CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Plastic films.

2.1.1 General features of plastic films [8].

Plastics generally are organic high polymers that are formed in a plastic state either during or after their transition from a small molecule chemical to a solid material. State very simply, the large chainlike molecule are formed by hooking together shortchain molecules of monomers in a reaction knows as polymerization. When unit of a single monomers are hooked together, the resulting plastic is a homopolymer, such as polyethylene, which made from the ethylene monomer. When more than one monomer is included in the process, for example, ethylene and propylene, the resulting plastics is a copolymer.

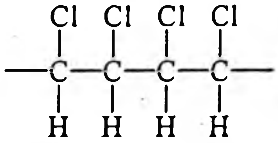
The two basic groups of plastic materials are the thermoplastics and the thermosets. Thermoplastic resins consist of long molecule each of which may have side chains or groups that are not attached to other molecules (i.e., are not crosslinked). Thus, they can be repeatedly melted and solidified by heating and cooling so that any scrap generated in processing can be reused. No chemical change generally take place during forming. Usually, thermoplastic polymers are supplied in the form pellets, which often contain additives to enchance processing or to provide necessary characteristics in the finished product (e.g., color, conductivity, etc.). The temperature service range of thermoplastic is limited by their loss of physical strength and eventual melting at elevated temperatures. Thermoplastic polymers such as ABS, nylons, polyethylene, polysulfone, poly(vinyl chloride), polypropylene, etc., see Table 2.1

Thermoset plastics, on the other hand, react during processing to form crosslinked structures that cannot be remelted and reprocessed. Thermoset scrap must be either discarded or used as a low-cost filler in other products. In some cases, it may be pyrolyzed to recover inorganic fillers such as glass reinforcements, which can be reused. Thermosets may be supplied in liquid form or as a partially polymerized solid molding powder. In their uncured condition, they can be formed to the finished product shape with or without pressure and polymerized by using chemicals or heat. The thermoset plastics such as epoxide, melamine, phenolics, polyesters, polyimides, silicones, ureas, polyurethanes, etc.

In this study, considered in thermoplastic polymers are PVC, LDPE, and PP. Therefore they have advantage in physical and chemical properties, shaping, processibility, and stability in atmosphere environment.

2.1.2 General features and properties of PVC films.

PVC is one of the world's most widely used plastics. Its acceptance comes from the polymer's versatility; it can be utilized in rigid compounds or blended with plasticizers to produce flexible grades. Most PVC is made via suspension polymerization. A small amount is made by mass polymerization, and plastisols and organosols are produced by the emulsion process. The simple for PVC molecule is completely unbranched chain of -(Cl)-CH- units as show:



$$-\underset{\displaystyle H}{\overset{\displaystyle Cl}{C}}-\underset{\displaystyle H}{\overset{\displaystyle Cl}{C}}-\underset{\displaystyle H}{\overset{\displaystyle Cl}{C}}-\underset{\displaystyle H}{\overset{\displaystyle Cl}{C}}-$$

Rigid PVC compounds normally contain resin, a heat stabilizer, and an impact modifier such as ABS or chlorinated polyethylene. Powder compounds are made by combining the ingredients in a high-intensity mixer. Pelletized compounds are made on twin-screw extrusion lines.

Flexible PVC compounds contain plasticizers to soften the resin. These additives are highvoiling solvents for PVC such as dioctyl phthalate (DOP) and didecyl phthalate (DDP). The plasticizers also act as processing aids.

Properties: PVC resin is self-extinguishing. In a fire, however, it produces hydrochloric acid and other toxic and corrosive chemicals. It can be burned in a property designed incinerator without releasing any of these chemicals into the atmosphere. A chief limitation of PVC is its heat resistance. Its heat distortion temperature is only about 160°F at 264 psi. Alloying with ABS and other polymers can improve PVC's performance at higher temperature. Other properties of PVC are shown in Table 2.1 [8].

TABLE 2.1 Typical property ranges for plastics

Thermo plastic	Symbol	Specific Gravity	Transpa rency	Tensile strength 10^3 psi	Tensile modulus, 10^5 psi	Impact strength Izod ft. lb/inch	Dielectric constant at 60 cps	Dielectric strength, volts/mil	Max use temp, F (no load)	DTUL at 66 psi	DTUL at 264 psi	Weather resist	Chemical resistance^c				
													W ac	S ac	W al	S al	Solv
ABS	GP	1.05-1.07	No		3.1	6	2.8-3.2	385	160-200	210-225	190-206	R-E	R	A^k	R	R	A^m-R
	Hi. imp.	1.01-1.06	No	4.8	2.4	7.5	2.8-3.5	300-375	140-210	210-225	188-211	R-E	R	A^k	R	R	A^m-R
	Ht. res.	1.06-1.08	No	7.4	3.9	2.2	2.7-3.5	360-400	190-230	225-252	226-240	R-E	R	A^k	R	R	A^m-R
	Trans.	1.07	Yes	5.6	2.9	5.3	-	-	130	180	165	R-E	R	A^k	R	R	A^m-R
Acetals	Homo	1.42	No	10	5.2	1.4	3.7	320	195	338	255	R^j	R	A	R	A-D	R
	Copoly	1.41	No	8.8	4.1	1.2-1.6	3.7	500	212	316	230	R^j	R	A	R	R	R
Acrylics	GP	1.11-1.19	Yes	5.6-11.0	2.25-4.65	0.3-2.3	3.0-3.7	450-500	130-230	175-225	165-210	R	R	A^k	R	A	A^m-R
	Hi. imp.	1.12-1.16	No	5.8-8.0	2.3-3.3	0.8-2.3	3.5-3.9	400-500	140-195	180-205	165-190	R	R	A^k	R	R	A^m-R
		1.21-1.28	No	8.0-12.5	3.5-4.8	0.3-0.4	3.5-5.1	400-440	125-200	170-200	155-205	R	R	A^k	R	A	A^m-R
	Cast	1.18-1.28	Yes	9.0-12.5	3.7-5.0	0.4-1.5	3.5-5.1	400-530	140-200	165-235	160-215	R	R	A^k	R	A	A^m-R
	Multi polymer	1.09-1.14	Yes	6.0-8.0	3.1-4.3	1.0-3.0	3.3-3.5	495	165-175	-	185-195	E	R	A^k	R	S	A^m
Cellulosics	Acetate	1.23-1.34	Yes	3.0-8.0	1.05-2.55	1.1-8.8	3.5-7.5	250-600	140-220	120-209	111-195	S	S	D	S	D	D-S
	Butyrate	1.15-1.22	Yes	3.0-6.9	0.7-1.8	3.0-10.0	3.5-6.4	250-400	140-220	130-227	113-202	S	S	D	S	D	D-S
Fluoro polymers	FEP	2.14-2.17	No	2.5-3.9	0.5-0.7	NB	2.1	500-600	400	158	-	R	R	R	R	R	R
	PTFE	2.1-2.3	No	1-4	0.38-0.65	2.5-4.0	2.1	400-500	550	250	-	R	R	R	R	R	R
	PVF_2	1.77	No	7.2	1.7	3.8	10.0	260	300	300	195	S	R	A^l	R	R	R
	ETEF & ECTFE	1.68-1.70	No	6.5-7.0	2-2.5	NB	2.4-2.6	400	300	220	160	R	R	R	R	R	R
Nylons	6/6	1.13-1.15	No	9-12	3.85	2.0	4.0	385	180-300	360-470	150-220	R	R	A	R	R	R-D^u
	6	1.14	No	12.5	-	1.2	4.0-5.3	385	180-250	300-365	140-155	R	R	A	R	R	R-A^u
Polyarylate		1.2	Yes	9.5	2.9	4.2	2.6	400	-	-	345	S	R	A^k	A	A	A
Polysulfone		1.36	No	13	3.7	2	3.94	350	500	-	525	Darkness	R	R	R	R	R
Polybutylene		0.910	No	3.8	0.26	NB	2.25	-	225	215	130	E	R	A^k	R	R	-
Polycarbonate		1.2	Yes	9	3.45	12-16	3.17	380	250	270-290	265-285	R	R	A^k	A	A	A
PC/ABS alloy		1.14	No	8.2	3.7	10	2.74	500	220	235	220	R-E	R	A^k	R	S	A
Polyesters	PET	1.37	No	10.4	-	0.8	3.65	-	175	240	185	R	R	A^k	R	A	R-A^o
Polyethylene	LD	0.91-0.93	No	0.9-2.5	0.20-0.27	NB	2.3	480	180-212	100-120	90-105	E	R	A^k	R	R	R
	HD	0.95-0.96	No	2.9-5.4	-	0.4-14	2.3	480	175-250	140-190	110-130	E	R	R-A^k	R	R	R
	HMW	0.945	No	2.5	1	NB	2.3	480	-	155-180	105-180	E	A	A^k	R	R	R
Ionomer		0.94-0.95	Yes	3.4-4.5	0.3-0.7	6-NB	2.4	1000	160-180	110	100-120	E	A	A^k	R	R	R
Polyimide		1.43	No	5-7.5	5.4	5-7	4.12	310	500	-	680	-	R	R	A	A	R
Polyphenylene sulfide		1.34	No	10	4.8	0.3	-	595	500	-	278	R	R	A^k	R	R	R
Polymethylpentene		0.83	Yes	3.3-3.6	1.3-1.9	0.95-3.8	-	700	275	-	-	E	R	A^k	R	R	A
Polysulfone		1.24	No	10.2	3.6	1.2	3.14	425	300	360	345	S	R	R	R	R	R-A

Table 2.1 (continued)

Polypropylenes	GP	0.90-0.91	No	4.5-6.0	1.6-3.0	0.4-1.2	2.20-2.28	650	225-300	200-230	125-140	E	R	A[k]	R	R	R
	Impact copolymer	0.88-0.91	No	3.5-5.0	1.3	2-NB	2.20-2.28	450-650	200-250	160-200	120-135	E	R	A[k]	R	R	A
	Random copolymer	0.89-0.91	No	4.0-5.5	1.0-1.7	1.1-12	2.25-2.30	450-600	190-240	185-230	125-140	E	R	A[k]	R	R	R
Polystyrenes	GP	1.04-1.07	Yes	6.0-7.3	4.5	0.3	2.45-2.65	400-600	150-170	-	180-220	S	R	A[k]	R	R	D
	Hi.-impact	1.04-1.07	No	2.8-4.6	2.9-4.0	0.7-1.0	2.45-4.75	400-500	140-175	-	175-210	S	R	A[k]	R	R	D
Polyurethane		1.11-1.25	No	4.5-8.4	0.1-3.5	NB	5.4-7.6	460	-	190	-	-	R-S	S-D	S-D	S-D	R
PVC Rigid		1.3-1.5	No-Yes	5-8	3-5	0.5-20	3.2-3.6	425-1300	150-175	135-180	130-175	R	R	R-S	R	R	R-A
PVC Flexible		1.2-1.7	Yes&No	1.4	-	0.5-20	5-6	250-800	140-175	-	-	S	R	R-S	R	R	R-A
Rigid CPVC		1.49-1.58	Yes-No	7.5-9.0	3.6-4.7	1.0-5.6	2.8-3.6	-	230	215-245	200-235	R	R	R	R	R	R
PVC/acrylic		1.30-1.35	No	5.5-6.5	2.75-3.35	15	3.9-40	400		180	170	R	R	S	R	R	A
PVC/ABS		1.10-1.21	No	2.6-6.0	0.8-3.4	10-15	-	600	-	-	-	S	R	R-S	R	R	R-D
SAN		1.08	Yes	10-12	5.0-5.6	0.4-0.5	3.0-3.8	1775	140-200	-	190-220	S-E	R	A	R	R	A
SMA		1.05-1.15	Yes-No	5-9	2.7-4.4	0.5-12	3.5	420	200	-	205-260	S-E	R	S	S	A	A
Alkyd -Glass filled		2.12-2.15	No	4-9.5	20-28	0.6-10	5.7	250-530	450	400-500	-	R	A	A	A	A	A
-Mineral filled		1.60-2.30	No	3-9	5-30	0.3-0.5	5.1-7.5	350-450	300-450	350-500	-	R	R	A	A	D	A
Epoxies(bis-A)No filler		1.06-1.40	Yes	4-13	2.15-5.2	0.2-1.0	3.2-5.0	400-650	250-500	115-500	-	R	R	A	R	S	R-S
Epoxies mineral filled		1.6-2.0	No	5-15	-	0.3-0.4	3.5-5.0	300-400	300-500	250-500	-	S	R	R	R	R	R-S
Epoxies (novolac) No filler		1.12-1.24	No	5-11	2.15-5.2	0.3-0.7	3.11-4.0	360-600	400-500	450-500	-	R	R	R	R	R	R
Phenolics Woodflour filled		1.34-1.45	No	5-9	8-17	0.2-0.6	5-13	260-400	300-350	300-370	-	S	R-S	S-D	S-D	A	R-S
Silicones -Glass filled		1.7-2.0	No	4-6.5	10-15	3-15	3.3-5.2	200-400	600	600	-	R-S	R-S	R-S	S	S-A	R-A
BMC -Mineral filled		1.8-2.8	No	4-6	13-18	0.3-0.4	3.5-3.6	200-400	600	600	-	R-S	R-S	R-S	S	S-A	R-A
Ureas -Cellulose filled		1.47-1.52	No	5.5-13	10-15	0.2-0.4	7.0-7.5	300-400	170	260-290	-	S	R-S	A-D	S-A	D	R-S
Urethanes No filler		1.1-1.5	No&Yes	0.2-10	1-10	5-NB	4.0-7.5	400-500	190-250	-	-	R-S	S	A	S	S-A	R-S

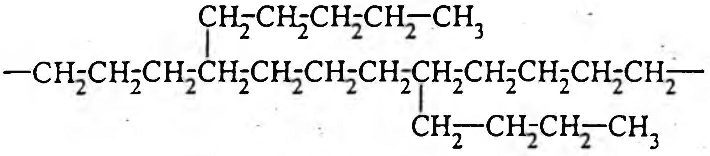
[A] All values at room temperature unless otherwise listed. [B] Per ASTM. [C] Notched samples. [D] Deflection temperature under load. [E] Ac is acid and Al is alkali; R is resistant, S is slight effects, E is embrittles and D is decomposes. [J] Chalks slightly. [K] By oxidizing acids. [L] By fuming sulfuric. [M] By ketones, esters, and chlorinated and aromatic hydrocarbons. [N] Hologenated solvents cause swelling. [O] Dissolved by phenols and formic acid.

2.1.3 General features and properties of LDPE films.

The polymerization of ethylene can occur over a wide range of temperatures and pressure but most commercial high pressure process utilize pressure between 1000 and 3000 atmospheres (1.45×10^4- 4.35×10^4 lb/in^2) and temperatures between 100 and 300°C. Temperatures higher than 300°C tend to cause degradation of the polyethylene. The simplest structure for the polyethylene molecules is a completely unbranched chain of - CH_2 - units as show:

$$-CH_2CH_2CH_2CH_2CH_2-$$

At the high pressure, the straight forward process chain growth and a great deal of chain branching occurs which has an important bearing on properties of low density polyethylene. Both short and long branch chains are produced, examples of which are shown below:



$$-CH_2CH_2CH_2\overset{CH_2CH_2CH_2CH_2-CH_3}{\overset{|}{C}H_2}CH_2CH_2CH_2\underset{\underset{CH_2-CH_2CH_2-CH_3}{|}}{CH_2}CH_2CH_2CH_2CH_2-$$

It will be noticed that each branch chain contains a terminal methyl (- CH_3 -) group. The occurrence of these branch chains prevent a close packing of the main polymer chains and this accounts for the fact that the process just described produces low density polyethylene.

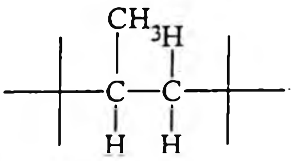
Properties: The structure of the low density polyethylene molecule also affects properties other than density (the density can vary between about 0.916 g/cm^3 and 0.935 g/cm^3). One important property is crystallinity. The great length of polymer chains means that a certain amount of entanglement normally occurs and this prevents complete crystallization on cooling ; there are thus disordered areas between the crystallinities. Areas where the chain are parallel and closely packed are largely crystalline while the disordered areas are atmospheres. The chain branching will tend to reduce the possibility of an ordered arrangement and so reduce the crystallinity of low density polyethylene usually varies between 55 and

70% (compared with 75 - 90% of HDPE). The other property of importance which is affected by the chain branching is softening. The fact that the chains cannot approach so closely to each other means that the attractive forces between them are reduced and less energy in the form of heat , is necessary to cause them to move relative to each other and thus flow. The softening point of LDPE is slightly below the boiling point of water and so the material cannot be used where boiling water or steam sterilization are involved.

Low density polyethylene is a tough, slightly translucent material and is waxy to the touch. It can be blow extruded into tubular film or extruded through a slit die and chill-roll casting process gives a clearer film but even blow film can be produced with good clearity with improvements in cooling of the bubble. Low density polyethylene film has a good balance of properties such as tensile strength, burst strength, impact resistance and tear strength. In addition, it retains its strength down to quite low temperatures (around -60°C to 70°C). It is a good barrier to water and water vapor but is not so good resistance, particularly to acids, alkalis and inorganic solution and, sensitive to hydrocarbons and halogenated hydrocarbons and to oils and greases. So that low density polyethylene is used in the fields of packing, building, horticulture and agriculture.

2.1.4 General features and properties of PP films.

The polymer, which has the basic structure unit is



$$\left[- \overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}} - \overset{\displaystyle H}{\underset{\displaystyle H}{C}} - \right]$$

was directed towards the use of Ziegler-type catalysts. Natta (in Italy) shown in 1954 that it was possible to prepare analogous polymers of propylene and polypropylene was first maketed in 1957. He found that in the Ziegler catalyst system, aluminium triethyl plus titanium tetrachloride, the titanium tetrachloride was replaced by titanium trichloride, a stereospecific catalyst was formed which yielded crystalline high molecular weight polymer of propylene. A stereospecific catalyst is one which controls the position of each monomer unit as it is added to the growing polymer chain, thus allowing the formation of a polymer of regular structure from an asymmetric monomer unit such as propylene.

Basically Natta's polymerization of PP is similar to Ziegler process for the preparation of HDPE. The gas, under a pressure of about 100 atm. (1.01×10^{-3} N/m^2 or 1.4×10^7 lb/in^2), is led into a reaction vessel in which is a well-stirred dispersion of catalyst in a liquid hydrocarbon. The temperature is kept low enough to ensure precipitation of the polypropylene as it is formed. Stirring is continued until the polymer content is between 35 and 40% when the sturry is pumped to flash drum where the unreacted propylene is removed and recycled. The slurry is then centrifuged to remove the liquid hydrocarbon. Catalyst removal from the polymer is carried out by extracting with a weak solution of hydrochloric acid gas in methyl alcohol. After removal of the extraction, the polymer is washed with water to remove the acid, steam to remove solid traces, dries, extruded and pelletised.

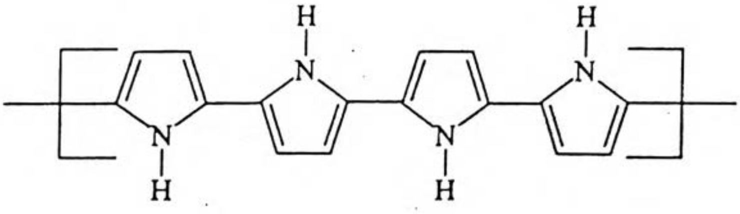
Properties : Polypropylene (about 0.90 g/cm^3), is harder and higher softening point. Polypropylene film can manufactured either by blow extrusion or by slit-die extrusion with subsequent cooling by chill-roll or water bath quench. The position is complicated by the fact that method have been used to produce a range of films which vary in the amount of orientation built into the film. Commercially, the films with unbalanced orientation, polypropylene films are used in the field of packing.

2.2 Polypyrrole [9,10].

Although polymers of pyrrole have been known for over 50 years, interest in these materials has greatly increased in the past decade because polypyrrole when doped become intrinsically electrically conductive. Efforts are underway to increase processibility of these polymers while maintaining electrical conductivity in ambient conditions.

Among the conducting polyheterocyclics, the most intensively studied polymers are polypyrrole. Polypyrrole has shown to be a conducting polymer in 1968. It was prepared by oxidation of pyrrole in sulfuric acid. The synthesized polypyrrole was a black powder with room temperature conductivity, of 8 S/cm. Polypyrrole is another class of electrically active polymer which are thermally and environmentally more stable. The five member ring heterocycles of pyrrole polymerize though α, α'- coupling (2,5-position).

The electrophysical properties of polypyrrole are determined by a variety of factors such as the degree of polymerization, nature of dopants and the heteroatom which incorperated into the π-conjugated system of carbon atoms, the band gap was 3.2 eV of polypyrrole. However, the effect of heteroatom on electrical properties of this polypyrrole may not be of that significance because electrical behavior of these highly conjugated polymers was governed by the polymer chain length since defect occur along the π-conjugated system of carbon atom.



(a)
Polypyrrole

(b)
Two inequivalent structures of the polypyrrole

Figure 2.1 (a) Chemical structure diagram of the polypyrrole.
(b) Two inequivalent structure of the polypyrrole.

Polypyrrole is of current theoretical interest since the two structures (Figure 2.1) sketched are not energetically equivalent. Thus, the coupling of electronic exitations to chain distortions (inherent in such linear conjugated polymers) will lead to polarons and bipolarons as the dominant charged species.

2.2.1 Theoretical consideration of conductive polymer.

In order to understand more about conductive polymer, a suitable starting point for consideration is band theory which is the essential basic of concepts for discussion of conduction in molecular solid. Since this thesis prepared polymer by CVD of pyrrole. Thus, effect of dopant was significant in this study. Furthermore, measurement of conductivity was described in section 2.3 .

(1) Band structure [9].

For simplicity, we assume that, one atom provided one atomic S-orbital at some energy (Figure 2.2(a)). When the second atom is brought up, it overlaps the first one and forms a bonding orbital and an antibonding orbital (Figure 2.2(b)). The third is brought up and overlaps its nearest neighbor (and only slightly its next-nearest) and from these three molecular orbitals are formed as show in Figure 2.2 (c) . The fourth atom lead to the formation of a fourth molecular orbital, and at this stage we can see that the general effect of bringing up successive atom is slightly to spread the range of energies covered by the orbitals, and also to fill in the range with orbital energies. When N atoms have been slotted on to the line there are N molecular orbitals covering a band of finite width. When N is indefinitely large, the orbital energies are indefinitety close, and form a virtually continuous band. Nevertheless this virtually continuous band consist of N different molecular orbitals, the lowest- energy orbitals in the band bring predominantly bonding, and the highest-energy predominantly antibonding.

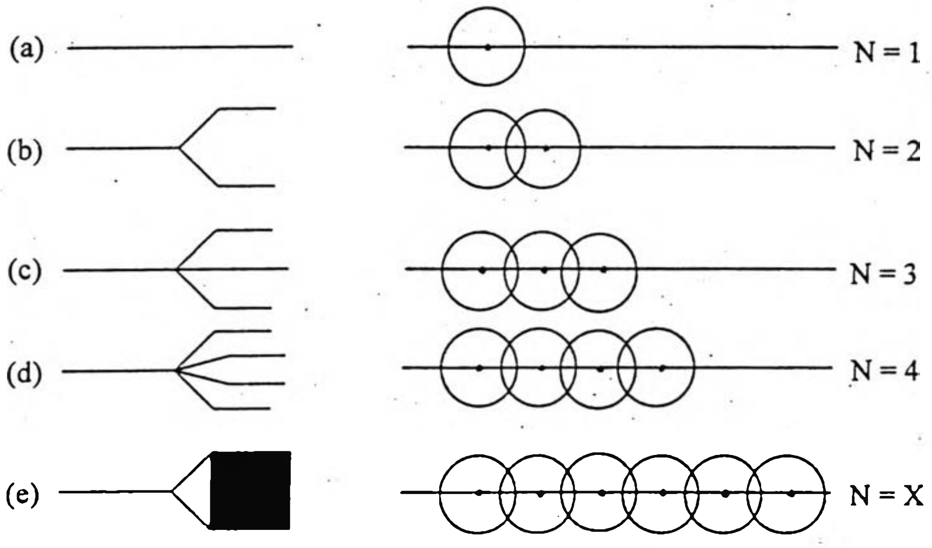


Figure 2.2 The formation of a band of N orbitals by the successive addition of atoms to a line.

The band formed from S-orbitals is call the S-band. If the atoms carry P-orbitals, the same procedure may be followed, and the band of molecular orbitals is call the P-band (Figure 2.3). If the atomic P-level lies higher than the atomic S-level, the P-band lies higher than the S-band, unless it is so broad (strong overlap) that the band overlap.

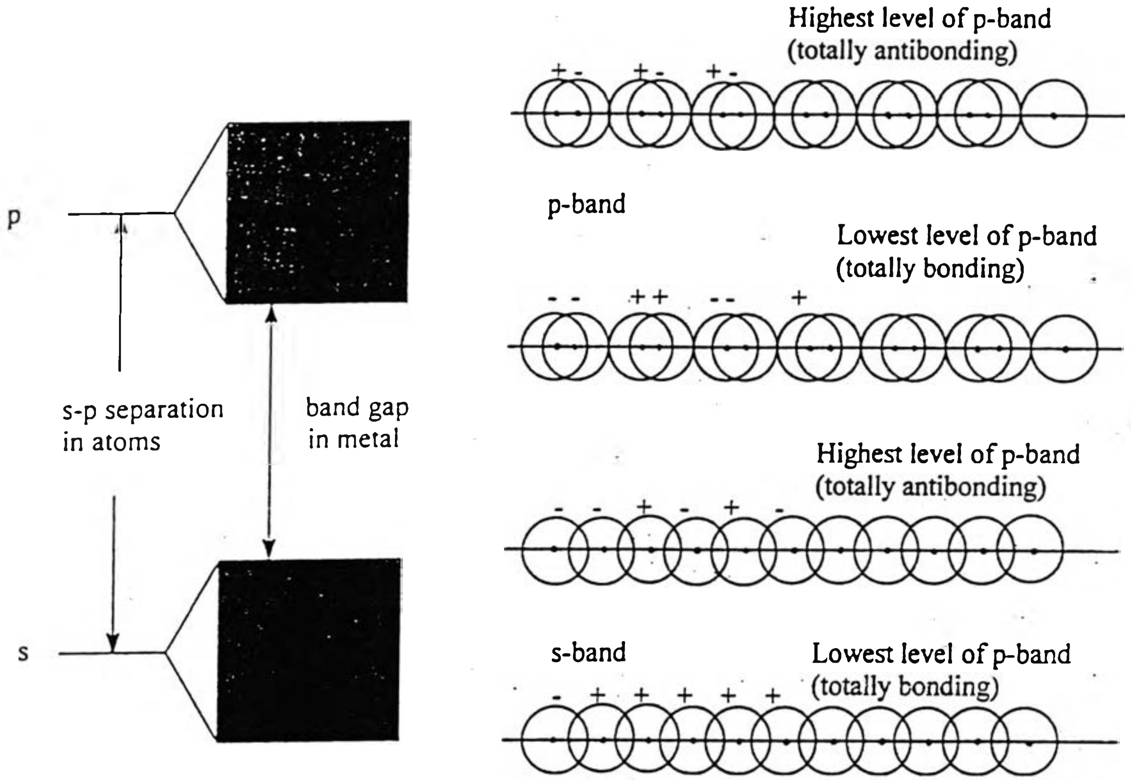
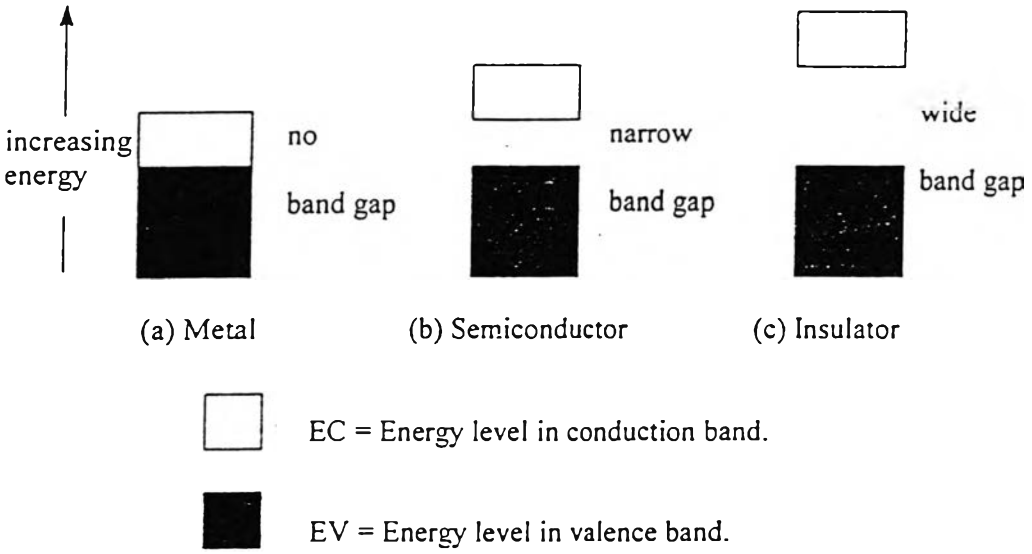


Figure 2.3 S-band, p-band, and the band gap.

(2) Metal, semicondutor and insulator [11].

Energy band diagrams may be used to illustrate the differences between metals, semiconductors and insulators. For sample model in metals the electrons completely fill the valence band and partially filled the conducting band. The higher energy conduction band is empty at absolute zero. This is shown in Figure 2.4(a), above absolute zero, electrons at the top of the highest occupied level can gain thermal energy and move into the low lying empty level of conductive bands. A substantial fraction of the electrons can be exited into singly occupied energy levels, even at relatively low temperature. Such unpaired electrons contribute to the electrical conductivity of a metal, and the substance is called a conductor.

In semiconductors and insulators, shown in Figure 2.4(b) and (c), the valence band is completely filled and an energy gap exists between it and the next higher energy band. If the energy gap is wide (large), there is little change for electrons to be exited into an empty conduction band and the material is and insulator. If there is only a small energy gap, the material is an intrinsic semiconductor, electrons being exited rather easily into the conduction band. If the gap is wide but impurity atoms are added, it may be possible to establish level within the gap that facilitate the movement of electrons into the conduction band. These latter systems are known as impurity semiconductor, or extrinsic semiconductors.



(a) Metal (b) Semiconductor (c) Insulator

Figure 2.4 The relationship of energy gaps in the three types of solids.

(3) Doping of semiconductors **[11,12]**.

Most technologically important semiconductors are the extrinsic type in which the charge carrier production is determined by trace amounts of impurities or by lattice imperfections. However, with the addition of an impurity (between about

0.1% to less than 1 ppm), the charge carrier type, its concentration and the conductivity of the sample can be controlled.

When the crystal lattice is disturbed by the addition of impurities or even by irregularity in the lattice arrangement, isolated centers are generated. Some centers can contribute electrons to the conduction band of the material. Such defects are called donors or donor centers. If the primary charge carriers are electrons, the material is called an n-type semiconductor. If the centers remove electrons from the chemical bonds, they are called acceptors and produce electron vacancies. These vacancies behave as positive charge carriers in the valence band and are called holes. If holes are the predominant charge carriers, a p-type semiconductor results.

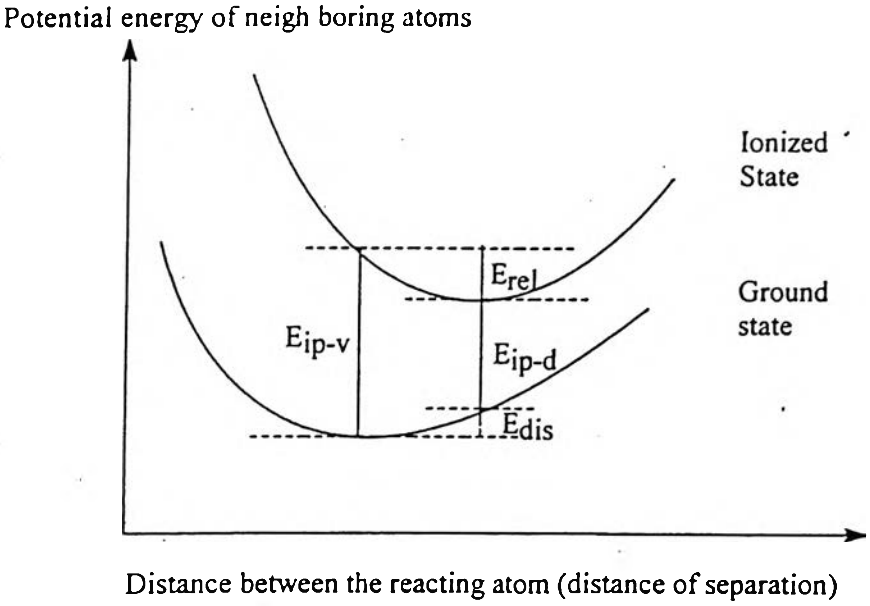
Conducting polymers are peculiar in that they conduct current without having a partially empty or partially filled band. Their electrical conductivity cannot be explain well by simple band theory. For example, simple band theory cannot explain why the charge carriers, usually electrons or holes, in polypyrrole are spinless. To explain some of the electronic phenomena in these organic polymers, concepts from physics that are new for chemists, including polarons and bipolarons, have been applied to conducting polymers since the early 1980s.

(4) Nature of the charges appearing on the polymer chain [11,12].

In crystal polymer, the interaction of a polymer unit cell with all its neighbors leads to the formation of electronic bands. The highest occupied electronic level constitutes the valence band (VB) and lowest unoccupied level, the conduction band (CB). The width of the forbidden band, or band gap (Bg), between the VB and CB determines the intrinsic electronic properties of the material. For all the organic conjugated polymers discussed so far, the band gap is much larger than 1.5 eV so that these materials are intrinsically insulating.

Initially, the high conductivity observed upon doping organic polymers was thought to result from the formation of unfilled electronic bands. It was simply assumed upon p-type or n-type doping, electrons were respectively, removed from the top of the VB or added to the bottom of the CB, in analogy to the mechanism of generation of charge carriers in doped inorganic semiconductors. This assumption was however quickly challenged by the discovery that polypyrrole which can display conductivity does not seem to be associated with unpaired electrons but rather with spinless charge carriers.

In organic molecule, it is usually the case that equilibrium geometry in the ionized state is different from that in the ground state, e.g., the geometry of polypyrrole is aromatic-like but becomes quinoid-like in the ionized state. The energies involved in the ionization process of a molecule are schematically depicted in Figure 2.5. A vertical, Franck-Condon like ionization process cost an energy $E_{ip\text{-}v}$. If a geometry relaxation then take place in the ionized state, a relaxation energy E_{rel} was gain back. Conceptually, going from the ground state to the relaxed ionized state can also be of in the following way. The geometry of the molecule is first distorted in the ground state in such away that the molecule adopts the equilibrium geometry of the ionized state. This costs a distortion (elastic) energy E_{dis} (Figure 2.5). For one-electron energy levels of the molecule, this distortion leads to an upward shift $\Delta\varepsilon$ of the highest occupied molecular orbital (HOMO) and a downward shift of the lowest unoccupied molecular orbital (LOMO), as illustrated in Figure 2.6. If we then proceed to the ionization of the distorted molecule, it requires an energy $E_{ip\text{-}d}$.



E_{ip-v} = The vertical ionization energy

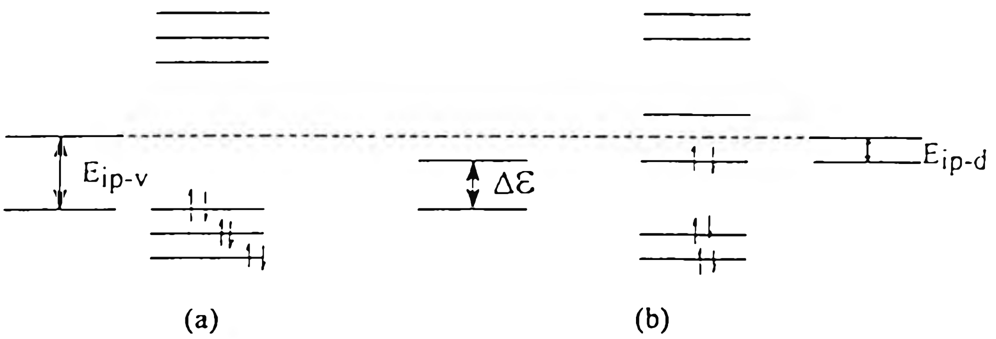
E_{rel} = The relaxation energy gained in the ionized state

E_{dis} = The distortion energy to be paid in the ground state in order that molecule adopts the equilibrium geometry of the ionized state.

E_{ip-d} = The ionization energy of the distorted molecule.

Figure 2.5 Illustration of the energies involved in a molecular ionization process.

From Figure 2.5, it is clear that it is energetically favorable to have a geometry relaxation in the ionized state when the quantity E_{ip-v}-E_{ip-d} (which actually corresponds to $\Delta\varepsilon$ as can be inferred from Figure 2.6) is larger than the distortion energy E_{dis}: or in other words, when the reduction, $\Delta\varepsilon$, in ionization energy upon distortion is larger than the energy E_{dis} required to make that distortion.



(a) The equilibrium geometry of the ground state.

(b) The equilibrium geometry of the first ionized state.

Figure 2.6 The one-electron energy levels for organic molecule in its ground state electronic configuration.

In a polymer, or any solid, a vertical ionization process $E_{ip\text{-}v}$ results in creating a hole on top of the valence band; see Figure 2.7(a). In this case, three remarks can be made. First, by the very definition of the process, no geometry relaxation (lattice distortion) takes place on the chain. Second, the positive charge on the chain is delocalized over the whole polymer chain. Third, the presence of a hole (unfilled level) on the top of the VB leads, as discussed above, to the appearance of a metallic character. This situation corresponds to the initial assumption made about the conduction mechanism in doped organic polymers. However, in an organic polymer chain, it can be energetically favorable to localize the charge that appears on the chain and to have, around the charge, a local distortion (relaxation of the lattices). This process causes the presence of localized electronic states in the gap due to a local upward shift, $\Delta\varepsilon$, of the HOMO and downward shift of the LUMO, Figure 2.7(b). Considering the case of oxidation, i.e., the removal of an electron from the chain, the ionization energy was lowered by an amount $\Delta\varepsilon$.

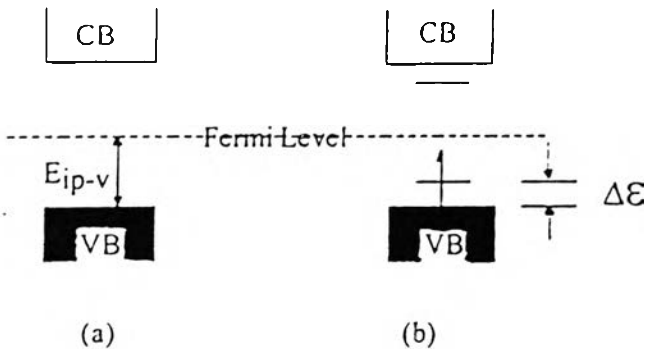


Figure 2.7 Band structure of polymeric chain in the case of
(a) a vertical ionization process
(b) the formation of polarons.

If ΔE is larger than the energy E_{dis} necessary to distort the lattice around the charge, this charge localization process is favorable relative to the band process. It was then formed what condensed matter physicists call a polaron. In chemical terminology, the polaron is just a radical ion (spinless) associated with a lattice distortion and the presence of localized electronic state in the gap referred to as polaron state. The quantity ΔE - E_{dis} (= E_{rel}) corresponds to the polaron binding energy. Calculation (based on Huckel theory with bond compressibility) has indicated that polaron formation is energetically favorable in all the organic conjugated polymers. The polaron binding energy is 0.12 eV in polypyrrole. It must be stressed that in the case of polaron formation, the VB remains full and the CB empty. There is no appearance of metallic character since the half-occupied level is localized in the gap, Figure 2.7(b).

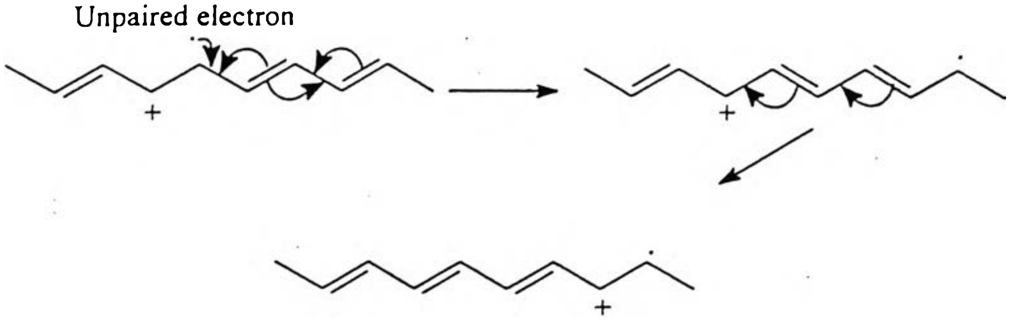
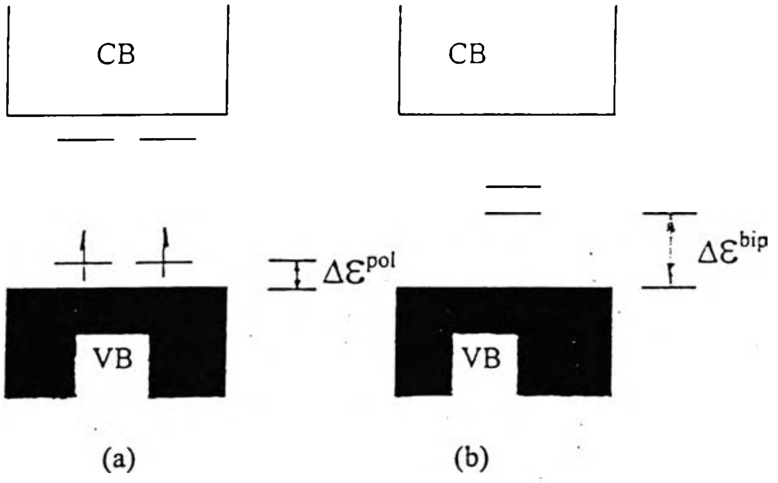


Figure 2.8 A radical cation that is partially delocalized over some polymer segment is called a polaron of polyacetylene.

If another electron is now removed from the already oxidized polymer containing the polaron, two things can happen [12]. This electron could come from either a different segment of the polymer chain, thus creating another independent polaron, or from the first polaron level (remove the unpaired electron) to create a special distortion, which solid-state physicist call a bipolaron. A bipolaron is defined as a pair of like charge associated with a strong local lattice distortion. The formation of a bipolaron implies that energy gained by the interaction with the lattice is larger than the Coulomb repulsion between the two charges of same sign confined in the same location. The two positive charges of the bipolaron are not independent, but act as pair.



(a) two polarons (b) one bipolaron

Figure 2.9 Band structure of polymer chain containing two polaron and one bipolaron

The electron band structure corresponding to the presence of two polarons and that of one bipolaron is depicted in Figure 2.9. Since the lattice relaxation around two charges is stronger than around only one charge, E_{dis} for the bipolaron is further away from the band edges than a polaron.

The creating of bipolaron relative to that of two polarons, the calculation for polypyrrole indicate that the distortion energy E_{dis} to form one bipolaron is roughly equal to that of forming two polarons. On the other hand, the decrease in ionization energy is much more important in the bipolaron case ($2\Delta\varepsilon^{bip}$) than for two polarons ($2\Delta\varepsilon^{pol}$); see Figure 2.9. This is the reason why one bipolaron is thermodynamically more stable than two polarons in these systems despite the Coulomb repulsion between two similar charges. Furthermore, the latter is also largely screened by the presence of dopants (couterion) with opposite charge. The bipolaron binding energy [= ($\Delta\varepsilon^{bip}$) - ($E_{dis}{}^{bip}$)] is calculated to be larger than that of two polarons by about 0.45 eV in polypyrrole.

In case of p-(n-) type doping, the bipolaron level in the gap is empty (fully occupied); see Figure 2.9(b). The bipolaron is thus spinless. The presence of bipolaron on polymer chains result in the possibility of two optical transitions below the band gap transition: for p-type doping, such as polypyrrole, from the VB to the lower bipolaron level and from the VB to the upper bipolaron level. In the case of polaron, a third absorption is possible below the gap, corresponding to an optical transition between the two polaron levels [Figure 2.9(a)].

Polypyrrole posses a non-degenate ground state since their grond state corresponds to a single geometric structure which, in this case, is aromatic-like. A quinoid-like resonance structure can be envisioned but has a higher total energy (Figure 2.10). The quinoid structure has a larger electron affinity than the aromatic structure. This explains why, on doping, the chain geometry in these compounds relaxes locally around the charge toward the quinoid structure [13].

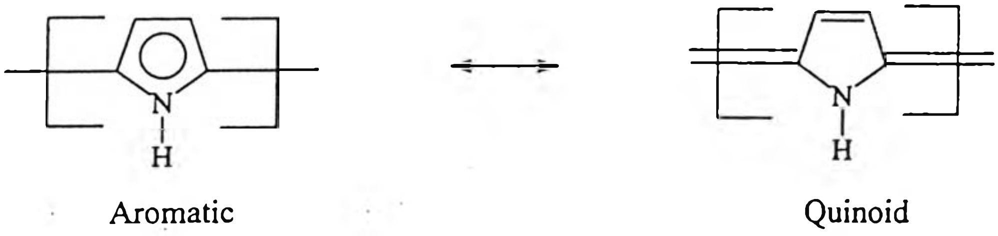


Figure 2.10 Aromatic (ground-state) and quinoid-like geometric structure for polypyrrole.

In summary, by polarons and bipolarons is now thought to be the dominant mechanism of charge transport in polymers. These concepts was dependent on the doping of these polymers, which its data demonstrate that:

(i) Polarons are formed on the chains at low oxidation level (slightly doped polymer),

(ii) At higher oxidation level, plarons combine to from spinless bipolaron (heavily doped polymer),

(iii) Wide bipolaron band are present in the gap in the highly conducting require (heavily doped polymer).

However, it should be emphasized that these models were device assuming ideal structure. The actual structure of most conductive polymers, both in the doped and undoped state, are unknown and all data show that certain polymers have a large number of defects. It shown in Figure 2.11 [14].

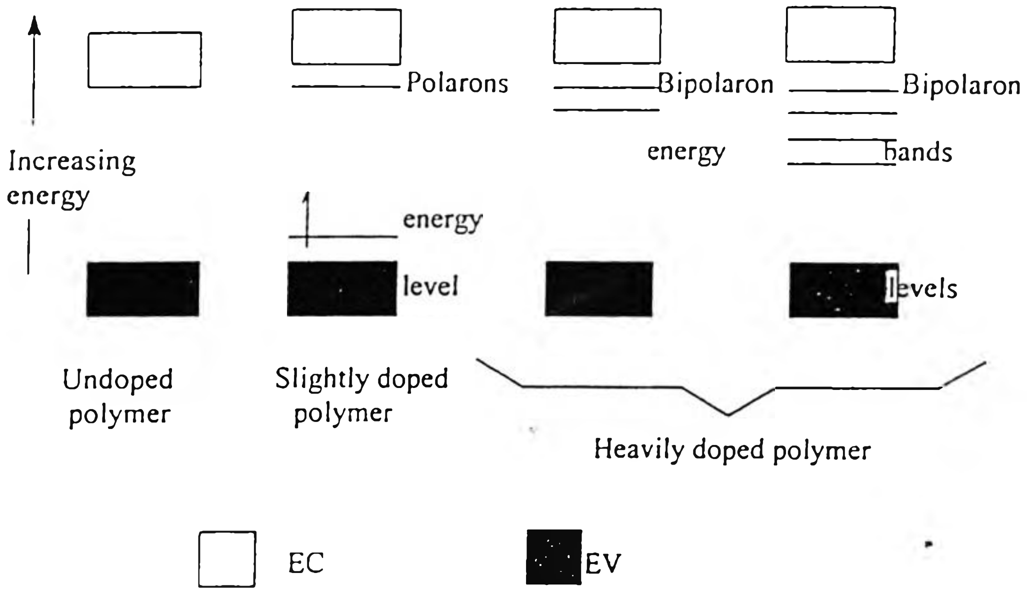


Figure 2.11 The band structure of a polymeric chain in case of polaron energy levels and bipolaron energy levels

2.2.2 The production of conducting polymers.

The field of synthetic metals remains an active area for fundamental research in experimental and theoretical solid-state physics as well as organic and polymer synthetic chemistry. The variety of new conducting polymeric solid have been continuously discovered. The area of synthesis is extremely fast moving and competitive.

Here, they summarize the major types of synthetic techniques used to prepare polypyrrole:

(1) Electrochemical polymerization
(2) Chemical polymerization
(3) Chemical vapor deposition polymerization

(1) Electrochemical polymerization **[15,16]**.

Passage of current thought a solution results in the loss of electrons, and compounds are oxidized at the anode. Electrons are gained and compounds reduced at the cathode. This process is referred to as electrochemical polymerization of pyrrole in a solvent such as acetonitrile, tetrafluoroborate or lithium perchlorate is present, and polymerization is carried out either at constant voltage or constant current.

The mechanism for polymerization involves oxidation of polypyrrole at the ∝-position to form a radical-cation (I) which undergoes radical coupling to yield the dimer dication (II). The latter loses two protons to yield the dimer (III). The dimer repeats the same reaction sequence-loss of an electron to form a dimer radical-cation, coupling with itself and (I) to form the tetramer-dication and trimer-cation, respectively, followed by two potrons less to yield tetramer and trimer. Propagation to polymer proceeds via repetition of the same sequence, one electron loss, coupling of difficulty-sized radical-cations, depotronation. This polymerization mechanism bears considerable resemblance to that for the oxidative polymerization of 2,6-disubstituted phenols.

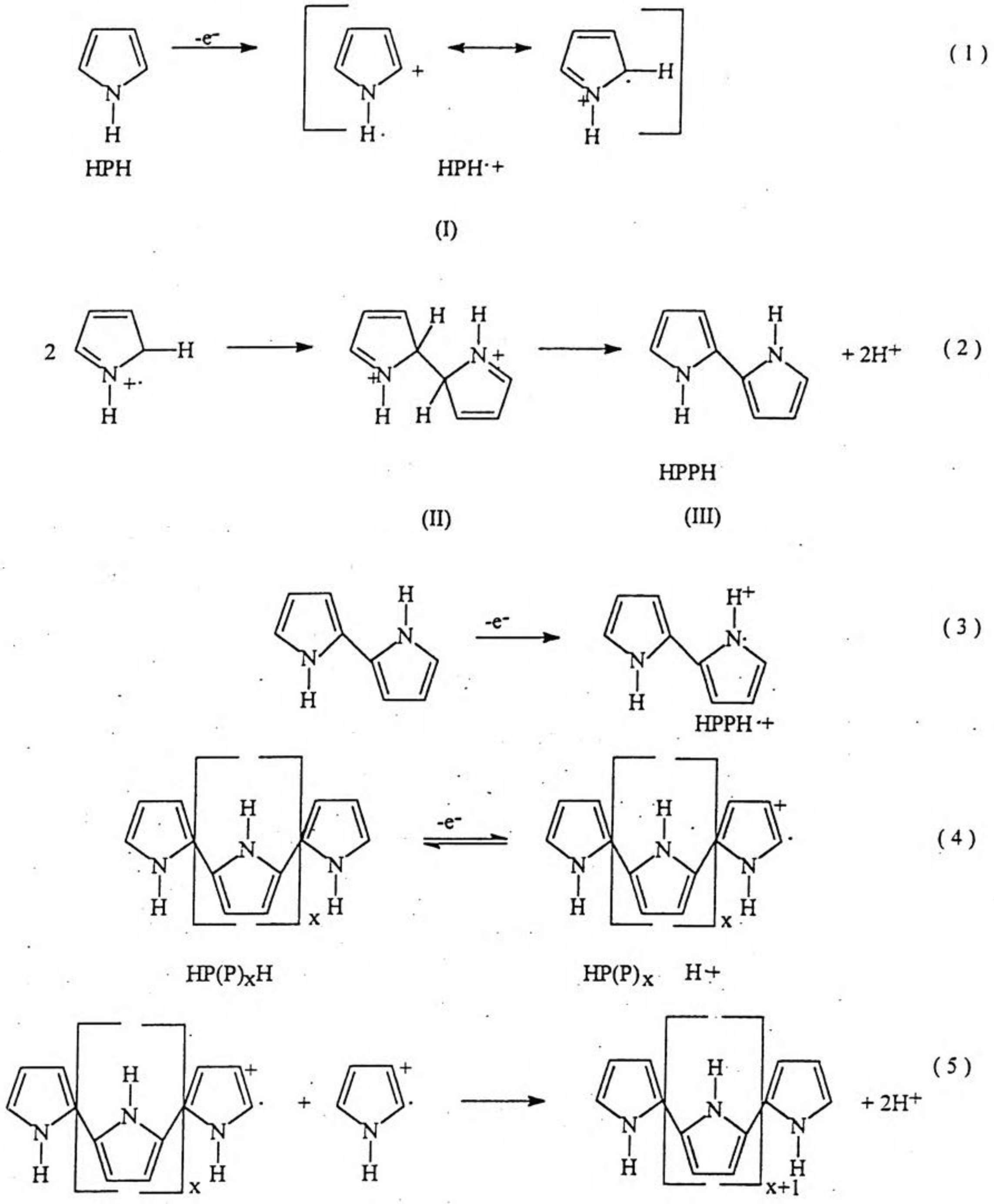
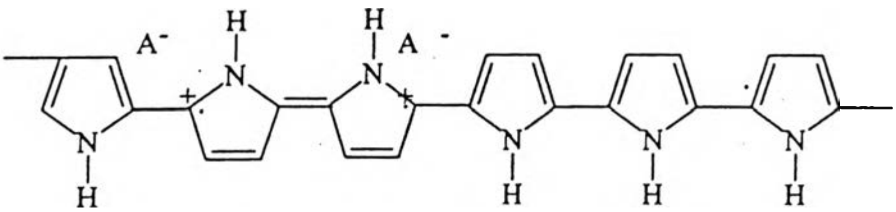


Figure 2.12 Polymerization mechanism bears considerable resemblance to that for the oxidative polymerization of 2,6-disubstituted phenols.

Electrochemical polymerization, as usually carried out, does not yield the neutral, nonconducting polypyrrole shown in Equation (4) but the oxidized (doped), conducting form, (one can cycle back and forth between the conducting forms, colored black and light yellow, respectively, by reversing polarity). The doped polymer would have a structure such as (IV),



(IV)

Figure 2.13 The structure of doped polymer

where A⁻ is the anion of the electrolyte. The doped polymer precipitates out and coats the surface of the anode during polymerization. The polymerization reaction and polymer properties (conductivity and mechanical strength) are dependent on such parameters as identity and concentration of electrolyte, reaction temperature, and current density.

(2) Chemical polymerization in solution [17].

The synthesis of conducting polymer via chemical method is less polymer, even though this method allowed a simple preparation of large quantities, more covenant and economical. The majority of the chemical synthesis method involves the polymerization and oxidation with oxidative transition metal ions, for example $FeCl_3$, $AgNO_3$, $Cu(NO_3)_2$, $AlCl_3$ and more. The use of other oxidants such as acid, halogens and organic electron acceptors have also been reported. Considerable chemical compositions and reaction stoichiometries for polypyrrole complexes were synthesized from $FeCl_3$, base on the observed chemical compositions of the complex, particularly the [Cl]/[N] ratio. At present time two reaction stoichiometries have been proposed.

$$4\,C_4H_5N + 9\,FeCl_3 \longrightarrow [(C_4H_5N)_4{}^{+}Cl^{-}] + 8\,HCl + 9\,FeCl_2$$

and

$$n\,C_4H_5N + 2.33\,n\,FeCl_3 \longrightarrow [(C_4H_5N + 0.33\,Cl^{-}]_n + 2.33nFeCl_2 + 2n\,HCl$$

Figure 2.14 Two reaction stoichiometries

Recently, polypyrrole obtained from chemical polymerization in solution can exhibit very high electrical conductivity when a suitable solvent is selected and the oxidation potential in the solution is controlled.

(3) Chemical vapor deposition (CVD) **[13]**.

In 1987, Takeaki Ojio and Seizo Miyata synthesized the conducting composite films of polypyrrole, which can be prepared by exposing polymeric matrix films containing $FeCl_3$ to pyrrole vapor. The composite films are, morever, highly transparent under the appropriate preparation condition. In that communication, the conductivity and the transparency of polypyrrole composite films by the gas state polymerization was discussed.

Poly(vinyl alcohol) was used as a polymeric matrix. $FeCl_3$ was an oxidizing agent for the polymerization. After dissolving PVA and $FeCl_3$ in the water, the solution was casted on a poly(ethylene teraphthalate) film substrate. The preparation of polypyrrole-PVA composite films was carried out in a desiccator at -15°C by exposing PVA films containing $FeCl_3$ on the PET film to the pyrrole and H_2O vapors which had been deoxygented sufficiently. The polymerization period was then dried under vacuum at room temperature. At optimum condition, the composite film shows about 10 S/cm conductivity.

2.2.3 General considerations of CVD **[13,18-21]**.

(1) Comparisons of CVD with other methods.

Polypyrrole can be prepared by either electrochemical or chemical oxidative means. Broadly, the chemical oxidative polymerization can occur via three mode:

(i) In a homogeneous solution

(ii) At an interphase of two immisible solutions

(iii)In the vapor phase

The properties of the polypyrrole, e.g. conductivity, strength and morphology, obtained are very dependent on the conditions and modes of polymerization. Various types of oxidizing agents have been used for chemical polymerization, e.g. copper(ll), silver(l) and iron(lll). Among them, $FeCl_3$ has been the most extensively used oxidizing agent. When pyrrole is in contact with an oxidant in the liquid phase, a dark, messy solution is formed and a great quantity of waste is generated. This problem may be resolved by vapor-phase polymerization, an area that has been rather neglected.

In vapor-phase polymerization, when a substrate precoated with an oxidant is exposed to pyrrole vapor, polypyrrole will be deposited on the substrate. In comparison with electrochemical polymerization, the vapor-phase and interphase chemical polymerization do not restrict the area of the film, this being a limitation due to the size of the electrode. Morever, uniformnity of the electrochemically prepared polypyrrole film is difficult to achieve.

(2) The factors on conductivity polymers by CVD.

The electrical conductivity of conducting polymers by CVD are dependent on various parameters as follows:

(i) $FeCl_3$ concentration in water

(ii) Pyrrole monomer concentration in water

(iii) Reaction temperature

(iv) Reaction time

In this study, the parameters show above mention are investigated, and polymer matrix are excepted. Furthermore, effects of iodine dopant upon electrical conductivity of prepared conductivity plastics.

2.3 Electrical conductivity measurement by van der Pauw method [22,23].

Van der Pauw method is a technique for measuring conductivity(σ) of samples which have constant thickness but arbitrary shape. First, four ohms contacts are made at edge of sample (Figure 2.15). (Then, the suitable current (I_{12}) was applied through contacts 1 and 2 and measured potential different (V_{34}) between contacts 3 and 4 and find ratio)

$$R_1 = [V_{34}] / I_{12}$$

Second, I_{23} is applied though contacts 2 and 3 and potential different, V_{41}, is measured thus obtain

$$R_2 = [V_{41}] / I_{23}$$

From these, the conductivity of the sample can be calculated from equation (2.1)

$$\exp(-\pi R_1 d\sigma) + \exp(-\pi R_2 d\sigma) = 1 \qquad \text{---------(2.1)}$$

When d is the thickness of the sample.

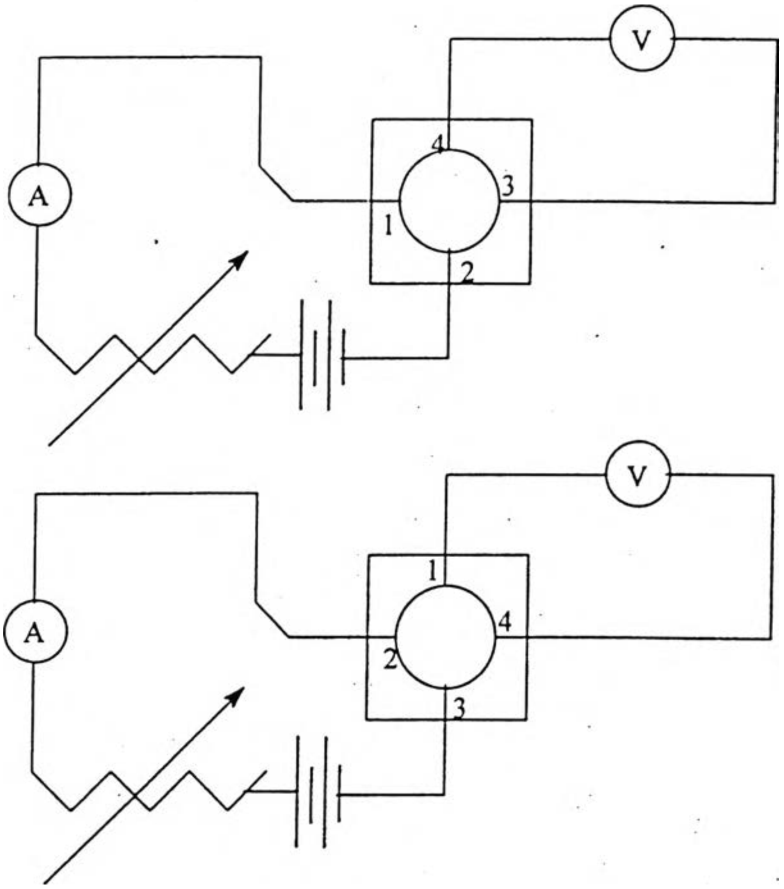


Figure 2.15 Conductivity measurement by van der Pauw method.

In principle, we can change the current electrodes around, get I_{12}, I_{34}, I_{41} and corresponding potential difference V_{34}, V_{41}, V_{12}, V_{23}, respectively. Then calculate σ_1, σ_2, σ_3, and σ_4 from equation (2.1) as show in Table 2.2. Finally obtain more accurate conductivity, equation (2.2)

Table 2.2 Various points for applied current.

σ_n	R_1		R_2	
	I	V	I	V
σ_1	I_{12}	V_{34}	I_{23}	I_{41}
σ_2	I_{23}	V_{41}	I_{34}	V_{12}
σ_3	I_{34}	V_{12}	I_{41}	V_{23}
σ_4	I_{41}	V_{23}	I_{12}	V_{34}

$$\sigma = (\sigma_1+\sigma_2+\sigma_3+\sigma_4) / 4 \qquad \text{---------(2.2)}$$

σ = average conductivity

The main problem in accurate measurement is the contact resistance between the measurement electrodes and the sample. Contact resistance may be reduced by painting electrodes directly onto the surface of the sample instead of relying on pressure contact with metal plates or foils. Suitable paints are silver dispersions or Aquadag (an aqueous dispersion of colloidal graphite)

The accuracy of conductivity measurement by van der Pauw method depends on the following conditions:

(i) Size electrical contact points at edge of the sample should be very small compared with the circumference of the sample.
(ii) Sample must have constant density, regular mass and thickness.
(iii) Sample must have no broken parts.
(iv) In the case of disc sample, separation distance between each contact should be approximately the same.

2.4 Literature survey.

Takeaki Ojio and Seizo Miyata **[13]** had been found that the conducting composite film of polypyrrole can be simply prepared by exposing polymeric matrix films containing ferric chloride to pyrrole vapor. Their composite films are, moreover, highly transparent under the appropriate conditions. Poly(vinyl alcohol) was used as a polymeric matrix. $FeCl_3$ was an oxidizing agent for the polymerization. After dissolving PVA and $FeCl_3$ in the water, the solution was casted on a poly(ethylene teraphthalate) film substrate.

The preparation of polypyrrole-PVA composite films was carried out in a desiccator at -15°C by exposing PVA films containing $FeCl_3$ on the PET film to the pyrrole and H_2O vapor which had been deoxygenated sufficiently. The polymerization period was then dried under vacuum at room temperature. At optimum condition, the composite film shown about 10 S/cm conductivity.

Marco-A De Paoli et. al [4] were prepared an electrically conductive plastic composite derived from polypyrrole and PVC by the electrochemical polymerization of pyrrole in a PVC matrix. The transmission electron microscopy shows that polypyrrole is uniformly distributed in the matrix. The conductivity of the composites fall in the range of 5-50 S/cm, and their mechanical properties, as measured in a stress-strain test, are very similar to those of pure PVC. These can be further improved by addition of poly(chloroprene) rubber as plasticizer.

Swee Ngin Tan and Hailin Ge [24] investigated the vapor-phase chemical polymerization of pyrrole in which a cotton thread coated with $FeCl_3$ oxidant was exposed to pyrrole vapor and electrical resistance of this conductive polypyrrole supported on cotton thread was measured using a specially designed four-point probe. In this work, they reported a systematic study of the vapor-phase chemical polymerization process of the pyrrole using $FeCl_3$ as the oxidant. They explosed the possibility of using cotton thread, another kind of cellulose materials that was widely available, as the support for the PPY under vapor-phase chemical polymerization. Moreover, the cotton thread has a well defined dimension, which is easily fabricated into various fixed lengths compared to using cotton fabric or filter paper, which would involved a more laborious fabrication process. They investigated the effects of the following factors, i.e. solvents, reaction time, pyrrole monomer and initiator concentrations, and temperature, on the process of vapor-phase chemical polymerization of pyrrole. It was found that the vapor-phase polymerization was a fast reaction. The resistance decreased with an increasing concentration of $FeCl_3$ and polymerization temperature. The presence of some solvents such as water, hexane and toluene in the vapor-phase did not after the polymerization process. However, some solvents such as methanol and acetone were found to be unsuitable for this process.

Kotaro Ogura et.al [6] prepared the electrically conducting PVC/PPY by photo-dehydrochlorination of prepared composite film. PPY was deposited electrochemically on a platinum plate from a nitric acid solution of pyrrole. The PVC/PPY composite film was finally obtained by casting poly(vinyl chloride) (PVC) onto the PPY electrode from a tetrahydrofuran solution of PVC. Figure 2.16 show the composite film under the irradiation of UV light, the prepared composite film was irradiated at 90°C with a low-pressure mercury lamp in the stream of hydrogen gas saturated with steam, and the PVC film was dehydrochlorinated, leading to the formation of conjugated polyene as following Figure 2.17. The electrical conductivity (σ) of PVC film in the irradiated composite film was revealed $2.5x10^{-5}$ S/cm. By iodine doping, σ was further enchanced up to $5.04x10^{-3}$ S/cm, as following in Table 2.3. The tensile strength of the irradiated composite film became larger than that of the original PVC film; i.e., the stress at break was: 461 (composite film): 401 kg/cm^2 (PVC). These results were brought about by the electrodeposition of PPY was photodecomposed to generate radical NO_2 and this species was doped to the polyene, resulting in the formation of electrically conductive PVC and mechanically improved composite film.

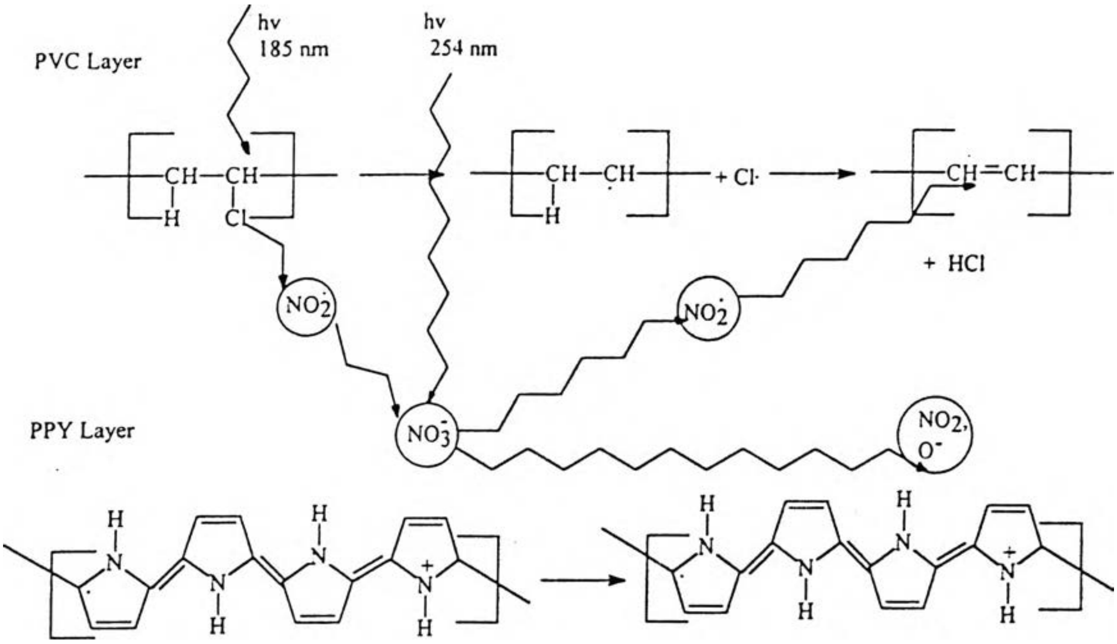


Figure 2.16 Schematic representation of the composite film under the irradiation of UV light.

Table 2.3 Electrical conductivity of the PVC in the Irradiated and Unirradiated Composite Films as a Function of Doping Time of Iodine[a]

Run	Sample	Irradiation Time (min)	Doping Time (min)	Conductivity (S/cm)
1	PVC[b]	120	0	$< 10^{-10}$
2	PVC/PPY	0	0	$< 10^{-10}$
3	PVC/PPY	0	30	$< 10^{-10}$
4	PVC/PPY	120	0	2.51×10^{-5}
5	PVC/PPY	120	10	8.48×10^{-4}
6	PVC/PPY	120	30	5.04×10^{-3}
7	PVC/PPY[c]	120	0	$< 10^{-10}$

[a] The film thickness of PVC was 2.9 μm,and that of PPY was 0.2 μm. The electical conductivity of the PVC film was measured by both the four-and two -probe methods.

[b] Original PVC film.

[c] The PPY film was electro-deposited from the HCl solution.

Bhat, N.V. and Yasmin, S.[5] prepared electrode in rechargeable batteries from cellophone and polypyrrole. They have used the interface technique for the preparation of conducting polymeric composites from cellophone plus polypyrrole [cello+PPY]. Cello has good mechanical properties and impacts flexibility and strength to the composites; PPY was electrically conducting and stable and makes the composite highly conducting and stable to ambient conditions. The conductivity of the composite was studies as a function of percentage content of PPY in the temperature range of 30-90°C. Besides the conduction mechanism, mechanical properties like tensile strength and percentage elongation of these composite were tested and these conductive composite were used as electrodes in rechargeable batteries using aqueous electrolytes.

Haddadi-AsL, V. et.al [25] studied in carbon-polymer composite electrodes for redox cells. Conductive polymer composite materials were fabricated by mixing PVC, nylon 6, nylon 11, LDPE, and HDPE with conductive fillers. To overcome the deterioration in the mechanical properties of carbon-polymer composites with high carbon loading, a range of chemically resistant rubbers was blended into the composites. Electrical, mechanical, permeation, and electrochemical studies show that the HDPE composite is the best electrode matrix material for the vanadium redox battery. The performance of a vanadium redox flow cell employing the best composite electrode was also evaluated and voltage efficiencies as high as 88% were obtained with electrodes employing graphite felt active layers bounded to the carbon-polymer composite substrates. Other applications of important conducting polymer are shown in Table 1.1[3].