic Methods of Conducting Polymers

Conducting polymers are classified into the cationic and anionic salts of highly conjugated polymers. They are obtained from the chemical oxidation / reduction and the electrochemical polymerization. In the oxidized conducting polymer, electrons have been removed from the backbone, resulting in a cationic radical. Whereas in the reduced conducting polymer, electrons have been added into the backbone, resulting in an anionic radical. However, this reduced conducting polymer is least stable than the cation counterpart (Jang, 2006).

In general, there are two synthetic methods for conducting polymers:

2.2.1 Chemical Oxidation Polymerization

This method is appropriate for generating mass production. On the other hand, it is constrained by the materials environment issues and by-products from the synthesis.

2.2.2 Electrochemical Polymerization

It is very useful particularly when thin films are desired. This thesis mainly describes the electrochemical polymerization using two electrolyte solutions to produce thin films.

2.3 Electropolymerization

Electropolymerization is a commonly technique used for the synthesis conducting polymers to prepare CP-based electrodes and devices (Ma et al., 2009). This was carried out at an electrode by using the positive potential. The method led to films being deposited directly on the ITO anode glass and the films thickness was easy to control (Ma et al., 2009). The electrochemical polymerization is usually carried out in a compartment cell equipped with three electrodes and containing supporting electrolyte, monomer, and an appropriate solvent (Arslan et al., 2007). This technique has received a wider attention because of its simplicity and the added advantage of obtaining a simultaneously doped conductive polymer (Arslan et al., 2007). The Organic films deposited by the electropolymerization on metallic surfaces present interesting properties in numerous domains, such as electrocatalysis, molecular microelectronics, biosensors, electrochromics devices, chemical modified electrodes, and the corrosion protection (Guenbour et al. 2000).

The electrochemical method led to films deposited straight on the anode. When a positive potential was applied at the electrode, a pyrrole monomer such as a heterocyclic compound was oxidized to form a delocalized radical cation, which included possible resonance forms. Radical-radical coupling reaction produced the dimerization of the monomer radicals at the α -position. Removal of $2H^+$ ions consequently formed the neutral dimer. Next step was the chain propagation which included the oxidation of the neutral dimer to form the dimer radical. The resultant radical can react with other monomer or a dimer, and this radical coupling and the electrochemical oxidation processes repeated themselves to extend the polymer chain length. The final step involved the termination of the chain growth and the resultant PPy film was formed on the anodic electrode (Jang, J., 2006).

In the case of the aniline electropolymerization, the radical cation of aniline monomer was formed on the electrode surface by oxidation of the monomer. This process was considered to be the rate-determining step. Radical coupling and the elimination of two protons made mainly the *para*formed dimers. Chain propagation proceeded with the oxidation of the dimer and the aniline monomer on the electrode surface. In this step, the radical cation of the oligomer coupled with a radical cation of aniline monomer. In the final step, PANI was doped by the acid (HA) present in solution. The growth of PANI was considered to be self-catalyzed. This means that the polymers were formed at the higher rate as the more monomers were deposited onto the polymer surface. It involved the adsorption of the anilinium ions onto the oxidized form of PANI, followed by the electron transfer to form the radical cation and subsequent reoxidation of the polymer to its most oxidized state (Jang, 2006).

2.4 Doping

There are two methods of doping a conductive polymer (Heeger *et al.*, 1988):

2.4.1 Chemical Doping

This method involves with the reaction of a polymer to an oxidant (e.g. iodine or bromine) or a reductant (e.g. alkali metals).

2.4.2 Electrochemical Doping

This method involves with chemical reactions which take place in a solution at the interface of an electron conductor (a metal or a semiconductor) and an ionic conductor (the electrolyte), and electron transfer between the electrode and the electrolyte or species in solution.

Doping is a reversible process which generally does not cause any degradation. Both the doping and the undoping processes (involving dopant counterions which stabilize the doped state) can be carried out chemically or electrochemically. The p-doping is the partial oxidation of the π -backbone of an organic polymer as shown in Figure 2.2, whereas the n-doping is the partial reduction of the backbone π -system of an organic polymer (Arslan *et al.*, 2007)

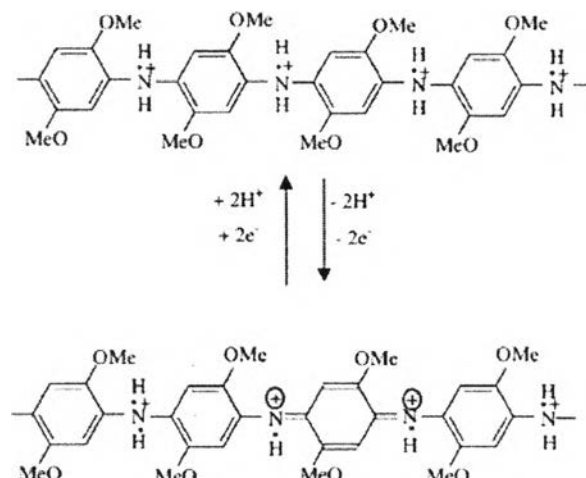


Figure 2.2 Removal of two electrons (p-doping) from PDMA.

Two kinds of doping allow the electrons to freely move from the valence band to the conduction band easily. So, the main cause that makes a polymer to conduct electrically is the jump of the electrons from the valence band to the conduction band (Pratt C., 1996).

2.5 Chromogenic Polymers

Chromogenic polymers are of many different types depending on the stimuli:

Materials	Stimuli	Chromogenic effects
photochromic	optical	photochromism
thermochromic	thermal	thermochromism
electrochromic	applied electric fields	electrochromism
piezochromic	pressure	piezochromism

2.5.1 Photochromic Polymers

This polymer can reversibly change color under an exposure to an ultraviolet light or an electromagnetic radiation. Examples of the photochromic polymer are diarylethenes, azobenzenes, spiropyrans and spirooxazines, as shown in

Figures 2.3 –2.5, respectively. The application of this polymer is color changing lenses for sunglasses.

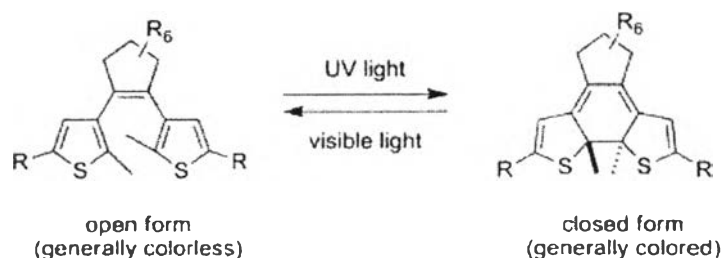


Figure 2.3 The chemical structure of Diarylethene polymer.

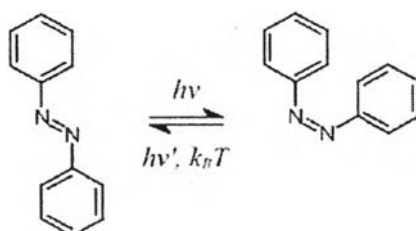


Figure 2.4 The chemical structure of Azobenzenes polymer.

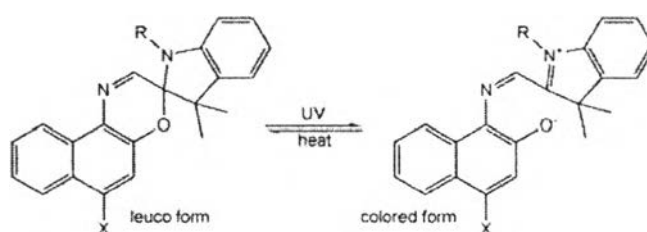


Figure 2.5 The chemical structure of Spiroyrans and Spirooxazines polymers.

Connal (2010) studied the synthesis and the use of a spiropyran functional polymer to form highly ordered honeycomb materials by the breath figure technique. Spiropyran was reacted with poly (acrylic acid) (PAA, $M_w = 450\,000$ Da) via the carbodiimide coupling protocols. The SP-functionalized polymer was no longer soluble in water and was isolated by the precipitation into methanol. When

this polymer was dissolved in chloroform, it displayed a photochromic behavior in response to UV or visible light, as depicted in Figure 2.6. Upon a UV exposure, the spiroopyran ring opened to form the merocyanine structure; this was clearly visible by the intense color change of the solution from light pink to an intense purple color.

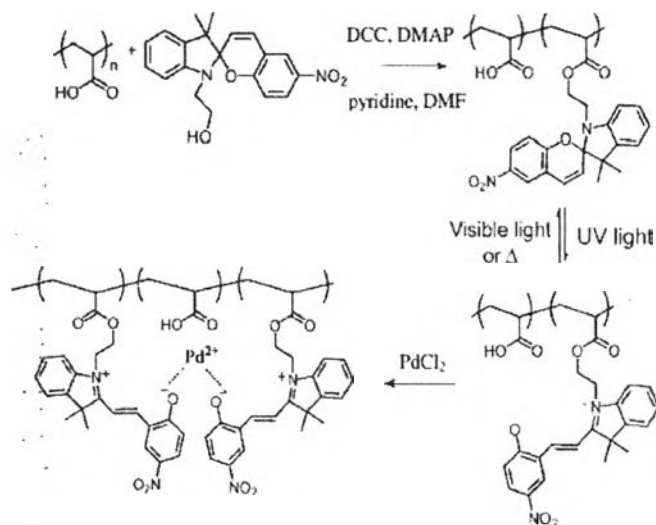


Figure 2.6 Synthesis of photochromic PAA.

Figure 2.7a shows the honeycomb film appearance to be an opaque color and its UV-vis absorbance before the exposure to UV light. This honeycomb film was then irradiated with UV light (366 nm), and it immediately changed to a deep purple color. A distinct change in absorption in the visible region was observed (Figure 2.7b). The film color could be reversed back to its original color state by irradiation with white light by leaving the film in the dark or by heating the film to 60 °C, as shown in Figure 2.7a. Heating the film resulted in a faster discoloration rate than did the light-induced methods. The film was completely decolorized within 10 min of heating to 60 °C, whereas the film took 4 and 24 h for complete discoloration by white light and dark conditions, respectively. Honeycomb films were cast again; however, this time the polymer casting solution contained PdCl₂ (100 ppm) then irradiated with UV light (366 nm). This polymer was analyzed by UV-vis spectroscopy before and after irradiation, as shown in Figure 2.7c and d. the results was similar to films without Pd²⁺. However, there is a distinct shift in the

absorption maximum from 600 to 550 nm for the palladium-containing honeycomb film demonstrating evidence of a new complex formed by the polymer with the palladium ions. The UV absorptions clearly demonstrated that this photochromic polymer can successfully coordinate to Pd^{2+} in a chloroform solution the protocols described here could be further developed for advanced sensor systems or novel catalytic supports.

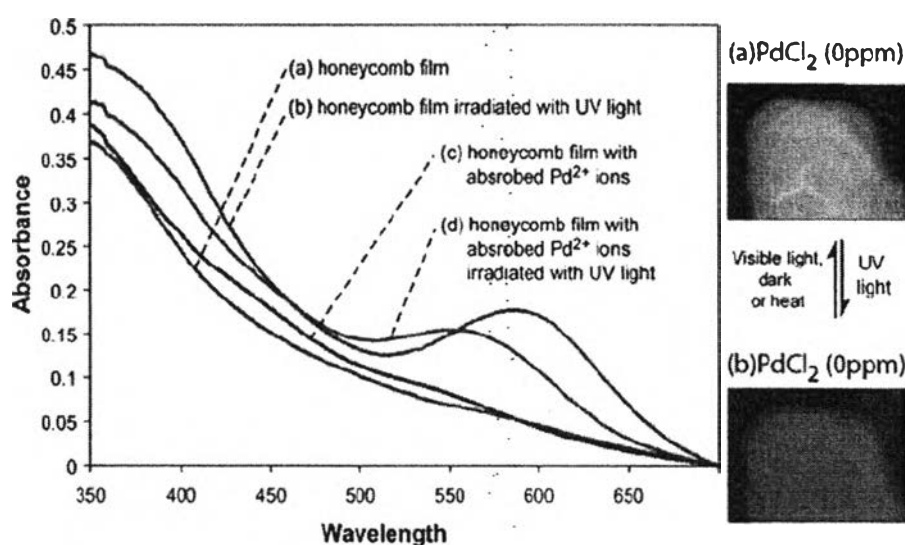


Figure 2.7 UV-vis spectroscopy of photochromic honeycomb films, with the right-hand side displaying digital photographs of two of these films: (a) a honeycomb film without irradiation, (b) a honeycomb film after irradiation with 366 nm UV light, (c) a honeycomb film containing PdCl_2 without irradiation, and (d) a honeycomb film containing PdCl_2 after irradiation with 366 nm UV light.

2.5.2 Thermochromic Polymers

Thermochromic Polymer can reversibly change color by an induced temperature. Examples of photochromic polymer are polydiacetylene (PDA) and crystal violet lactone (CVL), as shown in Figure 2.8. The applications of these polymers is the thermochromic ink which changes color in response to body heat as shown in Figure 2.9.

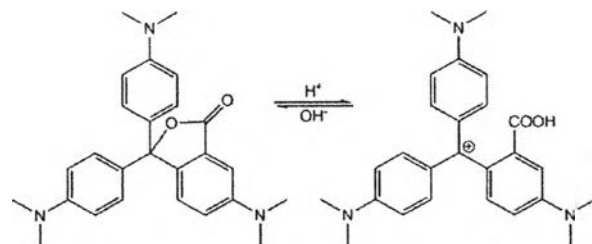


Figure 2.8 The chemical structure of Crystal violet lactone (CVL).

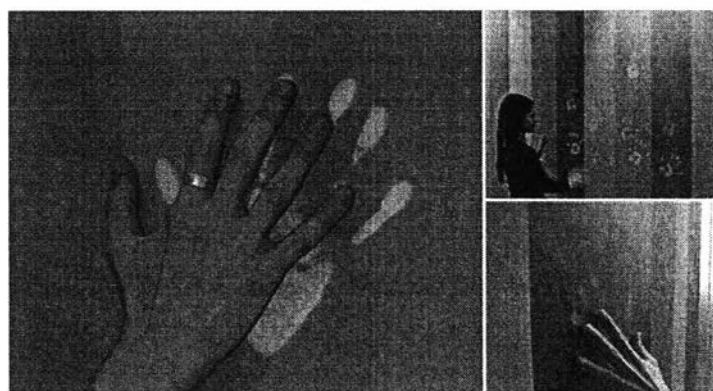


Figure 2.9 Thermochromic ink changes colour in response to body heat.

Phollookin (2010) and co-workers reported the synthesis and the thermochromic properties of bisdiynamide monomers with various lengths of the methylene spacer between the diyne and amide headgroup (m) and various number of methylene groups within its tail (n), forming thermochromically reversible PDAs with a color transition temperature near or below ambient temperature. The synthesis of the diamide diacetylene as shown in Figure 2.10, began with the copper-catalyzed cross coupling reaction as shown in Figure 2.11, between an iodoalkyne (2 or 3) and an alkyne acid (4-6) under a modified Cadiot-Chodkiewicz condition¹² to afford the diynoic acids (7-12) moderate to good yields (49-75%). The competitive homocoupling of the iodoalkyne sometimes lessened the diynoic acid yield. A subsequent treatment of the diynoic acids with 0.5 equiv of ethylenediamine in the presence of N,N' -dicyclohexylcarbodiimide (DCC) coupling reagent afforded the desired bisdiynamide monomers (1a-1f) as white solids with good yields (68-78%).

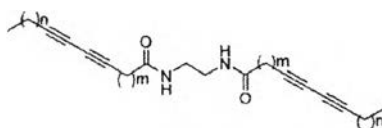


Figure 2.10 The chemical structure of diamide diacetylene.

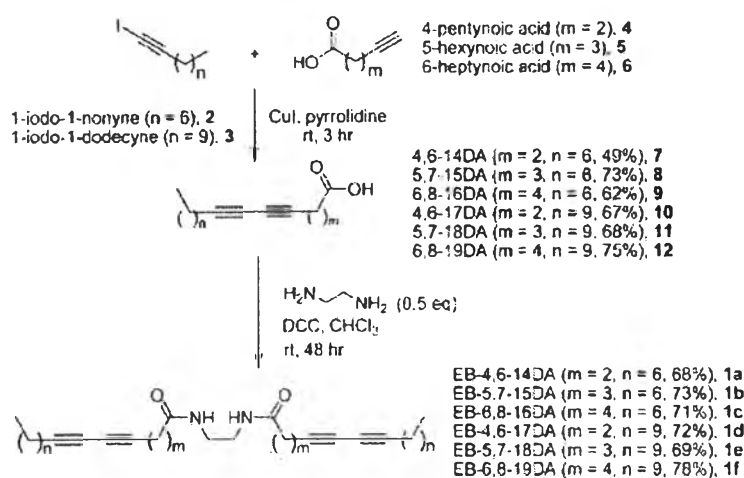


Figure 2.11 Synthesis of Diacetylene Lipid Monomers.

The phospholipid-liked monomers 1a-f, containing two hydrophobic tails, were well dispersed in Milli-Q water under a sonication at 80-85 °C to form either transparent or semitransparent sols. The corresponding fatty acid-liked monomers, containing only one hydrophobic tail, i.e. diynoic acids and monoamide diacetylenes with $m=2, 3$ and $n=6, 9$, formed a large aggregate and precipitated under the same preparative condition. Upon UV-irradiation (254 nm, 900 $\mu\text{w}/\text{cm}^2$) in an ice bath, the diacetylene sols rapidly turned intense blue or purple color within 5 min. The sizes and shapes of the lipid assembled particles within the PDA sols were characterized by the dynamic light scattering (DLS) technique and the atomic force microscopy (AFM). The DLS size distribution revealed the average hydrodynamic diameter of the particles in the range of 75-195 nm as shown in Figure 2.12. The PDA sol obtained from EB-6,8-19DA showed the smallest particle size of 75 nm while the largest size of 195 nm was observed for the sol obtained from EB-4,6-17DA indicating that the particle size tended to increase with the decreasing m value.

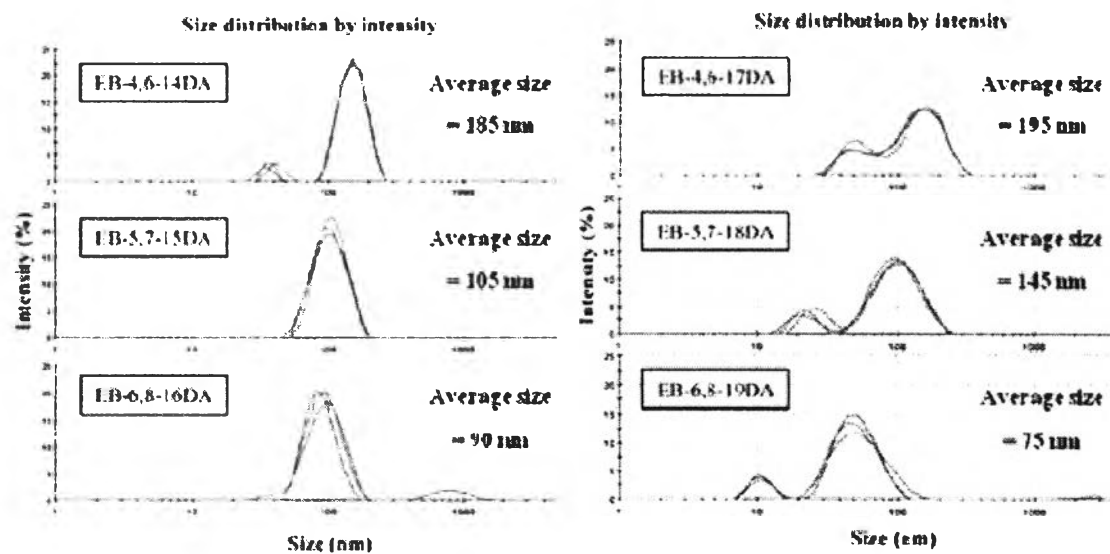


Figure 2.12 Size distribution of the PDA sols obtained from dynamic light scattering.

The AFM image of the dry sample of poly(EB-4,6-17DA) sol showed mainly spherical structures while those of poly(EB-5,7-18DA) and poly(EB-6,8-19DA) sols illustrated mixtures of spherical and rod-like structures as shown in Figure 2.13, that is in good agreement with the decreasing packing parameter (F) of the lipids.

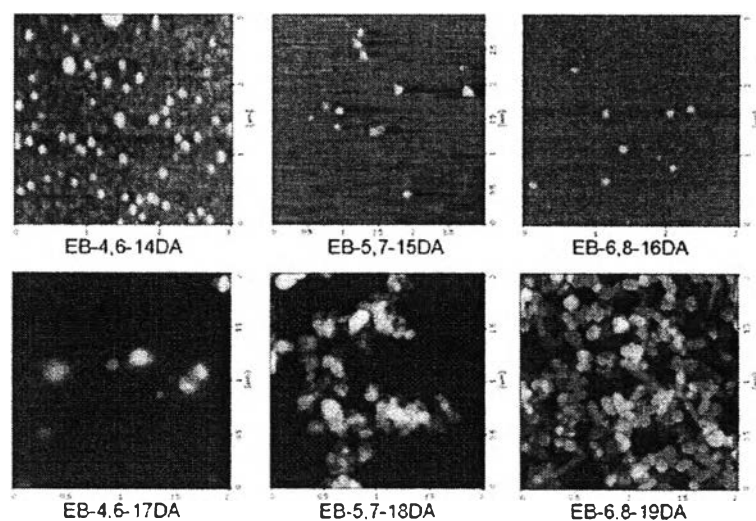


Figure 2.13 AFM images of poly(bisdiynamide).

2.5.3 Electrochromic Polymers

This polymer can reversibly change its color by an electric field. Examples of electrochromic polymers are polyaniline, viologens and polythiophene, as shown in Figures 2.14 – 2.16, respectively. The applications of these polymers are electrochromic windows or smart glasses, as shown in Figure 2.17.

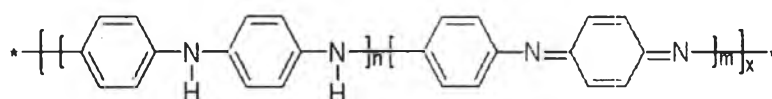


Figure 2.14 The chemical structure of Polyaniline.

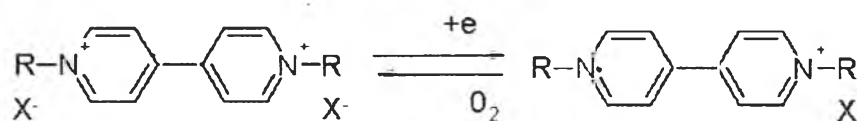


Figure 2.15 The chemical structure of Viologens.

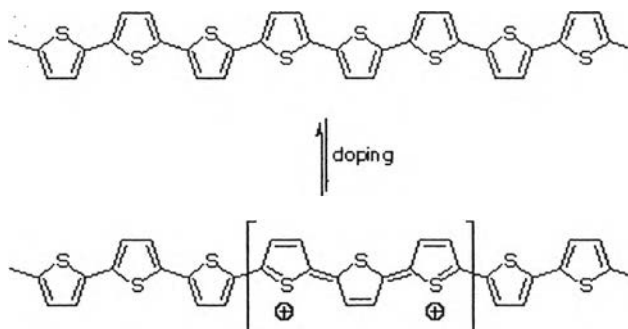


Figure 2.16 The chemical structure of Polythiophene.

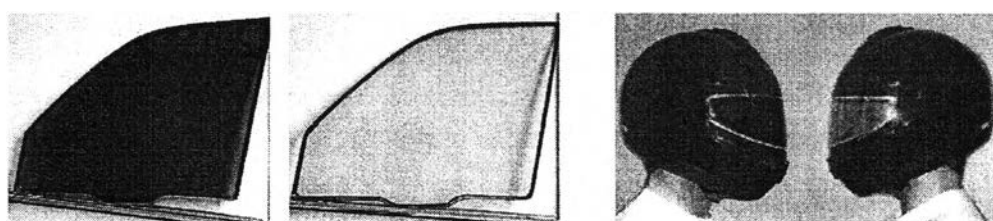


Figure 2.17 Electrochromic windows and smart glass

Jianfu Ding and co workers (2010) reported that the electrochromic properties were achieved by the electrochemical reduction of n-type polymers, such as PF_4O_x as shown in Figure 2.18, an alternating copolymer of quater(9,9-dioctylfluorene), and oxadiazole. The introduction of the strong electron-accepting oxadiazole unit into the poly(9,9-dioctylfluorene) main chain promoted the stability of the polymer in the electrochemical reduction. The copolymer film displayed an excellent electrochromic property upon the electrochemical reduction, which turned the colorless film at the neutral state to rosy-red at the electron charged state with a switching time of 1.1 s. The film exhibited a high stability during the electrochromic test, having only 30% loss of the transmittance change in 500 potential square-wave cycles.

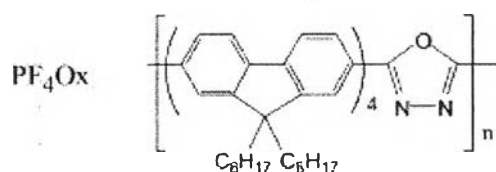


Figure 2.18 Chemical Structure of PF_4O_x .

2.5.4 Piezochromic Polymers

Piezochromic polymers can change color under an applied pressure. Examples of this polymers are poly(5,8-dihexadecyloxyanthraquinone-1,4-diyl) (PAQ), poly(di-n-alkylsilane)s (PDASi), poly(p-phenylene) (PPP), and Chemical Structure of trans-polyacetylene (trans-PA), as shown in Figures 2.19 – 2.22, respectively. The application is as a pressure indicator.

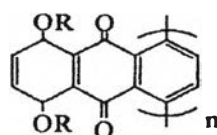


Figure 2.19 Chemical structure of poly(5,8-dihexadecyloxyanthraquinone-1,4-diyl) (PAQ).

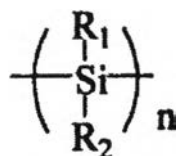


Figure 2.20 Chemical structure of poly(di-n-alkylsilane)s (PDASi).



Figure 2.21 Chemical Structure of Poly(p-phenylene) (PPP).



Figure 2.22 Chemical Structure of trans-polyacetylene (trans-PA).

2.6 Electrochromic Polymers

Electrochromic polymers are reversible in color and the visible change in transmittance and/or reflectance occurs by applying an electrical potential. This phenomenon, is called Electrochromism, results from the generation in different visible region of electrochromic absorption bands upon switching between two redox states (Camurlu *et al.*, 2005). The color of polymers is determined by the band gap energy, defined as the onset of the π -to π^* transition (Sahin *et al.* 2005). A number of conjugated polymers have colors both in the oxidation and reduction states. The important point to study of electrochromic polymer has been to control colors by main-chain and pendant group structural modifications (Coskun *et al.*, 2004). The electrochromic measurements; the spectroelectrochemical analysis, and the switching studies of the polymers were carried out by a UV-vis spectrophotometer in a UV-cuvette as a single compartment with three electrodes (Sacan *et al.*, 2006).

The remarkable advances of electrochromics performance can be viewed from several fronts. First, the range of colors now available effectively spans the entire visible spectrum and also extends through the microwave, near-infrared and mid-infrared regions. This is due to the ability to synthesize a wide variety of polymers with varied degrees of electron-rich character and conjugation. For example, a fine adjustment of the band gap, and consequently of the color, is possible through modification of the structure of the polymer via monomer functionalization, copolymerization and the use of blends, laminates and composites. Second, it has been the marked increase in device lifetimes. The key to this is the control of the degradation processes within the polymeric materials (by lowering the occurrence of structural defects during polymerization) and the redox system. Third, the polymer based ECDs have achieved extremely fast switching times for large changes in optical density. This fast switching is attributed to a highly open morphology of electroactive films, which allows a fast dopant ion transport. Other beneficial properties of polymers are outstanding coloration efficiencies along with their general processability. These techniques are employed in optical displays, camouflage materials, space craft control, car rear-view mirrors, variable reflectance mirrors, variable optical attenuators and variable transmittance windows. For example, the Gentex electrochromic mirror system has been successfully commercialized in the automotive industry, (Coskun *et al.*, 2004). Table 2.1 provides examples of complementary electrochromic polymers which have ability to change color when induced to the change in the redox state and are suitable for use in electrochromic devices.

Table 2.1 The example of complementary electrochromic polymers and colors

Chemical Names	Reduction Color	Oxidation Color	REF
Poly(3,4 ethylenedioxythiophene) (PEDOT)	Transparent	Blue	Hung Xuan, (2004).

Poly(3,4-ethylenedioxyppyrrrole) (PEDOP)	Transparent	Red	Hung Xuan , (2004).
Poly(3-methylthiophene) (P3MTh)	Blue	Red	Nicho, <i>et al.</i> (2004).
Poly(3,6-(2-ethylenedioxythienyl) carbazole) (PBEDOT-Cz)	Yellow	Blue	Hung Xuan, (2004).
Poly(3,3-diethyl-3,4-dihydro-2H- thieno[3,4-b][1,4]dioxepine) (PProDOT-(Et) ₂)	Purple-blue	Transmissive sky blue	Argun, (2004).
Poly(2,2'-[10-methyl-3,7- phenothiazylene]-6,6'-bis[4- phenylquinoline]) (PPTZPQ)	Yellow	Red	Argun, (2004).
Poly(2,7-carbazole)	Blue	Red	Kawabata, <i>et al.</i> (2010).
Poly(4,4-dioctylcyclo- pentadithiophene-alt-3- octylthiophene) (PDOCPDT-OT)	Red	Light blue	Wu, <i>et al.</i> (2009).
Poly[4,4- dioctylcyclopentadithiophene-alt- 4,7-(2,1,3-benzothiadiazole)] (PDOCPDT-PT)	Green	Gray	Wu, <i>et al.</i> (2009).
Poly[4,4- dioctylcyclopentadithiophene- alt-3,6-(9H-carbazol)] (PDOCPDT-Cz)	Yellow	Blue	Wu, <i>et al.</i> (2009).

2.7 Polyaniline

Electrochromic polymers such as polyaniline are very important because their color can be controlled electrically. Light emitting polymers are also important and are used in devices known as organic light emitting diodes (OLEDs) which are beginning to be used in modern displays. Polyanilines refer to a class of polymers which can be considered as being derived from a polymer, the base form of which has the generalized composition, as shown in Figure 2.23, consisting of alternating

reduced and oxidized repeat units, as shown in Figures 2.24 and 2.25 respectively. The average oxidation state, $(1-y)$ can be varied continuously from zero to give the completely reduced polymer to 0.5 to give the "half-oxidized" polymer, to 1 to give the completely oxidized polymer. The terms "leucoemeraldine", "emeraldine" and "pernigraniline" refer to the different oxidation states of the polymer where $(1-y) = 0$, 0.5 and 1, respectively as shown in Table 2.2, (MacDiarmid, 1992).

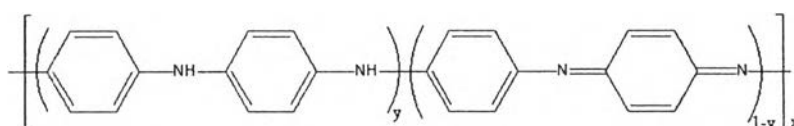


Figure 2.23 The structure of PANI repeating units.

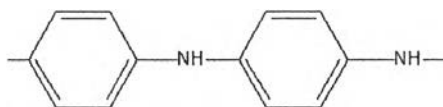


Figure 2.24 The structure of PANI in the reduced repeating units.

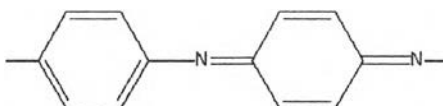
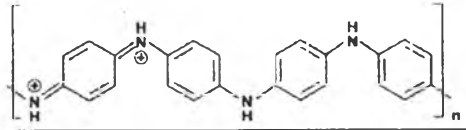
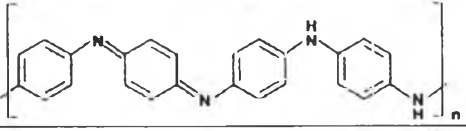
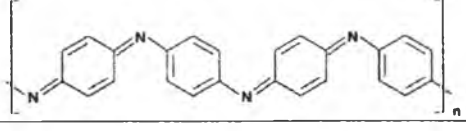


Figure 2.25 The structure of PANI in the oxidized repeating units.

Table 2.2 The chart below shows the different colored forms of the polymer

Name of Color States	Colored Forms	Colors
Leucoemeraldine		Colourless (Fully reducing Insulating)

Emeraldine salt		Green (Partially oxidized Conducting)
Emeraldine base		Blue (Partially oxidized Insulating)
Pernigraniline		Purple (Fully oxidized Insulating)

In principle, the imine nitrogen atoms can be protonated in whole or in part to give the corresponding salts, the degree of protonation of the polymeric base depending on its oxidation state and on the pH of the aqueous acid. Complete protonation of the imine nitrogen atoms in emeraldine base is by aqueous HCl (MacDiarmid, *et al.* 1989).

2.8 Poly(2,5-dimethoxyaniline) (PDMA)

PDMA film was deposited potentiostatically (0.4 V) on an ITO glass coated electrode with a specific conductivity of ca. $10 \Omega/\text{cm}^2$. Before each experiment, the ITO coated glass electrode was cleaned with acetone and double distilled water. In situ UV-VIS spectroelectrochemical experiments were carried out in a quartz cuvette of 1 cm path length, assembled as an electrochemical cell with PDMA film coated ITO plate as working electrode, a platinum wire as the counter electrode and Ag/AgCl as the reference electrode (Huang *et al.*, 2002).

In 2002, Potential-time curve (E-t curve) was used to record during the synthesis of PDMA coating on LCS at room temperature with an applied current density of $0.66 \text{ mA}/\text{cm}^2$ as shown in Figure 2.26. It is clearly seen that initially, the electrode potential is negative and it remains fairly constant at 470 mV for a certain time (101 s) known as an induction time. This was followed by a sudden increase of potential to a positive value (546 mV) and it decreased sharply and eventually reached to a steady state value (1313 mV). Then, the decomposition of the interphase was followed by the EPC (Patil *et al.*, 2002).

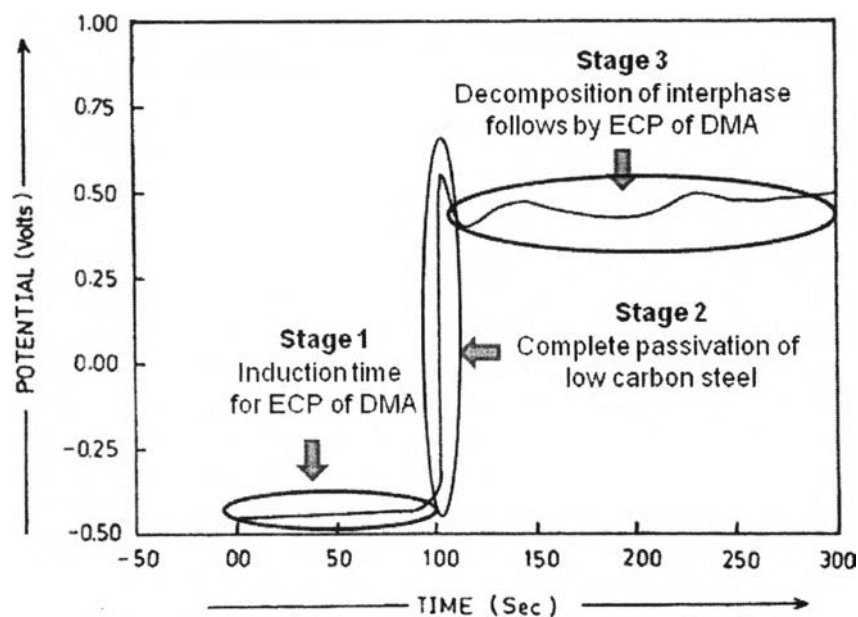


Figure 2.26 E-t curve of electrochemical polymerization of PDMA under galvanostatic condition at applied current density of 0.66 mA/cm^2 .

Cyclicvoltammogram of PDMA film showed two redox processes corresponding to the transition from leucoemeraldine to emeraldine and also emeraldine to pernigraniline state. Figure 2.27 represents the CV of the PDMA film in $0.5 \text{ M H}_2\text{SO}_4$. PDMA film was deposited by a reversible cycling of the potential in the range of $0.0 - 1.0 \text{ V}$ versus Ag/AgCl in a solution of DMA (10 mM) and $0.5 \text{ M H}_2\text{SO}_4$. Two redox peaks at $0.17 \text{ V}/0.11 \text{ V}$ (A/A') and $0.27 \text{ V}/0.20 \text{ V}$ (B/B') along with a very weak redox shoulder at $0.38 \text{ V}/0.28 \text{ V}$ (C/C') were noticed. The observed redox peaks have been earlier assigned to the transition from the totally reduced leucoemeraldine form to the emeraldine form, the transition from the emeraldine form to the fully oxidized pernigraniline form, and for the incorporation of a linear or cyclic dimer or to the degradation products of polymer (Huang *et al.*, 2002).

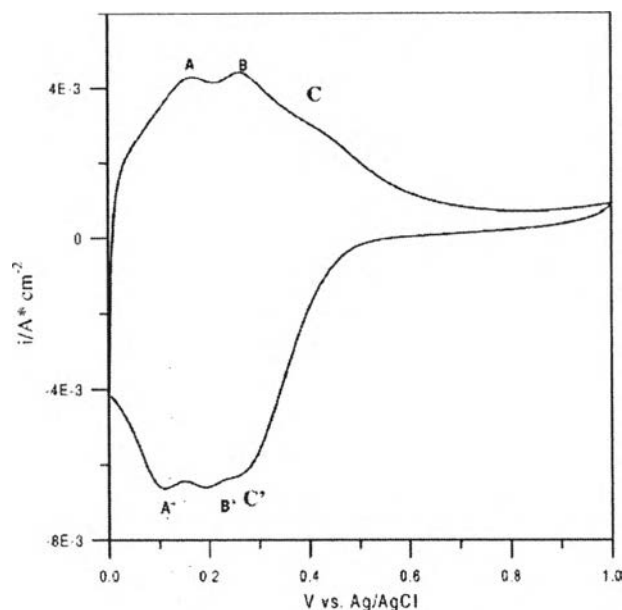


Figure 2.27 Cyclic voltammogram of PDMA-modified Pt electrode in 0.5 M H_2SO_4 . Film deposition: (DMA) = 10 mM, no of cycles = 50, potential range = 0.0 – 1.0 V and scan rate = 50 mV/s.

The FTIR spectrum of PDMA, as shown in Figure 2.28, exhibits the following spectral features. The strong band at 3350 cm^{-1} corresponds to the O–H stretching vibration. The strong band at 1647 cm^{-1} is an indicative of the presence of the carbonyl group C=O contained in the oxalate ion. The presence of the sharp duplex peaks at 1317 and 1361 cm^{-1} correspond to the C–O group. The 817 cm^{-1} absorption band represents the O–C=O in-plane deformation and the appearance of the band at 717 cm^{-1} may be due to O–C=O in-plane deformation and the Fe–O stretching (Patil *et al.*, 2002).

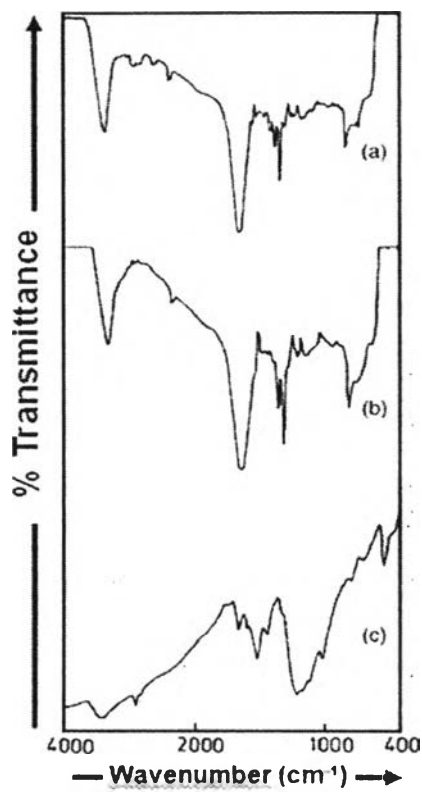


Figure 2.28 FTIR spectra of the PDMA coating synthesized on LCS substrates with an applied current density of 0.66 mA/cm^2 for the duration of: (a) 50s; (b) 101 s; and (c) 2000 s.