PREPARATION AND CHARACTERIZATION OF CONDUCTING
POLYANILINE AND POLYANILINE-TITANIUM(IV) OXIDE
COMPOSITE BLENDED WITH POLY(VINYL ALCOHOL)

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Specially dedicated to

my parents and siblings with love and
to Leong Mun Hon, my best friend
for their patience and encouragement

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ABSTRACT

Conductive polyaniline (PAni) and polyaniline-titanium(IV) oxide (PAni-TiO_2) composites were prepared by chemical oxidative polymerization of aniline in the presence of dodecylbenzene sulfonic acid (DBSA) in HCl medium, which played both the role as dopant and surfactant. Such processable conductive PAni and its composite were blended with poly(vinyl alcohol) (PVA) in water, which was then cast into film by solution casting, resulting a flexible, free-standing and conductive blend films. The morphology of the PAni/PVA and PAni-TiO_2/PVA blends was confirmed by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Generally, the thermogravimetric analysis (TGA) curves of the blends showed gradual weight loss due to absorbed moisture and solvent upon initial heating up to around 100 ^{o}C, followed by a slow weight loss until around 225 ^{o}C, which could be attributed to the elimination of dopant. The final degradation of the polymer occurs from around 227 to 900 ^{o}C. The presence of a single T_g as revealed by differential scanning calorimetry (DSC) and its shifts to higher value with increasing PAni and PAni-TiO_2 content, revealing the miscibility between PAni and PAni-TiO_2 with PVA through hydrogen bonding as shown by FTIR. The X-ray diffraction pattern of the blends revealed that the degree of crystallinity of PAni-TiO_2/PVA blends was lower than that of PVA and TiO_2, showing that the amorphous nature of PAni may inhibit crystallization of TiO_2 and PVA. The electrical conductivity of the PAni-TiO_2/PVA blends increase with the increase of TiO_2/aniline weight ratio and reaches a saturation value at weight ratio of 0.13. All the blends samples exhibit similar pattern, i. e. the conductivity increases with temperature from 30 ^{o}C to 50 ^{o}C, following with decreasing conductivity, and reach the maximum at 140 ^{o}C, then decrease with further increasing temperature. PAni/PVA and PAni-TiO_2 (I)/PVA show maximum conductivity at 40 ^{o}C, 1.69 and 1.78 S/cm, respectively. The blends films exhibited good conductivity even at low weight fraction of conductive components, with conductivity value around 10^{-5} S/cm. The electrical conductivity of the films increases with increasing content of conducting PAni and PAni-TiO_2 content in the PVA matrix; indicating the dependence of the blended film conductivity upon the PAni and PAni-TiO_2 content. This was due to the growing of continuous network formation, which is confirmed by TEM. The percolation threshold was about 2.0 wt. % for both PAni/PVA and PAni-TiO_2/PVA blends. From the Hall effect studies, the conductivity and carrier mobility are linearly related while the carrier mobility are inversed of the carrier density. At room temperature, PAni-TiO_2 (I)/PVA blend (40 wt. %) shows the highest carrier mobility (4878 cm^2 $volt^{-1}$ sec^{-1}) among the samples. Finally, the conductivity of the blends decreases as the temperature is increased and deviates strongly from variable range hopping equation above 300 K.

ABSTRAK

Polyaniline (PAni) dan polyaniline-titanium(IV) oxida (PAni-TiO$_2$) yang bersifat mengkonduksi telah disediakan secara pempolimeran pengoksidaan kimia dengan kehadiran asid dodecylbenzene sulfonik (DBSA) dalam medium HCl. PAni dan PAni-TiO$_2$ yang bersifat mengkonduksi dicampurkan dengan poly(vinyl alcohol) (PVA). Dengan menggunakan kaedah "solution casting", filem yang berciri terlenturan, "free-standing" dan mengkonduksi telah dihasilkan daripada larutan "blend". Morfologi PAni/PVA dan PAni-TiO$_2$/PVA telah dipastikan dengan menggunakan mikroskop electron pengimbas (SEM) dan mikroskop electron penghantar (TEM). Secara umum, corak analisis termogravimetrik (TGA) 'blends' tersebut menunjukkan kehilangan berat yang perlahan akibat air dan pelarut yang terserap semasa dipanaskan hingga kira-kira 100 ^{o}C, diikuti dengan kehilangan berat hingga kira-kira 225 ^{o}C, mungkin disebabkan oleh penghapusan dopan. Penguraian terakhir polimer berlaku kira-kira dari 227 hingga 900 ^{o}C. Kehadiran T$_g$ tunggal seperti yang ditunjukkan oleh *differential scanning calorimetry* (DSC), dan didapati menganjak ke nilai yang lebih tinggi dengan penambahan kandungan PAni dan PAni-TiO$_2$ dalam 'blends' menunjukkan keterlarutcampuran antara PAni dan PAni-TiO$_2$ dengan PVA. Corak pembelauan sinar X menunjukkan bahawa darjah kehabluran 'blends' PAni-TiO$_2$/PVA adalah lebih rendah berbanding dengan PVA dan TiO$_2$. Sifat amorfus semula jadi PAni mungkin mengurangkan darjah kehabluran PVA dan TiO$_2$. Kekonduksian elektrik PAni-TiO$_2$/PVA meningkat dengan peningkatan nisbah berat TiO$_2$/aniline hingga suatu tahap (0.13). Kesemua sampel menunjukkan corak yang hampir sama, iaitu kekonduksian elektrik meningkat dengan peningkatan suhu dari 30 ^{o}C hingga 50 ^{o}C, diikuti dengan pengurangan kekonduksian elektrik, mencapai maksimum pada suhu 140 ^{o}C, kemudian menurun dengan peningkatan suhu seterusnya. PAni/PVA and PAni-TiO$_2$ (I)/PVA menunjukkan kekonduksian elektrik maksimum pada 40 ^{o}C, masing-masing 1.69 and 1.78 S/cm. Filem-filem itu menunjukkan kekonduksian elektrik yang bagus dengan nilai sebanyak 10^{-5} S/cm walaupun pada komposisi komponen bersifat mengkonduksi yang rendah. Kekonduksian elektrik filem-filem meningkat dengan peningkatan kandungan PAni dan PAni-TiO$_2$. Ini menunjukkan kekonduksian filem bergantung kepada kandungan PAni dan PAni-TiO$_2$ akibat pertumbuhan jaringan yang terbentuk secara berterusan dan telah dipastikan dengan menggunakan TEM. 'Percolation threshold' untuk kedua-dua PAni/PVA and PAni-TiO$_2$/PVA adalah sebanyak 2.0 % berat. Daripada kajian kesan Hall, kekonduksian dan mobility cas berkaitan secara linear, manakala mobility cas dan ketumpatan cas adalah berkaitan secara songsang. Pada suhu bilik, PAni-TiO$_2$ (I)/PVA (40 wt. %) menunjukkan mobility cas yang tertinggi (4878 cm^2 volt^{-1} sec^{-1}). Kekonduksian elektrik menurun dengan peningkatan suhu dan tidak mematuhi persamaan model lompatan pelbagai-jarak (variable-range hopping) pada suhu melebihi 300 K.

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LIST OF ABBREVIATIONS

PA	-	Polyacetylene
PAni	-	Polyaniline
PEO	-	Poly(ethylene oxide)
PT	-	Polythiophene
PPY	-	Polypyrrole
PPV	-	Poly(phenylenevinylene)
PPS	-	Poly(phenylene sulfide)
PPP	-	Poly(p-phenylene)
E_g	-	Energy gap
eV	-	Elektron volt
LEB	-	Leucoemeraldine
PNB	-	Pernigraniline
EB	-	Emeraldine base
ES	-	Emeraldine salt
Cl^-	-	Ion chloride
CSA	-	Camphorsulfonic acid
DBSA	-	Dodecylbenzene sulfonic acid
APS	-	Ammonium persulphate
S/cm	-	Siemen per cm
HCl	-	Acid hidrochloric
Na	-	Sodium
K	-	Kalium
Li	-	Lithium
Ca	-	Calcium

BF$_4$	-	Boron tetrafluoride
PVA	-	Poly(vinyl alcohol)
TiO$_2$	-	Titanium(IV) oxide
UV	-	Ultra violet
SEM	-	Scanning electron microscopy
TEM	-	Transmission electron microscopy
AFM	-	Atomic force microscopy
FTIR	-	Fourier transform infrared
TGA	-	Thermal gravimetry analysia
DSC	-	Differential scanning calorimetry
XRD	-	X-ray diffraction
Ge	-	Germanium
ρ	-	Resistivity
σ	-	Dc conductivity
W	-	Sample thickness
S	-	Probe distance
DC	-	Direct current
I	-	Current
V	-	Voltage
V$_H$	-	Hall voltage
R$_H$	-	Hall coefficient
n	-	Carrier density
μ	-	Carrier mobility
H	-	Magnetic field
q	-	Electron charge
PAni-TiO$_2$	-	Polyaniline-titanium(IV) oxide composite
PAni-TiO$_2$/PVA	-	Polyaniline-titanium(IV) oxide composite blend with poly(vinyl alcohol)
PAni/PVA	-	Polyaniline blend with poly(vinyl alcohol)
Å	-	Angstrom
2θ	-	Angle of incidence of X-rays diffracting planes
CB	-	Conduction band
VB	-	Valence band

E_F	-	Fermi energy
T_g	-	Glass transition temperature
T_m	-	Melting temperature
σ_{dc}	-	Conductivity of direct current
Wt.	-	Weight
VRH	-	Variable range hopping
I_2	-	Iodine
PSiPy	-	Poly[(6-N-pyrrolylhexyl)hexylsilane]

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CHAPTER 1

INTRODUCTION

Plastics, fibers, elastomers, coatings, adhesives, rubber, protein and cellulose − are all common terms in our modern vocabulary, and all part of the fascinating world of polymer chemistry. Plastic materials have displaced traditional materials such as natural polymers (e. g. wood), metals, ceramics and glass in many applications owing to their physical and mechanical properties (light weight combined with physical strength) and ease of processability (the ability to mold the shape of plastic materials or extrude into sheet and rod through a die).

The combination of conventional polymers with conductive polymers or fillers is an important alternative to obtain new polymeric materials with designed properties. In such blends, the insulating polymer provides good mechanical properties and processability while the conducting polymer would provide electrical conductivity. In addition, through blending, the brittleness and lack of processability that are the main drawbacks hindering conducting polymers better utilization could be overcomed by new polymeric materials with improved processability, flexibility and controllable conductivity [1–2].

An essential requirement for the commercial breakthrough of conducting polymers in blend applications requires that conductivity is achieved at a small

weight fraction of the conducting polymer. Further, there is increasing demand for polymeric materials whose electrical conductivity can be tailored for a given application, and that have attractive combined mechanical and other properties. Thus, this have been the driving force for many of the researches in conductive blends to obtain a wide range of conductivity, which is controllable with varied weight fraction of the conducting polymer for various potential applications [3–4].

Consequently, there are many approaches towards preparation of such blends with desirable properties and are finding a growing number of applications in commercial market, including antistatic (microelectronic packaging), electrostatic dissipation (ESD), static discharge and electromagnetic interference shielding (EMI) [4–5]. For ESD and EMI, the required conductivity levels are approximately 10^{-5} — 10^{-9} S/cm and > 1 S/cm, respectively [4–5]. At present, conducting plastics in these applications are prepared by mixing conductive solid fillers, such as special carbon black or metal fibers into the matrix, or coating the material with a conducting layer. Percolation takes place at volume fraction of approximately 16 % vol. spherical rigid fillers used. Though mixing of solid fillers stiffens the material, it may cause undue brittleness and processing difficulties at the same time.

1.1   Percolation Theory

Percolation theory deals with the effects of varying, in a random system, the richness of interconnections present [6]. It can be used to model many things including flow of liquid through a porous medium, spread of disease in a population, polymer gelation, and conductor-insulator composites.

From the perspective of condensed-matter physicists (who have been the main ones to adopt this mathematical subject for use in their own discipline), the single most seductive aspect of the percolation model is the presence of a sharp phase transition at which *long-range* connectivity suddenly appears. This percolation transition, which occurs with increasing connectedness or density or occupation or concentration makes percolation a natural model for a diversity of phenomena.

The classic example of a percolation theory problem is an array of wires connecting one communication station with another. The communication network, represented by a large square-lattice network of interconnections, is attacked by a crazed saboteur who, armed with wire cutters, proceeds to cut the connecting links at random. Thus, what fraction of the wires must be cut to sabotage the communications array? This fraction, which is 0.5, is the percolation threshold [6]. When half of the bonds are broken, the communications array fails to work.

There are three major categories of percolation – bond, site, and continuum. Bond and site are used when talking about arrays. Site percolation occurs when there is a connected path of sites from one side of the array to the other. Bond percolation is utilized when there is a connected path of bonds across the array. Continuum percolation is used for system where an array model is inappropriate.

Imagine an array of squares (Figure 1.1). Now randomly shaded in one square at a time. A group of touching shaded squares is called a cluster. When enough squares are shaded to make a path across the array, the cluster to which the path belongs is called the spanning cluster [7]. Now, as this cluster grows, the path across the array becomes less tortuous. At the same time, other paths may be forming – parallel paths. This concept of parallel paths explains the increase in conductivity of a system even after the percolation threshold has been passed. The same thinking exercise above can be done by throwing random circles on a sheet of

paper (Figure 1.2). These circles can overlap. This is an example of continuum percolation [6].
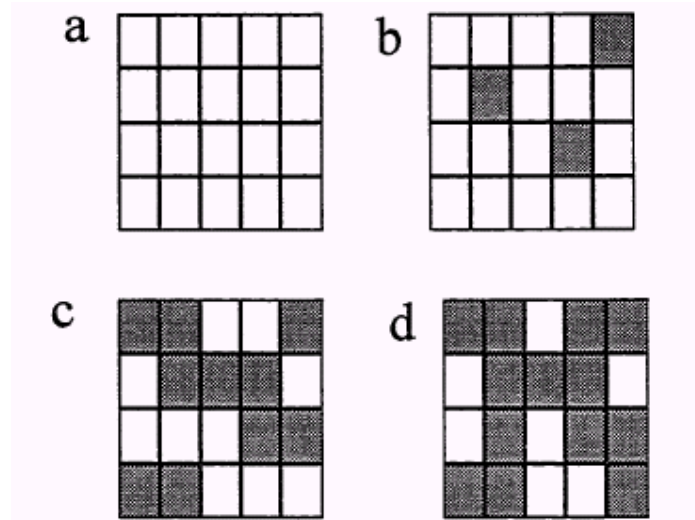
Figure 1.1: Square array percolation problem. (a) First is the empty array (b) Then, squares are randomly filled in (c) The cluster of squares that creates a complete path across the lattice is called the spanning or infinite cluster (d) Parallel paths are created (Adapted from reference [7])
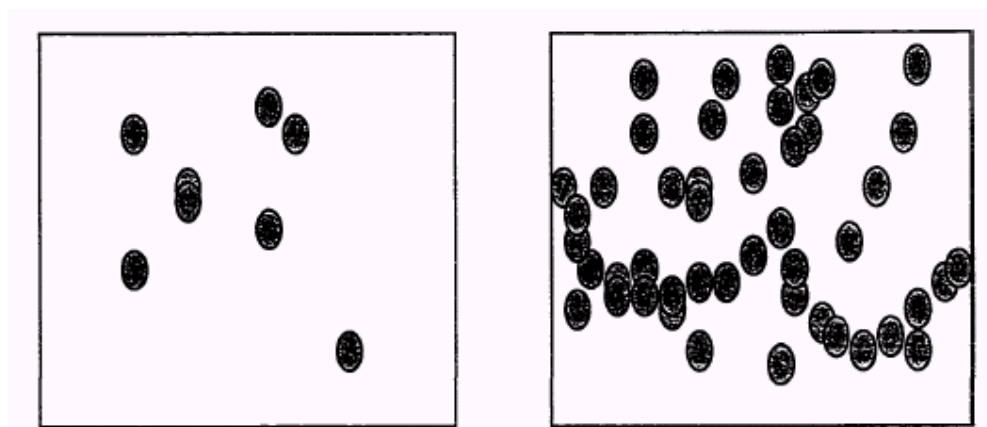
Figure 1.2: Random circle problem − demonstrate continuum percolation (Adapted from reference [6])

Before addressing the specific issues associated with suspension-based conductive composites, it is important to understand the basic concepts of these types of materials in general. Figure 1.3 illustrate the key features of a generic polymer-based conductive blend and Figure 1.4 is a generalized loading curve that represents the changes in electrical conductivity that occur as a function of conducting polymer loading. As conductive filler, such as conducting polymer, is added to an insulating polymer matrix a network begins to form and begins to span large distances. Once this conductive network reaches a critical size, on the order of the composite sample size, the two-component material makes a transition from insulator to conductor. The critical amount of filler (usually expressed as a volume fraction or percent) required to cause this insulator-to-conductor transition is known as the percolation threshold. Composite electrical conductivity typically obeys a power law as a function of conducting polymer concentration [6]:

$$\sigma = C \, (f - f_c)^t \tag{1.1}$$

where σ is the property of interest, C is a proportionality constant related to the conductivity of the filler (e. g. conducting polymer), f is the probability of a site (or bond) being filled or in other words the volume fraction of conductive filler, f_c is the critical volume fraction of filler associated with the percolation threshold and t is the power law exponent (typically 1.6 — 2.0 in 3−dimension) [6, 7]. This is graphed in Figure 1.4. In continuum percolation, f and f_c can be thought of in terms of volume fractions. In an insulating matrix composite with conductor inclusions added, f would be the volume fraction of the conductor at any time, and f_c would be the volume fraction of conductor it took to make a complete path across the material.

One problem with percolation is that it never allows for a leveling out of the property. The property in question keeps increasing as the second phase is added. Since properties tend to level out away from the percolation threshold, a balance
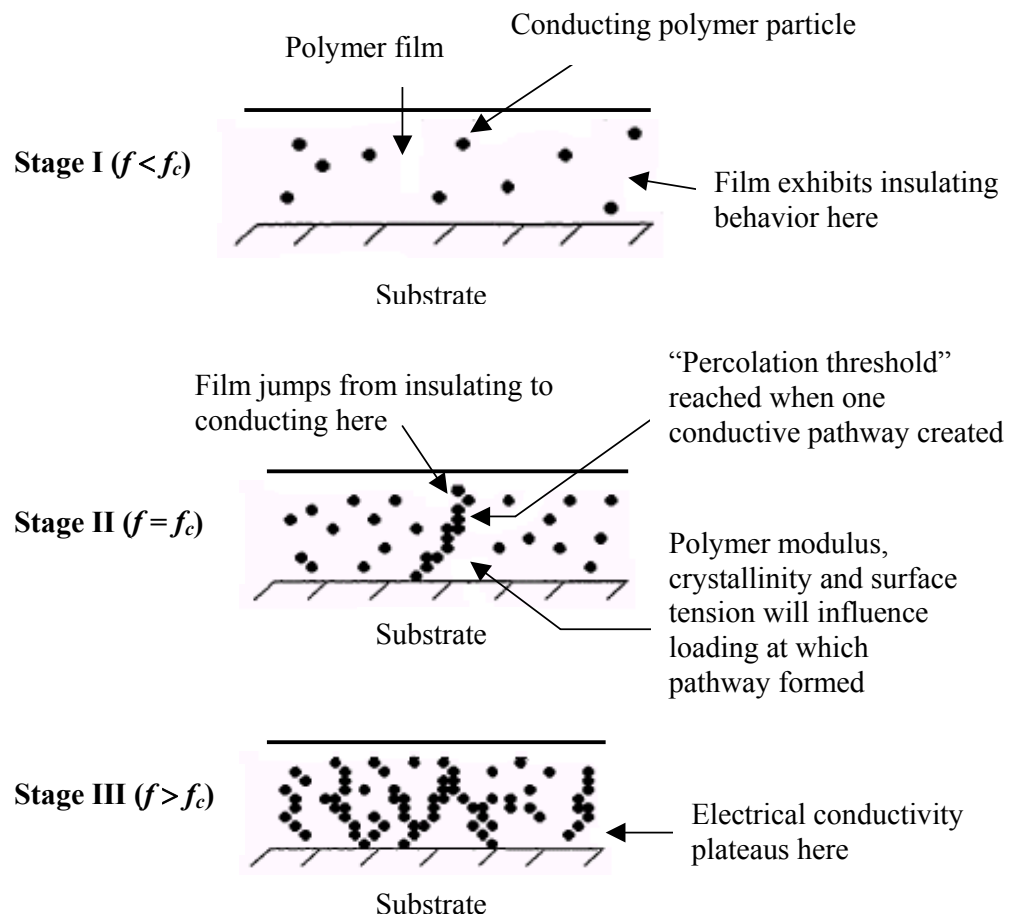
Figure 1.3: Electrically conductive polymer blend (Adapted from reference [8])
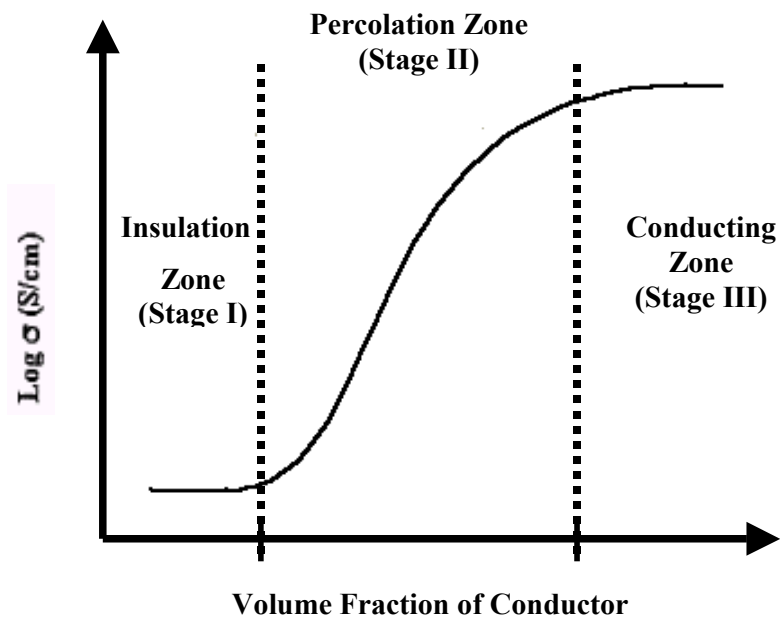
Figure 1.4: Typical percolation theory plot (Adapted from reference [8])

between percolation theory and effective media theory is a good way of modeling material behavior.

1.2   Conducting Blends

In a limited way, all polymers can be considered blends since their diversity in molecular weight and microstructure makes it unlikely that two adjacent macromolecules are identical. However, the term "blend" is usually reserved for a mixture of two or more polymers with noticeable differences in an average chemical composition or microstructure. It is not necessary for both polymers to mix at a molecular level. However, mixing at the molecular level occurs if the polymers are miscible. The great majority of polymer pairs are immiscible but this does not preclude their effective use. However, the mixing and subsequent fabrication procedures are crucial to performance since they determine the final morphology of the composite.

Polyaniline has been categorized as an intractable material. Nonetheless, it is possible to process polyaniline from its solution in concentrated acid such as HCl, *p*-phenolsulfonic acid (PSA), camphorsulphonic acid (CSA) and other acids with a polymer concentration ranging from extremely dilute to more than 20 % (wt/wt) [9–11].

1.2.1 Blends With Water-Soluble Polymers

The strong affinity of polyaniline for water has motivated many groups to investigate the compatibility of polyaniline with water-soluble polymer such as polyvinyl alcohol and carboxy methyl cellulose. A. Mirmohseni [12] reported the preparation of a homogeneously dispersed polyaniline by chemical polymerization of aniline in a media containing 10 % polyvinyl alcohol, which can be cast to form a mechanically robust film. The uniform composite films of nanostructured polyaniline (e. g. nanotubes or nanorods with $60 - 80$ nm in diameter) were fabricated by blending with PVA as a matrix [13]. It was found that the electrical, thermal and mechanical properties of the composite films were affected by the nanostructured PAni-β-NSA content in the PVA matrix. The composite film with 16 % PAni-β-NSA showed the following physical properties: room temperature conductivity is in the range of 10^{-2} S/cm, tensile strength ~ 603 kg/cm^2, tensile modulus ~ 4.36 x 10^5 kg/cm^2. Pallab Banerjee [14] had reported conductive polyaniline composite films formed by chemical oxidative polymerization of aniline inside carboxymethylcellulose matrix films, exhibiting extremely low percolation threshold ($f_c \sim 1.12$ x 10^{-3}).

Manisara Peesan *et al.* [15] have reported the preparation of blend films of β-chitin and PVA by solution casting from corresponding solutions of β-chitin and PVA in concentrated acid. The glass transition temperature of the blend films was found to increase slightly with an increase in the β-chitin content.

1.3   Materials
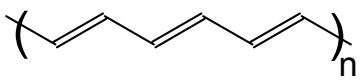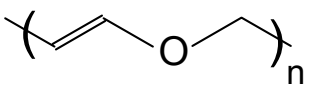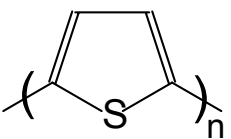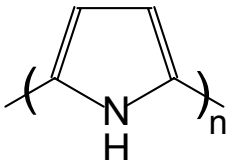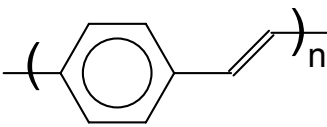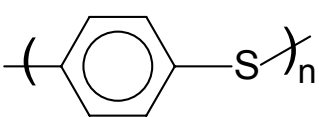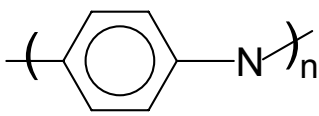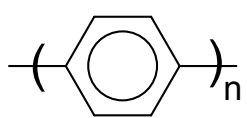
1.3.1   Electrically Conductive Polymer

From the initial discovery of nearly 12 orders of magnitude of enhancement in conductivity in the first intrinsic electrically conducting organic polymer, doped polyacetylene, in 1977 [16], spurring interest in "conducting polymers". These polymer systems containing highly loosely held electrons in their backbones, usually referred to as π-bonded or conjugated polymers or conducting polymers, with a wide range of electrical and magnetic properties, are a field of increasing scientific and technical interest. Inspired by by polyacetylene, many new conductive polymers were developed, including polypyrrole (PPy), polythiophene (PT), polyaniline (PAni), poly(*p*-phenylene) (PPP), poly(phenylene vinylene) (PPV) and etc (Table 1.1).

Later generations of these polymers were processable into powders, films, and fibers from a wide variety of solvents, and also air stable although these intrinsically conducting polymers were neither soluble nor air stable initially. Some forms of these intrinsically conducting polymers can be blended into traditional polymers to form electrically conductive blends. The conductivities of these polymers spans a very wide range from that typical insulators ($< 10^{-10}$ S/cm) to that typical of semiconductors such as silicon ($\sim 10^{-5}$ S/cm) to greater than 10^4 S/cm (nearly that of a good metal such as copper, 5 x 10^5 S/cm), depending on doping [17].

The principal interests of researchers on conductive polymers are the potential applications of conductive polymer in the electronic industry. They could

Table 1.1: Chemical structure of some conjugated polymers

(a) Polyacetylene
(PA)

(b) Poly(ethylene oxide)
(PEO)

(c) Polythiophene
(PT)

(d) Polypyrrole
(PPy)

(e) Poly(phenylenevinylene)
(PPV)

(f) Poly(phenylene sulfide)
(PPS)

(g) Polyaniline
(PAni)

(h) Poly(*p*-phenylene)
(PPP)

be applied in antistatic and electromagnetic shielding protection, as capacitors, electrode in polymer batteries, sensors and actuators, protective coating materials, light-emitting polymer for electronic display devices (such as polymer-based LED, monitor or large area display) and much more. The advantages of conductive

polymer over conventional materials are the relative ease of processing, cost effectiveness by mass production and fabrication of smaller electronic devices. But conductive polymers not remained as an "ideal" material as long as some basic problems regarding its properties unresolved. Two main problems that greatly affect the performance of conductive polymers include environment instability (stability against thermal heating, water vapour and sunlight irradiation) and difficult of processing (where most conductive polymers are in- or weakly soluble in organic or inorganic solvents). Technological uses depend crucially on the reproducible control of the molecular and supramolecular architecture of the macromolecule via a simple methodology of organic synthesis.

1.3.1.1 Electronic Properties of Conductive Polymer

The essential feature of the conjugated polymer is that it provides bands of delocalised molecular orbitals, the π bands, within which the full range of semiconductor and metal behaviour can be achieved through control of the degree of filling. At the same time, the integrity of the chain is preserved by the strong sp^2 π bonds which are unaffected by the presence of the excitations within the π-electron manifold [18]. From the point of view of the solid-state physicists, what distinguishes these semiconductors from inorganic materials, which are well used in technology, is the strong anisotropy of the lattice and of the electronic excitations. This has the effect of allowing very strong local interactions between the geometry of the polymer chain and electronic excitations, such as injected charges or excitons. This coupling between lattice and electrons is an important example of a non-linear system, and there has been great interest in the characterization of resulting excitations.

Conjugated polymers in the undoped state possess one p_z electron per site, thus giving occupation of one half of the molecular orbitals within the manifold. All these polymers show an energy gap (E_g) between filled, π states (for bonding) and empty, π^* states (for antibonding) so that semiconducting behaviour is observed. The semiconducting gap or energy gap (E_g), which is the energy separation between π and π^* states, ranges from around 1 eV for poly(isothionaphthene), 1.5 eV for polyacetylene, to 3 eV for poly(p-phenylene) [18]. The size of this gap is directly related to the magnitude of the alternation of bond lengths along the chain.

The conducting properties of conjugated polymers are seen when band filling is altered away from the semiconducting ground state. This is accomplished by chemical doping, photoexcitation of electrons and holes, or by charge injection to form regions of space or surface charge density, and each of these methods for introducing excitations is considered in the following sections. Chemical doping, through formation of charge transfer complexes, can either remove electrons from the π valence band (oxidative doping) or add electrons to the π^* conduction band (reductive doping), and in the usual band models, should then give metallic properties. However, the coupling of the π band structure to the size of the local geometry of the polymer chain (in the form of bond alternation amplitude) gives a range of novel non-linear excited states.

All conjugated polymers, such as polyaniline, poly(thienylene), polypyrrole, poly(p-phenylene) and etc except polyacetylene, show a preferred sense of bond alternation. For these polymers the ground-state geometry is the so-called aromatic configuration, with long bonds between rings, and an aromatic structure within the ring. The other sense of bond alternation gives the quinoidal configuration, with shortened bonds between rings, and a quinoidal structure in the ring. The electronic excited states are described as polarons [19–20] and the excited-state geometry of the chain is shifted towards the quinoidal structure; this geometrical change pulls a pair of states away from the band edges into the gap. Polaron-like excitations can exist in different charge states, as is shown in Figure 1.5.

For conjugated polymers which preserve electron-hole symmetry (hydrocarbon polymers such as poly(phenylenevinylene), polyaniline and poly(phenylene), the polaron has associated with it two gap states pulled away symmetrically from the band edges, as illustrated in Figure 1.5. The presence of the gap stated allows several new sub-gap optical transitions, as indicated in Figure 1.5; for the charged polaron and bipolaron these are commonly detected through induced sub-gap optical absorption, and for the neutral singlet polaron-exciton transition from upper to lower gap state can be detected through photoluminescence.
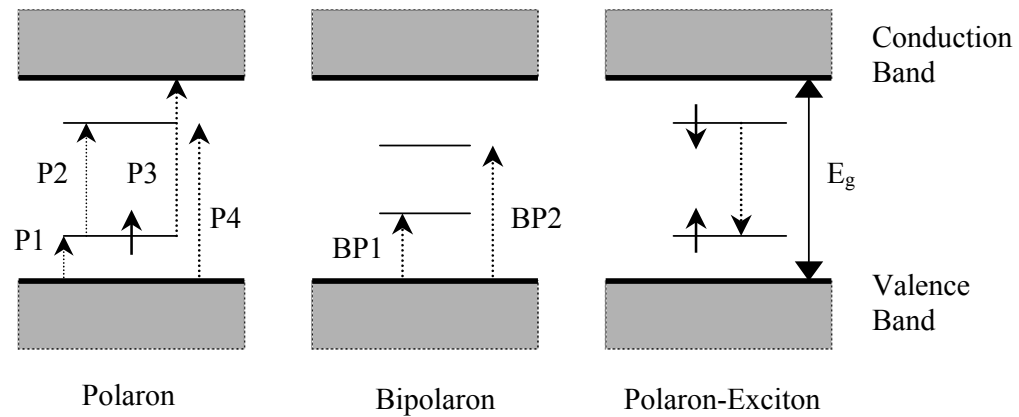
Figure 1.5: Schematic diagram shows the energy level scheme and optical transition for the positively charged polaron, bipolaron and the neutral polaron-exciton (Adapted from reference [18])

1.3.1.2 Polyaniline (PAni)

Electrically conducting polymers in their pristine and doped states have been the materials of great interest for their applications in modern technologies. Among all conducting polymers polyaniline (PAni) has a special representation, probably due to the fact that new applications of PAni in several fields of

technology are expected. The first report on the production of "aniline black" dated back to 1862 when Letheby used a platinum electrode during the anodic oxidation of aniline in a solution containing sulfuric acid and obtained a dark-green precipitate [21]. This green powdery material soon became known as 'aniline black'. The interest in this material retained almost academic for more than a century since "aniline black" was a powdering, intractable material, a mixture of several products which is quite difficult to investigate. Green and Woodhead [21] performed the first organic synthesis and classification of intermediate products in the "aniline black" formation and five different aniline octamers were identified and named as leucoemeraldine base, protoemeraldine, emeraldine, nigraniline and pernigraniline. These names are still used, indicating various oxidation states of PAni (Figure 1.6).
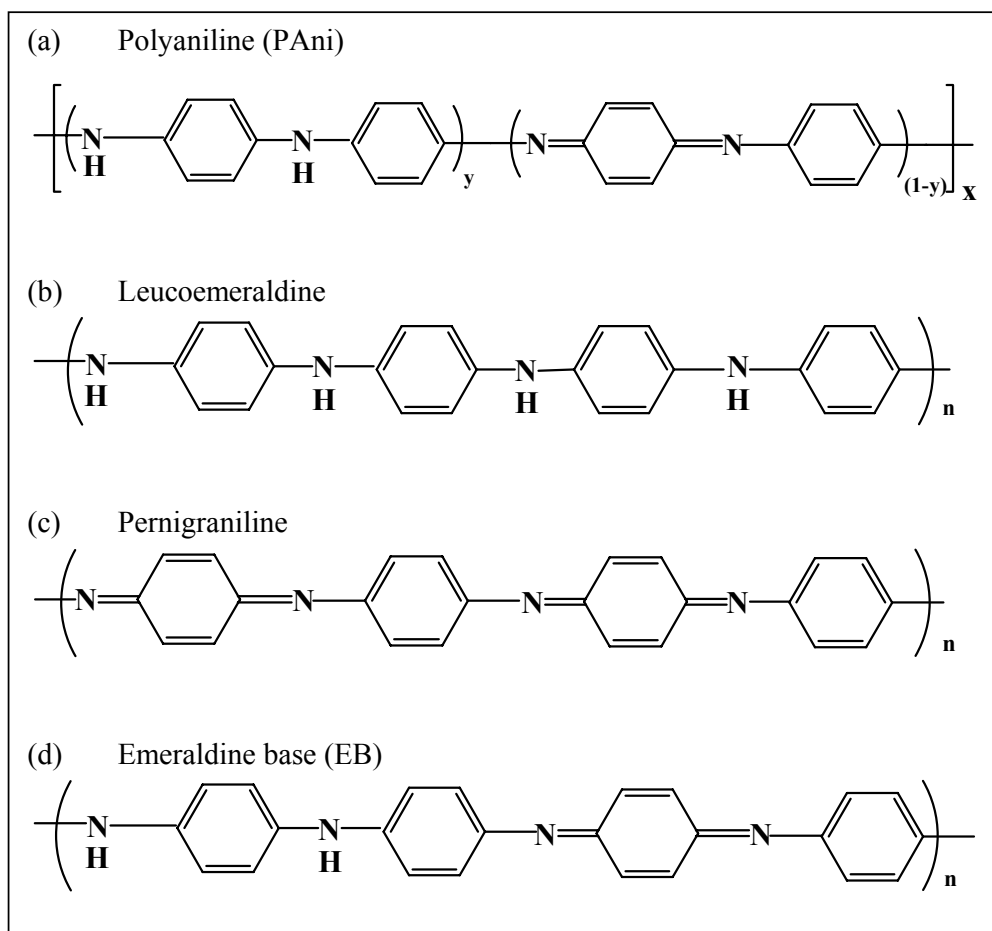
Figure 1.6: Various states of oxidation and protonation of polyaniline (Adapted from reference [17, 22])

Polyaniline is a typical phenylene-based polymer having a chemically flexible —NH— group in a polymer chain flanked either side by a phenylene ring. It is a unique polymer because it can exist in a variety of structures depending on the value of (1–y) in the general formula of the polymer shown in Figure 1.6 (a) [17, 22]. The electronic properties of PAni can be reversibly controlled by protonation as well as by redox doping. Therefore, PAni could be visualized as a mixed oxidation state polymer composed of reduced {–NH–B–NH–} and oxidized {–N=Q=N–} repeat units where –B– and =Q= denote a benzenoid and a quinoid unit respectively forming the polymer chain (Figure 1.6 (a)), the average oxidation state is given by 1–y. Depending upon the oxidation state of nitrogen atoms which exist as amine or imine configuration, PAni can adopt various structures in several oxidation states, ranging from the completely reduced leucoemeraldine base state (LEB) (Figure1.6 (b)), y–1 = 0, to the fully oxidized pernigraniline base state (PNB) (Figure 1.6 (c)), where 1–y = 1. The "half" oxidized (1–y = 0.5) emeraldine base state (EB) (Figure1.6 (d)) is a semiconductor and is composed of an alternating sequence of two benzenoid units and a quinoid unit. The protonated form is the conducting emeraldine salt (ES).

The electronic structure and excitations of these three insulating forms (LEB, PNB, EB) are contrasted. However, the LEB form can be *p*-doped (oxidatively doped), the EB form can be protonic acid doped and the PNB form can be *n*-doped (reductively doped) to form conducting ES systems. The EB, intermediate forms of PAni can be non-redox when doped with acids to yield the conductive emeraldine salt state of PAni as demonstrated in Figure 1.7. It can be rendered conductive by protonating (proton doping) the imine nitrogen, formally creating radical cations on these sites. This doping introduces a counterion (e.g. Cl^- if HCl was used as the dopant), and recently, the counterion was affixed to the parent polymer by partially sulfonating the benzene rings in the polymer, resulting in a so-called "self-doped" polymer. Both organic acids such as HCSA (camphor sulfonic acid), and inorganic acids, such as HCl, are effective, with the organic sulfonic acids leading to solubility in a wide variety of organic solvents, such as chloroform and m-cresol. The protonic acid may also be covalently bound to the

PAni backbone, as has been achieved in the water-soluble sulfonated PAni (Figure 1.7). Similar electronic behavior has been observed for the other nondegenerate
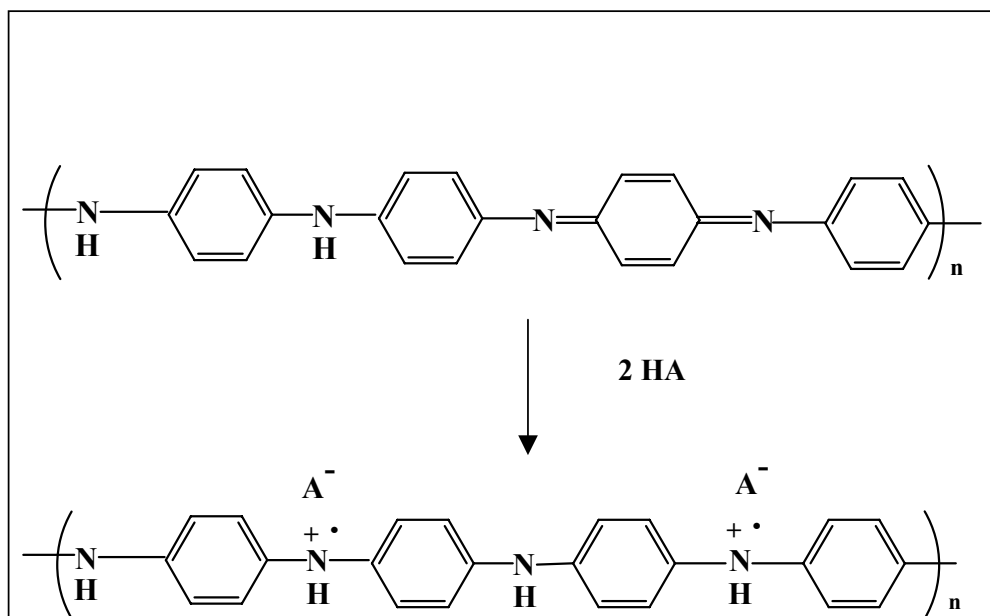
Figure 1.7: Protonic acid doping of PAni (emeraldine base) to PAni (emeraldine salt) (Adapted from reference [17])
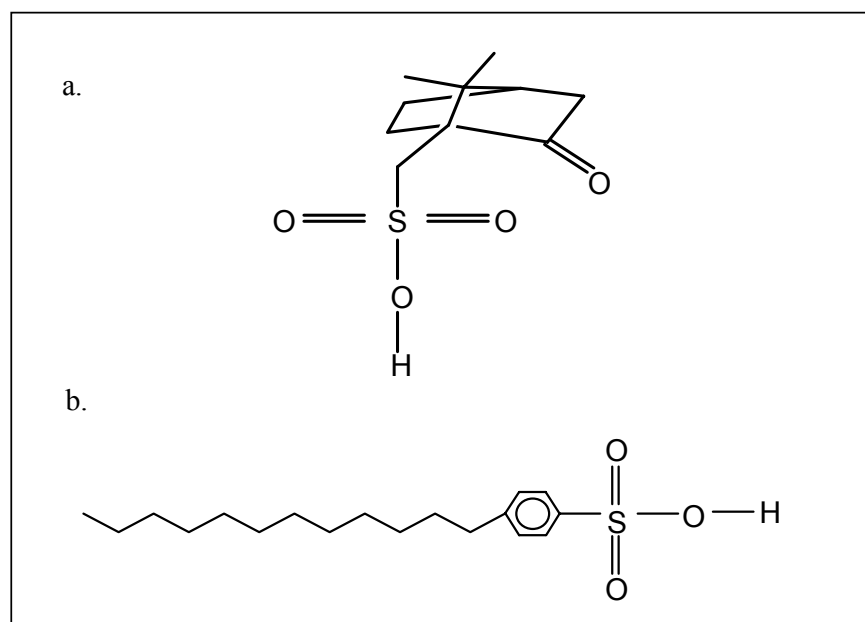
Figure 1.8: Chemical structures of (a) camphorsulfonic acid, CSA and (b) dodecylbenzenesulfonic acids, DBSA (Adapted from reference [21])

ground state systems as for protonic acid doped PAni. That is, polarons are important at low doping levels. For doping to the highly conducting state, a polaron lattice (partially filled energy band) forms. In less ordered regions of doped polymers, polaron pairs or bipolarons are formed.

During doping all the hetero atoms in polymer, namely the imine nitrogen atoms of the polymer become protonated to give a polaronic form where both spin and charge are delocalized along the entire polymer backbone. The conductive emeraldine salt state can be converted back to the insulating emeraldine base state through treatment with a base, indicating that this process is reversible.

This protonated emeraldine salt form is electronically conducting, the magnitude of increase in its conductivity varies with proton (H^+ ion) doping level (protonic acid doping) as well as functionalities present in the dopant [22]. In the doping acid, the functional group that present, its structure and orientation can influence the solubility of a conducting form of PAni or for obtaining aqueous dispersion and compatibility with other polymers. The chemical structures of two organic acids, which are recently used in doping PAni are shown in Figure 1.8.

Thus, PAni owns advantages over other conducting polymers owing to its moderate synthesis route, superior environmental stability and undergoes simple doping by protonic acids easily.

1.3.1.3 Conduction Mechanism in PAni

Before the details of conduction in polyaniline are discussed, three frequently used physical terms in describing conduction in solid have to be

understood; namely soliton, polaron and bipolaron as shown in Figure 1.9 [23]. Soliton, sometime called as conjugational defect, is lone electron created in the polymer backbone during the synthesis of conductive polymer, in very low concentration. Conjugational defect is a misfit in the bond alternation so that two single bonds will touch. Soliton can be generated in pairs, as soliton and anti-soliton. Three methods were used to generate additional solitons – chemical doping, photogeneration and charge injection. An electron will be accepted by the dopant anion to form a carbocation (positive charge) and a free radical during the chemical doping (oxidation) of the polymer chain, known to organic chemists as radical cation or polaron to physicists. Both the soliton and polaron can be neutral or charged (positively or negatively) as shown in Figure 1.9.

The conductivities of PAni can be transformed from insulating to conducting through doping. Both n-type (electron donating, such as Na, K, Li, Ca) and p-type (electron accepting, such as I_2, BF_4, Cl) dopants have been utilized to induce an insulator-to-conductor transition in electronic polymers. The common dopants for PAni are hydrochloric acid, sulfuric acids and sulfonic acids. For the degenerate ground state polymers, the charges added to the backbone at low doping levels are stored in charged soliton and polaron states for degenerate polymers, and as charged polarons or bipolarons for nondegenerate systems. Such a situation is also encountered in PAni, which do not have two degenerate ground states. That is, the ground state is non-degenerate due to the non-availability of two energetically equal Kekule structures. Therefore there cannot be a link to connect them. In the doping process, the heteroatoms – nitrogen will be protonated and become a bipolar form (Figure 1.10). The motionless charged states are known as carbonium (+ve) and carbanion (-ve) radicals by organic chemist. The conventional distortion of molecular lattice can create a localized electronic state, thereby lattice distortion is self-consistently stabilized (Figure 1.10).

Thus, the charge coupled to the surrounding (induced) lattice distortion to lower the total electronic energy is known as polaron (i. e. an ordinary radical ion)
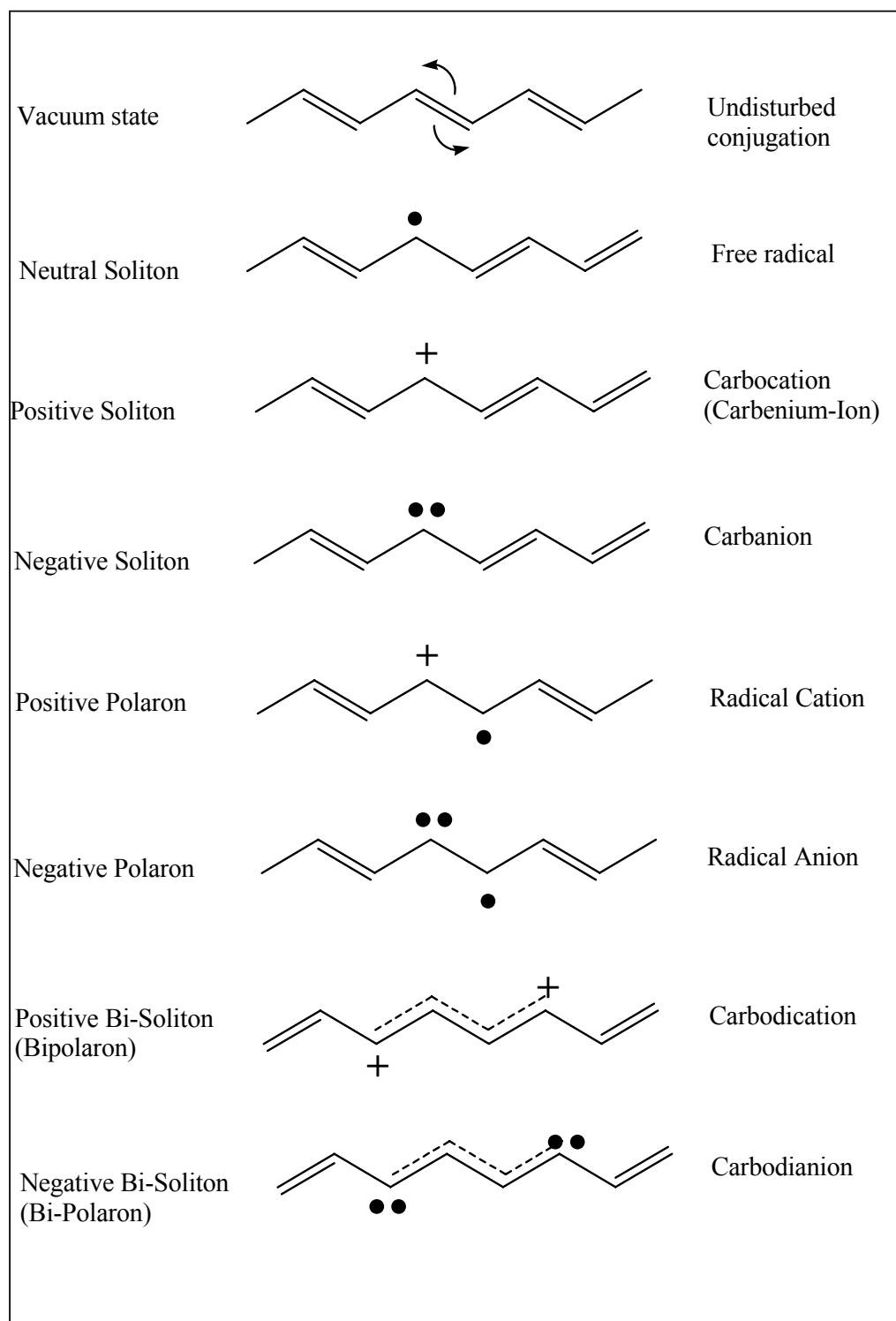
Figure 1.9: Defects in conjugated chains: a "physical – chemical dictionary" (Adapted from reference [23])
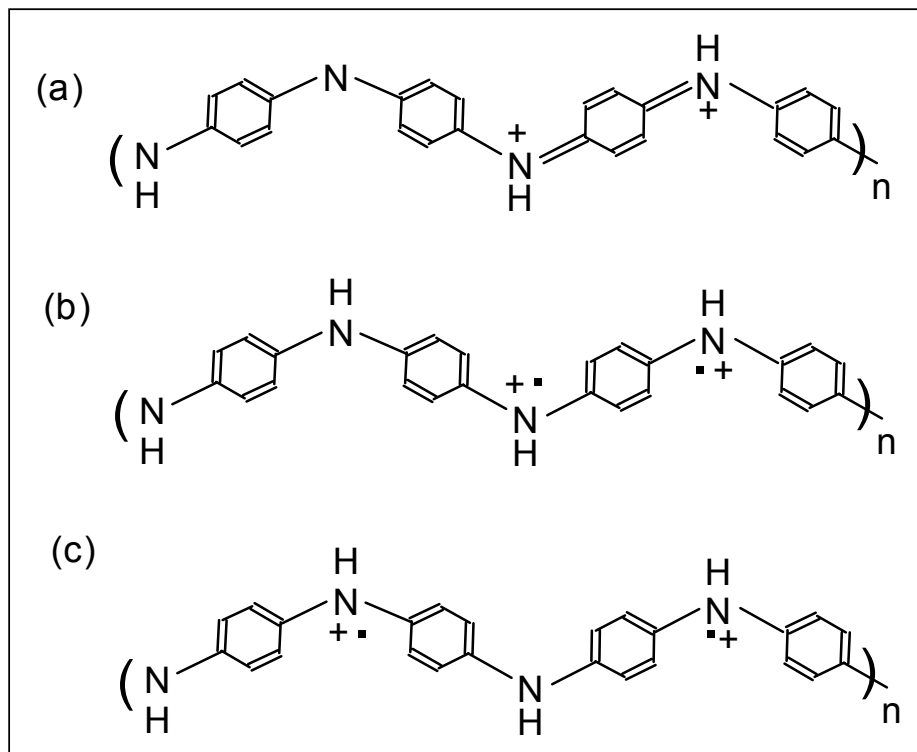
Figure 1.10: Polaron and bipolaron lattice. (a) Emeraldine salt in bipolar form. (b) Dissociation of the bipolarons into two polarons. (c) Rearrangement of the charges into a 'polaron lattice' (Adapted from reference [24, 25])
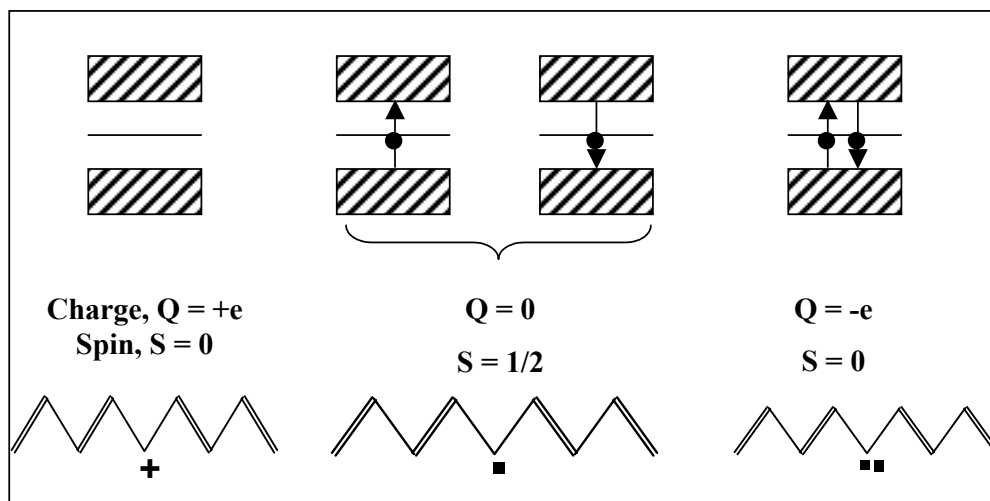
Figure 1.11: Spin-charge inversion of a conjugational defect. Charged solitons are spinless; neutral solitons carry a magnetic moment [26]

with a unit charge and spin = ½. A bipolaron consist of two coupled polarons with charge = 2e and spin = 0. The polaron and bipolaron have a unique property called "spin-charge inversion": whenever soliton bears charge, it has no spin and vice versa (Figure 1.11) [26]. Bipolarons are not created directly but must form by the coupling of pre-existing polarons or possibly by addition of charge to pre-existing polarons (Figure 1.12) [21, 27–28].

At the molecular level a polymer is an ordered sequence of monomer units. The degree of unsaturation and conjugation influence charge transport via the orbital overlap within a molecular chain. The charge transport becomes obscured by the intervention of chain folds and other structural defects. The connectivity of the transport network is also influenced by the structure of the dopant molecule. The dopant not only generates a charge carrier by reorganizing the structure (chemical modification) it also provides intermolecular links and sets up a microfield pattern affecting charge transport. Any disturbance of the periodicity of the potential along the polymer chain induces a localized energy state. Localization also arises in the neighbourhood of the ionized dopant molecule due to the coulomb field.

The conductivity of various conducting polymer tends to be relatively insensitive to the identity of the doping agent. The most important requirement for a dopant is sufficient oxidizing or reducing power to ionize the polymer. For example, though I_2 is a relatively weak electron acceptor, it induces conductivity in polyacetylene (550 S/cm), which is comparable to that achieved on doping with AsF_5, a strong electron acceptor (1100 S/cm) [29].

It is well known that polyaniline with conjugated π-electron backbones can be oxidized or reduced more easily and more reversibly than conventional polymers. Charge-transfer agents (dopants) effect this oxidation or reduction and in doing so convert an insulating polymer to a conducting polymer with near metallic conductivity in many cases. Since PAni behave like amorphous solids and the
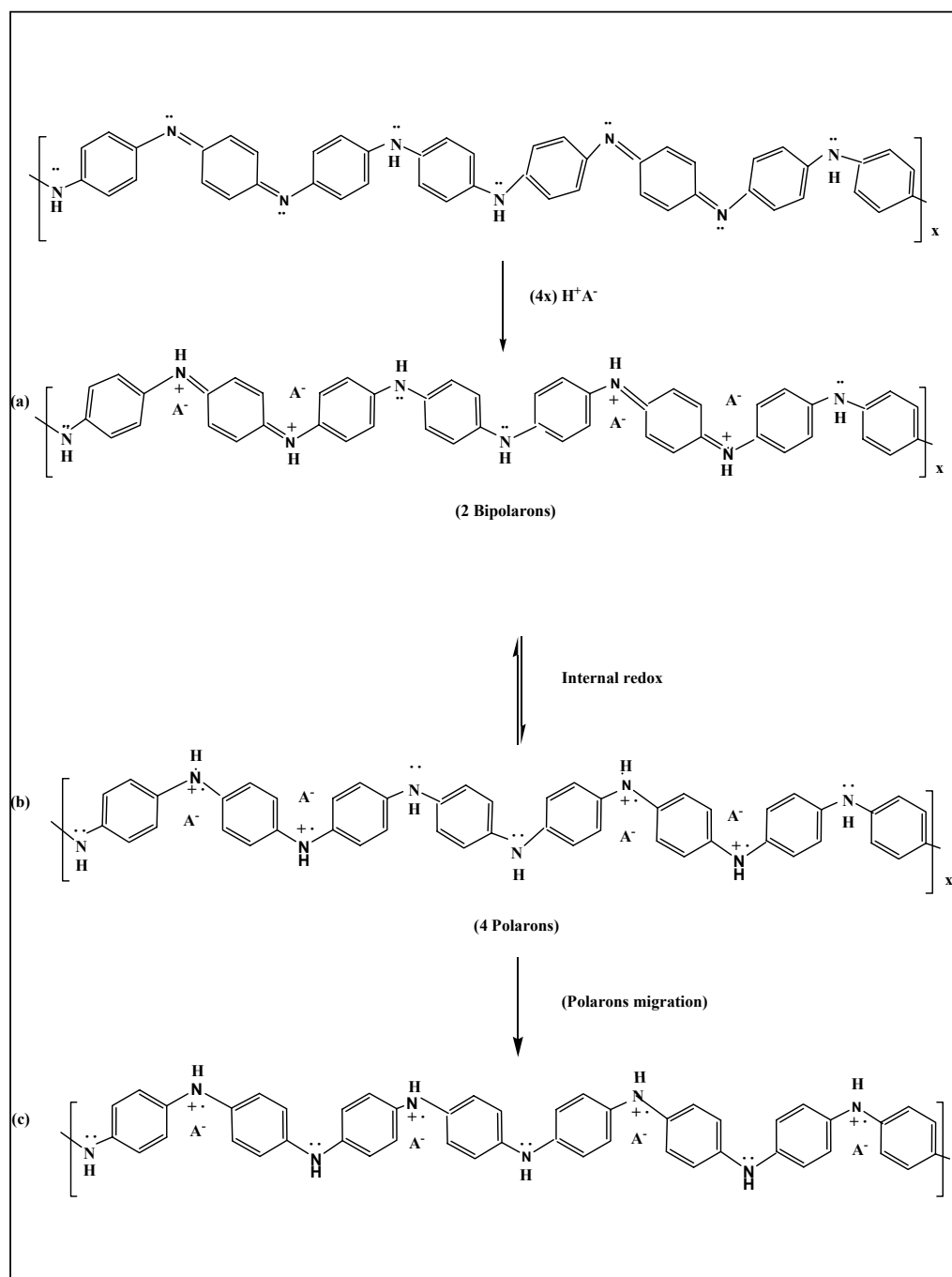
Figure 1.12: Scheme of the protonation process leading to formation of polaron and bipolaron in doped PAni (a) Emeraldine salt in bipolar form (b) Dissociation of the bipolarons into polarons (c) Rearrangement of the charges into a "polaron lattice". (Adapted from references [21, 27–28])

simple band theory fails to explain the conduction of electricity in polymers, we have to assume the validity of the band theory of solids for polymers to the nearest approximation to explain the conduction in polymers [30]. Further, we have to look at the basis of doping effects on the PAni in order to wholly understand the conduction mechanism in PAni.

During the synthesis of PAni, the polymer backbone can have inherited a certain concentration of conjugational defects, which is also known as solitons (Figure 1.9). On doping of PAni with oxidizing DBSA (*p*-doping) in present study, protonation is realized in which DBSA accept the electrons, conferring positive charges on the PAni chain and the positive charges of the cationic PAni chains are balanced by the anionic part of the acids [31]. When electron is removed from the top of the valence band (by oxidation) of PAni, conjugational defects are generated from the distorted PAni's backbone lattice as PAni is a one-dimensional material, resulting in a vacancy (a radical cation or called positive polaron, which composed of neutral and positively charged solitons) equivalent to a hole is created [30, 32]. A polaron give rise to two levels (polaron bands) in the band gap due to the formation of polaron lattice defect state. The dopant, DBSA itself on the other hand, would be incorporated into the PAni and sits as counter-ions somewhere between the polymer chains. If the concentration of defects on the PAni backbone is high enough, the wave functions of the individual defects will overlap and the Peierls distortion[†] will be suppressed not only locally but also globally, leading to the disappearance of energy gap and PAni chain will becomes metallic [23]. Figure 1.12 indicates the formation of polaron and bipolaron states in polyaniline.

Nevertheless, before the wave functions of the polarons (combination of neutral and charged solitons) overlap are suggested, the electrostatic interaction between the charge of the polarons and that of the counterions has to be taken into account. One may proposes that the charged solitons themselves might move and

[†] Peierls distortion: The typical one-dimensional phenomena for metal-to-insulator transitions described by Bloch wave where a gap opens between the electronic density of states (Ref [23]).

thus contribute to the conduction mechanism. Yet, this is not very likely, because the charged solitons will be electrostatically bound to the counter-ions and therefore they are not expected to be mobile [23, 26]. Thus, the remaining unpaired electron on the PAni chain contributes to the propagation of polaron through a conjugated polymer chain by shifting of double bonds alternation that give rise to electrical conductivity (Figure 1.13) [30].

Such polaron is not delocalize completely, but is delocalized only a few monomeric units deforming the polymeric structure. The energy associated with this polaron represents a destabilized bonding orbital. It has a higher energy than the valence band, (to the nearest band theory approximation) and lies in the band gap. If another electron is subsequently removed from the already oxidized polymer, another polaron or a bipolaron will be created. Low doping level gives rise to polarons and with increase in the doping level more and more polarons interact to form bipolarons [30, 33]. The energy levels in polymers as a result of doping are indicated in Figure 1.14.

Moreover, the midgap states could acts as hopping centers and the electrical transport mechanism could well be variable-range hopping (VRH) for PAni, as has been proposed in amorphous semiconductors [23, 26, 29].

In general, doping will not be homogeneous and a sample doped moderately will consist of lightly and heavily doped regions. Owing to the local anisotropy of the samples caused by the polymer chains (one-dimensionality), the percolation behavior (formation of connected paths of highly doped regions) is very difficult to predict and the observed conductivity will very often be a combination of variable-range hopping in lightly doped regions and tunneling between more heavily doped domains in the PAni and its composites.
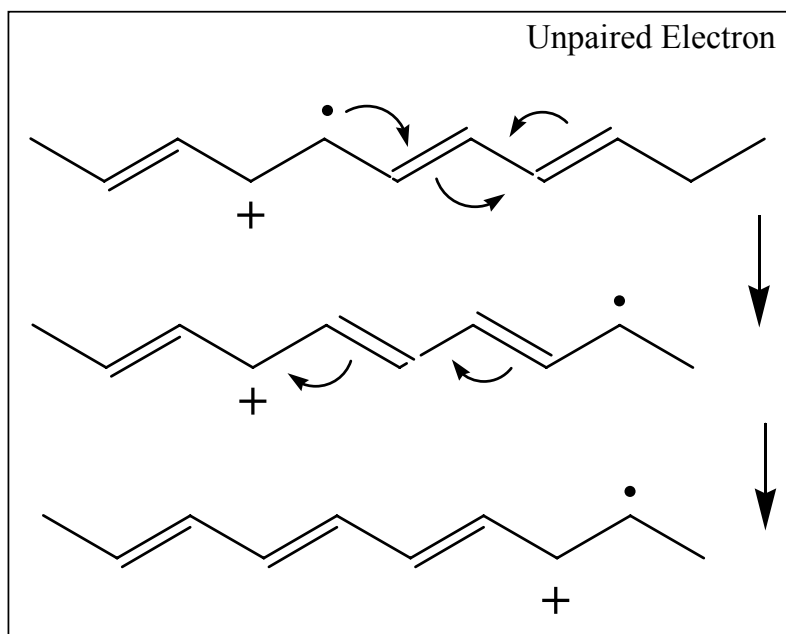
Figure 1.13: Propagation of polaron through a conjugated polymer chain by shifting of double bonds (alternation) that give rise to electrical conduction (Adapted from reference [30])
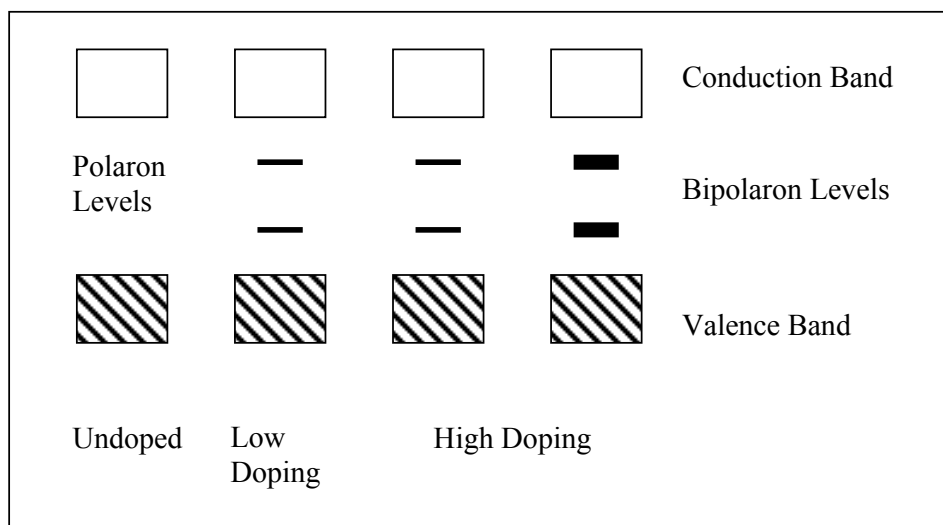
Figure 1.14: Energy band diagrams and defect levels for polarons and bipolarons in undoped, lightly doped and heavily doped conducting polymers (Adapted from reference [30])

In a VRH model [26], the conduction of charge carriers could be explained by the hopping mechanism (Figure 1.15). Hopping is like a man crossing a river by jumping from stone to stone, where the stones are spread out at random, as illustrated in Figure 1.15 (a). It is obvious that the more stones available, the higher the conductivity, σ_{dc} because he can jump effortlessly from stone to a nearer stones compared to hopping from stone to a far apart stone.
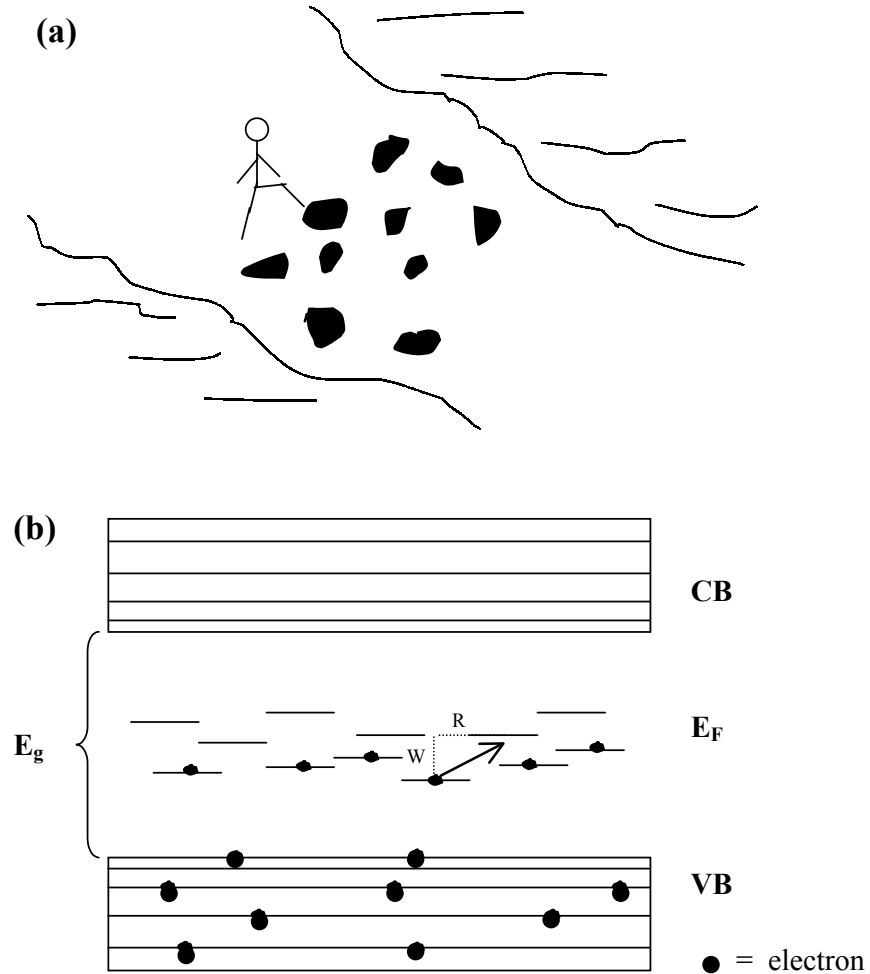
Figure 1.15: (a) Hopping transport: a man crossing the river by jumping from stone to stone and (b) Electronic level scheme of disordered PAni to demonstrate the hopping conductivity (CB = conduction band, VB valence band, E_F = Fermi energy, W = energetic distance between states, R = local distance between states, E_g = energy gap) [26]

To discuss the temperature dependence of hopping conductivity, it is more reasonable to look at the band structure represented in Figure 1.15 (b). There are localized states in the energy gap (E_g), distributed randomly in space as well as in energy. The Fermi energy level (E_F) is about at the center of the E_g with the states below E_F is occupied and the states above empty (except for thermal excitations). Electrons will hop (tunnel) from occupied to empty states. Most of the hops will have to be upward in energy. There are many phonons available at high temperature, which can assist in upward hopping. As these phonons freeze the electron has to look further and further to find an energetically accessible state. As a result, the average hopping distance will decrease as the temperature decreases – hence the name "variable range hopping". Since the tunneling probability decreases exponentially with the distance, the conductivity also decreases.

It is well known that doping process produces a generous supply of potential carriers, but to contribute to conductivity they must be mobile. And, it is found that the hopping conduction of conducting polymer (including PAni) may be hampered by three elements contributing to the carrier mobility [29], namely single chain or intramolecular transport, interchain transport and interparticle contacts. These three elements comprise a complicated resistive network (illustrated in Figure 1.16), which determines the effective mobility of the carriers. The polarons and bipolarons are mobile and under the influence of electric field, can move along the polymer chain, from one chain to another and from one granule to another. At higher temperature, softening process will eventually alter the macroscopic and microscopic properties of PAni.

However, there are many other factors that also influence such conduction mechanism, such as doping level, method of preparation [32] and temperature [34].
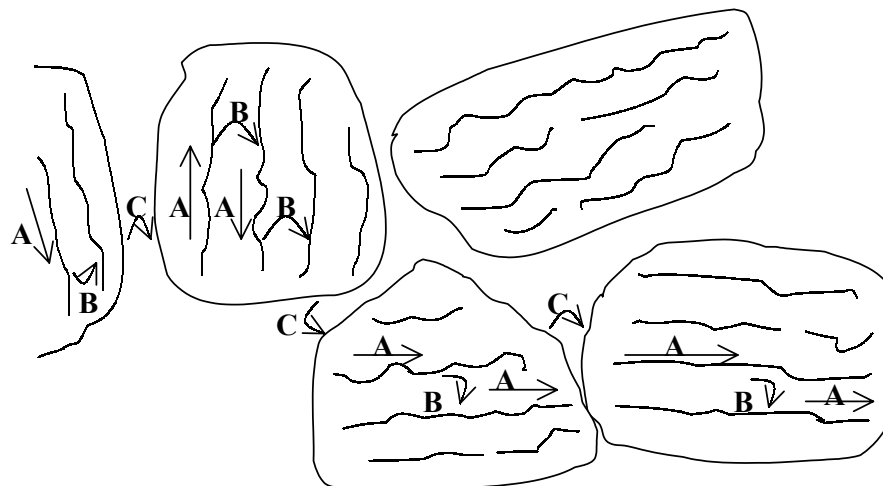
Figure 1.16: Conducting network of a conducting polymer with A indicating intrachain transport of charge, B indicating interchain transport, C indicating interparticle transport and arrows showing path of charge carrier migrating through the material [26]

1.3.2   Water-soluble Polymer — Poly(vinyl alcohol) (PVA)

Water-soluble polymer provide the best matrix for a model blend because polyaniline can be incorporated into a blend system with the presence of dodecylbenzene sulfonic acid (DBSA) which helps in the form of dispersing.

Poly(vinyl alcohol), a polyhydroxy polymer, is the largest volume, synthetic, water-soluble resin produced in the world. With the gradual reduction in cost, various other end uses began to be exploited. Figure 1.17 shows the chemical structure of PVA.
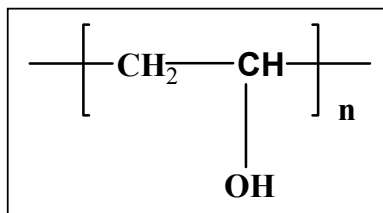
Figure 1.17: Structure of PVA

The biodegradable and non-toxcity PVA is highly soluble in highly polar and hydrophilic solvents, such as water, acetamide and glycols. The solvent of choice is water and the solubility in water depends on the degree of polymerization and hydrolysis. The polymer is an excellent adhesive for corrugated board, paper and paper board and in general purpose adhesives for bonding paper, textile and porous ceramic surfaces. It possesses solvent, oil and grease resistance matched by few other polymers.

The excellent chemical resistance and physical properties of PVA resins have led to broad industrial use [35]. PVA forms tough, clean films, which have high tensile strength and abrasion resistance, oxygen-barrier properties under dry conditions are superior to those of any known polymer. Furthermore, the unsupported films cast from aqueous solutions of PVA and plasticiser have resistance towards organic solvents. The use of PVA film in the cold water-soluble packaging of materials such as detergent, bleach, for pesticides, herbicides, fertilizers and other materials which pose health or safety risks, enable dissolving in water without the removal of the package. Owing to low surface tension, emulsification and protective colloid properties are excellent. Moreover, it has high electrical resistivity $(3.1 - 3.8)$ x 10^7, leading to the extremely excellent antistatic properties of the film [35–36].

The main uses of PVA are in fibers, adhesives, emulsion polymerization, production of poly(vinyl butyral) and paper and textile sizing. Furthermore,

significant volumes are also used in joint cements for building construction. In addition, it is used in water-soluble films for hospital laundry bags, temporary protective films and other applications.

In this study, water-soluble polyvinyl alcohol (PVA) was selected to blend with the electrically conducting polyaniline (PAni) and polyaniline-titanium(IV) oxide (PAni-TiO$_2$) composite to form a free-standing conducting film and investigate the electrical properties of the films.

1.3.3 Metal Oxide

Nowadays, the physical and chemical requirement of a material has been even greater than ever. This demand cannot be fully met neither a handful of elements having semiconducting properties nor some relevant chemical compounds, which are already understood. Therefore, increasing attention is being paid to studies on less known chemical compounds able to act as semiconductors to meet the need of the future technology. One of the most important aspects of a "new" material is most probably the electrical property. This is because the development of the technology has put electronic and electrical appliances in our daily life.

Among them, semiconductor oxides may be considered as most promising. Owing to their electrical properties like conductivity, magnetic, ferroelectric, piezo-electric, electroluminescence and optical property, some of the metal oxides have been successfully applied in electronic and microelectronic for the production of electronic components such as transistor, capacitor, resistor, microchip and others.

In this study, titanium(IV) oxide (TiO_2) was utilized to form composite with PAni and then blended with water-soluble PVA.

1.3.3.1 Titanium(IV) Oxide (TiO_2)

Titanium(IV) oxide, occurring in three polymorphic forms − rutile, anatase, brookite, is a very common pigment utilized in various industries. Rutile and anatase are produced commercially in large quantity for the use as pigments, catalysts and in the production of ceramic and electronic materials. Their electrical conductance is between 1.1 x 10^{-5} − 3.4 x 10^{-3} S/cm [37]. TiO_2 is widely used in welding-rod coatings, specific paints, inks, acid-resistant vitreous enamel, etc. owing to its high refractive index, durability, dispersion, tinting, strength, chemically inert nature and non-toxicity.

However, below a critical size, TiO_2 clusters can absorb the energy of ultraviolet (UV) to release electron and radical by oxidation under irradiation of UV. Thus, they are also used as protectant against external irridiation and sunlight. Thus, it is used as a sunblock in suncreams because it reflects, absorbs, scatters light, does not irritate skin and it is water-resistant. In plastic industries, TiO_2 is incorporated on the package of fat-containing food to prevent UV radiation. It is also utilized in the production of anti-static plastic and as electrically conducting materials.

Further, the absorbed organic compounds on TiO_2 clusters can be decomposed by oxidation owing to the presence of a radical released by irradiation. So, TiO_2 is known as photocatalyst [31]. Anatase TiO_2 have high potential for

application in diverse areas of environmental purification, such as purification of water and air due to the unique properties.

The polyaniline-TiO$_2$ composite had been investigated on its electrical property, effect of thermal treatment and TiO$_2$ content [31]. According to Somani and co-workers [38], this composite exhibits high piezosentivity and being maximum at certain PAni-TiO$_2$ composition.

1.4   Characterization of Polymer Blends

There are several methods could be employed to evaluate a material or composite, whether they are in the category of nano- or submicron-sized materials. The most common methods used are Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM). For the SEM, the resolution ranges from sub-milimeter to sub-micron while the TEM and AFM could go up to nanometer. Both SEM and TEM are very useful to determine the morphology and particle sizes of samples where direct imaging of the material structures can be perform. The AFM is suitable for scanning the 3-dimension surface morphology and surface imaging of the samples.

Apart from the morphology and particle sizes of the conducting polymer blends, we have to look also into another important physical properties, i.e. electrical properties of the blends. The electrical properties of a conducting polymer blends involves the charge transfer within the nanocomposite matrix whereby is a complex and difficult to study. Two of the measurements used in this research are described below.

1.4.1   Four-probe Method

Resistivity measurements are generally made on desired materials to determine their suitability as materials for electronic components. The resistivity must be measured accurately since its value is critical in many devices.

Many conventional methods for measuring the resistivity are unsatisfactory for semiconductors because metal-semiconductor contacts are naturally rectifying. An excess concentration of minority carriers will affect the potential of other contacts and hence modulate the resistance of the material.

The four-probe method overcomes the difficulties mentioned above and also offers other advantages. It permits measurements of resistivity in samples having a wide variety of shapes, including the resistivity of small volume within bigger pieces of semiconductor. This method of measurement is also applicable to silicon and other semiconductor materials such as conducting polymer [10, 39–42].

1.4.2   Hall Effect Measurement

Conductivity measurements could not distinguish the types of carriers present. But Hall effect measurement, which is basic tools for determination of mobilities could. This method was discovered by Hall in 1879 [43] when he was attempting to prove the magnetic field effect on a current. With this method, parameters such as Hall coefficient, carrier density, mobility and other values could be derived from the measured resistivity data.

1.5   Research Background and Challenges

The principal problem encountered with the potential utilization of conducting polymers is their poor processability and environmental stability. Attempts have been made earlier to incorporate plastics or rubber with conducting polymer in order to improve the processability of the said mixed material without losing the mechanical properties [14].

Currently, polyaniline (PAni) is one of the most investigated intrinsically conducting polymers due to its easy synthesis and good conductivity. Significant progress in the preparation of processible forms of polyaniline has been reported in recent years. The use of selected sulphonic acids [42], phosphonic acids [11] and hydrochloric acid [9, 44] as protonating agents has led to the solubilisation of the conductive polyaniline; enabling its processing from solution. Furthermore, some of the polyaniline dopants plasticize it upon ptotonation which, in turn, facililitates thermal processing of PAni. For all these reasons, polyaniline is considered as one of the most promising candidates for the fabrication of conductive blends with industrially important classical polymers.

Such a great demand for flexible, conductive plastic film and the latest progress on the fabrication of polyaniline and its blends has attracted enormous industrial interest. The ability to process PAni into tough, free-standing, air stable films has been a pulling factor for the intense research and great number of published material related to this promising conducting polymer. Nevertheless, one of the difficulties associated with the processing of conjugated polymers is their poor solubility in common volatile organic solvents. PAni in its emeraldine form (PAni-EB) is commonly processed by dissolving the polymer in N-methylpyrrolidone (NMP) or m-cresol, both high boiling point solvents, resulting in cast films containing a non-negligible amount of residual solvent, often associated with residual water from the polymerization reaction [45–46]. The resulting PAni film normally contains a considerable amount of N-methylpyrrolidone (NMP),

about 18 % by weight due to the high boiling point of NMP (202 $^{\circ}$C) and the presence of the hydrogen bonding interaction of the carbonyl group with the NH group in PAni. The residual solvent will affect the electrical conductivity and degree of crystallization and crystalline structure apart from mechanical and thermal properties [47].

Interactions between the two blended polymers would greatly influence the conductivity and physical properties of the films. In terms of percolation theory [6], the conductivity is very small at sufficiently low concentration where there is no connected path. As the concentration of the conducting polymer is increased, the conductivity shows a sharp increase at a certain concentration of conducting polymer, which is called the percolation threshold.

Several works have been reported on the preparation of interpenetrating composites of polyaniline (PAni) with several matrix polymer such as poly(methyl methacrylate), poly(vinylalchohol), polycarbonate etc [2, 12, 15, 48–50]. Several studies also reported conducting polyblends prepared with polyaniline and a classical polymer (polystyrene, poly(vinyl acetate), polyimide, etc) in organic solvents, which exhibit good mechanical properties associated with interesting electrical properties [9–10, 45]. Those polyanilene blends are all in an organic system. Recently, Shi-Jian Su and Noriyuki Kuramoto had reported that polyaniline blends in organic system obtain higher conductivity than in aqueous system [46]. The information about the polymer blends in aqueous is much more scarce. In this respect, in this works we explored and studied polyaniline blends in aqueous system.

1.6   Research Scope

The scope of this research is as listed below:

a)   To synthesis conductive polyaniline (PAni) and polyaniline-titanium(IV) oxide composites through *in situ* polymerization method.

b)   To form conductive, free-standing films of PAni/PVA and PAni-TiO$_2$/PVA by using solution casting method.

c)   To study the effect of TiO$_2$ content on the conductivity behavior of the blends with varying TiO$_2$/aniline weight ratio, ranging from 0.13 – 0.53.

d)   To study the heating effect on conductivity behavior within temperature range from 30 $^{\circ}$C – 160 $^{\circ}$C.

e)   To study the influence of weight fractions of conductive components (PAni and PAni-TiO$_2$), ranging from 0.1 wt. % – 40 wt. %, on the blends' conductivity behavior.

1.7   Research Objective:

Polymer blends have been extensively studied in recent years due to their significant importance in applied as well as basic sciences. They are formulated to provide a material with an appropriate balance of thermal performance, processability and toughness among other properties that cannot be met with single polymers. Even though the metallic conductivity of certain conductive polymer blends came close to those of metal, the main problems of long-term stability of charge carrier and its mobility in conductive polymer blend yet to be addressed.

The focus of this research is to synthesis conductive polyaniline (PAni) and polyaniline-titanium(IV) oxide, and consequently to process PAni and PAni-TiO$_2$ conducting blends into tough, free-standing, flexible and conductive films in

aqueous system through blending with water-soluble poly(vinyl alcohol). PAni has been selected as the conductive polymer candidate to be synthesized and used to composite with titanium(IV) oxide by *in situ* polymerization, doped with dodecylbenzenesulfonic acid in hydrochloric acid medium. The chemical and physical characterizations of these systems were emphasized on those related to antistatic films properties, such as electrical conductivity and charge carrier mobility.

These two activities, namely synthesize and characterization, were carried out in tight interaction with each other. On one hand, the aim of physical investigation is to account for the influence of TiO_2 content, temperature and weight fractions of conductive components (PAni and PAni-TiO_2) on the conductivity behavior of the films. Besides, the electrical transport properties such as electrical conductivity, charge carrier mobility and density are studied and correlated by using the four-probe and Hall effect measurement. On the other hand, the objective of the chemical study is to confirm and defined feature of the polymer and its composite blends and is meant to innovate better synthetic method for better quality conducting films.

It can be concluded that the wt. % of conductive fractions, TiO_2 content, temperature, charge mobility and the conductivity behavior of the films are in tight interaction with each other. The blending procedures could lead to innovation in synthetic method for better conducting films.

4.2   Suggestions

To further understand the PAni and PAni-metal oxide composites blended with water-soluble polymer in aqueous system, future effort should focus on the study of how the carrier density and mobility of the samples are affected by the preparation method; namely the synthesis temperature, the duration of the polymerization, the choice of dopant, metal oxides and water-soluble polymers used and finally the way of film preparation method. In addition, the thermal heating and ageing effect on the microscopic and macroscopic level of the sample could be carried out to investigate the conduction and transport properties. The investigation on the low temperature conductivity of the films is suggested.

This research could be extended by varies the choice of water-soluble polymer used, such as polyvinylpyrrolidone (PVP), polymethacrylamide (PMAAm) and etc. The chemical reactivity of the PAni and PAni-metal oxide blending with different water-soluble polymer casting on different substrates should also be explored to expand the potential application of PAni films in the future.

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