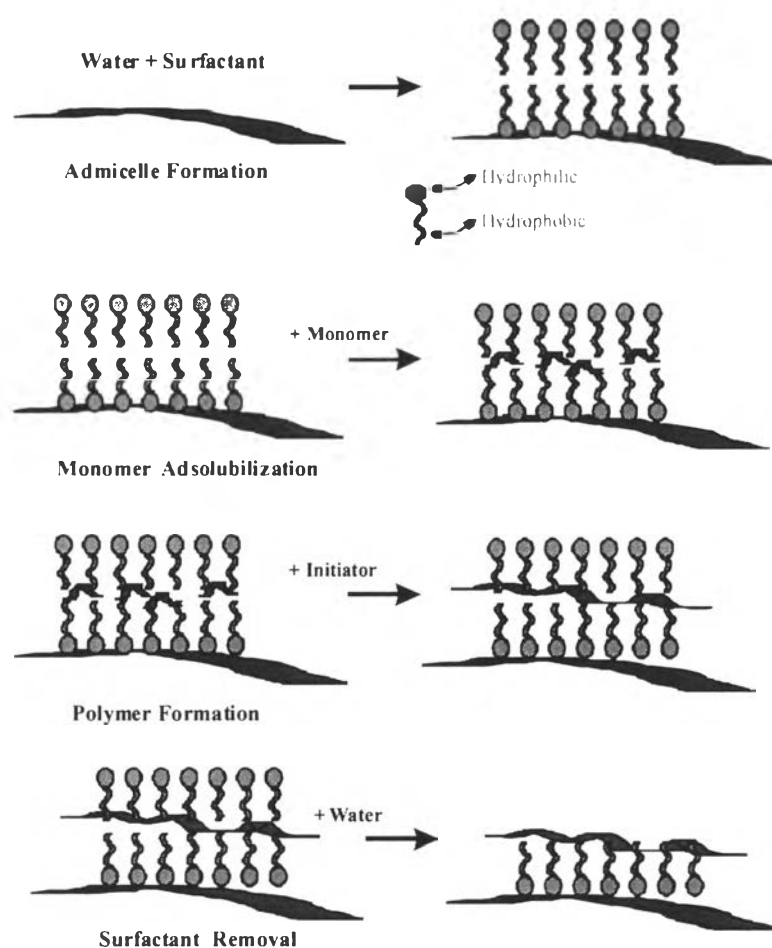# CHAPTER II
LITERATURE REVIEW

2.1 Admicellar Polymerization

Thin film coating by admicellar polymerization process can be divided into four steps as shown in Figure 2.1.

Figure 2.1 The admicellar polymerization process.

Step 1. *Admicelle Formation:* Adsorption of a surfactant bilayer onto the surface of the substrate. Adsorption is accomplished through the use of a suitable surfactant under appropriate system conditions.   The choice of

surfactant is influenced by the point of zero charge (PZC) of the substrate. At pH values below the PZC, the surface becomes protonated and more positively charge, above the PZC, the surface is negatively charged. Thus, anionic surfactants adsorb well below the PZC and cationic surfactants adsorb well above the PZC. The concentration of surfactant used is close to the critical micelle concentration (CMC) to prevent emulsion polymerization in the micelles. Figure 2.2 shows the adsorption isotherm of an ionic surfactant on a solid surface.
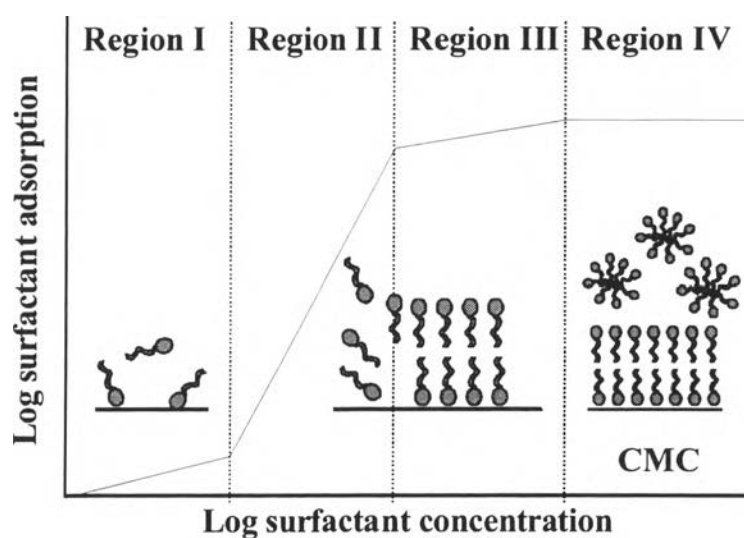
Figure 2.2 Typical adsorption isotherm of surfactant on a solid surface.

Step 2. *Monomer Adsolubilization*: Monomers which are hydrophobic go into the hydrophobic interior of the admicelle. This process is called adsolubilization.

Step 3. *Polymer Formation*: The polymerization takes place in the admicelle by adding initiator. The mechanism of polymerization is similar to that occurs in the conventional emulsion polymerization.

Step 4. *Surfactant Removal*: After the polymerization is complete, the upper layer of surfactant is removed by washing.

This technique is simple with low energy consumption and more economically than other coating techniques.

2.2 Thin Film Coating by Admicellar Polymerization

The method for coating a thin film of polymer on a substrate by using admicellar polymerization technique has been widely studied.

Wu *et al.* (1987) used sodium dodecyl sulfate (SDS) as two-dimensional solvents for the formation of ultrathin film of polystyrene on alumina surface. Results from polymerization show 75% or higher conversions of adsolubilized monomer to polymer after 25 minutes. A uniform film was formed on the alumina oxide surface. Under varying conditions, film thickness of 13 nm was obtainable.

The method has been expanded to cover another substrate, an amorphous precipitated silica, using other surfactant types (O'Haver *et al.*, 1994). Results from polymerization in cetyltrimethylammonium bromide (CTAB), octylphenoxypoly(ethoxy) ethanol (a nonionic surfactant), and methyltri(C8-C10) ammonium chloride (a cationic surfactant) show effective conversion of adsolubilized styrene monomer to polystyrene. Only approximately 25% of the polymer was extractable after refluxing for 4 h in tetrahydrofuran. The process has shown that, on precipitated silica substrates at least, the organic polymer is quite firmly attached to the surface even though it is not chemically bonded. This process also offers a potentially inexpensive method for modifying chemical and physical surface properties of various substrates.

Lai *et al.* (1995) studied the polymerization of tetrafluoroethylene (TFE) in admicelle of sodium perfluoroheptanoate on alumina oxide powder. The effects of surfactant and initiator concentrations were studied. A main factor to control TFE gas monomer adsolubilization into surfactant bilayers was pressure variation. The measurement of friction coefficients and contact angles also verified that thin PTFE films were formed on the alumina plates.

The effect of adding sodium chloride (0-0.5M) on the solubilization behavior of pyrrole in admicellar sodium dodecyl sulfate (SDS) solution was determined (Funkhouser *et al.*, 1995). Pyrrole was found to decrease surfactant adsorption in contrast to alcohol, alkane, and aromatic hydrocarbon.

A particular pyrrole adsolubilization value can be attained with a lower equilibrium SDS concentration by adding salt. The interfacial concentration of pyrrole is increased by the addition of salts, enabling the use of admicellar-assisted polymerization with ammonium persulfate to produce thin, well-connected films of polypyrrole salts on alumina plates, demonstrating the applicability of the technique to monomers with moderate water solubility. The resistance of the film is comparable to much thicker films produced in the absence of salt and surfactant. The film formation was not observed by using solution of SDS without added salt.

Sakhalkar *et al.* (1995) studied the formation of thin polystyrene films on glass fiber. The process of producing the thin film includes three steps, the formation of surfactant admicelle, the partitioning of the styrene monomer into the admicelle, and the *in situ* polymerization of the adsorbed monomer. Scanning electron microscopy (SEM) was used to observe the treated fibers and evaluate the film formation. This micrograph shows a non-uniform coating on the fiber surface. Experiments conducted also revealed that polymerization was not restricted to the admicelle and that some polymerization occurred in the supernatant as well.

Thin films of polypyrrole (PPY) were deposited on alumina particles using hexanoic acid adsorbed on the particles as a template (Cho *et al.*, 2000). From the solubilization studies under appropriate conditions, it was concluded that pyrrole diffuses into the interface and condenses at the interface. The amount of pyrrole solubilized increases with the increase of the initial concentration of pyrrole. Surface polymerization of pyrrole at the interface yields polypyrrole-coated alumina, which was characterized by contact conductivity, calcination, and AFM. Even with a fairly low amount of PPY in alumina (12wt %), a high contact conductivity of 4.7×10^{-2} S.m^{-1} was obtained, which is more than 3 times that of pure polypyrrole powders. The product has potential application as conducting fillers, and the method used may be extended to prepare other types of core-shell type composites for novel materials

Yuan *et al.* (2001) studied chemical deposition of electrical conducting polypyrrole (PPY) thin films on mica and alumina in aqueous solutions with and without surfactant. Examination of film morphology and thickness indicated a strong dependence of structure on the method of preparation. PPY films polymerized in the presence of cationic surfactant-cetylmethyl ammonium bromide (CTAB) are thin, free of wrinkles, and as thick as those polymerized in anionic surfactant-sodium dodecyl sulfate (SDS) salt solutions. This means that, with a fixed pyrrole concentration and with sufficient oxidant, film thickness does not strongly depend on the type of surfactant.

Formation of polymeric films on cellulosic surfaces was investigated (Boufi and Gandini, 2001). The interaction of cellulosic fibers and surfactant was studied using two different surfactants, hexadecylpyridinium chloride (CTP) (a cationic surfactant), and sodium dodecylbenzenesulfate (SDBS) (an anionic surfactant). No adsorption was achieved with the anionic surfactant, whereas the cationic one strongly adsorbed. The addition of alkenyl monomers (styrene, methymethacrylate, and 2-ethylhexylacrylate) to these systems and their subsequent polymerization resulted in the formation of polymer both in the aqueous medium and around the fibers. The latter 'coating' which was rather irregular in coverage, produced a strong increase in the hydrophobic character of the cellulose surface.

Pisuntornsug *et al.* (2002) used admicellar polymerization method to modify the surface of cotton fabric. Sodium styrene sulphonate, a polymerisable anionic surfactant, was polymerized on cotton to impart a negative charge on the fiber surface to enable the fiber to be dyed with a cationic dye with no need for salt addition. The treated cotton was dyed with a cationic dye to determine the amount and uniformity of coating. The results show that the treated and dyed fabric gives good washing fastness at 30°C and excellent dry rub fastness.

In the same year, cotton fabric was also modified to increase the hydrophobicity by coating the thin film of styrene using admicellar polymerization method (Pongprayoon *et al.*, 2002). The polystyrene film

formed was characterized by SEM, FTIR, and GPC. The increase in the hydrophobicity of treated cotton surface was determined by the drop test. Results show clear evidence of a layer of coating polystyrene thin film on the fiber surface, and the coated cotton fabric can resist wetting by a water droplet for longer than 30 minutes.

2.3 Preparing Conductive Fabric

Many techniques for preparing conductive fabric have been widely studied. The effect of dopants, their properties and their applications are also investigated.

Khun *et al.* (1990) prepared electrically conductive fabric under agitation by contacting the textile material with an aqueous solution of pyrrole or aniline compound, oxidizing agent, and a doping agent. After oxidation polymerization, a uniform conductive polymer film on the textile was achieved by controlling the type and concentration of polymerizable compound. The electrical resistivities of the fabrics are in the range 500 to 5,000 ohms per square (measured at 70°F and 50% RH). In addition, good conductivity can be achieved by using sulfonic acid derivatives as the counter ion dopant for polymers.

Jin *et al.* (1996) studied diffusion and chemically oxidative polymerization of polyaniline (PANI). PET fibers and Nylon fabrics were used as substrates. The effect of dopants was investigated. Results show that PANI-PET fibers and PANI-Nylon fabrics doped with HCl have an electrical conductivity as high as 0.42 S/cm and 0.45 S/cm respectively. For other dopants, p-toluensulfonic acid (p-TSA), dodecylbenzene sulfonic acid (DBSA), and 5-sulfosalicyclic acid (SSA), the conductivity of the final composites is one or two orders of magnitude lower than that with HCl. To determine the interfacial adhesion of PANI on textiles, a washing test was used and results showed that the conductivity and interfacial adhesion of composites improved greatly by preliminary aniline diffusion treatment of textiles. Results of SEM, WAXS, and DSC indicated that the improvement in

properties of composite textiles is mainly attributed to the increased interaction of macromolecules at the interface caused by the diffusion of PANI chains in the surface layer of the substrates.

Thin films of conductive polymers, polypyrrole or polyaniline, coated onto poly(ethylene terephthalate) or nylon woven fabric used for chemical sensing based upon electronic changes arising in the polymeric films with the gas-phase adsorption of electronically active vapors, were studied (Collins *et al.*, 1996). The polymers were formed by an *in situ* solution polymerization process that is based on oxidative coupling of the monomer species and simultaneous incorporation of the dopant. The resistivities of polypyrrole doped with naphthalene-disulfonic acid (NDSA) on PET were 211, 775, and 3000 Ω/cm^2. The resistivity of polypyrrole on PET doped with anthraquinone-2-sulfonic acid (AQSA) was 129 Ω/cm^2, polypyrrole on nylon doped with NDSA was 100 Ω/cm^2, and polyaniline on PET doped with Cl⁻ was 75Ω/cm^2. The resistivity of these materials was monitored following exposure to several toxic gases.

The insulating natural fibers, such as cotton, silk, and wool become electrically conducting by polymerization of electroactive monomers (Bhadani *et al.*, 1996). They are subjected to electrical treatment in the polymerizing solution of pyrrole in acetonitrile containing p-toluene sulfonic acid as a supporting electrolyte. The conductivity is in the range of 0.2 to15 S/cm and dependent on the nature of fibers.

Kuhn *et al.* (1997) studied the adsorption at the liquid/solid interface of the conductive textiles based on polypyrrole. The electrical properties and environmental stability of the product depend on a number of variables such as concentration of the chemicals and particularly the dopants used. Different counterions or doping agents can affect not only the degree of conductance, but also the degree of stability. The performance, in terms of conductance and stability, improves with the concentration of sulfonic acid used. The performance is further improved if soluble aromatic sulfonic acids, such as naphthalene-2-sulfonic acid and particularly anthraquinone-2-sulfonic acid are

used. This is due to their relatively planar structure which allows stacking of these molecules between the layers of the conjugated polymer. This facilitates hopping of electrons from chain to chain where defects in the chain occurrs. The surface resistance of 10-10,000 ohms/square can be produced, and no significant differences could be found by the use of different fibers.

Anbarasan *et al.* (1999) studied graft copolymerization of polyaniline (PANI) and poly (o-toluidine) (POT) onto poly(ethylene terephthalate) fiber by using peroxydisulfate as a lone initiator under nitrogen atmosphere in aqueous hydrochloric acid medium. The grafting was verified by recording cyclic voltametry of the grafted fiber, conductivity measurements, and thermal analysis. The variations in % grafting, % efficiency, rate of grafting and rate of homopolymerization of aniline or o-tuluidine, indicated that POT could be better grafted onto PET than PANI. The % grafting and % efficiency values also show the same trend. Grafting was always accompanied by homopolymerization. The conductivity value of PANI-grafted PET (1.50 $Mohm^{-1}cm^{-1}$) was higher than the POT-grafted PET (3.30 $Gohm^{-1}cm^{-1}$).

Two methods of obtaining electrically conductive fabrics by *in situ* polymerization of aniline were compared (Oh *et al.*, 1999). Conductive fabrics were prepared by immersing the nylon 6 fabrics in 100% aniline or an aqueous hydrochloride solution of aniline followed by initiating successive polymerization in a separate bath (DPSB) or in a mixed bath (DPMB) of oxidant and dopant solution with aniline. The higher conductivity of composite fabrics, whose value reached up to 0.6×10^{-1} S/cm, was obtained by the DPMB process. No significant changes in the fabric conductivity were observed after abrading the composite fabrics over 50 cycles and multiple acid and alkali treatments. The stability of conductivity was slightly decreased by less than 1 order after exposure to light for 100 h. But the fabric conductivity could be recovered by acid redoping with proper dopant.

A method for synthesis and covalent bonding of electrically conductive polypyrrole to a poly(ethylene terephthalate) fabric for biomedical application was studied (Tessier *et al.*, 2000). It involves a three-step process.

In the first step the fiber surfaces are activated using phosphorus trichloride. Then, 1-(3-hydroxypropyl) pyrrole is introduced and grafted to the phosphorus chloride to create an ester bond between the fibers and the pyrrole. Finally, the pyrrole-grafted fibers are dipped in an aqueous $FeCl_3$ catalyst and exposed to pyrrole monomer vapor for the final polymerization. This last step creates an electrically conductive polypyrrole layer covalently linked to the poly (ethylene terephthalate) fabric. The smooth and uniform surface coating of polypyrrole was achieved. The surface resistivity values of the product are in the range of 10^4-10^5 Ω/square, which are considered attractive for biomedical applications. The PPY-coated samples were found to be more hydrophilic than the untreated ones.

The electrical properties of conductive polypyrrole-coated polyester fabric under various experimental conditions were investigated (Lian *et al.*, 2000). The properties studied include the volume and surface resistivities. The results show that both the surface and volume resistivities of the coated textiles dropped by more than 10 orders of magnitude compared with the uncoated fabric. The volume resistivity of the coated materials varied between 10^1 and 10^2 Ω.m, while the surface resistivity changed from 10^2 to 10^4 Ω/square depending on the coating thickness. It was also found that their electrical properties were not affected significantly by environmental factors, such as humidity, and sterilization by gamma radiation.

Kim *et al.* (2001) studied the effect of dopant mixture on the conductivity and thermal stability of polyaniline/Nomex conductive fabric. The composite fabric was prepared by *in situ* polymerization of aniline doped by a mixture of hydrochloride (HCl) and various sulfonic acids such as benzenesulfonic acid (BSA), sulfosalicylic acid (SSA), and dodecylbenesulfonic acid (DBSA). The results show that PANI/Nomex composite fabrics doped by a mixture of protonic acids exhibited higher conductivity than those doped by other single dopants such as camphor sulfonic acid (CSA), p-toluenesulfonic acid (TSA), BSA, SSA, and HCl. The conductivity of PANI/Nomex fabrics doped by a mixtureof HCl and DBSA

was evenly maintained up to 100°C without depression of mechanical properties of Nomex. Their conductivity was also maintained under extension of the composite fabric.

The thermal stability of polyaniline-Nylon composite fabrics doped by a mixture of hydrochloric acid (HCl) and various organic aryl sulfonic acids such as benzenesulfonic acid (BSA), dodecylbenzenesulfonic acid (DBSA), and p-toluenesulfonic acid (TSA) was studied (Oh *et al.*, 2001). Conductive fabric was prepared by oxidation polymerization of 0.5M aniline in aqueous HCl solution and in various doping solutions. The highest fabric conductivity was obtained with HCl/BSA (3.122×10^{-2} S/cm). This conductivity increased as the concentration of BSA in the polymerization bath increased from 0.05M to 0.5M. The conductivity of all doped PANI-nylon 6 composite fabrics decayed at elevated temperatures in air. Among the various dopants, HCl/DBSA showed the best thermal stability.

Oh *et al.* (2001) studied the effect of plasma treatment on the surface characteristics and conductivity of polyaniline (PAn)-nylon 6 composite fabrics. Oxygen, argon, and ammonia gases were applied for the plasma treatment of nylon 6 fabrics to improve the adhesion and rate of polymerization. Oxygen-plasma-treated nylon fabric retained the highest conductivity and PAn deposit. The surface of nylon 6 fibers was strongly etched by oxygen plasma treatment and various functional groups such as COOH and C=O could be produced on the nylon 6 fiber surface, which was confirmed by XPS. Oxygen was revealed as the most aggressive and effective plasma gas compared with ammonia and argon plasma in this system. The conductivity of oxygen-plasma-treated PAn-nylon 6 fabric was more stable with repeated washing and abrasion cycles than PAn-nylon 6 fabric without plasma pretreatment. Fabric conductivity increased as the monomer concentration increased up to 0.5M and then leveled off. Fabric log conductivity in the range of −2.2 to −1.6 S/cm could be reached in a single deposit and a further increase could be achieved with an increase in the number of multiple deposits.

PET fabric/polypyrrole (PPy) composite with high electrical conductivity was prepared by chemically and electrically polymerization used for electromagnetic interference shielding (EMI SE) (Kim *et al.*, 2002). In the chemical polymerization, pyrrole dissolved in an aqueous solution without or with polyvinyl alcohol as a surfactant was first sprayed on the PET fabric and oxidized by spraying an aqueous solution of an oxidant and a dopant. Electrochemical polymerization was carried out in an aqueous electrolyte solution by applying a constant current density to the PET fabric coated with chemically polymerized PPy and a stainless steel plate as the working and the counter electrodes, respectively. The results show that the specific volume resistivity of the composite was as low as 0.2 Ω cm, giving rise to EMI SE of about 36 dB over the wide range of frequency, where 7% of the power of the incident wave was absorbed by the composite.

Preparation of conductive polymer-coated fabric was carried out by admicellar polymerization (Lekpittaya *et al.*, 2004). By this method, a thin layer of conductive polymers, namely, polypyrrole, polyaniline, and polythiophene, was formed on cotton and polyester fabrics via a surfactant template. The effects of monomer concentration, oxidant to monomer ratio and addition of salt on the resistivity of the resulting fabrics were studied. The results showed that the apparent surface and volume resistivity decreased with increase in monomer concentration in the range 5-15 mM, but was not strongly dependent on the oxidation to monomer ratio over the range of 1:1 to 2:1. Addition of 0.5 M salt was found to reduce the resistivity significantly. The lowest resistivity obtained was with polypyrrole-coated fabric with resistivity around 10^6 ohm.

2.4 Concept of Doping

Conjugated polymers are either electrical insulators or semiconductors, but their resistivity can decrease by several orders of magnitude by "doping". Since 1977, polyacetylene $(CH)_x$ was known as the

prototype conducting polymer which can be p- or n-doped, either chemically or electrochemically. The development in the field of conducting polymers has grown rapidly. A variety of other conducting polymers and their derivatives have been discovered. In the "doped" state, the backbone of a conducting polymer consists of a delocalized π-system. The doping process can be classified into three processes, which are redox doping, non-redox doping and doping involving no dopant ions.

Redox doping

The doping of all conducting polymers had previously been accomplished by redox doping. This involves the partial addition (reduction) or removal (oxidation) of electrons to or from the π-system of the polymer backbone. This can be done by chemical and/or electrochemical processes, during which the number of electrons associated with the polymer backbone changes. The examples of conductive polymers are presented below.
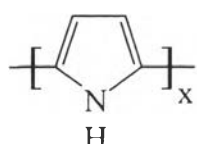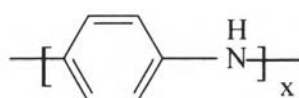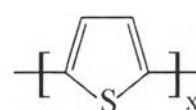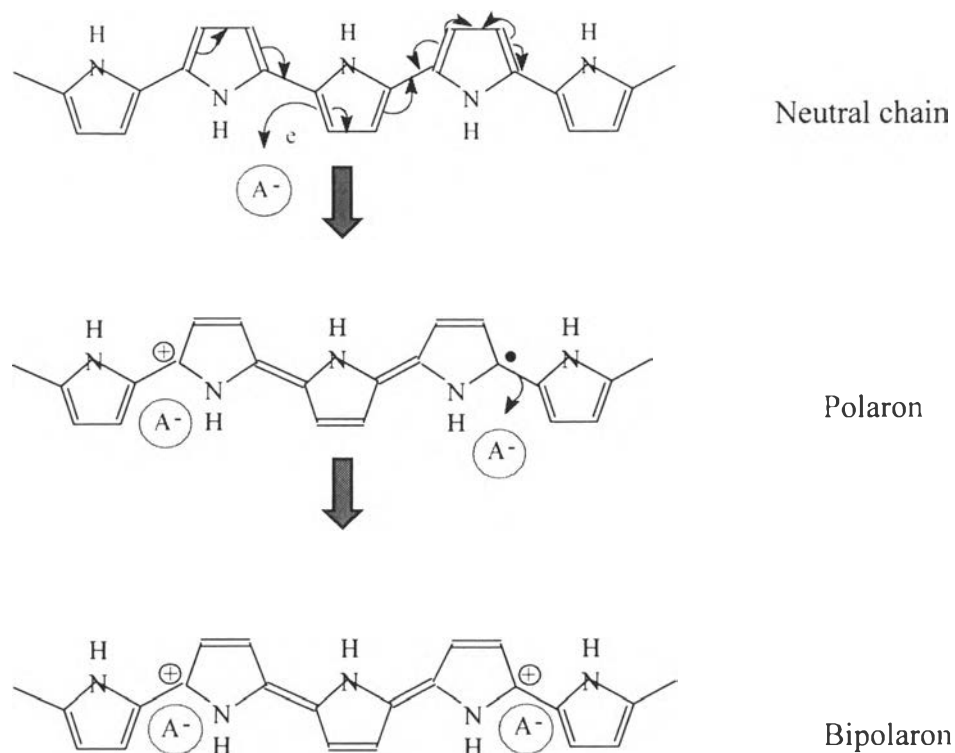

| Polypyrrole | Polyaniline | Polythiophene |

In the doping process, counter 'dopant' ions are introduced which stabilize the charge on the polymer backbone. The polymer may store charge in two ways. In an oxidation process it could either lose an electron from one of the bands or it could localize the charge over a small section of the chain. Localizing the charge causes a local distortion due to a change in geometry, which costs the polymer some energy. In each case, spectroscopic signatures, e.g. those of solitons, polarons, bipolarons, etc. are obtained characteristic of the given charged polymer. Examples of polaron and bipolaron structure of a polymer are shown in Figure2.3.

Figure 2.3 P-type doping of polypyrrole resulting in a polaron and bipolaron.

Doping of polyaniline

Polyanilines refer to a very important class of electronic/conducting polymers. The average oxidation state (1-y) can be varied continuously from zero to give the completely reduced 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, either in the base form, e.g. emeraldine base, or in the protonated salt form, e.g. emeraldine hydrochloride, which possesses green color. 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 depends on its oxidation state and on the pH of the aqueous acid. The most highly conducting doped form can be reached by two completely different processes, protonic acid doping and oxidative doping. Protonic acid doping of emeraldine base units with, for example 1 M aqueous HCl, results in complete protonation of the imine nitrogen atoms to give the fully protonated emeraldine hydrochloride salt.
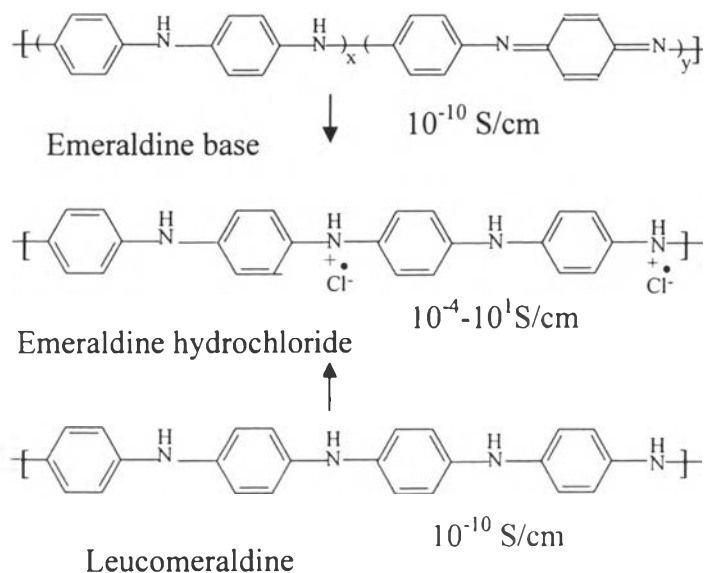
Figure 2.4 Protonic acid doping and oxidative doping of polyaniline

Doping of polythiophene

In 1986, electrochemical and chemical synthesis of polythiophene (PTH) was accomplished. Transition-metal halides such as $FeCl_3$, $MoCl_5$, and $RuCl_3$ were used for the chemical oxidative polymerization. To enhance the conductivity, it can be doped by many dopants such as iodine, $FeCl_3$, $NOSbF_6$, and SO_3CF^-. PTH can exist in a variety of redox forms as shown in Figure 2.4. However, the electrical conductivity is assigned usually to only one of them. The withdrawal of one electron from the PTH molecule (Fig.2.4 (a)), followed by its doping with a solution anion (x^-), leads to its conducting half-oxidized polaronic state (b), whereas the loss of a second electron leads to the oxidized bipolaronic form (c).
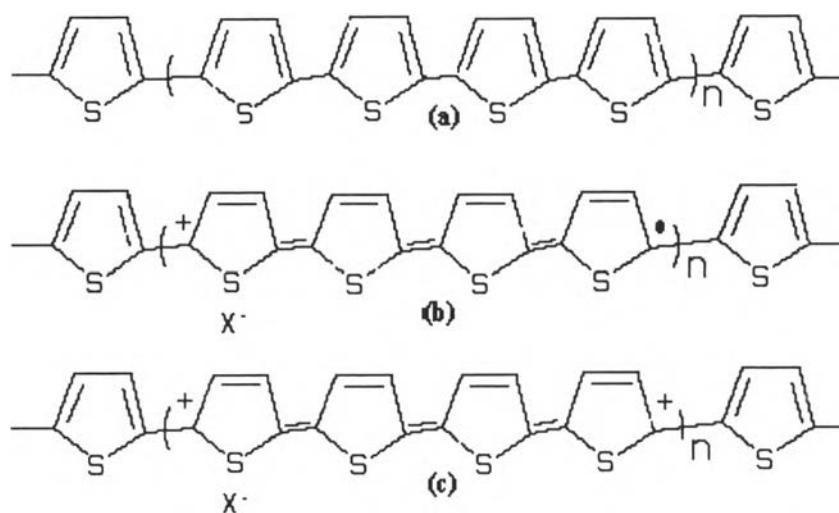
Figure 2.4 Different redox forms of PTH: (a) reduced, (b) half-oxidized (polaronic), and (c) oxidized (bipolaronic).

2.5 Volume and Surface Resistivity Measurements

Since the current encountered in textile materials and other insulators are usually so small, as low as 10^{-17} A. Therefore sensitive instrument and appropriate test methods should be applied. ASTM D-257 is one of the test standards for measuring the surface and volume resistivity of insulating material. By using the appropriate electrode systems, surface and volume resistance can be measured separately. The resistivity or conductivity can be calculated when the required specimen and electrode dimensions are known. By using KEITHLEY 8009 Models 6517 A, the surface resistivity, can be calculated from the following equation:

$$\rho_s = \frac{WV}{LI} \qquad \text{ohm/sq}$$

Where V is the applied voltage, I is the measured current, W is the width of electrodes, and L is the distance between electrodes. The unit of ρ_s is ohm per

square. Volume resistivity, ρ_v, is obtained by measuring the current leakage through a specimen. Volume resistivity determination is often used in checking the uniformity of an insulating material, either with regard to processing or to detect conductive impurities that affect the quality of the material. Volume resistivity, ρ_v can be determined from the following equation:
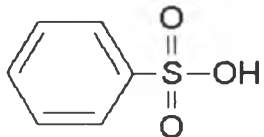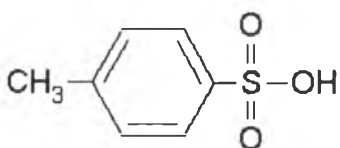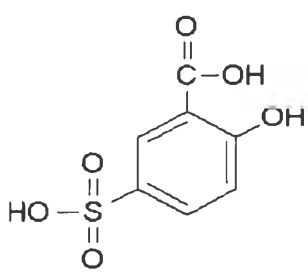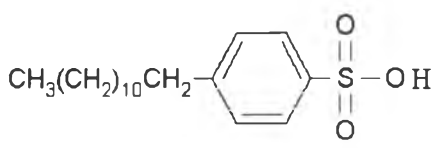
$$\rho_v = \frac{AV}{It} \qquad \text{ohm-cm}$$

Where V is applied voltage, I is the measured current, A is the effective area of the guarded electrode for the particular electrode arrangement in cm^2 and t is the average thickness of sample in cm.

Various techniques have been used to prepare conductive fabric especially coating a conductive polymer onto a fabric could be made very simple and effective. As mentioned previously, admicellar polymerization method has been used to prepare thin films of conductive polymers on many substrates. Thus, applying this method for coating thin films of conductive polymers on a fabric surface should be an interesting subject for investigation. In order to increase the conductivity of the coated fabric, some authors have studied the effect of dopants such as hydrochloric acid (HCl), which can destroy the fabric if the coated fabric is left in acid solution for a long time. Furthermore, the chloride anion (Cl⁻) can be easily removed (de-doping) when washing the doped fabric. Therefore, in this research work, five types of organic sulfonic acids including, dodecylbenzene sulfonic acid, sodium salt (DBSA), benzene sulfonic acid (BSA), 5-sulfosalicyclic acids dehydrate (5-SCA), p-toluenesulfonic acid monohydrate (PTSA), and (+)-camphor-10-sulfonic acid (β) (CSA) were used as a dopants. Their structures are shown in Table 2.1. The effects of these dopants on the resistivity of polyaniline- and polythiophene-coated polyester fabrics were investigated.

Table 2.1 The structures and molecular weight (MW) of all dopants used in the present study

Dopant	Structure	MW
BSA		158
PTSA		190
CSA		232
5-SCA		254
DBSA		348