PHYSICO-CHEMICAL STUDIES ON CONDUCTING POLYMERS

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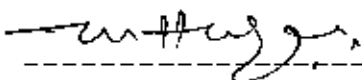
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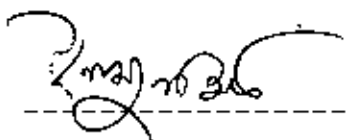   Department of Chemistry
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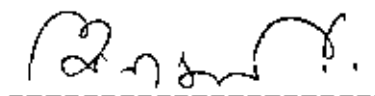   BUET, Dhaka.

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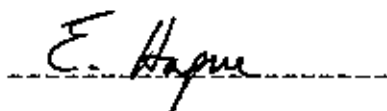   BUET, Dhaka.

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Certified that the work incorporated in this thesis PHYSICO-CHEMICAL STUDIES ON CONDUCTING POLYMERS submitted by Mr. Golam Haider has been carried out by the candidate under our supervision. The work embodied in this thesis is original and we declare that it has not been submitted in part or in full for any degree or diploma of any other university.

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ABSTRACT

The elemental analysis of polyaniline synthesized in this study supports the emperical formula of polyaniline as : $(C_6H_4NH)_4$ 2 HSO_4. The mechanism of polymerisation inferred that one anion (HSO_4^-) is substituted for every two phenyl rings.

In the infrared spectra of polyaniline, a strong absorption band at around 480 cm^{-1}, gives an evidence of 1, 2, 4- substituted aromatic ring. This indicates the bonding in polymer is through 1, 4- position of benzene ring.

From the scanning electron micrograph of polyaniline at 25°C and at a current density of 5mA/cm^2 exhibits grain like morphology. The average bundle size of the grains of polyaniline increases with the increase of current density. Also, with the change of polymerization temperature there is a dramatic change in morphology of polyaniline. The grains take microspherical morphology for polyaniline prepared at 25°C temperature have been changed to a fibrillar one when synthesis is carried out at 9°C.

The electrical conductivities of both the polymers (polyaniline and poly o-toluidine) synthesized at differenct temperature and different current density increases with the decrease of temperature and the maximum condictivity is observed at 9°C. The highest electrical conductivity is also observed in both the polymer prepared at the current density of 10 mA/cm^2.

In the case of uv-visible spectra of the polymers synthesied at a current density of 10 mA/cm^2 shows the smaller band gap energy than that synthesized at 5 and 15 mA/cm^2. It is also observed that the absorption band appears always at lower energy in the case of polyaniline than that of poly o-toluidine.

In the X-ray diffraction patterns, the peaks are broad and diffused for the polymers synthesized at 5 mA/cm^2. The peaks become sharper as deposition current density increases. In case of poly o-toluidine the existance of the broad diffuse peak indicates amorphous nature deposited at room temperature and current density ranging from 5 to15 mA/cm^2. It is also found for both for polyaniline and poly o-toluidine, that lower deposition temperature results in sharper of diffraction peaks suggesting more crystallinity. Although in case of polyaniline, increased deposition current density increased crystallinity, this is not so evident for poly o-toluidine.

From TGA curves, by applying the Sharp-Wentworth method, it is found that both the polyaniline and poly o-toluidine have higher activation energy (E_a) synthesised at intermediate current density viz. 10 mA/cm^2. It is further seen that the activation energy of polyaniline is always higher than that of poly o-toluidine. Activation energy calculated from TGA curves further show that polyaniline deposited at current density of 10 mA/cm^2 possesses the highest thermal stability in air.

CONTENTS

1.1. General Introduction :

From the ancient period metals are being used as the materials of tools, utensils, weapons etc. With the development of civilization peoples are using metals as the construction and engineering materials. But because of limited resource and for specific properties peoples had to look for the alternative materials. As the substitute of metal, polymers have made an enormous impact in the tweentieth century. The ever increasing applications of artificial fibres, plastics, elastomers etc., have rendered man more dependent on molecular materials. The greater workability, lighter weight and economy have made the polymer more advantageous over metals.

However, there is an important fundamental difference in the properties of metal and polymer which distinguishes metals from the polymers. Most of the metals are heavy (except a few), electrically and thermally conductive. On the otherhand, polymers are in general lighter substances and are electrical and thermal insulators. The electrical conductivity of metals lies in the range of 10^4 to 10^6 Ω^{-1} cm^{-1} while that of organic polymers is around 10^{-14} Ω^{-1} cm^{-1}. Generally polymers including plastics, rubbers and synthetic fibres are regarded as insulators because of the intrinsic property of carbon-carbon covalent bonds. PVC, natural as well as synthetic rubbers etc., therefore, were used as insulating sheath and polyester polyamides, polyimides etc. were used as insulating enamel or varnish for copper or aluminium cables.

Common organic polymers generally consists of carbon atoms covalently bonded to each other forming long chain molecules. Polymer chains depending on

the arrangements of atoms may be linear, branched or net work structure as shown in Fig. 1.1, given below :

(a)   (b)

(c)   (d)
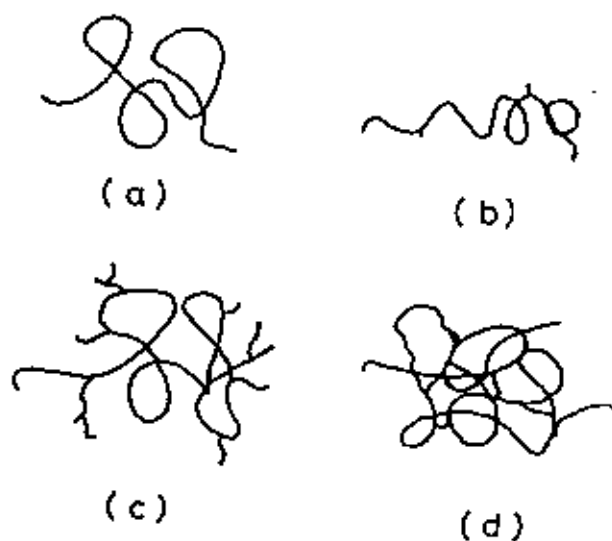
Fig. 1.1. Schematic structures of various types of polyethylene :

(a)   Linear (high density) polyethylene (HDPE).

(b)   Linear low density polyethylene (LLDPE)

(c)   Branched (low density) polyethylene (LDPE) and

(d)   Crosslinked polyethylene (XLPE).

LLDPE is essentially linear having a few short branches while LDPE is highly branched having both short and long branches. Linear structure ensures close packing of long polymer chains making HDPE more dense density 0.96 gm/cm^2 and mechanically stronger and thermally more resistant against the density 0.92 - 0.93 gm /cm^2 and mp 110 − 112°C of LDPE. By crosslinking both the mechanical and thermal properties are increased. Some polymer chain may also contain other than

carbon and hydrogen atom, heteroatoms like oxygen, nitrogen and sulphur in the branches as well as in the back bone. These polymers resist the flow of electric charge carriers through the chain. These polymers usually consists of well separated molecules within a given class of materials, the conductivity is usually enhanced if the size of the molecule is increased. But this was not sufficient to guarantee a reasonable conduction. Practically the question of producing macromolecular materials which exhibit a conductivity similar to that of metals has long been posed. The importance of this question lies in the significance of being able to process such material in the forms of film, foils or fibres according to the standard procedures of plastics industry. So that they can act as a substitute for metals.

One of the early approaches to make polymer conducting is to prepare a composite of polymer using conducting filler, such as metal powder, flake or wire, graphite powder etc[1-3]. Conductive fillers remain embedded more or less evenly dispersed in the polymer matrix and conduct electric current. For example, nickel and copper powders were mixed with polyethylene, PVC and polymethyl-methacrylate powder[4-6]. The weight fraction of metallic powder in the field plastics may be as high as 20% or even higher. Kusy and Turner[4] and latter Bhattacharya et al.[6] reported the use of 6 to 10% metallic powder for comparable conductivity. They proposed that the enhanced conductivity at comparatively lower loading metallic powder is due to formation of hexagonal ring structure of metal powder under optimum condition in the polymer matrix[5,6]. The conductivity of these charged polymers varies with the function of the charge incorporated in the polymers and for charges upto 20% by weight of polymers, it ranges between 10^{-6} to $10^{-1}\Omega^{-1}$ cm^{-1}. The concentration of these charges is usually not increased beyond this limit because after that the charged polymer loses their mechanical properties and becomes less useful.

Some charge transfer molecular complexes exhibit enhanced conductivity. This is owing to the unique structure of these complexes in the form of parallel stacks of molecules having very high degrees of intermolecular overlap giving rise to an electronic conduction band along the stack (Fig. 1.2).
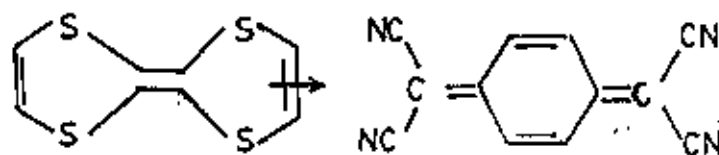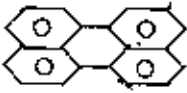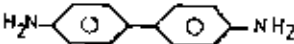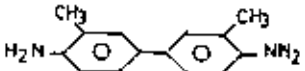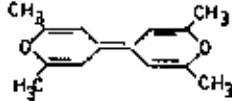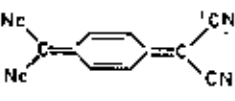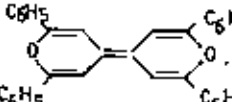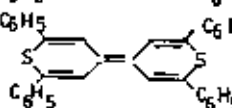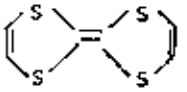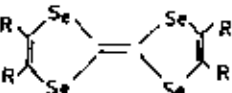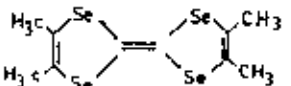
Fig. 1.2 TTF - TCNQ Complex

Examples of such complexes are : Tetrathiafulvalene (TTF) or tetramethyltetra-seleniumfulvalene (TMTSF) and Tetracyanoquinodinethane (TCNQ) etc.. These molecules form 1:1 donor acceptor complex having the room temperature conductivity of 500 Scm^{-1} or even higher [7,8]. Table 1(a) represents the conductivity of some donor acceptor complexes of AsF_5, PF_5, BF_3 etc. also form salt with TMTSF. Some of them [e.g. $(TMTSF)_2 PF_6$] show superconductivity at 9K under a pressure of 12 kbar[7].

Table 1.a. Electrical conductivity of donor acceptor complex at room temperature.

Donor	Acceptor	Donor/Acceptor Stoichiometry	Conductivity $S cm^{-1}$
Penylene	Iodine	1:3	0-1
H_2N — O — O — NH_2	Iodine	1:2 5	0-45
CH_3 / CH_3 H_2N — O — O — NH_2	Iodine	1:25	0-034
CH_3 CH_3 O O H_3C CH_3	(TCNQ)	1:1	10^{-6}
C_6H_5 C_6H_5 O O C_6H_5 C_6H_5	TCNQ	1:1	1-7
C_6H_5 C_6H_5 S S C_6H_5 C_6H_5	TCNQ	1:1	38
(TTF)	TCNQ	1:1	500
R Se Se R / R Se Se R, R=H or CH_3	TCNQ	1:1	800
H_3C Se Se CH_3 / H_3C Se Se CH_3 (TMTSF)	PF_5 or $As F_5$ or $Sb F_5$ or BF_3	2:1	500–800

Encouraged by these results attempts were made to synthesize conducting polymers by incorporating such donor acceptor complexes in the polymer chain. But such attempts were not successful.

Despite numerous and concerted attempts specially by preparative chemists, it was not until very recently that the production of macromolecular materials whose conductivity and conductivity characteristics were same or closely similar to those of metal was possible. From the monographs[8-11] and review articles[12-14] it can be gleaned that ideas concerning the relationships between the molecular structure and the structure and electrical properties of macromolecular solids have not been fully developed. However, a considerable amounts of work have been done in this area.

1.2. Historical Background to the Development of Conducting Polymer :

From the begining of 1950s peoples are trying to manufacture conducting polymer because of their wider and advantageous applicability over metals. In 1950s plastic manufacturers succeeded in making polymers having electrical conductivity by incorporating conducting charges, metal powders, metal fibres or carbon black in a conventional polymer acting as host matrix. But these matrix cannot be regarded as conducting polymers because the polymers present in such composites are nonconducting.

Although the syntheis of polyacetylene (PA) using Zieglar catalyst was first reported by Natta et al.[15] But paractically synthesis of PA in its conducting form was reported by Hatano et al.[16] Hatano and his co-workers prepared high molecular weight PA with both crystalline and amorphous variety by using various Zieglar Natta catalyst. They reported that crystalline form of PA was a conducting polymer and its electrical conductivity decreases abruptly almost by five orders and its colour also changed from greenish black to pale yellow. This is due to gradual oxidation of PA by air. It was assumed that previously Natta obtained only the amorphous form of PA which was electrically insulator.

Real interest in conducting polymers arose after the work of Walatka et al.[17] on polysulphurnitride (SN)$_x$. Although (SN)$_x$ was first reported by Burt[18], its exciting metallic conductivity was discovered only by Walatka[17]. Work on (SN)$_x$ was further stimulated by the observation that it behaves as superconductor at- 272. 76°C[19]. Despite of its metallic conductivity (SN)$_x$ (known as synthetic metal) could not find wider use due to its extreme reactivity.

Shirakawa et al.[20-22] prepared two types of PA using Zieglar - Natta catalyst. The colour of these two types of PA was completely different. The copper coloured was found to be trans– PA and the silver coloured was found to be cis– PA. The electrical conductivity of trans– PA and cis– PA was found 4.4 × 10^{-1} S cm^{-1} and 1.7 × 10^{-9} S cm^{-1} respectively[23]. But when these polymer are exposed to vapours of bromine and chlorine at room temperature a dramatic change in their IR spectra occured without any visible change in their appearance[24]. However, there is no report that these workers measured the conductivity of these PA films after the exposure to the vapours of bromine and chlorine. But latter Shirakawa et al.[14,24] have reported that PA exhibited dramatic increase in conductivity on treatment with strong oxidizing and reducing agents.

These reports provide a base for the research in conducting polymers. Diaz et al.[25] have reported on a new route to conducting polymers by electrochemical synthesis of polyaniline and polypyrrole. Conducting polyparaphenylene (PPP) was reported[26] followed by conducting poly phenylene sulphide (PPS)[28]. Now a days these are considered as the basic conducting polymers.

The chemical structure of these conducting polymer are shown in Fig. 1.3.

Poly acetylene

Poly aniline

Poly (P-Phenylene) (PPP)

Poly (P Phenylene Sulphide) (PPS)

Poly Pyrrole (PPY)

Poly thiophene (PTP)
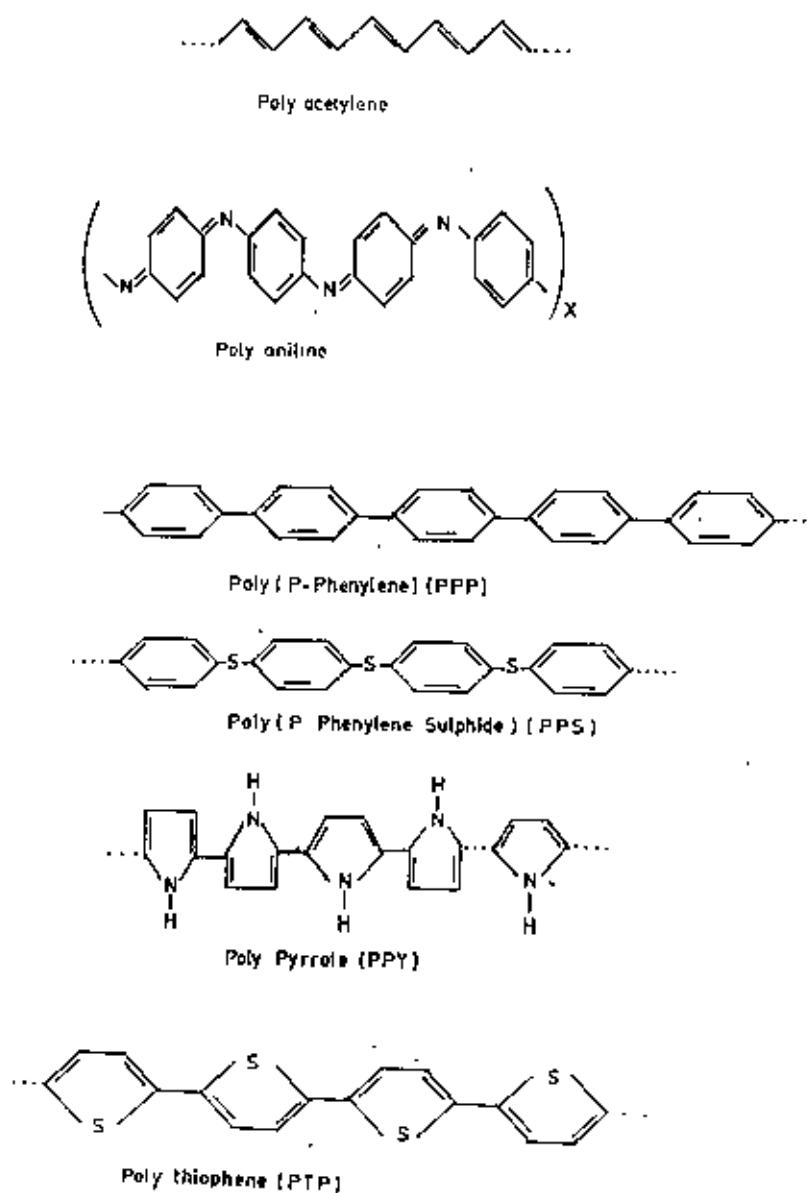
Fig. 1.3 Chemical structure of some important conducting polymers.

The chronology of the development of work on conducting polymer is shown in Table. 1.b.

(SN)$_X$ Synthesized by Burt[18] ⟶ | 1910 |

| | 1973 | ⟵ Metallic conductivity of (SN)x reported by Walatka et al.[17]

Semiconducting polyacetylene | 1971 |

discovered by Shirakawa et al.[20-22] ⟶ | 1974 |

| | 1977 | ⟵ Doping of poly acetylene by Shirakawa et al.[14,24]

Electrochemical synthesis of poly pyrrole by Diaz et al.[25] ⟶ | 1979 |

Conducting poly para phenylene by Ivory et al.[26] ⟶ | 1979 |

| | 1980 | ⟵ Conducting poly para phenylene sulphide by Rabolt et al.[28]

Conducting polyaniline Mac Diarmid et al.[29,30] ⟶ | 1986 |

| | 1989 | Poly ethynyl sulphide by Maiti et al.[31]

Poly (paraphenyl acetylinic phosphine) Maiti et al.[32] ⟶ | 1989 |

| | 1991 | ⟵ Conducting polyaniline by Mac Diarmid et al.[29,30,34], Gupta et al.[35-38]

Table. 1.b. Chronology of development of conducting polymer.

The new insights into conducting polymer introduced by Shirakawa et al. in 1977. In their work they demonstrated for the first time that PA is a semiconductor with a large band gap. It exhibits a dramatic increase in specific conductivity if it is treated with strong oxidizing and reducing agent[14,24,27]. When a thin film of cis-polyacetylene obtained by polymerization of acetylene on the surface of a solution

of suitable catalysts in an inert solvent was treated with iodine, bromine, AsF_5 or sodium naphthalide, its conductivity increased from an initial value of approximately $10^{-9} \Omega^{-1}$ cm^{-1} to approximately $5.10^2 \Omega^{-1}$ cm^{-1}.

1.3. Nature of Bonding and Conductivity :

The nature of bonds within the materials plays an important role on the conductivity of the material. Metals are highly conductive. Bonding of metal atoms is neither covalent nor ionic. The metal atoms are held in their crystal lattice by a special type of bonding known as metallic bonds. Lorentz[39] has suggested a theory of metals in which a metal is regarded as a crystalline arrangement of hard spheres (the metal cations) with free electrons moving through the interstices of the crystal lattice. These free electrons act as the charge carriers for electrical conduction of metals. Valence electrons in normal covalent molecules are all shared between two bonding atoms and held tightly. These localised tightly held electrons are not available as the charge carriers for electrical conduction.

However, the $\pi-$ electrons of carbon-carbon double or triple bonds are relatively free compared to σ electrons. In conjugated double bond systems in an organic molecules delocalization of $\pi-$ electrons is possible through the interaction of neighbouring π electrons. Thus, in a completely conjugated system, the delocalization can make the $\pi-$ electrons freely mobile over the entire length of the molecule. Little[40] has postulated that polyacetylene exhibits superconductivity. The support for this theory of augmentation of electrical conductivity by delocalization of electrons was received from the examples of graphite. All the carbon atoms in graphite are sp^2 hybridised and exist in planar hexagonal structures (Fig. 1.4). Remaining single electron of each carbon atom exists in the delocalized state. It can move freely over that plane making graphite electrically conducting to a level of metals.
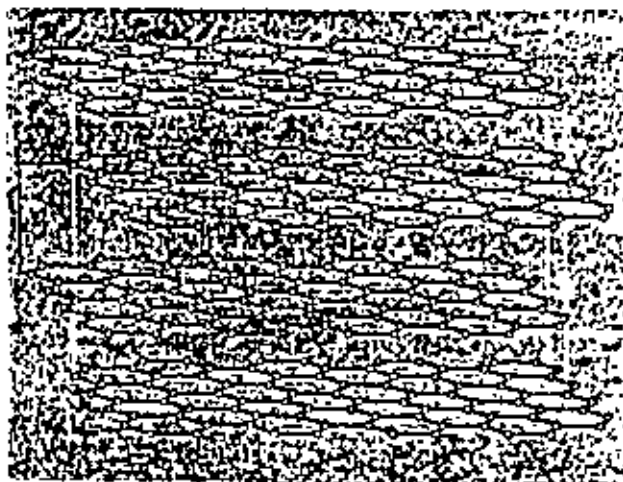
Fig. 1.4. Structure of graphite molecules.

From the above stated theory it is clear that for electrical conductivity there must be delocalized or freely mobile electrons in the molecules.

1.4 Conducting Properties of Organic Polymers :

The electrical properties of materials are described by four categories: insulators, semiconductors, semimetals and metals. The boundaries between categories are somewhat arbitrary and are defined using either the resistivity (Ω cm) or the conductivity (Ω^{-1} cm^{-1} or Scm^{-1}) of the materials. The insulators have conductivity's below 10^{-7} Scm^{-1}, semiconductors span 10^{-7} to 10^{2} Scm^{-1} and the metals have conductivity above 10^{2} Scm^{-1}. The extreme conductivity's are of the order of 10^{-8} Scm^{-1} for insulator such as ordinary organic polymers e.g., rubber, plastics etc. and 10^{6} S cm^{-1} for metals e.g., silver, copper etc.

The conductivity of a material depends on its electronic energy level structure. When atoms or molecules are assembled to make a crystalline solid, the degenerate energy level produced spread to form non degenerate energy bands. The width of these bands reflect the strength of interactions between the individual atoms or molecules. The wave functions describing electrons in these band states extend throughout the solid. For a current to flow the applied electrical field must impart kinetic energy to electrons by promoting them to higher energy band states. For reasonable field strength this requires a small gap between filled and empty states, e.g., a partially filled band. The level of conductivity is dependant on the density of available and empty states.

In insulators, there is an energy gap of several electron volts (eV) between the highest field electronic state in the valency band and the lowest empty state in the conduction band. Thus the empty state are inaccessible by either electric field or thermal excitation. semiconductors have energy gaps of less than about 2eV at which point thermal excitation across the gap is possible. True metallic behaviour results when the energy gap between filled and empty states disappears. Applied field can then cause current flow even at a very low temperatures. Thus, the conductivity of semiconductors falls at low temperatures as thermal excitation is quenched, while that of metals increases, as the thermal motion of the lattice and scattering process are reduced. In Semi-metals the density of electronic states in the vicinity of the highest filled level, the Fermi level (E_F) is very low and so is the conductivity. For good conductors, such as copper, the density of electronic states at E_F is high.

The conductivity of polymer span values from insulating to metallic regimes. Applying the band model to polymers with saturated chemical structures. Here all the valency electrons form strongly localised chemical bonds and the energy gap is

large e.g. polyethylene (PE) has a gap of 8eV. For polymers with unsaturated (conjugated) backbone structures, the simplest picture is of a chain with equal bond-lengths and one unbonded electrons per carbon atom e.g., polyacetylene (PA). Because two electrons Fig.1.5(a) of opposite spin are needed on each site to fill the available states, this chain has a half filled energy bond. This chain is unstable with respect to dimerization as the π- electrons form additional bonds. This costs elastic deformation energy but gains from the lowering of electric energy by localizing the electrons in the multiple bonds and opening an energy gap Fig. 1.5(b). These bond alternation or peierls transition[42] produces a semiconducting material.
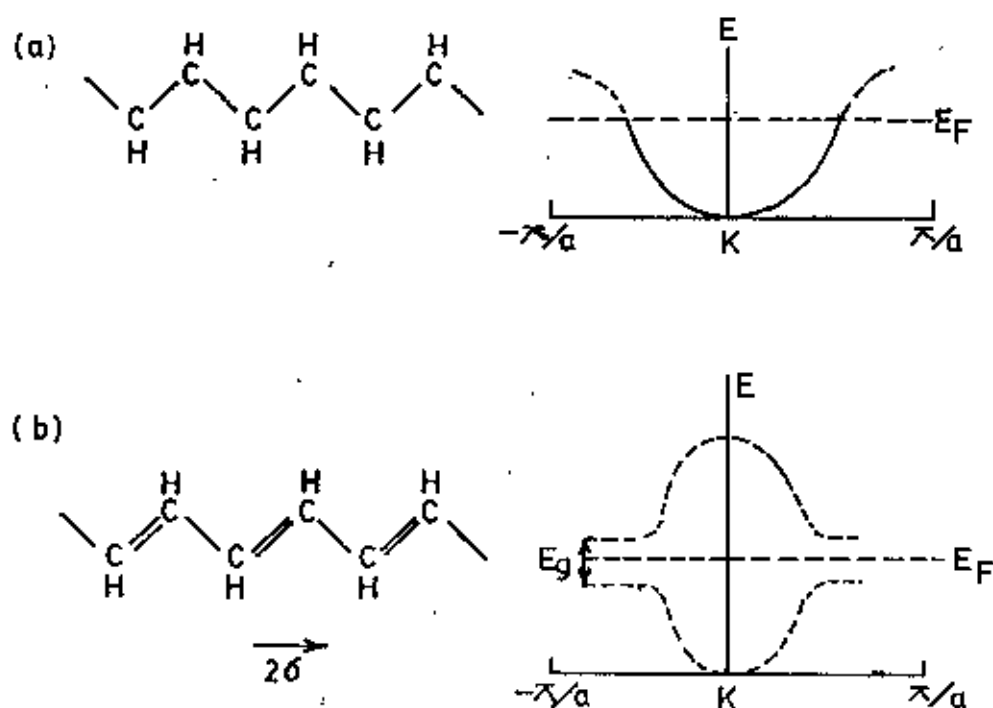
Fig.1.5 Chemical and electronic band structure of non alternated (a) and alternated (b) PA. E_F indicates the Fermi level and E_g the energy gap H = 2π. Filled band states are shown by the full curve and the empty band states by broken curve.

These ideal models are modified when the real morphology of polymers is taken into account chain ends, chain folds, amorphous regions, impurities and defects will swear out the band states resulting in whole or partial filling of the gap. Disorder will also tend to lead localised states. The energy gap which seperates the valence and conduction band states in crystalline solids is replaced by a mobility gap in disordered solids[43]. Carrier motion is accomplished by hopping between localised states below this gap and is band like for states above the gap. Thus polyethylene exhibits a small defect–induced conductivity of about 10^{-13} Scm^{-1} with very low carrier mobility. In addition in an ideal one dimensional polymer chain, disorder will localise all states at 0° k^{41}. Such Anderson localisation will render polymeric semiconductors insulating at low temperature. The coulombic interaction of electrons and holes can also produce localised states (excitons) giving a low temperature exicitonic insulators[43]. Thermal excitation at room temperature can be sufficient to overcome these localization effects.

The conducting properties of polymers can also be further explained by the band theory of solids. According to this theory, when a large number of atoms or molecules are brought together to form a polymeric chain an energy band is formed through the interaction of the constituent atomic or molecular orbitals. Convincing evidence for the existence of such energy bands is obtained from X-ray emission and absorption spectra. The band of highest energy which is completely filled by electrons is called valence band. Electrons associated with this band, involved in chemical bonding are localized and are not free to move throughout the solid. Bands of lower energy are usually not considered as they involve primarily core electron and are even more localized to the individual atoms. The lowest lying unoccupied band is generally called as a conduction band. There is a forbidden energy region between the valency band and the conduction band.

This energy region is generally called the energy gap (E_g) or band gap Fig. 1.6.

E_g = Energy gap
E_F = Fermy energy
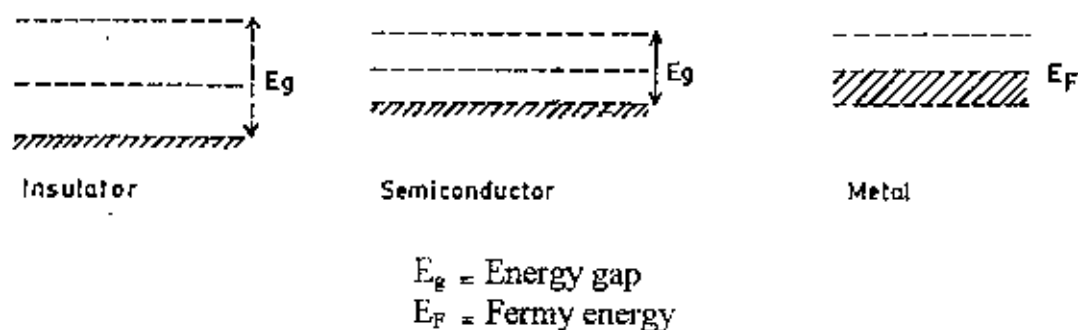
Fig. 1.6. Electronic band structure

According to the Fig. 1.6, when the energy gap is large, the material is an insulator. As this gap decreases, thermal excitation of electrons from the valence band to conduction band is possible and then the materials becomes an intrinsic semiconductor. But when this energy gap becomes negligible or becomes very small, the material behaves like a conductor or metal.

Insulating polymers :

One of the principal application of polymers is as electrical insulators. Polymers with saturated structures and those with unsaturated groups, in either the back bone or side groups which are well separated by saturated groups will have intrinsically large energy gaps and be insulators. The mobility of carriers in these polymers is controlled by the quasi-continuous set of impurity and defect induced energy level within the band gap. Typical conductivities and mobilities are 10^{-15} Scm^{-1} and 10^{-14} m^2 v^{-1} S^{-1} for PE, 10^{-16} Scm^{-1} and 10^{-13} m^2 S^{-1} cm^{-1} for poly-teterafluoroethylene (PTFE) and 10^{-15} S cm^{-1} and 5×10^{-11} m^2 v^{-1} S^{-1} for polystyrene (P). Thus in addition to a knowledge of band structure it is necessary to investigate the motion of carriers and its dependence on simple morphology.

Semiconductors :

In semiconductors all valence electrons are situated in around states at T=O (i.e. the valence band is filled and the conduction band is empty). The band gap may be interveted to be the bonding energy of the valence electrons.

At finite temperatures, some of the atoms or molecules are thermally ionised, with the number of electrons in the conduction band being equal to the number of holes (defect electrons) in the valence band. The electrons in the conduction band serve to maintain a current in an external electrical field as described for metals. In addition, these holes move in the opposite direction.

This motion of electrons (holes) ceases when they recombine with the holes (electrons) and return to a bound state. In thermal equilibrium, these recombination events, along with the thermal excitation events, are in equilibrium. The equilibrium concentration of both the holes and the conduction electrons is equal and dependent of temperature. If the concentration of the conduction electrons is n and that of the holes in the valence band ρ, then the expression for the electrical conductivity is (isotropic solid)=e $(n\mu_e + \rho\mu_p)$ where μ_e and μ_p being the mobility of the electrons and holes respectively. In otherwords, according to their mobility, the electrons and the holes contribute independently to the total conductivity. The magnitude of the conductivity depends on the number and the efficiency of the scattering process occurring via phonons and defect sites, in the same way for metals.

In contrast to the behaviour of metals, n and p are characteristically temperature dependent for individual semiconductors. In the simplest case, where the current is maintained by electron and hole pairs and all charge carriers have the

same isotropic mobility, the concentration of the charge carriers at temperature T is given by

$$n = p = (n_o p_o)^{\frac{1}{2}} \exp(-E_A/2kT) \text{ ----------------------- (1.1)}$$

and the temperature dependence of σ by

$$\sigma(T) = e\,\{\mu_e(T) + \mu_p(T)\,n_o p_o^{\frac{1}{2}} \exp(-E_A/2kT)\} \text{---- (1.2)}$$

E_A represents the activation energy for the formation of the charge carriers (i.e., the electron hole pairs) and may be identified as the magnitude of the band gap, k is the Boltzmann constant.

When $E_A \gg kT$, the behaviour of a semiconductor is determined essentially by the exponential term of eq (1.1) thus, increases exponentially with temperature. If it is the case however, that $E_A \leq 2kT$ or that the charge carriers are formed athermally as for example by photoexcitation. The temperature dependence of the conductivity is determined by the pre-exponential factor of eq (1.2). By analogy to eq. (1.2), an equation has been formulated by Epstein and Conwell[46] as:

$$\sigma(T)/\sigma(T_R) = AT^{-\alpha} \exp(-E_A/KT)$$

which describes the temperature dependence of the conductivity, normalized with regard to a reference temperature T_R. Experimentally[45-47] it has been found that $0.5 \leq \alpha \leq 2.5$ in organic metals.

The anisotropic mobility of the charge carriers in organic materials has seldom been experimentally determined. Karl[48] has impressively demonstrated, using anthracine that the magnitude and temperature coefficient of the mobility does not only significantly depend on the purity of the molecular crystal, but also that both are extremely anisotropic. For the temperature interval 100 K < T < 300 K, almost isotropic mobility of the holes $\mu_p \approx T^{-1.5}$ is found. The mobility of the

electrons is however, strongly anisotropic $\mu_{ca} \approx 10^{-1\,57}$ $\mu_{cb} \approx 10^{-0\,84}$ and $\mu_{ba} \approx 10^{-0.16}$. The indices a,b,c refer to the axes of the anthracene unit cell. For organic metals (e.g TFF–FCNQ) Weger[49] has developed a comprehensive, if not undisputed[50] theory by means of which the proportionality $\sigma \sim T^{-2}$ frequently found in this class of materials, can be interpreted by Invoking special scattering processes. Weger correctly points out that one should differentiate between conductivity at constant pressure and constant volume. Because of the usually strong anisotropic temperature and pressure dependence of the lattice constant in organic materials, the conductivity should only be considered normalized for constant lattice dimensions.

Charge Transport and Structure :

The electrical conductivity of doped PA and similar polymers must be discussed on the basis of available information pertaining to the charge transport and structure of organic metals. While it is not necessary to refer to the comprehensive theoretical background developed for organic materials, it must be noted that the high conductivity observed always accompanies certain packing modes of the molecules in the conductive crystals. All organic metals consists of molecular crystals of charge transfer complexes. Almost all complexes of donors and acceptors crystallize in the form of mixed stacks, as indicated in Fig. 1.8. Crystals which exhibit this type of packing are insulating. Only those crystals, in which the donating and accepting molecules after charge transfer are found in segregated stacks, are conducting.
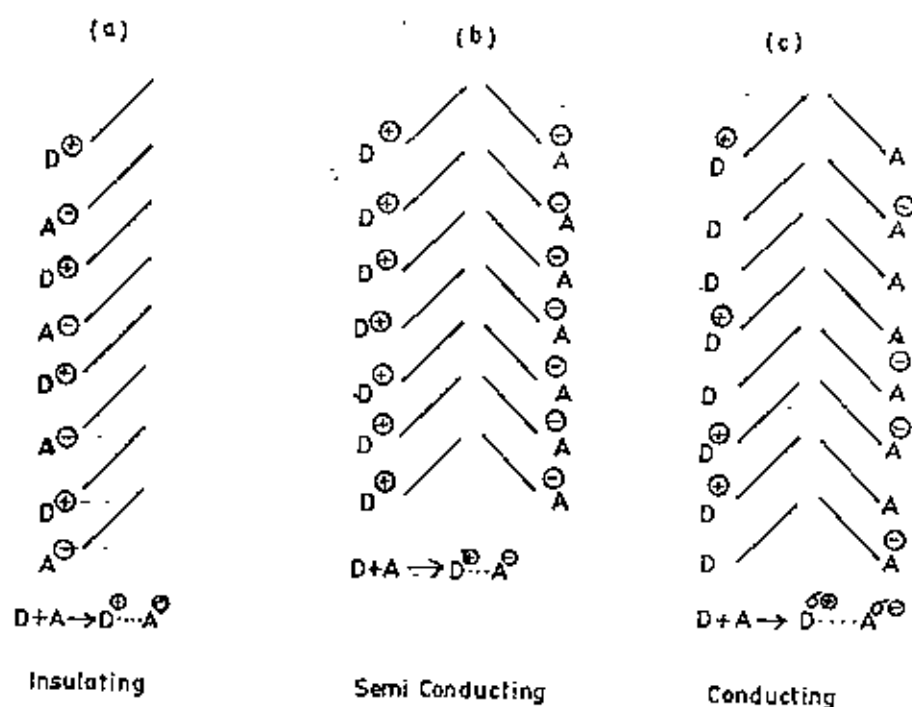
Fig. 1.7 Schematic view of the packing in organic CT–Crystals (a) Insulating (b) semiconducting and (c) conducting CT–Complex.

If however, a full charge is transferred as shown schematically in Fig. 1.7 (b), a semiconductor results. An organic metal is only formed if there is a partial transfer of charge and therefore, the stack of the acceptor molecules consists of a mixture of neutral and negatively charged units while the donor stack consists of a mixture of neutral and positive units Fig. 1.7 (c). This is the pattern found in the conductive crystals of TTF–TCNQ. Such a crystal may also be described as an organic salt, consisting of two independent but interpenetrating lattices of stacks of TTF–cations and TCNQ-anions. It has, in fact, been demonstrated[51,52] that the charge transport proceeds independently in the two stacks; the TCNQ stack supporting a current of electrons, the TTF stack a current of holes.

The charge transport may be described, in a quasi–chemical formulation as an exchange process. This is sketched in Fig. 1.8 (b) which depicts the situation inside the TCNQ stack.

(a)

$$TCNQ^{\ominus} + TCNQ^{\ominus} \rightleftharpoons TCNQ + TCNQ^{2\ominus}$$

(b)

$$TCNQ^{\ominus} + TCNQ^{0} \rightleftharpoons TCNQ^{0} + TCNQ^{\ominus}$$
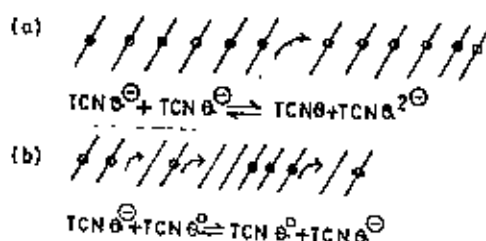
Fig 1.8 Model of charge transport within C.T. complex using TCNQ as an example : (a) at complete charge transfer from the donor to acceptor (TCNQ); (b) at only partial reduction of the acceptor.

A partial charge transfer from the donor to the acceptor stack is understood as resulting in a random placement of neutral and negatively charged (radical anion) TCNQ molecules along a single stack. Electron transport is now described as a diffusive exchange of charge between free and occupied positions along a chain of such molecules.

If, however, complete charge transfer has taken place as depicted in Fig.1.7 (b) and 1.8 (a) (i. e., if each TCNQ molecule carries a negative charge), the transport of charge must be described in the present context, as a disproportionation. This requires considerable energy, since an electron has to travel to a lattice site already occupied by a negative charge, thus a large coulomb potential has to be overcome and hence a semiconductor results.

The bonding relationship within the stacks of an organic metal can be characterized from Fig. 1.8 (b) as a CT interaction between neutral molecules and

the radical ions formed from them. The numerous successful synthesis of salts exhibiting metallic conductivity[51-54] prove this description to be correct. Among others mention must be made of the salts derived from TTF and its derivatives with simple anions x^- of low nucleophilicity exhibiting the general formula (TTF) x^{+-} as well as compounds of TCNQ with cations K^+ of low electrophilicity of composition $(TCNQ)^-_y$ k^+ with $1 < y < 3$.

According to this concept, the conductivity relates essentially to the structure of the lattice and to the packing of the molecules and not so much to structural peculiarities of the individual molecules, as was previously assumed[55]. In particular, the question of under what conditions the desired structure of stacks may be formed is principally a problem of the kinetics of crystallization and not a question of the electronic structure of the individual molecules[56].

The radical cation salts of simple aryls may serve as suitable examples to demonstrate some of these ideas. These materials exhibit conductivities of the order $1 < \sigma$ (300k) < 1000 Ω^{-1} cm^{-1}. In addition, they may be considered as excellent models for doped PA and other conductive polymers. They are obtained by electro-chemical oxidation (using a suitable supporting electrolyte such as nBu$_4$N$^+$x$^-$ with x=ClO$_4$,PF$_6$, AsF$_6$, SbCl$_6$ etc.) of naphthalene[57,58], fluoroanthene, perylene, Pyrene[45], as single crystals having metallic lustre and exhibit the general formula $(Aryl)_2^+ x^-$.

The desired packing shown in Fig. 1.7 (c) is realised in the crystals; the aryls are stacked with a distance of 3.2 Å between the planes of the rings. The projection of the crystal structure of (fluoroanthene)$_2^-$ PF$^-_6$ on to and along the stacking axis is exhibited in Fig. 1.9.
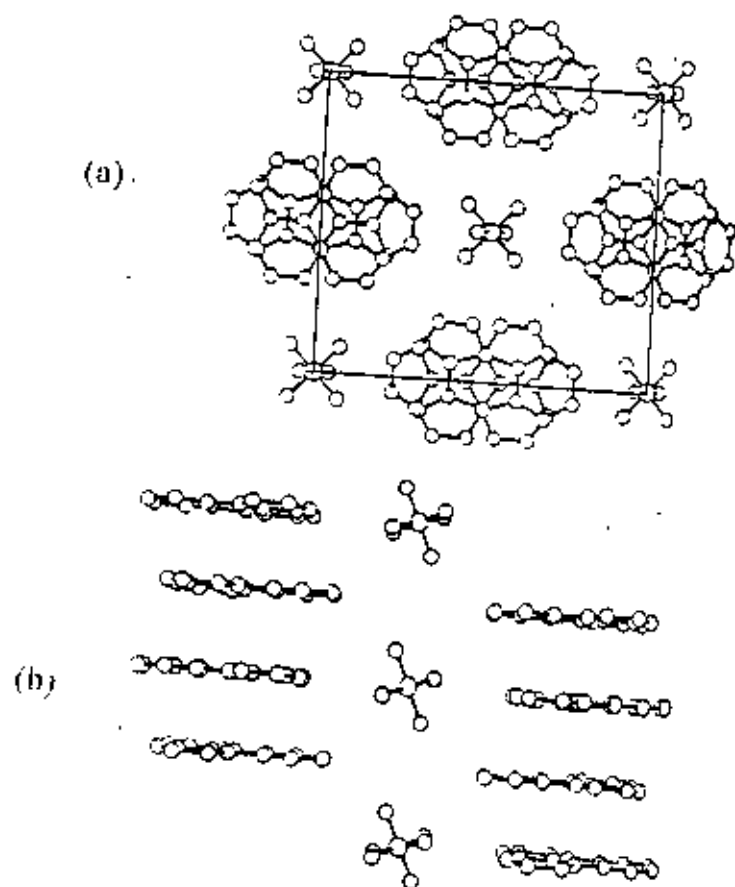
Fig. 1.9 Crystal structure of the organic metal (a) on the stack axis and (b) along the stack axis.

With this background and considering nature of the chemical reactions which proceeds in the doping of PA it is concluded that the conductivity in doped PA relies on the same type of interactions as are sketched in Fig. 1.7 (c) and 1.8 (b) for the radical ion salts of simple aryls. Within the frame work of these ideas, radical ions of individual polymer sequences consisting of n double bonds are formed when the

doping agent reacts at and with the surface of the morphological units of PA. These sequences extend between the surfaces of the lamellar structures and stabilize themselves by forming CT complexes with adjacent and still neutral sequences. The doping proceeds to the extent at which in the average, each conjugated chain sequence between conformative defects or cross links has been transformed into the complex structure. The charge of the radical ions, which is situated on the sequences delocalized along the chains is compensated by counter ions. These are either intercalated in layers between the chains or deposited on the surfaces of the morphological units.

The original lattice breaks down in the course of doping PA. This is shown experimentally by the disappearance of the Bragg's reflections. The latter remain, however, for some period of time during the doping albeit with decreasing intensity. This is due to the fact that the doping proceeds inhomogeneously and individual morphological units become doped at different rates. Samples which have reached maximum conductivity are however, amorphous as revealed by X-ray investigation. Hence, exact data on the packing of the chains and counter ions are not available at present and analogies have to be relied upon.

Presumably, charge transport takes place within a morphological unit normal to the chain direction as indicated by the exchange process sketched in Fig. 1.8 (b). In other words it is expected that a high mobility of the charge carriers exists normal to the chain direction, even in the absence of perfect crystalline order. It is another problem as to how the electric contact is made where the surfaces of the individual morphological units touch each other and where contact resistances be build up which have not thus far been characterised.

These ideas are contradictory to those proposed by among others Heeger et al.[59,60], Chien et al.[61] and Rice et al.[62,63]. These authors claim that the conductivity mainly arises from the transport of charge along individual chains. Apart from the fact that they incorrectly assumed that PA as obtained the Shirakawa procedure, consists of a network of extended fibres and fibrils of infinitely long, extended chains they did not take in to account the expected interactions been neighbouring chains. Rather, these authors believe that the charge carriers migrate along a single chain in a manner similar to delocalization of charge along an extended π–bonded system and that the constraints are strictly one dimensional diffusion apply. Such a state of a charged π–bonded within may be described mathematically as a soliton[62,63]. The chemical structure as shown below envisaged in this context is the radical cation. Any interaction with adjacent chains are, however not allowed. The radical site in below is termed a neutral soliton and the site of the positive charged soliton. It is only the latter which is able to transport a charge if an external electrical field is applied.

Unfortunately, until now, no successful measurements on samples in which the orientation of the chains with regard to the direction of the field was known have been reported. Hence, the question whether the charge transport occurs in a direction across the chains or along the individual chains which is basic to the understanding of the electrical phenomena in doped polymers, cannot yet been answered experimentally.

Electrical Conductivity and Mechanisms of Charge Transport: Definitions and Concepts :

Investigation on the conductivity of organic metals requires a basic understanding of the electrical behaviour of the solid state. Some of the most

important definitions and relationships are summarized in the following short section, without claim to their completeness, in order to facilitate a discussion concerning the mechanisms of charge transport. For additional information, the reader is referred to the literature[51,52,64,65].

Electrical Conductivity of Metals :

The electrical behaviour of metals is described by Ohm's Law, which states that at constant temperatures a current density, j, will adjust itself proportional to an external electrical field, E. The tensor (σ) describing the electrical conductivity is independent of time and electrical field strength.

$$j = (\sigma) E$$

j is maintained by a flux of charge carriers in the field direction. Assuming a conduction by n electrons of charge e per unit volume, j corresponds to an average drift velocity v dr

$$v \, dr = - \, j \, / en$$

For the case of direct current, j and v dr are constant with time and therefore,

$$j = -e \cdot n \, v \, dr = (\sigma) \, E.$$

The conductivity may hence be expressed as, $\sigma = n. \, e \, \mu \, (\Omega^{-1} \, cm^{-1})$.

The constant μ termed mobility, is equivalent to σ and is defined as $\mu = | \, v \, dr \, | \, / |E| \, [cm^2 v^{-1} s^{-1}]$. μ can be experimentally determined by measuring σ if n is known. The electrons do not move freely in the field, rather they are scattered by phonons; that is by the thermal density fluctuations of the lattice and by lattice defects. The phonon density increases with increasing temperature. Lattice defects may normally be considered as static and temperature independent scattering centers. Therefore, the temperature dependence of the resistivity $\rho = \sigma^{-1}$ follows

Matthiesen's rule $\rho^{(T)} = \rho_R + \rho_p^{(T)}$, where ρ_R is the portion of the total resistively of an isotropic metal due to the scattering by defects and ρ_p is that portion caused by the phonons.

As a consequence ρ increases with temperature of metals $\rho_p^{(T)}$ increases proportionally to T^5 at $T<<\theta$ and proportion. Usually to T at $T>>\theta$. The residual resistively ρ_R is controlled by additives.

If the dimensions of a metal sample decrease in comparison to the mean free path of the charge carriers between two scattering events at the surfaces, consequently, the resistivity calculated from the sample dimension is no longer a material constant in small samples.

This may be importance when the conductivity data of doped PA are evaluated, since the charge transport takes place in this material inside very small particles, the dimensions of which are of the same order of magnitude as the expected value of the mean free path.

This charge transport concept in polymer molecules can be described as follows.

In polyacetylene and other conjugated polymers there is an initial increase in conductivity on doping. It is assumed that upon doping, oxidants remove electrons from the filled valency band and reductants add electrons in the vacant conduction band. In polymers, the conduction is not associated with unpaired electrons but with charge carriers. Brazovskii used the term "polaron" to point the combined effect of electron localization and lattice polarization[66]. Soliton model was proposed in this view in 1980[67]. The model suggests the conduction mechanism in polymers. According to this model solitons are assumed to be the conducting species for charge

transport. Charged solitons are a type of charge defects introduced with electron acceptors or donors. The case of doping with electron acceptor of PA and PPP are shown in Fig. 1.10
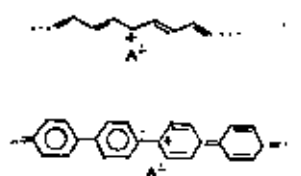
Fig. 1.10 Charged Solitons in PA and PPP

This theory of model was initially appealing as these charged solitons do not carry any spin and experimentally too, the conducting polymers are found to possess spinless transport. However, among the conducting polymers only PA can support soliton defects because it possesses a degenerate ground state i.e., two geometric structures corresponding exactly to the same total energy.

But PPP and other conducting polymers can not support this theory because unlike PA they have energetically non-degenerate ground state and therefore the structures on either side charged defects would be of different energy.

Failure of the solitonic theory necessitated the invention of newer type of charge carriers i.e., polarons and bipolarons Fig. 1.11.

Polarons (Radical cations)

Bipolarons (Dications)
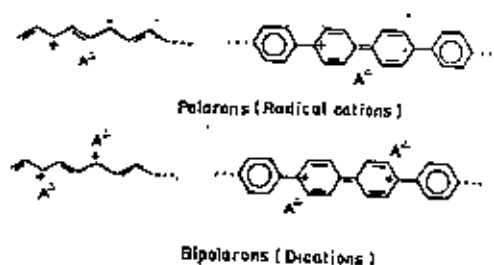
Fig. 1.11 Polaron and bipolarons in PA and PPP

The polaron chain gets ionized on dopping and this ionization process creates a polaron i.e., redical ion on the chain. It is thought that the polaron is a result of an interaction of a charge soliton and a neutral soliton. Polarons have half spin. At low doping level, these polarons are carriers of electricity. On increased doping, tho concentration of polaron increases resulting in large probability of interaction which results to form bipolarons. Biplarons are doubly charged but spinless species. A single bipolaron is thermodynamically more stable then two polarons.

1.5   Application of Conducting Organic Polymers :

Polymeric conductors pose a serious challenge to the established inorganic semiconductor technology. Interest in conducting polymers is primarily duc to various novel applications envisaged for such polymers.

Application of conducting polymers in the development of a rechargeable battery appears to be feasible and is at the threshold of commercialization. A number of conducting polymers such as polyacetylene, polyaniline and other polyheterocyclics has been used as electrode materials for rechargeable batteries. Polyaniline lithium battery has already been marketed[68,69].

A number of electronic devices such as schottky diodes, plastics transistors, p–n junction etc. have been developed using semiconducting and conducting polymers. For the fabrication of these devices the same polymer through control of doping or two different polymers onc polyhetrocyclics and the other polyaniline have been used. Plastic field effect transistor (PET), for example, have been fabricated with polythiophene as the semiconductor and p-toluene sulphonate doped polypyrrole as the source drain electrode[70].

Light–emitting diodes (LEDs) have been made by depositing a film of semiconducting polymer such as poly (2–methoxy 5–(2–ethyl hexoxy)–1,4 phenylene vinylene) on indium-tin oxide coated glass surface[71,72]. Some of the new

fields for application of conducting polymers include gas separation membrane[73], photo electrochemical cell[74], optical devices[75,76], ion gates[77,78], memory storage devices[79,80], non-linear circuit elements[81], etc.

1.6   Aim of Present Research Work :

In view of the importance, Physico–chemical studies on organic conducting polymers have received wide attention because of their application in various field mentioned above. From the literature survey it appears that although a wide spectrum of study has been done on conducting organic polymers particularly on polyaniline, poly o–toluidine, poly-pyrrole, poly–furan and poly–thiophene and their derivatives, a limited number of work has been reported on electrochemically synthesized polymers. Thus to widen this spectrum the proposed work is planned in order to study the effect of different parameters like deposition current density, bath temperature and composition on electrochemically synthesized conducting polymers of polyaniline and poly o–toluidine.

CHAPTER- 2

2.1 Review of Literature

The search to replace traditional inorganic semiconductors, metals and superconductors by organic macromolecular materials has led to the interdisciplinary field of molecular electronics. This new area of research containing organic chemistry, electrochemistry, solid state physics and microelectronic engineering have received much attention in the recent past, although the works on synthetic metals have practically been originated in 1910 through the synthesis of poly sulphur nitride $(SN)_x$. Although $(SN)_x$ was first reported by Burt: its exciting metallic conductivity was discovered only Walatka et al.[82]. Work on $(SN)_x$ was further stimulated by the observation that it behaves as a superconductor at $-277.76°C$ [83]. Despite its metallic conductivity, $(SN)_x$ (known as synthetic metal) could not find wider use due to its extreme reactivity. In the literature it is seen, that most of the work on conducting polymer has been done on polyacetylene, polyaniline, polyphenylene, polypyrrole, polythiophene and their derivatives, because of their diversity, ease of fabrication, low cost and wider application. Work done on some important conducting polymers is disscused below:

2.1.1 Polyacetylene

Polyacetylene is the first conjugated polymer to attract attention and is the most throughly studied[84,85]. Natta et al.[15] have reported the polymerization of acetylene by using Ziegler catalyst and obtained polyacetylene (PA) in the form of a red insoluble powder. The red powder was found to be an insulator. Hatano et al.[86] have also obtained high molecular weight polyaniline, both crystalline and amorphous variety by using various Ziegler–Natta catalyst expecting that PA

containing chain of conjugated double bonds might have semiconducting properties They reported that the crystalline form of PA was gradually oxidized by air and the electrical conductivity decreased abruptly by almost five orders and the colour changed from greenish black to pale orange. It may therefore, be assumed that Natta et al.[84] have obtained only the amorphous form of PA (red colour powder) which may be cis– polyacetylene.

Shirakawa et al.[20-22] reported the preparation of a free standing PA film by passing dry pure acetylene gas over the Ziegler–Natta catalyst of titanium tetrabutoxide triethyl aluminium in toluene at −78°C. They prepared two types of PA films, one is flexible copper coloured and other one is silver coloured. The former is cis and the latter is trans-PA. The conductivities of the films of trans and cis- PA 4.4×10^{-5} Scm^{-1} 1.7×10^{-9} Scm^{-1} respectively. When these films were exposed to the vapours of bromine and chlorine at room temperature a dramatic change in their IR spectrum occured without any visible change in the appearance. Shirakawa et al.[14] have again reported that PA exhibits increase in conductivity on treatment with strong oxidizing or reducing agent. Aldiss M[87] reported the preparation of PA in arsenic trifluoride solvent by using arsenic pentafluoride as a catalyst. PA obtained in this method was claimed to be soluble in acetone and THF. Indirect method for the preparation of PA was reported by Soga et al.[88]. In this method polyvinyl chloride solution in THF was treated with potassium salt of t– butyl alcohol under nitrogen atmosphere to yield PA.

$$\cdots\cdots CH_2\text{-}CH\text{-}CH_2\text{-}CH \cdots\cdots$$
$$\qquad\quad | \qquad\quad |$$
$$\qquad\quad Cl \qquad Cl \longrightarrow CH = CH - CH = CH \cdots\cdots$$
$$\qquad\qquad\qquad\qquad\qquad\qquad + 2\ HCl$$
$$\qquad\quad PVC \qquad\qquad\quad PA$$
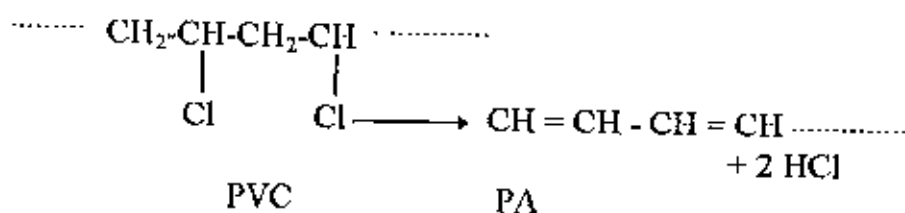
A new polymerization initiator for PA preparation was reported by Lutting[89] and Green et al.[90]. This initiator consists of a hydroiodic reducing agent with a salt or complex of gr. VIII-metal.

H. Munstedt[91] reported the effect of aging on electrical conductivity of polyacetylene. It has been reported that polyacetylene which is an insulating material as polymerized becomes conductive only on its oxidized or reduced state. Upon exposure to air, the conductivity of polyacetylene first increases. In parallel to the conductivity increase an oxygen uptake can also be observed. After some time of exposure to air, the conductivity reaches a maximum and then falls again. The decrease of conductivity is accompained by a further oxygen uptake. This oxygen uptake and loss of conductivity are reversible.

Chen et al.[92] have reported the importance of polyacetylene as the materials for use in batteries. photovoltaic cells, electromagnetic screening etc. Electrochemical preparation of polyacetylene is difficult, as a result majority of workers have used Ziegler–Natta catalysts. Many attempts have been taken to obtain a greater degree of orientation in the structure of PA. But none of these methods has proved as successful as the orientation of precursor polymer.

Cis–PA prepared at low temperatures is converted into the trans– PA form on heating. Cis–PA has an orthorhombic crystal structure while both orthorhombic and monoclinic forms have been reported for trans-PA for samples prepared at different routes[93-95]. Reaction condition determines the ratio of cis to trans–PA structure, defect density and crystallinity of the product. Block poly (acetylene co–styrene) have been reported to have a hexagonal structure. which has been attributed to PA. However, IR spectra and theoretical calculations do not support this suggestion[96,97].

In the literature considerable amount of work have been reported on the effect of doping on the conductivity of PA. Doping can be achieved either by exposure to dopant vapour or solution e.g., potassium naphthalide solution or electrochemically[98,99]. In some cases the doping reaction is relatively straight forward e.g for potassium naphthalide as shown below :

$$(CH)_x + xy\ (naphth^-) \rightarrow [(CH)^{y-}]_x + xy(naphth)$$

$$[(CH)^{y-}]_x + xy(Na^+) \rightarrow [yNa^+\ (CH)^{y-}]_x$$
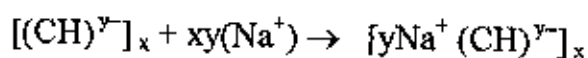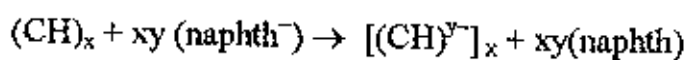
Here, naphtha$^-$ = naphthalide anion.

In others it is complex e.g., iodine produces I_3^- and I_5^- ions, while for AsF_5, the ions that have been postulated are AsF_5^-, $As_2F_{10}^{2-}$ and $As\ F_6^-$ with products such as AsF_3, $HAsF_6$ and $HAsF_5\ OH$. Mac Diarmid et al.[100] reported that in a cell with Li and PA electrodes containing $LiClo_4$, on external connection of the electrodes current flows as a result of the electrochemical reactions shown below :

$$Anode + xyLi = xyLi^+ + xye^-$$

$$Cathode\ (CH)_x + xye^- = [(CH^{y-})_x]$$
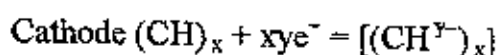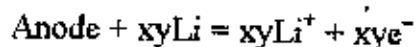
Li^+ liberated at the anode is incorporated in to PA as a counter- ion

The physics of PA–metal and PA–semiconductor interfaces and the applications of PA for photovotaic devices has been explored quite extensively[98,101]. The photoefficiencies observed are low in the range of 10^{-3} to 10^{-4}, reflecting the high defect density in PA[102]. The application of PA to batteries has been extensively investigated[98,103]. Most attention has been focused on Li/PA electrode with an electrolyte of $LiClo_4$ or $Li\ BF_4$ in a nonaqueous solvent.

In addition to PA related polymers with substituent groups e.g., poly (pheny acetylene), Poly (1,6-heptadiene) and co-polymers have been investigated[104,105]. In general the conductivity achieved on doping is less than that for PA.

2.2 Poly Paraphenylene (PPP)

Another class of polymer that has received attention is based on PPP e.g., poly (1,3-phenylene), poly (thio 1,4-phenylene), poly (p-phenylene sulphide, PPS) etc[106]. A major advantage of PPP and PPS is that the undoped polymer is solution and melt processable. PPS is also available commercially. The physical properties of these polymer doped and undoped have been interpreted in terms of bipolaron model[107,108]. The validity of this approach has been questioned by chemical analysis, which has shown that these materials are complex mixtures of dissimilar oligomers rather than distinct polymer[109]. Furthermore, doping is accompanied by side reactions leading to crosslinking. PPS was the first to be shown not be soluble in conducting form. The nature of the solvent, AsF_3 and the rapid development of other soluble conducting polymer rendered this of academic interest. PPP has been used successfully as a battery electrode[110]. PPP alkali metal alloy composite electrode have a greater cyclability and discharge rate than bare metal electrodes[111]. Extensive reviews of these and a wide range of related polymers have been reported[113,114].

2.3 Polypyrrole (PPy.)

Electrically conducting polypyrrole has attracted much interest recently because of its superior stability to that of polyacetylene. H Munstedt[91] has reported that the conductivity of polyacetylene drops by a factor two in less than one hour at $80^{\circ}C$. Whereas in the case of polypyrrole it takes about one week. H Munstedt also reported that the temperature dependence of polypyrrole is very weak. The conductivity increases with temperature as is typical of semiconducting materials. It is also reported that the band energy is calculated as $E_g = 0.04$ eV, which is markedly lower than that for polyacetylene. Hagiwara et al.[115] have reported that the electronic and optical properties of neutral and oxidized PPy have analysed in terms of polarons and bipolarons. At low doping levels, polarons (radical cations)

are produced but above 1% doping these combine to form bipolarons (di-cations). Electrical conductivities for fully oxidized ppy fall in the range 1-300 Scm^{-1} depending on the preparative conditions. A maximum value of 10^3 Scm^{-1} has been reported for stretched samples. Electrically conductive compositive with good mechanical strength have been prepared by electropolymerizing pyrrole through porous membranes. However, with careful preparation thick mechanically strong films can be produced directly. PPy films exhibit excellent stability in inert gases and dry air at elevated temperature but degrade much more rapidly in moist air. Reversible absorption of water has been observed but this can be reduced and film stability improved if appropriate counterion is used[116]. A study on chemical bonding of the counter ion to PPy has also been reported[117]. In the literature it is also reported that with n-Si or TiO_2 electrodes PPy deposition requires photoexcitation to liberate the electrons, participating in the polymerization. This has been studied for pattern definition and to mediate photo electrochemistry at the semi conductor surface[119,120]. Use the PPy as an electrochromic material has been investigated but this application is limited by side reaction occurring in reduced films, considerable effort has been expended on developing PPy electrodes for batteries. Self discharge is a problem and side effects reduce cycling efficiency and lead to failure of the Li-electrode of Li/PPy cell after about 200 cycles. Electrochemical plastic field effect transistor(PET) devices have been made by bridging gold microelectrodes with ppy and other electropolymerized materials. These have been used to detect low levels of oxidizing species. A promising use of PPy is the production of chemically modified electrodes. Redox groups can be substituted in the pyrrole nitration without affecting polymerization behaviour. Efficient electrocatalytic groups can be incorporated into the conductive polymer[120]. PPy can be prepared by acid and transition metal halide catalized polymerization from solution and gas phases. These routes have been used for the production of composite material for sensor, battery and other applications[121].

Kanazawa and Diaz et al.[122] have reported the electrochemical polymerization of pyrrole which proceeds with simultaneous doping. When a solution of pyrrole (0.06M) in 99% aqueous acetonitrile is electrolized in the presence of tetraethyl ammonium fluoroborate (0.1M) as the supporting electrolyte, a blue black film of an insoluble polymer precipitates on the anode. If IR spectra exhibits bands which are characteristics by pyrrole ring. The films contain BF_4^- ions in a molar ratio c,a 1:4 with respect to pyrrole ring. They assume that the constitutive units of polymer are linked to each other or via the a-c atoms of the pyrrole rings. Consequently, the following idealized structure is proposed.

The films exhibit a conductivity of 100 Ω^{-1} cm^{-1} which is readily reproducible. conductivity is weakly dependent on temperature and decreases from 100 Ω^{-1} cm^{-1} at 300 k to 30 Ω^{-1} cm^{-1} at 80 k. It assumed that defect electrons (holes) act as the charge carriers. The conductive film of density 1.48g cm^{-1} are stable in air for long period of time and can be heated to temperatures approaching 100°C without any essential alteration of their electrical properties. These are X-ray amorphous. A diffuse halo, which is obtained electron diffraction, corresponding to a d-value of 3.4 Å is presumed to be caused by the characteristic distance between the ring planes of pyrrole rings in adjacent chains[122,123].

Dall Olio et al.[124] have reported that a brittle films of oxy–poly (pyrrolene) were formed by anodic oxidation of pyrrole in dilute sulphuric acid giving a conductivity of 8 ohm^{-1} cm^{-1}. From the elemental analysis it is reported that the formula $C_{4.0}H_{3.4}N_{0.99}$ $S_{0.15}O_{0.92}$ suggesting the presence of 0.15 sulfate diane per pyrrole unit. This relationship implies that there is one positive charge for every 2-3 pyrrole units. Although a more complete characterization of this material is not available, it must be similar to the pyrrole black powders generated when pyrrole is oxidized chemically e.g., with H_2O_2[125]. The formula for this material obtained from

chemical analysis is $C_{4.0-4.5}$ $H_{3.0-3.4}$ $N_{1.0}$ $O_{1.0-1.5}$ which indicates that the material consists of linked pyrrole units. The anion in this material could be formate, in which case it would be present in the ratio of one formate ion for every two pyrrole units. The electrical transport behaviours of the thicker free standing film of poly pyrrole show a marked similarity to those of conducting PA.

The electrical conductivity of polypyrrole fluoroborate films is reported by Vander Pauw[126]. The temperature dependence of the conductivity showed that conductivity is increased with increasing temperature. Unlike the behaviour that is expected for a simple metal it was not unlikely that the variable range of hopping picture of Mott[127] is appropriate in this case at high temperature, it is likely that some localization effect is also being made.

Kanazawa and Diaz et al.[122] have measured the thermal conductivity of polypyrrole tetra fluoroborate. They have reported that by using a modification technique of Bidean et al.[128], the thermal conductivity was found to be 9×10^{-3} cal/s. This value is intermediate between that of metal and insulating polymers and indicates that the carriers contribute substantially to the thermal transport.

Seeger and Gill[129] have measured the Hall effect by using a double ac technique. By implying electronic or n-type conduction they observed anamolous behaviour where the Hall constant is negative. Burnay and Pohl[130] have reported the similar results for polythalocyanine.

Kanazawa and Diaz et al.[122] have also reported that there are two absorption band in the spectrum of thin free standing films of polypyrrole tetrafluoroborate. The higher energy absorption is presumably an interband transition while the lower energy absorption which appears in the infrared region is associated with the polymer conductivity.

Kanazawa and Diaz et al.[122] have reported the amorphous nature of poly pyrrole as their X–ray analysis revealed no peak in the spectrum.

It is reported in the literature that the cylic voltammogram study on polypyrrole showed the interaction between redox sites in the polypyrrole film is less severe than in those cases involving pendent molecular redox centres and the difference probably reflects the fact that the redox reaction of polypyrrole involves an extended π–electron system[131]. In this article it is also reported that the electroactive behaviour observed with the polypyrrole films is not unique to this material but is a characteristic of many of the π–conjugated polymers that are conducting in the oxidized state.

Diaz[132] has reported that the anions in polypyrrole produces a variation of 10^5 in the conductivity of the films.

Maddison et al.[133] have studied the pressure dependence of electrical conductivity in polypyrrole. In their study they have prepared polymer sample electrochemically using a solution of 0.1 M pyrrole and 0.1 M nap-toluene sulfate. The samples were then subjected to isostatic argon gas pressure in order to prevent sample deformation. High pressures were applied by pumping argon gas in to a pressure vessel via a pneumatic pump to 200 MPa and finally with a 10.1 hydraulically pump intensifier to apply pressures in the range 200-1100 MPa. It is reported in this study that the electrical conductivity of polypyrrole is strongly dependent on pressure and to fit the experimental results Maddison et al.[133] have used the second order function equation $\sigma = \sigma_0 + \sigma_1 p + \sigma_2 p^2$, Here σ_0 is the residual conductivity, σ_1 and σ_2 are constants and p is the pressure.

Salmon and Kanazawa et al.[134] have reported that the films of polypyrrole polymer prepared by a chemical method are different from the electropolymerized PPy films. These are hydrogen rich, transparent and insulating.

Murthy et al.[135] have reported the results on electrochemical oxidation of pyrrole in aqueous acidic, basic and neutral media as examined by cyclic voltametry. In their results similar voltammograms were observed in H_2SO_4, NaOH and KCl solutions. They have reported the peak potentials and peak currents in all media at different scan rates. Much broader anodic peaks were obtained in KCl medium than in the acidic and basic media. The peak potentials were also more positive in KCl medium than in acid and basic media. This indicates that it is difficult to oxidize pyrrole in a KCl medium than in acidic one.

Dietmar et al.[136] have reported the results on oxidative polymerization of some N–alkyl pyrrole with ferric chloride. In their study they have synthesized polymers of N–(2–hydroxyl ethyl) pyrrole, 2–(N–pyrrole) ethyl acetate and 2(N–pyrrole) ethyl stearate via oxidative polymerization with $FeCl_3$ poly 2–(N–Pyrrole) ethyl acetate and poly 2(N–pyrrole) ethyl stearate were partially soluble in organic solvents and transparent films were cast from solution.

Gandhi and Murray et al.[137] have reported the mechanism of electro-mechanical actuation in polypyrrole. In their report they have said that polypyrrole undergoes unusual mechanical responses when subjected to applied electric potentials. Akira Adachi and Jun Yamanchi[138] have investigated the effect of UV irradiation on polypyrrole doped with benzene sulfate by ESR. They have observed that during UV radiation, the line width of the ESR spectrum increased probably due to the production of localized spin when fission of the polymer chains starts to

occur. After UV was switch off, the line width reverted to its initial value due to the reunification of the polymer structure.

Yue Sun and Eli Ruckenstein[139] have reported the morphology of polypyrrole bearing conductive composite. They have prepared polypyrrole rubber composites and studied the morphology by scanning electron microscope and determined the composition by energy dispersive spectroscopy and elemental analysis.

2.4 Poly Thiophene

Doped polythiophene films prepared by electrochemical polymerization are known to be conductive[140,141]. However, reported values of the electrical conductivity lie in a wide range between 10^{-2} and 10^2 Scm^{-1} [140-145]. Akimoto and Furukawa et al.[146] have synthesized the polythiophene films under several different conditions. A part of the polymerized film was once undoped and vibrational spectra of the film was recorded. The remaining part was doped with iodine to the maximum and the conductivity was measured. As a result they have reported a high degree of polymerization alone is not adequate for a doped film to have high electrical conductivity but abundance of long conjugated coplanar segments is the requisite condition.

It is reported in the literature[147-150] that among polypyrrole, polythiophene, polyfuran, polyaniline and so one, polythiophene (PT) has been intensively studied with respect to fundamental properties, because PT prepared by electrochemical oxidation can be made in the shape of a tough and flexible film with strong stability in air. In addition to this successive undoping, redoping cycles for PT and its derivatives can be controlled by an electrochemical procedure[144,151,152].

Tanaka K et al.[153] have studied the change in characteristics of polythiophene film at various electro polymerization temperatures. They have reported that the electronic properties of polythiophene samples prepared at higher temperatures (40°C) are poor compared with those prepared at lowest possible temperature for the polymerization system.

Ymaoto et al.[154] have reported the conductivity of poly– (2.5-thiophene). They have observed that the conductivity increases if it is treated with iodine However, the values so far measured are comparable to very poor semiconductors.

In a report Munstedt[114] has compared the conductivities of BF_4^- salt of poly thiophene [PTh $(BF_4^-)_y$] and polyaniline and polypyrrole sulfate film. In the report they have mentioned that [$PTh^{-y} (BF_4)_y$] film has significantly lower conductivity than that of poly pyrrole phenyl sulfonate film. Both the polythiophene and polyaniline do not exhibit an over whelmingly good stability.

In a review report Sukumar Maiti[155] has mentioned that substitution of long alkyl sulfonate group in the 3-position of thiophene molecule makes the polymer more soluble in water. Substitution of bulky groups in the 2-position of thiophene also results in soluble polymers which on heating produce 2,5-thienyl vinylene. This may be regarded as the alternating copolymer of thiophene and acetylene.
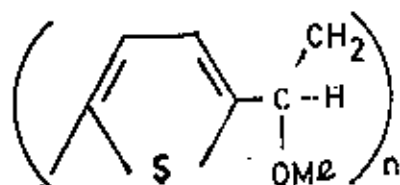
Magnetic resonance measurements of polythiophene doped with BF_4^- ion were reported by Mizoguchi K et al.[156]. In this report measurement of temperature dependence of magnetic susceptibility by Shumacher-Slichter technique was described. They have observed that the Pauli susceptibility appeared at 8 mol % BF_4^- concentration. The density of states at the Fermi energy was also comparable order with that reported for $As\ F_6^-$ doped poly -p-phenylene and poly acetylene.

The stability of $AuCl_3$ and $FeCl_3$ doped poly (3-hexyl thiophene) has been studied by Ahlskog[157]. He has observed that at room temperature $AuCl_3$ doped poly (3 hexyl thiophene) is substantially more stable than $FeCl_3$ doped poly (3-hexyl thiophene). At elevated temperature even $AuCl_3$ is a thermally unstable dopant, still more stable than $FeCl_3$. Kreja et al.[158] have studied the structural and electrical properties of chemically modified poly (3-alkyl thiophenes). They have observed that the substitution of aromatic hydrogen atom in the 4-position of poly (3-alkyl thiophene) by a nitrogroup ($-NO_2$) or by a chlorine atom ($-Cl$) lowers the conductivity of the initial polymer.

2.5 Polyaniline

Although huge amount of work and a good number of publications has been made on polyaniline even then some aspects of polyaniline are far from being fully understood. Electronically conductive polyaniline is the simple 1,4- coupling product of simple monomeric aniline molecules. This coupling reaction is dominated in acidic media pH 0-1. If the reaction is carried out in less acidic media, the appearance of more or less branched phenylene quinoneimines which are not electronically conductive becomes more and more pronounced [159,160].

The molecular weight of as prepared polyaniline is not well defined. Mac Diarmid et al.[161] have observed the molecular weight Mw = 64000 and Mn = 25000 for polyaniline in the course of their gel permeation investigations. On

the other hand, Adams et al.[162] have estimated an Mn value of 2500-6000 for polyaniline prepared under similar conditions to those used by Mac Diarmid et al. by the use of end group technique.

An important feature of undoped PANI is its solubility in NMP[163]. This offers the possibility of producing stifle free standing films and fibres of PANI and composite materials if a conventional polymer is dissolved in the same solution. Pure PANI films and fibres offer the opportunity of checking the influence of orientation of the individual molecules on the conduction properties of the material. Indeed a large increase in the conductivity has been observed upon stretching PANI films by a factor of three or four[164]. Unfortunately the high boiling point of NMP represents a serious draw back to this way of overcoming the unprocessibility of PANI.

Another standard solvent for PANI, but in the undoped and doped states, is concentrated sulfuric acid. Like NMP, such solutions offer the opportunity of producing films and fibres of PANI, with improved mechanical and conduction properties if a stretching treatment is applied in the course of the preparation and/or composite materials with other polymers, like poly(p-phenyleneterephthalamide) (PPTA), are produced[165].

The low solubility of doped PANI in the more conventional organic solvents is quite a difficult problem to solve. Nevertheless, only recently the group of Heeger and Smith at the University of California at Santa Barbara has claimed that the use of camphor sulfonic acid (CSA) and dodecyl benzenesulfonic acid (DBSA) renders doped polyaniline soluble in m-cresol and o-xylene, respectively[166,167]. According to these authors, such solutions allow the preparation of pure and composite films having d.c conductivities of up to 450 S cm^{-1}. However, a word of

caution must be said with respect to the findings of Heeger et al.. According to the findings of other groups[168,169], it is not possible to get a soluble product on treating undoped PANI with DBSA. Furthermore, m-cresol is suspected to be a cancer-causing substance thus counting out this route for obtaining soluble, doped PANI on a large scale immediately.

With respect to the charge carriers in PANI, there is quite a large difference in opinion in the scientific world. Whereas, Nechtschein et al.[170] have observed spinless bipolarons as the responsible carriers in most of their samples, Epstein, MacDiarmid and their coworkers[171,172] strongly favour spin-carrying polarons for the intramolecular charge transport process. Furthermore, some other groups[173-176] recall the possibility of polaron-bipolaronn transformations.

The mechanism by which the existing polarons and/or bipolarons effect the conductivity is still not clear. The simple idea that these heavy carriers (the mass of a polaron lies somewhere in the region of six to 30 times the electron mass[177]) should be able to move along the individual chains like free electrons and even more, be able to hop from one chain to a neighbouring one or across the grain boundaries of macroscopic PANI crumbs seems rather unreasonable. On the other hand, the possibility that the lower mobility of the polarons/bipolarons might have some influence on conduction mechanism involving free electrons or holes hopping from one fixed polaron/bipolaron to another cannot be discounted. Note that the latter mechanism necessarily involves a timely confined transormation of a polaron into a bipolaron and vice versa.

The importance of a better intermolecular arrangement, i.e., a higher level of crystallinity in the PANI samples, for obtaining a higher conductivity has become a well accepted factor all around the world recently, and this idea is not restricted to

PANI but involves most of the more prominent electronically conductive polymers. The observation that the conductivity of PANI films and fibres can be increased upon stretching is direct evidence for the importance of a good intermolecular arrangement (the latter being detectable with the aid of X-ray diffraction studies).

The arrangement of PANI molecules within the crystalline parts of powders, films and fibres and the total amount of the crystalline phase in the samples under investigation have been treated in several studies by Pouget et al.[178,179] These authors found two readily discernible arrangements, i.e., the emeraldine base 1/emeraldine salt 1 (EB1/ES1) and emeraldine base 2/emeraldine salt 2 (EB2/ES2) systems, respectively. Both crystalline arrangements belong to the orthorhombic system. The difference between them is found in the packing of the chains and the counterions within the individual cells[178]. It is necessary to point out that Pouget et al. claim that all the observable crystalline structures in differently prepared PANI samples can be accounted for by the EB1/ES1 and EB2/ES2 crystalline arrangements. Furthermore, it is important to stress the following statements of Pouget et al. concerning the EB1/ES1 and EB2/ES2 systems.

1. The undoped ES1 salt has in every case almost completely amorphous structure. On the other hand, ES2 itself shows in every case a semicrystalline structure.

2. Doped and undoped ES2 salts can show either a totally amorphous structure or a semicrystalline one, depending on the details of the preparation.

3. If the ES2 salt has a semicrystalline structure and undergoes an undoping process, a totally amorphous material results in every case

It is well accepted that PANI is a member of the family of the more environmentally stable electronically conductive polymers. Nevertheless, it undergoes a certain amount of degradation if exposed to heat and/or the

environment. The observable changes in mass and conductivity are caused by the uptake/loss of water, the loss of dopant molecules, different chemical reactions between the PANI chains themselves or with dopant molecules, or by more complex reactions between the doped material and the substances absorbed during the environmental and/or thermal exposure.

CHAPTER- 3

Experimental

3.1 Electrochemical Synthesis of Conducting Polymer :

There are two important methods for the synthesis of organic conducting polymers.

(a) Electrochemical method and

(b) Chemical method

Despite, the versatility of the chemical methods of polymerisation electrochemical synthesis of polymers offers an effective alternative in some instances. This is because electrochemical reaction are often much clear with respect to possible pollutants than chemical reactions. Moreover, electrons as a reagent, are inherently pollution free, at least at the point of use. Thus, there are a number of examples where electrochemical routes produce unique products and do so in reaction pathways which in themselves are unique. An appeal of electrochemical polymerization is that they can be controlled so well by means of the electrode potential to give a high selectivity of desired products.

In this study electrochemical method was used to synthesize polyaniline and polyo-toluidine.

Procedure

Reagents and solvents are purified by distillation. In this method conducting polymers are synthesize from an electrolytic solution containing aniline/o-toluidine in sulfuric acid medium by anodic electrodeposition on platinum sheet.

In the synthesis processes the effects of the following major variables on the structure and properties of synthesized polymers are observed:

(i)   Bath composition : Monomer 5-20cc/l, H_2SO_4 100 cc/l

(ii)   Bath temperature : $5°C$-$25°C$

(iii)   Deposition current density : 5-15mA/cm^2

One litre of solution was prepared by adding 100 c.c of sulphuric acid of specific gravity 1.84 (BDH, Analargrade) and 5-20 c.c.aniline/o-toluidine in the proper amount of water. The solution was then mixed with 20 gm of charcoal, heated up to boiling point and boiled for 15 minutes. The solution was then cooled, decanted and filtered. The clear and colourless solution thus obtained was subsequently used for electrochemical polymerization.
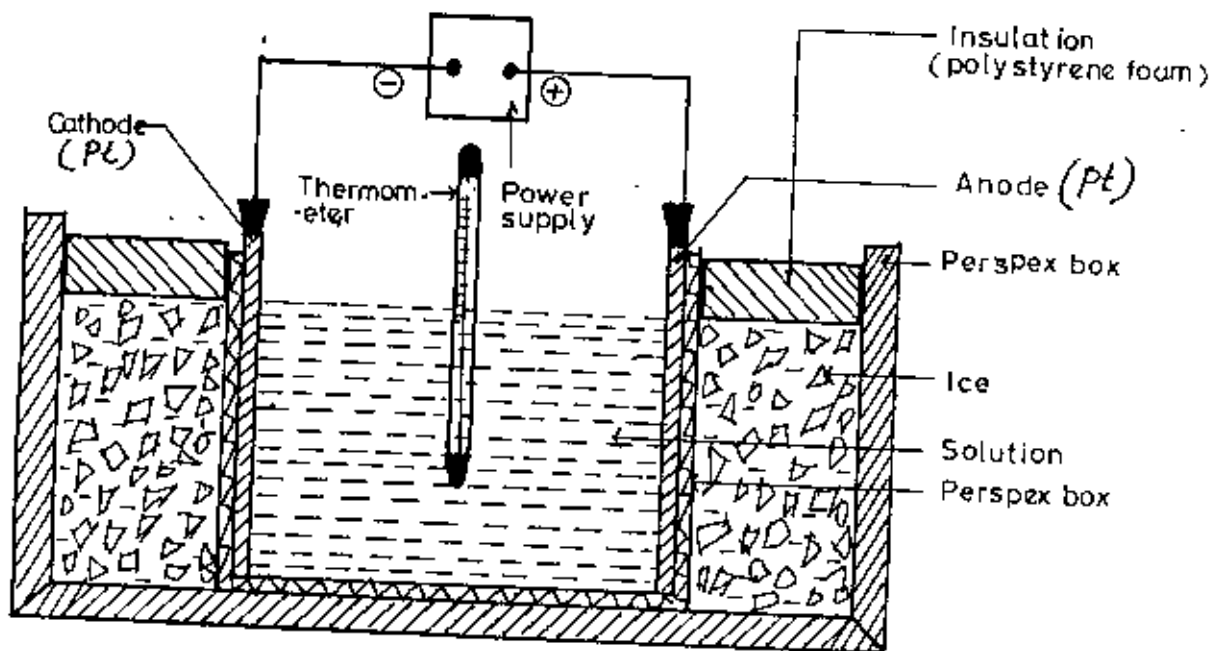

Fig. 3.1: The experimental set up for the electrochemical synthesis of polymers.

Two litres of aniline solution was placed in a perspex container of 20 cm × 14 cm × 14 cm size (Fig. 3.1). For deposition below room temperatures, the cell was kept in another perspex box filled with ice. Two platinum sheets each of 13 cm length and 12 cm width were placed vertically inside the cell and were used as anode and cathode. One side of the anode was covered with lacquer. The anodic area was measured where the polymers were deposited. A constant current power source (Kenwood Model PD 3-10) was used to deposit polyaniline at the anode under galvanostatic condition. The polymer was deposited as film on the anode surface. Deposition was conducted out for about six minutes after which the anode was taken out of the cell and polyaniline was scrapped out of the anode by using a perspex knife. Deposition was carried out several times to collect enough material for subsequent investigations. The sample was then washed thoroughly with distilled water to remove of any free sulphate. After washing, the sample was dried in a at 60°C under vacuum for about 20 hours. It was then stored in a desiccator under embient atmosphere. Following this some procedure polyaniline and poly o-toluidine samples were prepared under various conditions of different current densities, bath compositions and temperature.

3.2   Chemical Synthesis :

Chemical synthesis of polyaniline was done using 0.4 mol solution of aniline in acidic medium. The solution was prepard by dissolving 3.65 ml aniline in 10 ml I M sulphuric acid. Nitrogen gas was passed through this solution to deoxygenate it. To this solution, dried ammonium peroxidisulphate was added in order to obtain 0.1 molar solution of ammonium persulphate. The solution was kept under constant stirring at room temperature and the stirring was continued for 7 (seven) hours. Black precipitate of the polyaniline was then collected by filtering the solution. It was then washed with distilled water and then with ethanol. Finally it was air dried.

3.3   Characterization :
3.3.1 Thermal Analysis (TG Analysis)

TG analysis is concerned with weight change of sample with temperature. The thermogravimetric curves thus obtained gives information about the sample composition, decomposition temperature and thermal stability of polymers. Activation parameters can also be determined by using various analytical methods. The thermogravimetric analysis was carried out in the House Building Research Institute (HBRI), Mirpur, Dhaka in air atmosphere in the temperature range 0°C to 1000°C with heating a rate of 10°C/minutes by using RIGAKU Thermogravimetric Differential Thermal Analyzer (TAS-100) with TG Basic unit 8110. Sample weight was 5 mg in each run. The temperature was recorded by using a chromel-alumel thermocouple.

Methods for Data Analysis :

Thermal stability of polymer can be studied by using TG analysis technique. It is very useful technique in which we can easily observed the change in weight of polymer sample with increase of temperature. The range at which polymers start degradation is called the degradation or decomposition temperature. But at low temperature say below 100°C there is loss of only moisture. At high temperature polymer starts degradation. The TGA curve of polymers follows relatively single sigmoidal path. The shape of TGA curve depends upon the kinetic parameters like (a) reaction order (n) (b) frequency factor (A) and (c) activation energy (E_a). From this value we can easily find out the mechanism involved in polymer degradation and an estimation of thermal stability. A number of methods have been proposed for estimating kinetic parameters from dynamic TGA studies[180,182]. All these methods are based on the assumptions that

(i)   Thermal and diffusion barriers are negligible, and

(ii)   Arrhenius equation is valid

In this work, Sharp-Wentworth[181] method is used to determine above mentioned parameters. In the reaction.

$$X \rightarrow Y + Z \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where X and Y are solids and Z could be a volatile or gaseous products.

The rate of disappearance of X may be expressed as

$$\frac{dc}{dt} = k\,(1\text{-}c)^n \ldots\ldots (2)$$

where c : fraction of X decomposed at time t,

n : order of reaction, and

k : rate constant which is related to temperature by the Arrhenius equation as

$$k = A.e^{-\frac{E_a}{RT}} \ldots\ldots\ldots\ldots (3)$$

where A : frequency factor,

E_a : activation energy of the reaction, and

R : gas constant.

For a linear heating rate, β in deg/min., $\beta = \frac{dT}{dt} \ldots\ldots\ldots\ldots(4)$

Therefore $\frac{dc}{dt} = \beta.\frac{dc}{dT} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$

On combining equation (2) ,(3) and (5),

we get $\frac{dc}{dT} . \beta = (1\text{-}c)^n . A.e^{-E_a/RT} \ldots\ldots\ldots\ldots\ldots\ldots(6)$

On rearrangement, we get $\dfrac{\frac{dc}{dT}}{(1-c)^n} = \frac{A}{\beta}\, e^{-E_a/RT} \ldots\ldots\ldots(7)$

Now taking logarithm

$$\log \frac{\frac{dc}{dT}}{(1-c)^n} = \log \frac{A}{\beta} - \frac{Ea}{2.303RT} \quad \cdots\cdots\cdots\cdots\cdots\cdots (8)$$

If $n=1$, i.e., for reaction having first order, the equation (8)

reduce to $\log \frac{\frac{dc}{dT}}{(1-c)} = \log \frac{A}{\beta} - \frac{Ea}{2.303RT} \quad \cdots\cdots\cdots\cdots (9)$

By applying equation (9) to simple TG curve, total mass loss at the end is taken as the active mass a_0 of the substance participating in the degradation process and this value a_0 is taken into account in calculating fractional mass loss (c) at given temperature. But the situation is somewhat different in a two stage degradation reaction. These two steps are theoretically separated from each other by using a method suggested by Papazian[183] and each step is individually analysed for evaluation of kinetic parameters by using Sharp-Wentworth method. In present investigation the degradation has been observed to follow a single sigmoidal path. Therefore the equation (9) can be applied to it. Now the activation energy E_a and frequency factor A, of reaction involved in the thermal degradation of polymers were calculated by means of Arrhenius equation

$$k = A.e^{-E_a/RT} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (10)$$

where k is the reaction rate constant Therefore a plot between $\log \left(\frac{\frac{dc}{dT}}{1-c}\right)$ as a function of $\frac{1}{T}$ is drawn, and the activation energy and frequency factor can be calulated as follows :

$$\text{Slope} = \frac{-E_a}{2.303R} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (11)$$

$$\text{and Intercept} = \log \left(\frac{A}{\beta}\right) \quad \cdots\cdots\cdots\cdots\cdots (12)$$

Therefore Activation energy, $E_a = -\text{Slope} \times 2.303R \quad \cdots\cdots (13)$

Frequency factor $\frac{A}{\beta}$ = antilog (Intercept) .... (14)

By using these equations (13) and (14) kinetic parameters can be calculated.

3.3.2 X-Ray Diffraction (XRD) :

This analysis gives an idea about the crystal structure, unit cell dimension and crystalline nature of the polymer. The X-ray structure analysis is based on the phenomenon of diffraction of X-ray by a substance. Wide angle X-ray diffraction spectra were taken by using Jeol JDX-8PJEOL diffractometer. Diffraction patterns using CuK_α radiation at 30 kV and 20 mA. were recorded with a scanning speed $\frac{1}{2}^\circ$ or 1°/min. The sample powder was put in the sample holder (aluminium specimen holder) or on the glass slide and the lid of the camera was sealed tightly. The X-ray was switched on and the window was opend to the X-ray. The patterns were recorded on chart recorder at a chart speed of 2.5 mm/min.

3.3.3 Electrical Conductivity:

Dry powdered samples were pressed into pellet in the laboratory of Chemical Engineering Department, BUET by using "SHIMADZU TABLETDIE" under a pressure of 330 kgf/cm². The pellets, thus obtained were crack free, hard and smooth. Before measuring the conductivity the thickness and area of pellet was measured with the help of screwgauge. The pellets were then stored in desiccator till the measurments.

After measuring the thickness and diameter of the pellet of the polymer sample,, the pellet was placed in the sample holder and the corresponding resistance was measured at room temperature by using the conventional two probe method

using a Kethley autoranging microvoltmeter (197A). Resistivity was calculated by using the equation.

$$\rho = R. \frac{A}{t} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

where R : Resistance of pellet.

       A : Surface area of the pellet.

       t : Thickness of the pellet.

       ρ : Resistivity of the polymer.

3.3.4 UV-Visible Spectroscopy :

UV-visible spectra of polyaniline and poly o-toluidine samples in DMF solvent were taken at room temperature in a Hitachi, Japan, double beam Spectrophotometer (model no 200-10) attached with synchronized recorder (model no-200) in the Department of Conservation Laboratory, Bangladesh National Museum, Sahbagh, Dhaka. Spectra were recorded between the wave length range from 200 to 700 nm.

Polymer samples were dissolved in dimethyl formamide (DMF) solvent to a visual extent. Polymer solution was the filtred by using Whatman No. 40 filter paper, The filtrate was used for spectral analysis. The sample solution was placed in one of the holes of the sample holder and the other hole was filled with the reerence dimethyl formamide (DMF) solvent. The spectrum was then recorded.

3.3.5 Infra Red Spectra :

5.0 mg of solid polymer samples were used for IR measuremants. Infrared spectra were recorded by using KBr pellet technique in 400-4600 cm^{-1} range at the Department of Polymer Physics, Technical University of Berlin,

Berlin, Germany, on Specord 75 Infrared Spectrophotometer by optically zero balancing technique.

3.3.6 Scanning Electron Microscopy (SEM) :

Scanning electron microscopy of the polymer samples was carried out using Cambridge Stareoscan S 250 MK III Scanning electron microscope at the SIRC, Technical University of Berlin, Berlin, Germany. The samples were coated with Au and thickness of coating was approximately 150 Å. The scanning electron micrographs were taken at a magnifications of 150.

3.3.7 Carbon, Hydrogen and Nitrogen Analysis (Elemental Analysis) :

The C, H and N analysis of polyaniline was done by microestimation technique by using CARLD ERBA STRUM, DP 200 at RSIC Lucknow, India.

CHAPTER- 4

Results and Discussions :

4.1 TGA and DTA Analysis for Polyaniline and Poly O-Toluidine :

TGA curves of electrochemically prepared polyaniline under different conditions are shown in Fig. 4.1 and 4.2. The TGA curves show an initial mass loss at temperature below 100°C. This is due to the loss of moisture from the sample. After the loss of low molecular mass moisture, weight decreasing at slow rate up to about 300°C, above which a rapid loss of weight takes place. The slower weight loss at intermediate temperature may be due to lose of lower molecular mass oligomers. The weight loss at higher temperatures is due to the thermal decomposition of polyaniline. The degradation of polyaniline is found to follow a single sigmoidal path. Similar behaviour has also been observed in the case of chemically prepared polyaniline[184]. The TGA curves of poly o-toluidine exhibit more or less similar behaviour as can be found in Fig. 4.3 and 4.4.

The DTA curves of polyaniline deposited under diferent conditions are given in Fig. 4.5 and 4.6. The curves shows small endothermic peak below 100°C. This endothermic peak corresponds with the intial mass loss indicated by TGA curves and is due to the removal of sorbed water from the polymer[185]. The curves then show an exothermic peak at around (250°C). This is thought to be due to phase transition. Upon further increase of temperature the DTA curves show a sudden jump followed by a couples of exothermic peaks. These sudden jump and exothermic peaks are linked to rapid oxidational degradation of polyaniline. The sudden rise in DTA curves corresponds with the rapid mass loss of the sample as

indicated by the TGA curves. The DTA curves of poly o-toluidine is shown in Fig.4.7 and 4.8. The curves are found to show characteristics similar to that of DTA curves of polyaniline (Fig.4.5 and 4.6). This indicates that similar degradation process is operative in both polyaniline and poly o- toluidine samples.

The activation energy for thermal degradation of polyaniline and poly o- toluidine was determined following the Sharp-Wentworth method and assuming reaction order equal to one[186].

Fig. 4.9 shows a typical log $[\frac{dc}{dt} / (1-c)]$ versus 1/T curve, the slope of which gives the activation energy (where c is the fraction decomposed at time t and T is temperature).The activation energy for the thermal degradation of polyaniline and poly o-toluidine obtained at various deposition current densities is shown graphically in Fig. 4.10. It is seen that in the case of both polyaniline and poly o-toluidine activation energy tends to have a higher value at intermediate current density viz. 10 mA/cm^2. It is further seen that the activation energy for polyaniline is always higher than that of poly o-toluidine.

The activation energy of polyaniline and poly o-toluidine deposited at various temperatures is shown in Table 4(a) and 4(b) respectively. It is found that activation energy of polyaniline deposited at different temperature lies in the range of 35.54 - 38.06 kj/mole while that of poly o-toluidine lies in the range of 32.57 - 37.03 kj/mole. No clear correlation between activation energy and deposition temperature is seen in either of the cases.

Among the three deposition current densities investigated (5,10 and 15 mA/cm^2) the current density of 10 mA/cm^2 is found to yield highest conductivity in both polyaniline and poly o-toluidine. Band gap energy calculated from UV-visible spectra supports this result. Activation energy calculated from TGA curves further

show that polyaniline deposited at 10 mA/cm^2 possesses the highest thermal stability in air. It is therefore concluded that for the electrodeposition of conducting polymer, there exists an optimum deposition current density at which best results are obtained and this optimum current density is found to be 10mA/cm^2 in the present study.

Table 4(a) Activation energy of polyaniline obtained at various deposition temperatures

Deposition Temperature °C	Other Deposition Condition	Activation energy kj/mole
5	A. Solution Composition	35.54
9	Aniline : 20 ml/l	37.37
18	H$_2$SO$_4$:100 ml/l	35.82
25	B. Current density 10 mA/Cm^2	38.06

Table 4(b) Activation energy of polyo-toluidine obtained at various deposition temperatures

Deposition Temperature °C	Other Deposition Condition	Activation energy kj/mole
5	A. Solution Composition	32.57
9	Poly o-toluidine: 20 ml/l	—
18	H$_2$SO$_4$: 100 ml/l	37.99
25	B. Current density 10 mA/Cm^2	37.03
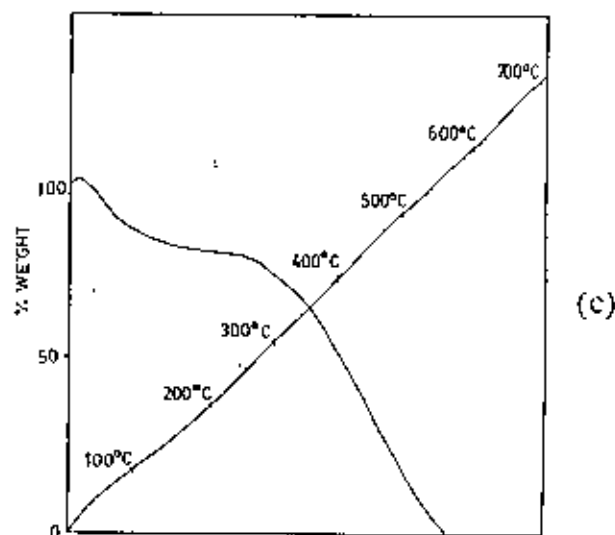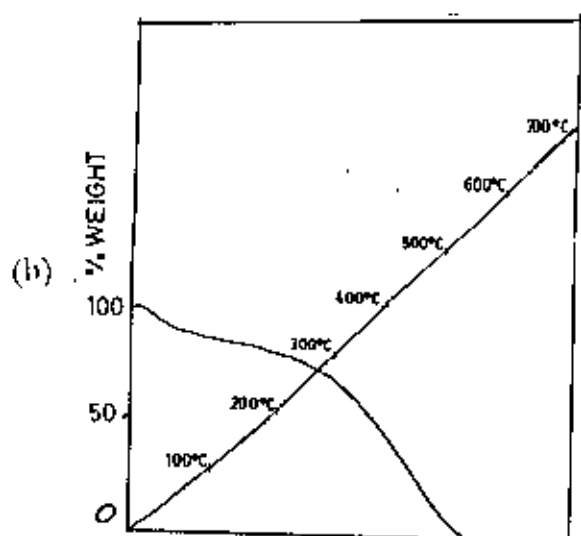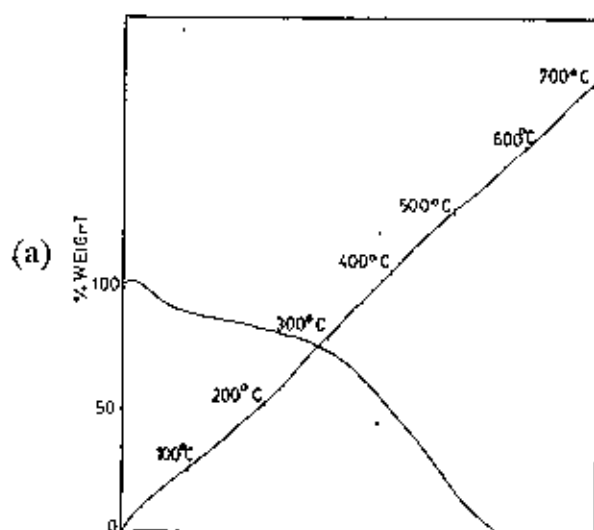
Fig. 4.1 TGA curves of polyaniline deposited at (a) 5mA/cm², (b) 10 mA/cm² and (c) 15 mA/cm². (Solution composition : 20ml/l aniline. 100ml/l H₂SO₄, temperature 25°c)
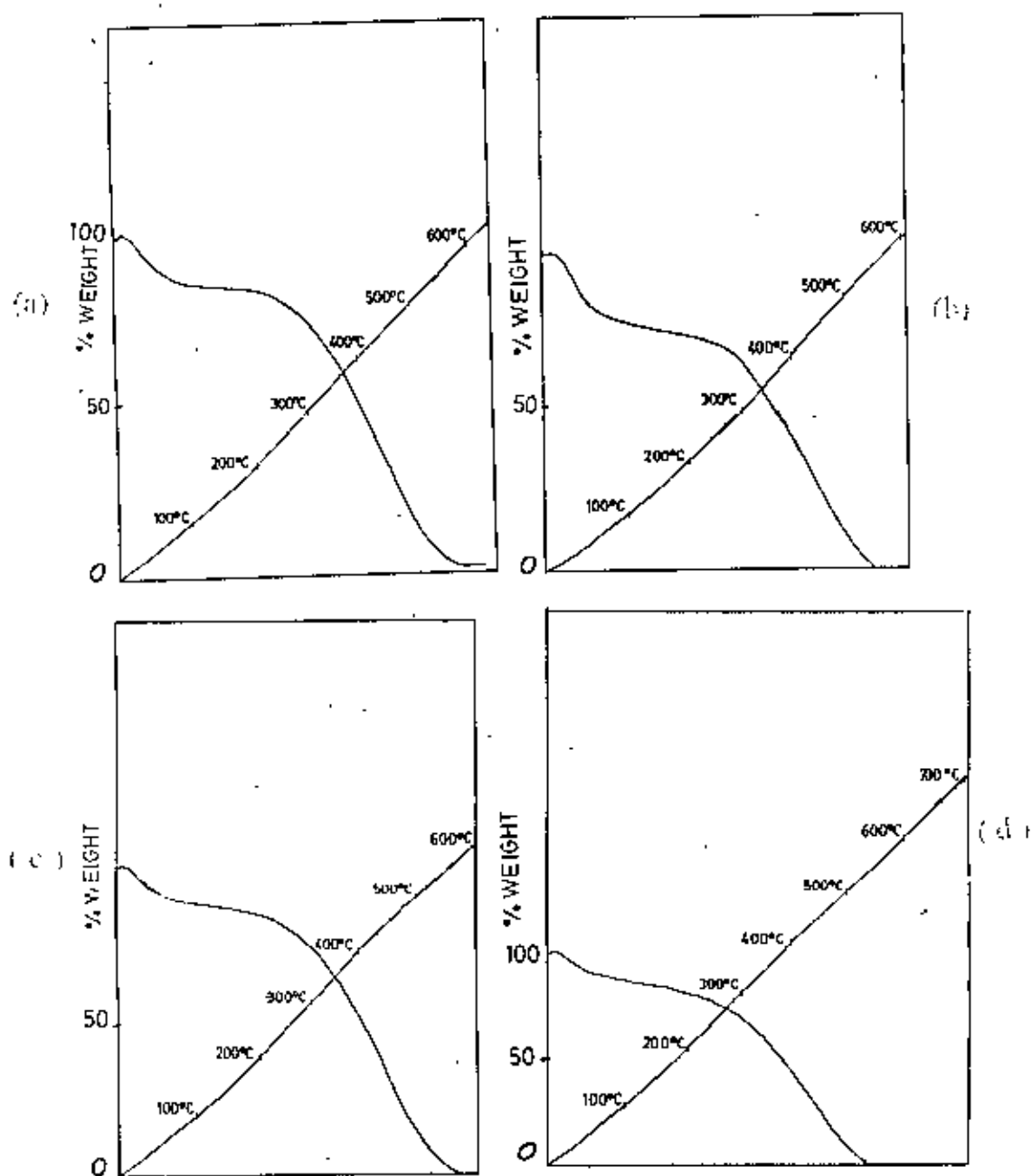
Fig. 4.2 TGA curves of polyaniline deposited at (a) 5°c, (b) 9°c © 18°c and (d) 25°c
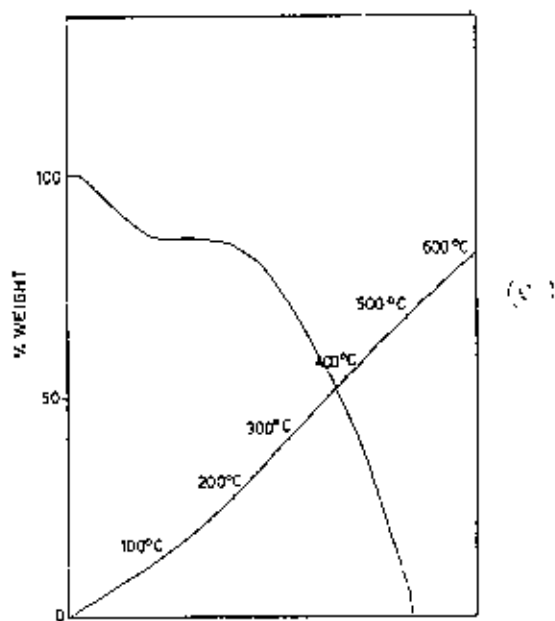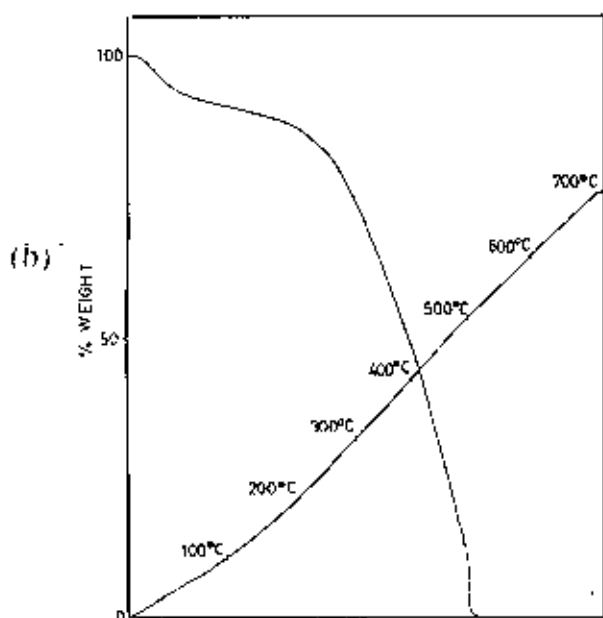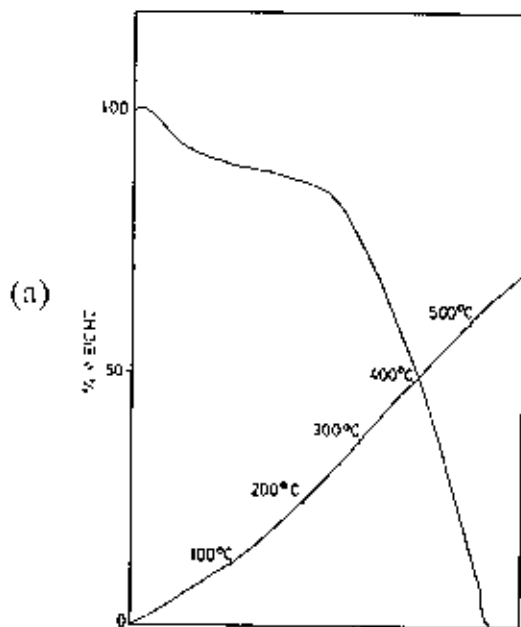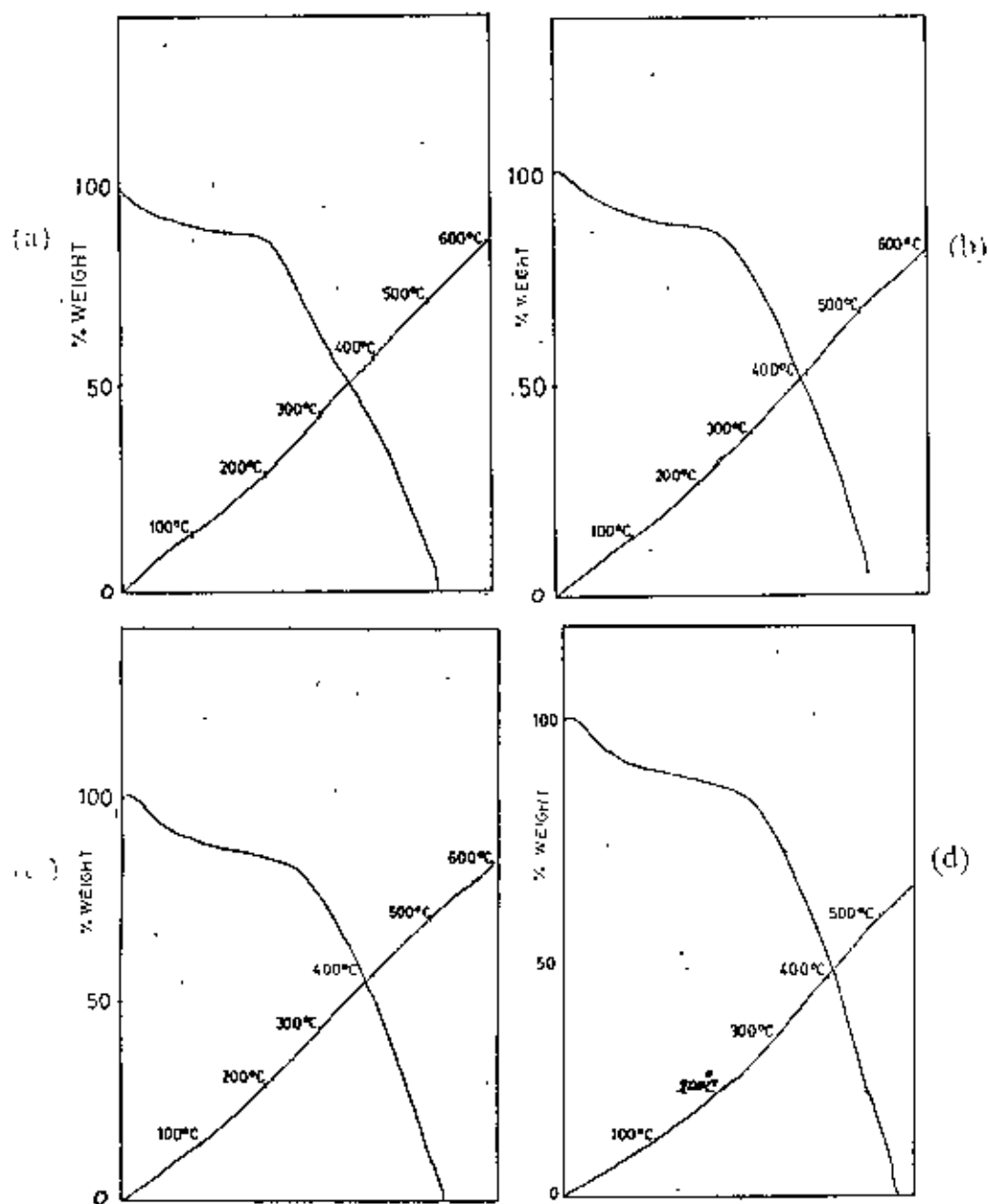(Solution Composition : 20ml/l aniline, 100ml/l H₂SO₄ and current density 10 mA/cm²)

Fig. 4.3 TGA curves of poly o-toluidine deposited at (a) 5mA/cm², (b) 10mA/cm² and (c) 15mA/cm² (Solution Composition : 20ml/l o-toluidine, 100ml/l H₂SO₄ and temperature 25°c)

Fig. 4.4 TGA curves of poly o-toluidine deposited at (a) 5°c, (b) 9°c © 18°c and (d) 25°c (Solution Composition : 20ml/l o-toluidine, 100ml/l H₂SO₄ and current density 10mA/cm²)

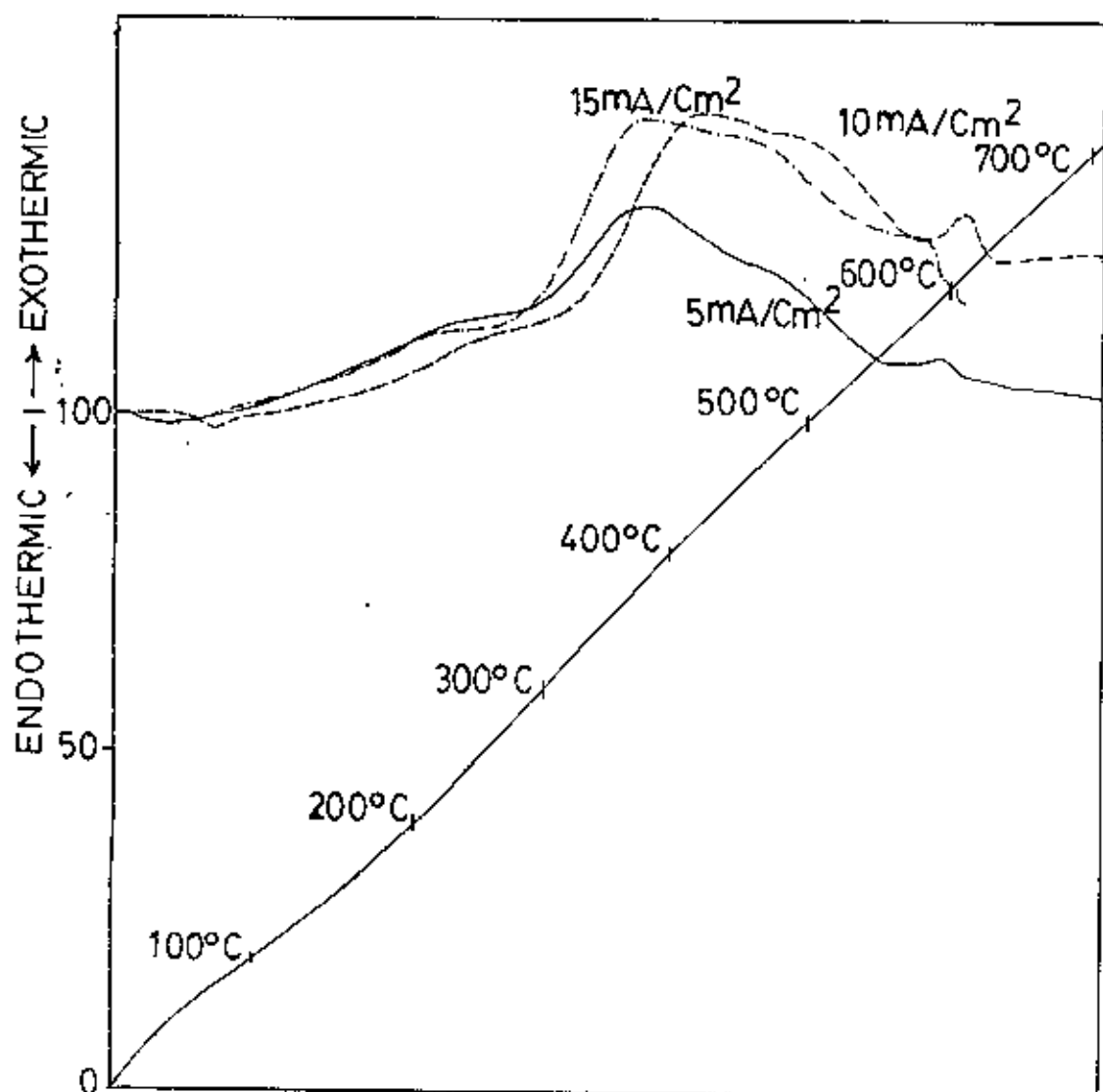Fig. 4.5 Typical DTA curves of polyaniline deposited at different current densities (Solution Composition : 20ml/l aniline, 100ml/l H₂SO₄ and temperature 25°C)
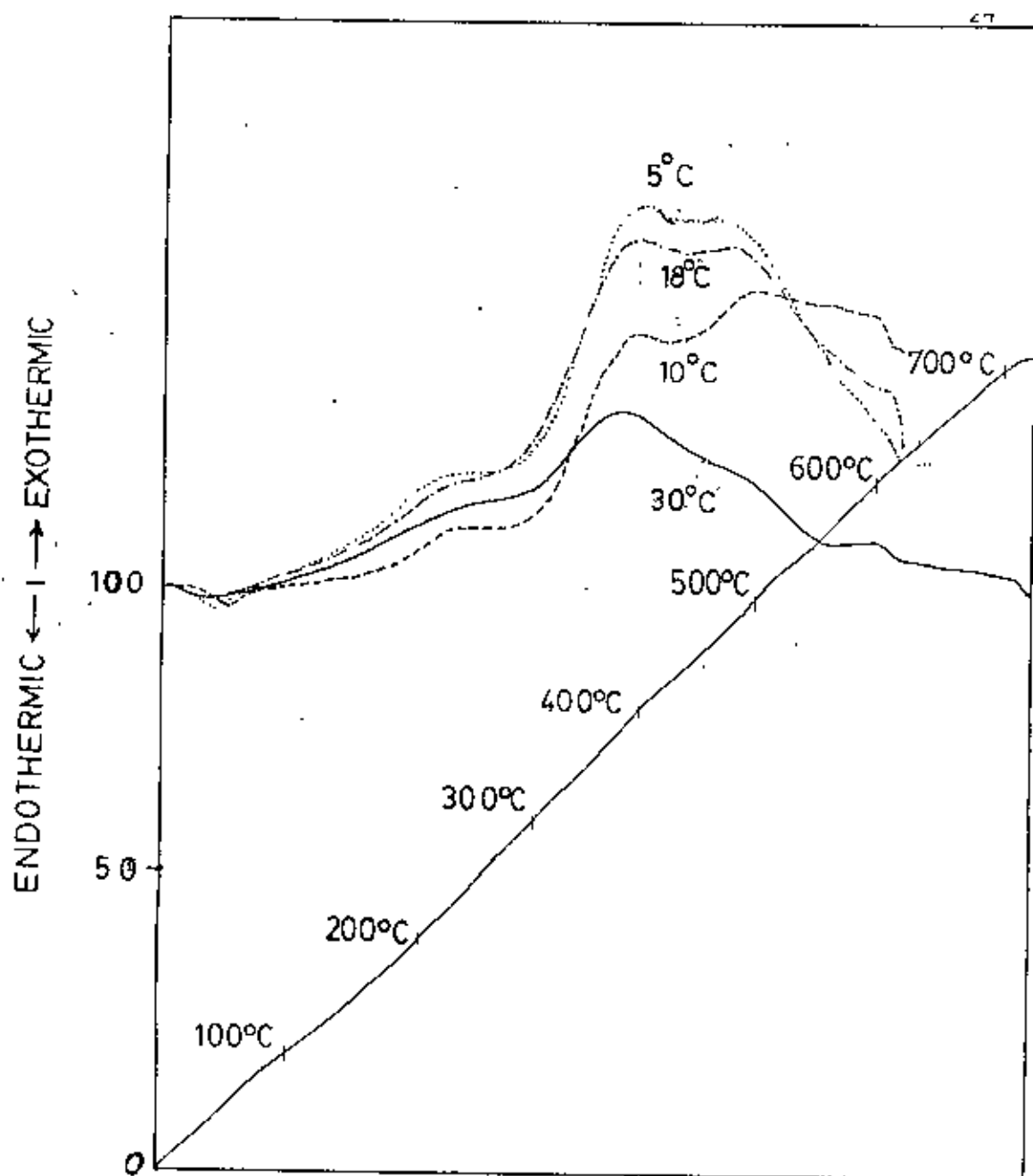
Fig. 4.6 Typical DTA curves of polyaniline deposited at different temperatures.
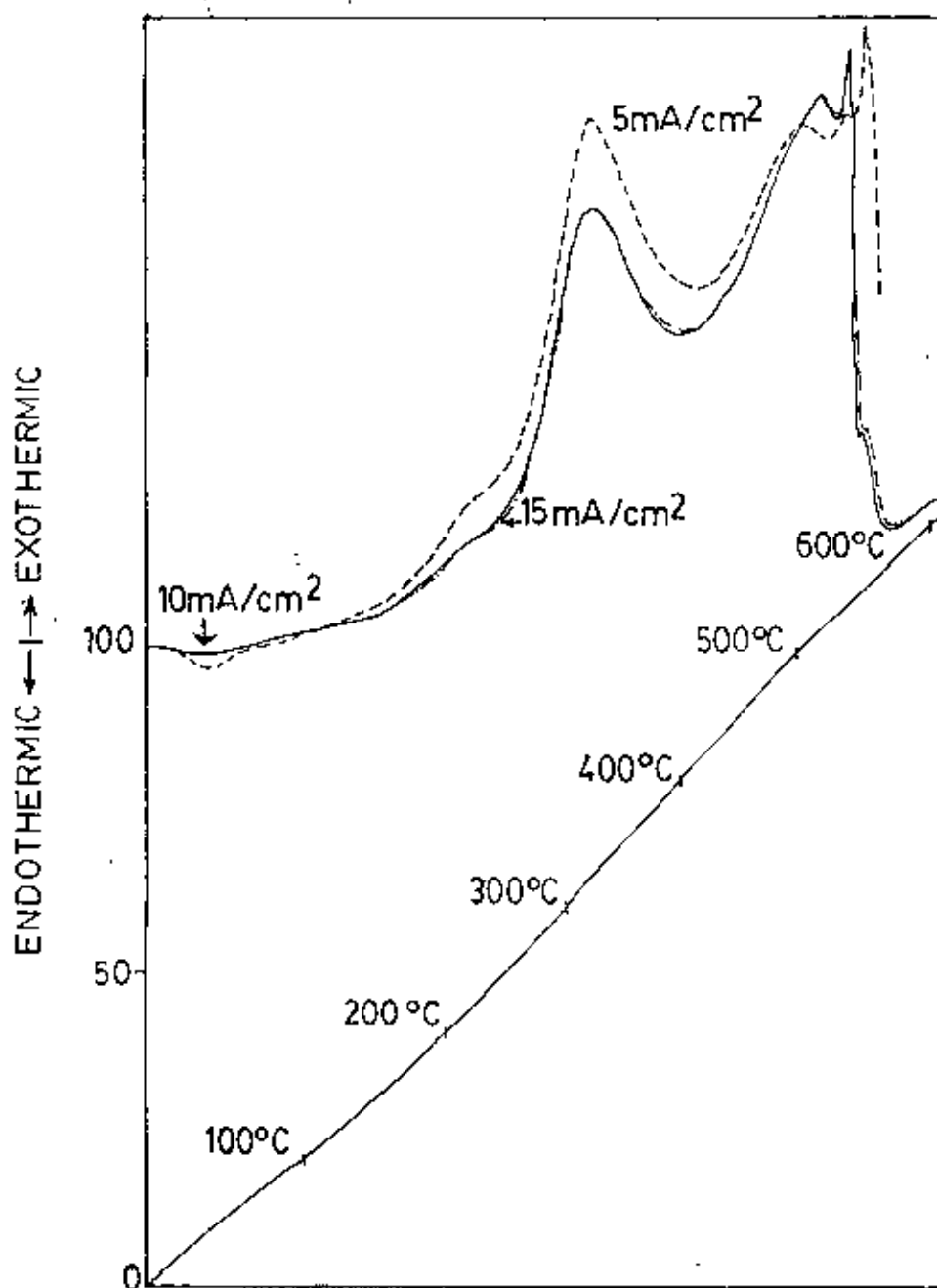(Solution Composition : 20ml/l aniline, 100ml/l H$_2$SO$_4$ and current density 10 mA/cm^2)

Fig. 4.7 Typical DTA curves of poly o-toluidine deposited at different current densities. (Solution Composition : 20ml/l o-toluidine, 100ml/l H₂SO₄ and temperature 25°C)
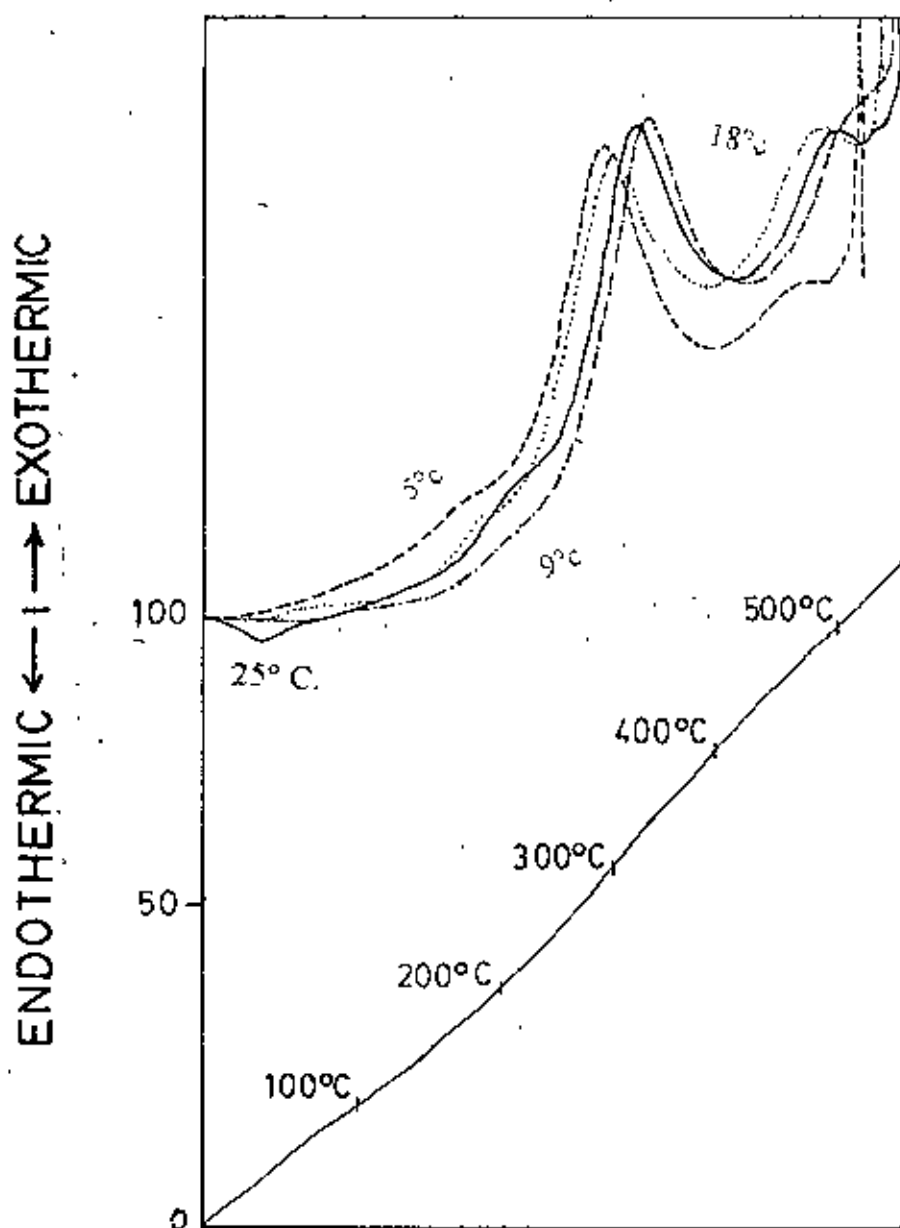
Fig. 4.8 Typical DTA curves of poly o-toluidine (Deposition temperature 5, 9, 18 and 25°c)
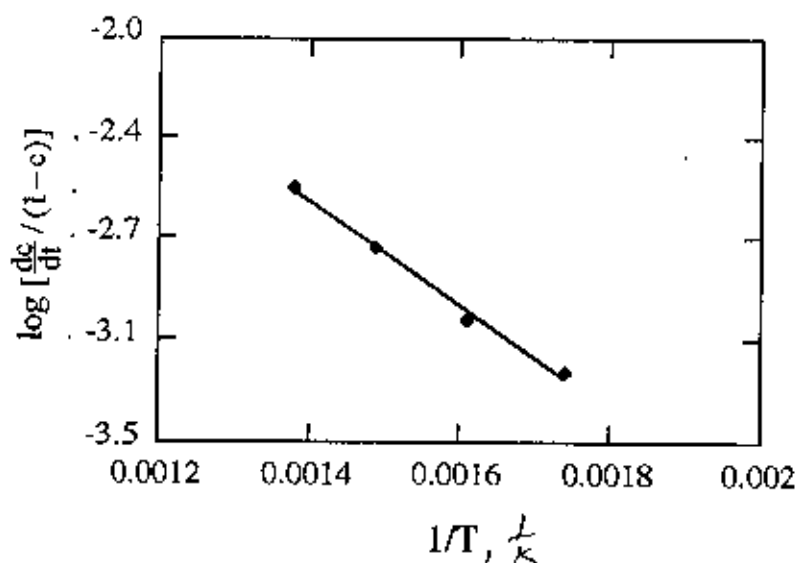(Solution Composition: 20ml/l o-toluidine, 100ml/l H₂SO₄ and current density 10mA/cm²)

Fig.4.9 A typical plot of log $[\frac{dc}{dt}/(1-c)]$ versus $\frac{1}{T}$ thermal degradation of polyaniline 5 mA/cm^2 and 25°C.
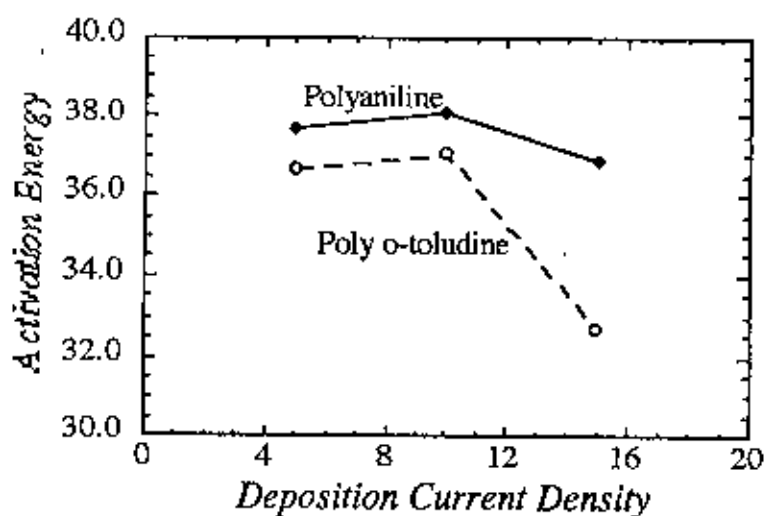

Fig. 4.10 Show the variation of activation energy of polyaniline and poly o-toluidine deposited at different current density 5, 10 and 15 mA/cm^2

4.2   X-Ray Diffraction Study of Polyaniline and Poly O-Toluidine :

Fig. 4.11 shows the X-ray diffraction patterns of polyaniline samples deposited at anodic current densities of 5, 10 and 15 mA/cm^2 respectively. All the patterns exhibit mainly two peaks which occur at 2θ values in the neighbourhood of 19 and 25°. Diffraction peaks at similar positions were also found for polyaniline by others[187,188]. Peak characteristics, however are observed to change with polyaniline deposition current density. The peaks are rather broad and diffused for the sample prepared at 5 mA/cm^2. The peaks become sharper as deposition current density increases. It can thus be concluded that lower deposition current density yields amorphous polyaniline while higher crystallinity of polyaniline is obtained when the deposition current density is higher.

X-ray diffraction patterns of polyaniline deposited at different temperatures are shown in Fig. 4.12. Two peaks at 2θ values around 19 and 25° are seen to occur in all the patterns. These peak positions are more or less similar to those of polyaniline deposited at different current densities at room temperatures (compare Fig. 4.11 and 4.12). The peaks are, in general, rather diffuse.

The X-ray diffraction patterns of polyo-toluidine deposited at various current densities at room temperature is shown in Fig. 4.13. All the patterns contain a broad hump around 2θ values of 20-25°. The existance of the broad diffuse peak indicates amorphous nature of polyo-toluidine deposited at room temperature at current densities ranging from 5 to 15 mA/cm^2.

Fig. 4.14 shows the effect of deposition temperature on the diffraction pattern of poly o-toluidine deposited at 10 mA/cm^2 from bath containing 20 ml/l o-toluidine. The diffraction pattern of poly o-toluidine deposited at 5°C shows a

rather sharp peak at 22.5° and some overlapping diffused peaks in the neighbourhood of 14-17°. The peaks of the samples deposited at 9°C and 18°C are very broad. These broad peaks occur more or less at the same position as those in samples deposited at 5°C.

Fig. 4.15 shows the diffraction pattern of poly o-toluidine deposited at 15 mA/cm² at room temperature from bath containing a lower amount of ortho-toluidine viz, 5 ml/l. The pattern exhibits rather sharp peaks at 2θ values 22.4° and 26.4° and two peaks of comparatively lower sharpness at 10.6° and 16.6°. Fig. 4.15 may be compared with Fig. 4.13 where the only difference between the two samples is bath composition, all other conditions being identical. It is thus observed that deposition from a dilute bath yields a more ordered poly o-toluidine.

It is found in the case of both polyaniline and poly o-toluidine that, in general, lower deposition temperature results in sharper diffraction peaks suggesting more caystallinity. Although in the case of polyaniline, increased deposition current density increases crystallinity, this is not so evident for poly o-toluidine. Polyaniline and its derivatives are known to have orthogonal crystal structure[189]. In the present case, fewer number of peaks and their diffused nature did not allow the determination lattice parameter. It is seen from Fig 4.11 and 4.13 that, generally polyaniline is more crystalline than poly o-toluidine. Shenglong et al.[190] also found that poly o-toluidine possesses lower crystallinity than polyaniline prepared under the same conditions. Thus the finding of the present study is in agreement with that Shenglong et al.. Similar finding was also reported by Warhadpande and Gupta[189]. The presence of methyl group in the structure of o-toludine may cause distortion in the lattice resulting in a loss of periodicity.

Fosong et al.[187] they studied effect of concentration of electrolyte. In this study concentration of monomer was lowered in the electrolytic solution on the crystallinity of undoped polyaniline. They found that crystallinity decreases with increasing HCl concentration over the range of 0.00-7 N HCl. In the present study, aniline solution of a single concentation viz. 20 ml/l aniline and 100 ml/l H_2SO_4 was used. However, in one experiment the concertation of o-toluidine was lowered to 5 ml/l and the resulting poly o-toluidine shows a higher amount of crystallinity.

Although diffused peaks in XRD pattern generally indicates amorphous structure, it can also be linked to the presence of very fine microcrystals. Shevchenko et al.[191] studied the structure of polyaniline by both X-ray diffraction and electron diffraction. They found that although X-ray diffraction pattern of polyaniline shows broadened peaks indicating the presence of amorphous structure, electron diffraction revealed the presence of highly ordered microregions within the sample. It is believed that further investigation of the present samples by electron diffraction would lead to better insight about their structure.

Furthermore, Shevchenko et al.. found that X-ray diffraction patterns of electrochemically and chemically synthesized sampls were different. The main peaks occured at about 2θ values of 18 and 24° for electrochemically polymerized sample while those for chemically polymerized samples occurred at about 8 and 12°. In the present study polyaniline was also synthesized chemically whose X-ray diffraction pattern is given in Fig. 4.16. A comparison of Fig. 4.11 and 4.16 shows that electrochamically and chemically prepared samples show similar XRD pattern i.e., the number and the position of the peaks are more or less the same in both cases. It is not clear if this discrepency could be linked to the fact that all the samples in the present case were prepared from sulphuric acid based baths while Shevchenko et al.. used hydrochloric acid based solution for their sample preparation.
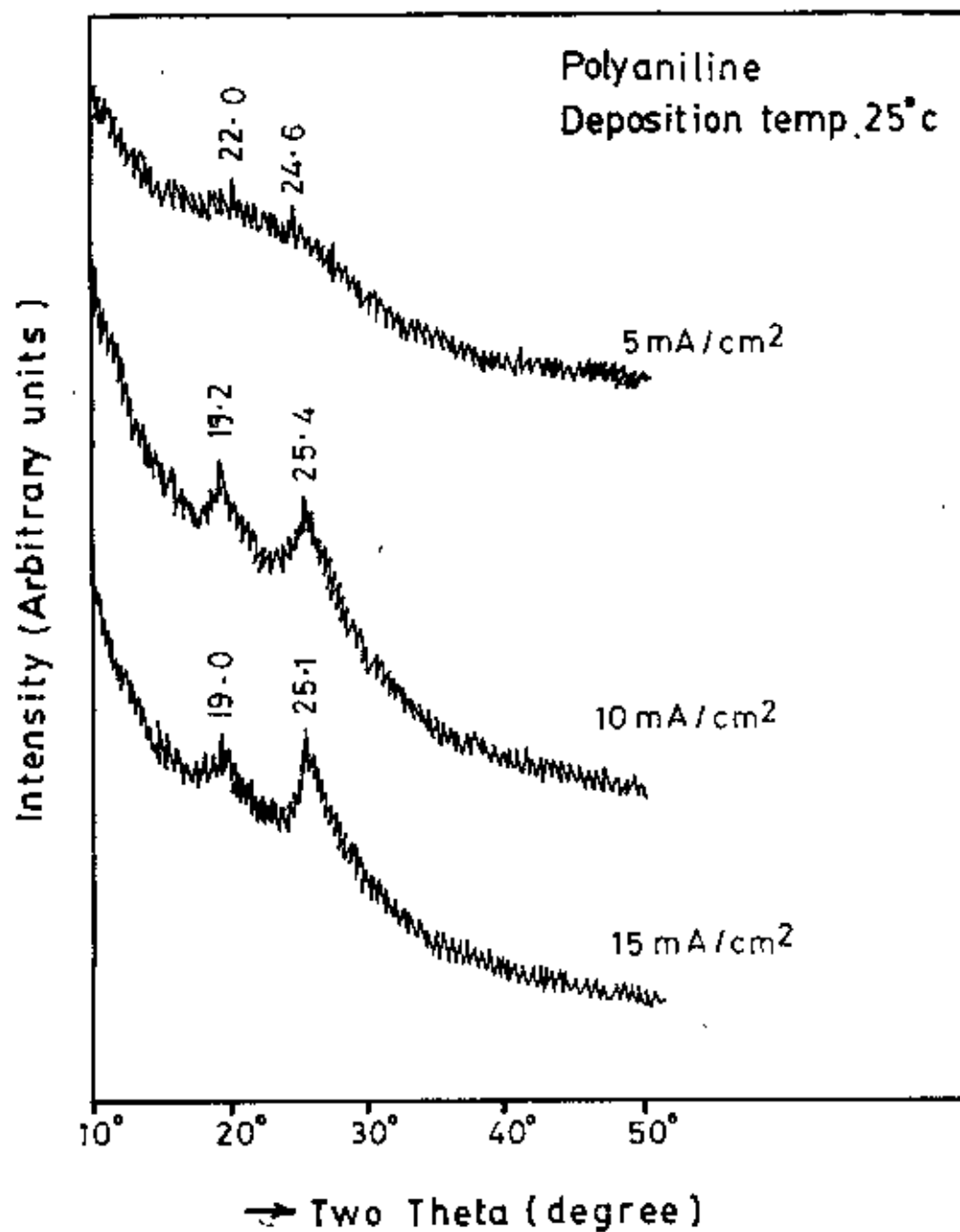
Fig. 4.11 X-Ray Diffration patterns of polyaniline deposited at different current densities (Solution composition 20 ml/l aniline, 100 ml/l H_2SO_4, temperature 25°c)
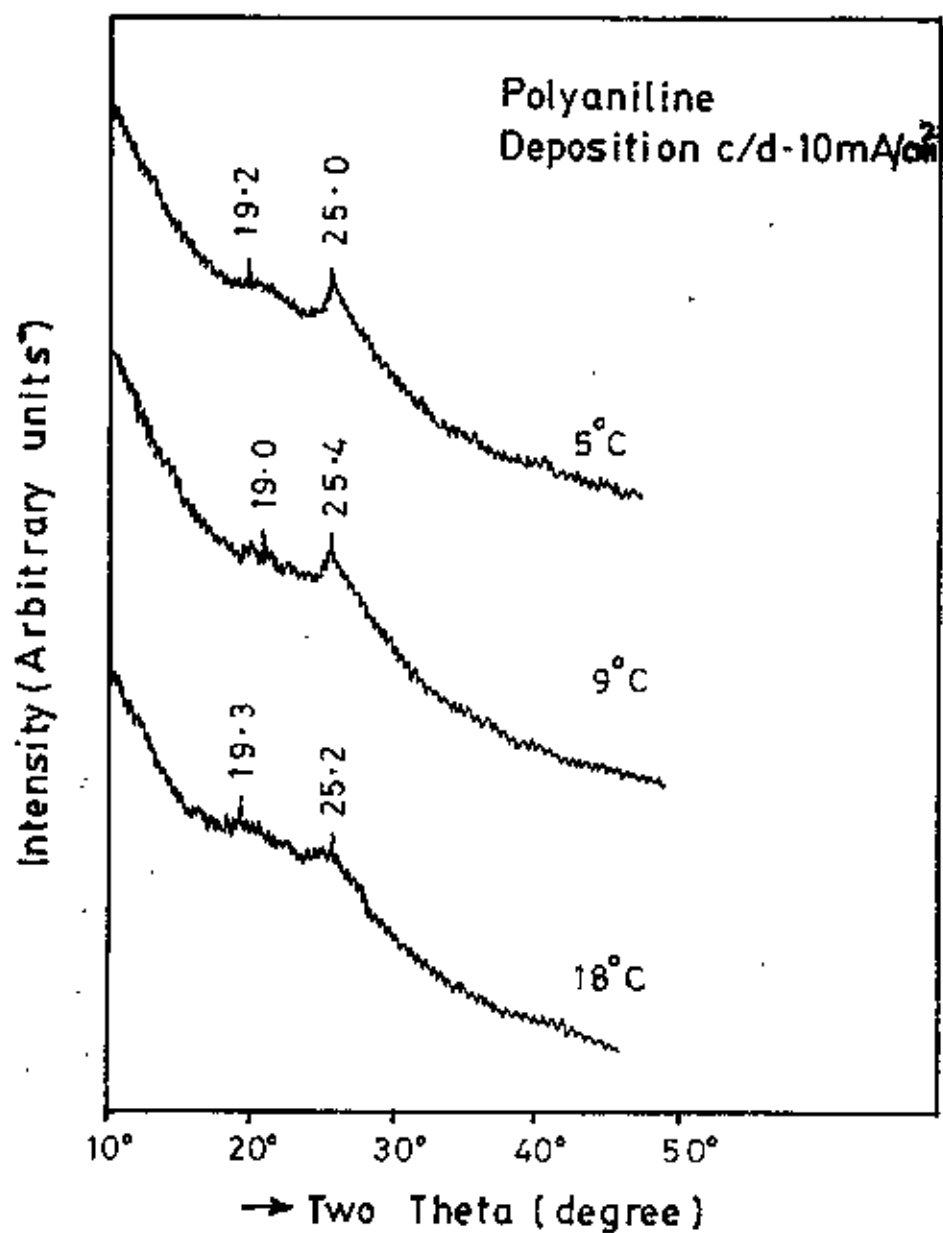
Fig. 4.12 X-Ray Diffration patterns of polyaniline deposited at different temperatures (Solution composition 20 ml/l aniline, 100 ml/l H_2SO_4 and current density 10 mA/cm^2)
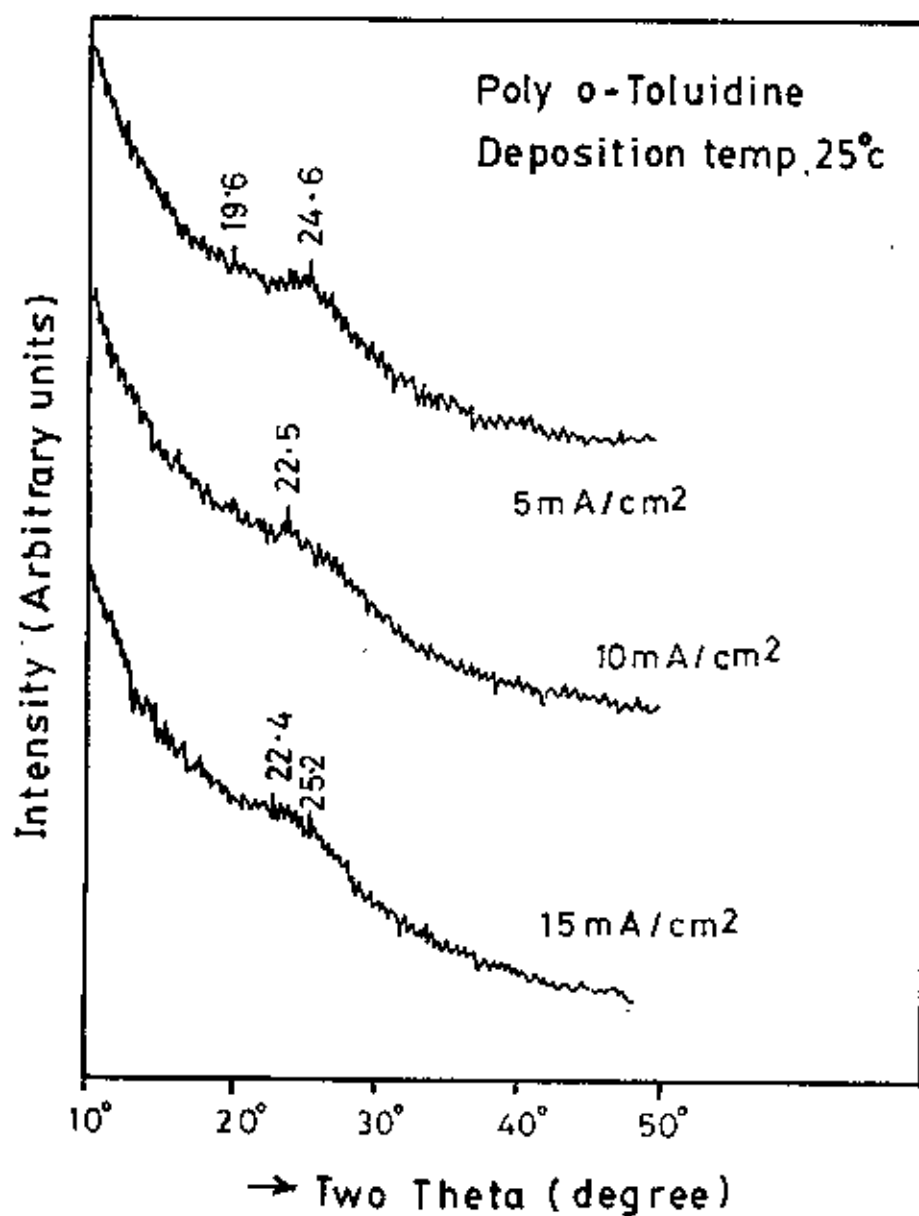
Fig. 4.13 X-Ray Diffration patterns of poly o-toluidine deposited at different current densities (Solution composition 20 ml/l o-toluidine, 100 ml/l H_2SO_4, temperature 25°C)
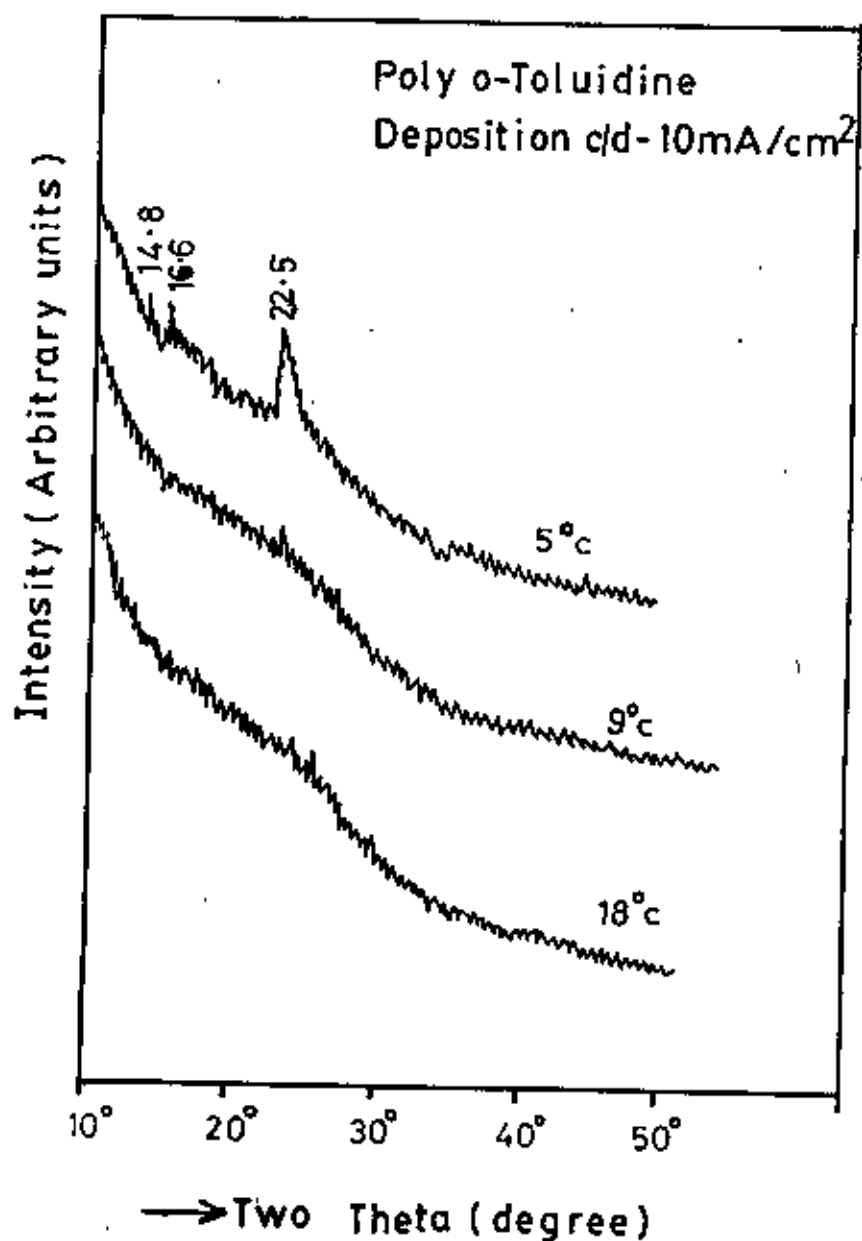
Fig. 4.14 X-Ray Diffration patterns of poly o-toluidine deposited at different temperatures (Solution composition 20 ml/l o-toluidine, 100 ml/l H_2SO_4 and current density 10 mA/cm^2)

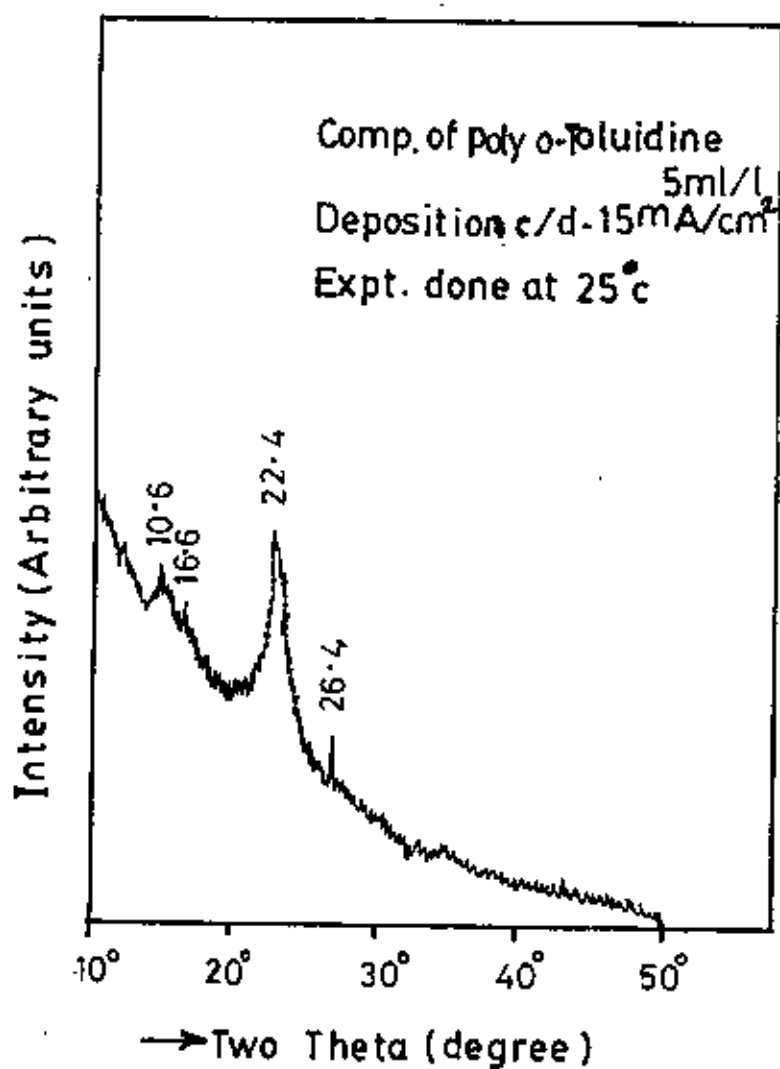Fig. 4.15 X-Ray Diffration patterns of poly o-toluidine deposited at 15 mA/cm^2 (Solution composition 5 ml/l o-toluidine, 100 ml/l H$_2$SO$_4$, temperature 25°C)
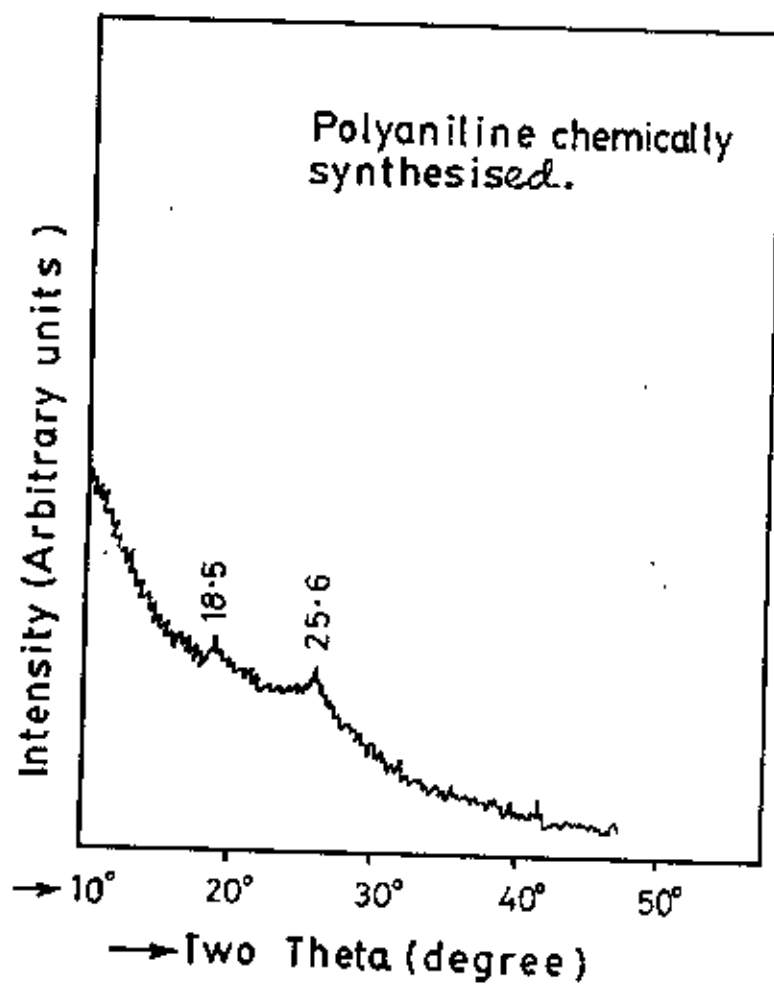
Fig. 4.16 X-Ray Diffration patterns of chemically synthesized polyaniline at 25°C.

4.3 Electrical Conductivity :

The electrical conductivity of polymer depends upon many factors such as the dopant concentration, the morphology of the polymer, orientation of conducting species, temperature, density, shape and moisture content in the sample. The electrical resistivity of all the polymer samples were measured by two probe techniques at room temperature. The electrical conductivity was computed from the measured resistance and sample dimensions by the following equation:

$$R = \rho \frac{t}{A}$$

Where

R = Resistance of the pellet,

A = Cross sectional area of the pellet,

t = Thickness of the pellet

ρ = Resistivity

The calculated conductivity values from the measured resistances are given in Table 4(e) and 4(f) and in Fig. 4.17 and 4.18

Table 4 (e) Conductivity of polyaniline and poly-o-toluidine synthesized at a constant current density (10 mA/cm^2.) at different temperatures.

Temperature in °C.	Conductivity in Ω^{-1} cm^{-1}	
	Polyaniline	Poly o-toluidine
25	1.838×10^{-3}	5.16×10^{-4}
18	7.96×10^{-3}	5.32×10^{-4}
9	1.14×10^{-2}	3.65×10^{-3}
5	8.48×10^{-3}	5.42×10^{-4}

It is evident from Table 4(e) and from the Fig. 4.17 that in general the electrical conductivity of both the polymer increases with the decrease of deposition temperature. Maximum conductivity is observed at 9°C for both the samples. On further decrease of temperature the conductivity of polyaniline and poly o-toluidine

decreases. This may be due to the fact that with the decrease of temperature the deposition of polymer becomes slower which produces better crystilline products. Similar results are also reported by Gupta et al.[193] for chemical synthesis of polyaniline and its derivatives. The decrease of conductivity at lower temperature than $9^\circ C$ may be due to the difficulty of deposition of polymer on the electrode. In the case of poly o-toluidine no deposition is observed at lower temperature ($5^\circ C$). Similar results are reported by Lux[192] for chemical synthesis of polyaniline. According to him the polymerization reaction does not takes place below - $10^\circ C$.

Table 4(f) Electrical conductivity of polyaniline and poly o-toluidine synthesized at different current density at a constant temperature ($25^\circ C$) :

current density mA/cm²	Conductivity in Ω^{-1} cm^{-1}	
	Polyaniline	Poly-0-toluidine
5.00	2.14×10^{-4}	2.79×10^{-5}
10.00	1.838×10^{-3}	5.16×10^{-4}
15.00	4.595×10^{-5}	6.03×10^{-5}

Table 4(f) shows the results of electrical conductivity of polyaniline and poly o-toluidine at different current densities. It is observed from the Table 4(f) that polymers prepared at the current density of 10 mA/cm² have the highest conductivity. Gupta et al.[193] also repoted similar results, in the case of chemically synthesized polyaniline and poly o-toluidine where they found 1:1.15 as the optimum monomer oxidant ratio. It seems probably that at lower current density (5 mA/cm²) polymerization does not takes place to a desire degree. Consequently the product has lower conjugation and exhibits lower conductance. On the other hand in the case of higher current density (15 mA/cm²), the formation of intermediate radical cation predominates over the polymerization. Therefore the product may contain low molecular weight oligomer which was evident from the

colour changes of the bath solution (pinkish colour). From these observation it may be said that there might be an optimum current density (10 mA/cm^2 for polyaniline and poly o-toluidine.) at which the polymer deposition will be better than at any other values of current density.

It is also observed from Table 4(e) and 4 (f) and also from Fig. 4.17 and 4.18, that the conductivity of poly o-toluidine is always lower than that of polyaniline. This may be due to the fact that the methyl group of phenyl ring in the poly o-toluidine increases the torsional angle between the adjacent rings, that prevent the polymer to grow to a longer chain. As a result number of conjugation in the polymer decreases that might lead to a decrease in conductivity. More over, the presence of methyl group may also lead to difficult electronic flow along the polymer chain then the parent polyaniline. Similar results are also reported by Ahmed et al.[194]
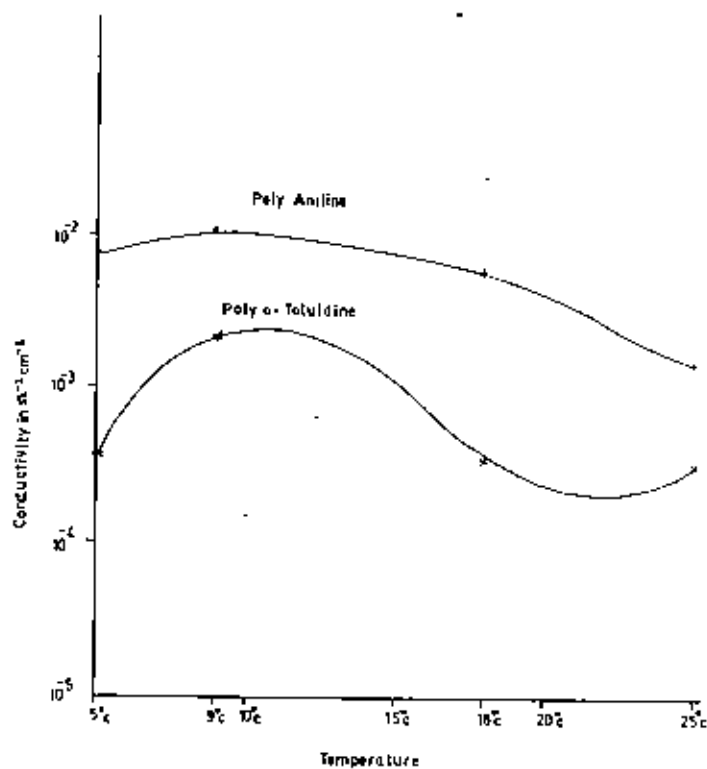
Fig. 4.17 Electrical conductivity versus deposition temperature for polyaniline and poly o-toluidine.
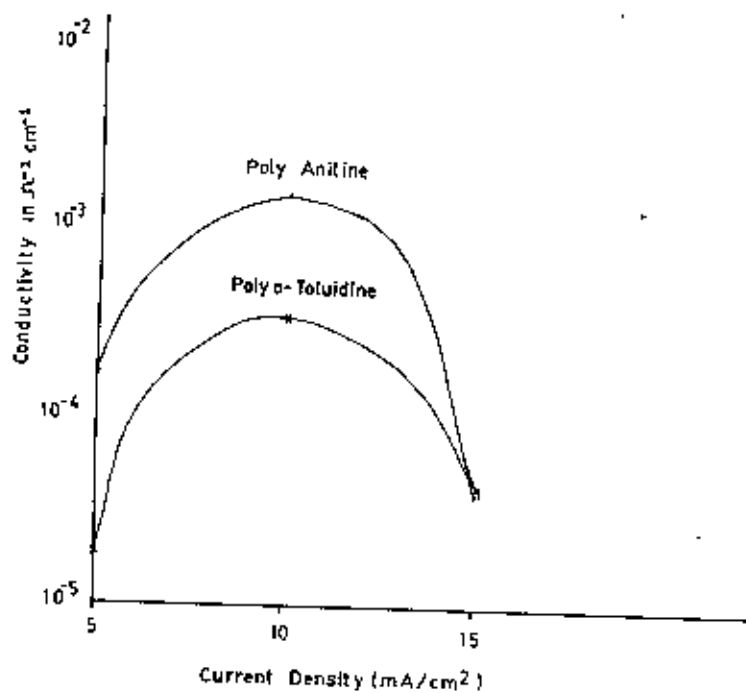

Fig.4.18 Conductivity versus current density for polyaniline and poly o-toluidine.

4.4   UV-Visible Spectra :

It is well known that absorption of electromagnetic radiation in the UV-visible region provides important information about the energy bands.

UV-visible spectrum of polyaniline and poly o-toluidine prepared under different polymerization conditions are recorded in DMF at room temperature are shown in Fig. 4.19,   4.20, 4.21 and   4.22 and the corresponding bands are presented in the Table 4(g) and 4(h).

Table 4(g) Effect of current density on UV-visible spectra of the polymers synthesized at room temperature (Bath composition: 20 ml/l of monomer, 100 ml/l H_2SO_4)

Current Density mA/cm^2	Polyaniline		Poly o-toluidine	
	Band gap in nm. (eV)	Exciton in nm (eV)	Band gap in nm. (eV)	Exciton in nm (eV)
5	315 (3.94)	600 (2.07)	310 (4.00)	580 (2.14)
10	370 (3.35)	550 (2.25)	318 (3.9)	595 (2.08)
15	325 (3.82)	600 (2.07)	310 (4.00)	595 (2.08)

Table 4(h) Effect of Temperature on UV-visible spectra of polymer synthesized at current density   10 mA/Cm^2 (Bath composition: 20 ml/l of monomer, 100 ml/l H_2SO_4)

Temperature °C	Polyaniline		Poly o-toluidine	
	Band gap in nm. (eV)	Exciton in nm (eV)	Band gap in nm. (eV)	Exciton in nm (eV)
25	370 (3.35)	550 (2.25)	318 (3.9)	595 (2.08)
18	330 (3.76)	620 (2.00)	310 (4.00)	600 (2.07)
9	330 (3.76)	615 (2.02)	330 (3.76)	600 (2.07)
5	330 (3.76)	620 (2.00)	--	--

From the Fig. it is observed that the spectra of these polymers show two absorption bands. The band at around 280 -370 nm (4.43-3.35 eV) is due to

$\pi \rightarrow \pi^*$ transition (from the valency band to conduction band). The broad band around 500-620 nm (2.48 - 2.00 eV) is due to $n \rightarrow \pi^*$ transition. The exciton band associated with the formation of benzenoid to quinoid ring[195-198]. The shift in these bands is observed by the change in polymerization conditions such as temperature of polymerization, and current density applied for polymerization.

It is evident from the Table 4(g) that the polymers prepared at a current density of 10 mA/cm^2 show the smaller bandgap energy (370 nm, 3.35 eV) (i.e. lower energy required for $\pi \rightarrow \pi^*$). At lower current density of polymerization (5 mA/ cm^2) the absorption band appears at lower wavelength (315 nm). And at higher current density (15 mA/ cm^2) the absorption band is observed also at lower wavelength (325 nm). From these data it may be said that for the polymerization of each polymer there may be an optimum current density at which deposition will be perfect. In this study for polymerization of polyaniline and poly o-toluidine the optimum value observed is 10 mA/cm^2. At lower and higher current density than the optimum value perfect deposition may not take place. When the applied current density is low the formation of radical cation might be less and the polymerization would be in complete. As a result, a bathochromic shift in the absorption spectra is observed. On the other hand when the applied current density is high, the intermediate radical cation formation is predominant in the polymerization. As a result the product may be lower in molecular mass. Consequently, the polymer might have shorter conjugation. This is supported by the conductivity results obtained in this study.

It is also evident from the results given in Table 4(h) that the band-gap and exciton band are also influenced by the temperature of polymerization. In this study the polymers (both polyaniline and poly o-toluidine) prepared at different temperatures (25°C, 18°C, 9°C and 5°C). It is found that polyaniline prepared at

25°C shows the smaller band-gap energy (370 nm ; 3.35 eV). A hypsochromic shift is observed with the decrese of temperature from 25 to 18°C. However at a further decrease in temperature no further shift is observed. In the case poly o-toluidine the band gap is influenced by the temperature little bit differently. In this case a hypsochromic shift in the band gap with the decrease of temperature from 25 to 18°C. However, on further decrease temperature ((9°C) a bathochromic shift is observed. No deposition (polymerization) took place at 5°C.

A careful observation of results presented in the Table 4(g) and 4(h) indicates that in general band gap transition increases in energy with the replacement of hydrogen atom in the benzene ring by the bulky methyl group. The methyl group in the benzene ring increases the torsion angle which makes the blue shift in the absorption band. Similar results are also reported by Ahmed et al.[199] and Gupta et al.[200]
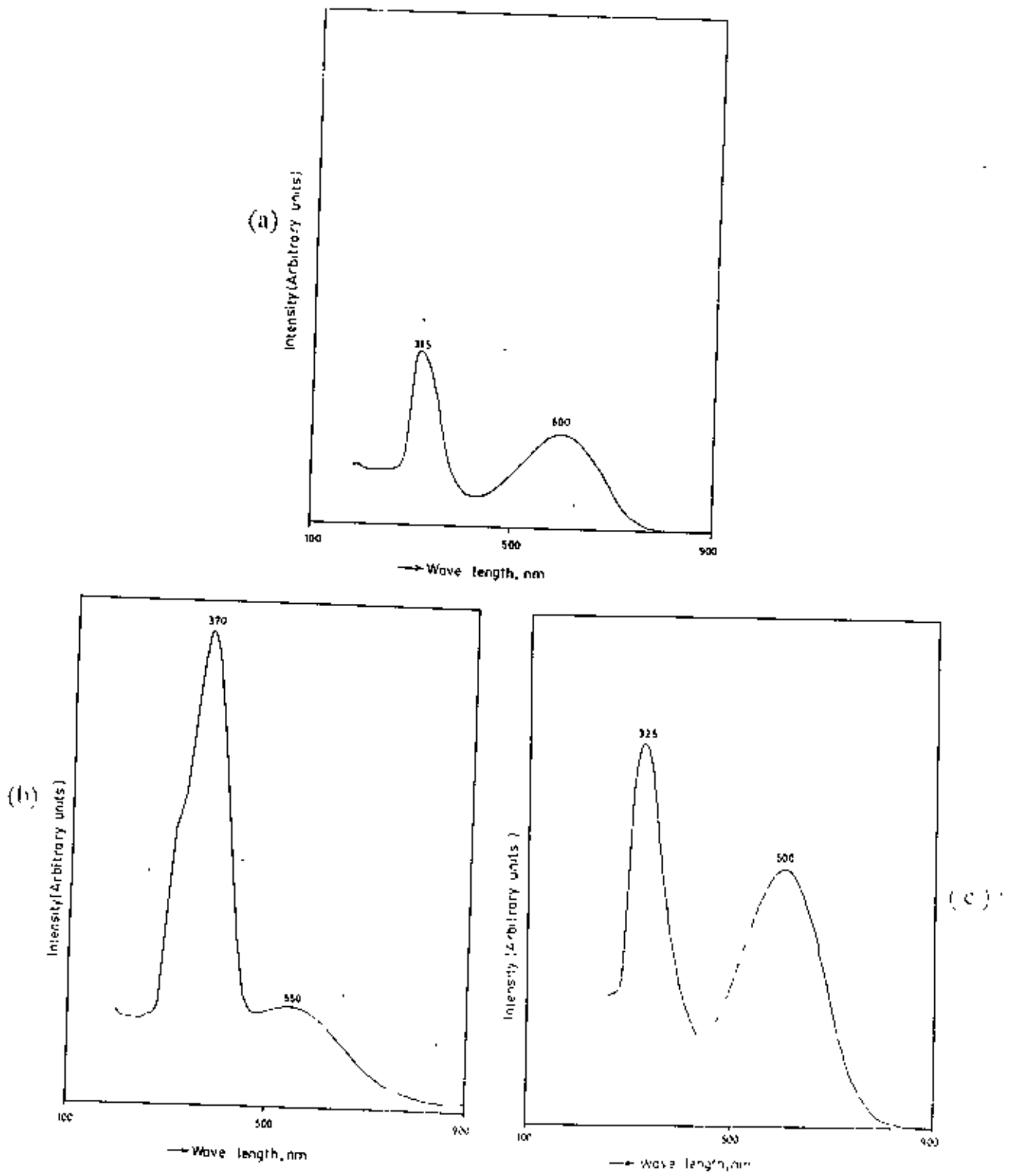
Fig. 4.19, UV-vis spectra of polyaniline deposited at (a) 5mA/cm², (b) 10 mA/cm² and (c) 15 mA/cm². (Solution composition : 20ml/l aniline, 100 ml/l H₂SO₄, temperature 25°C)
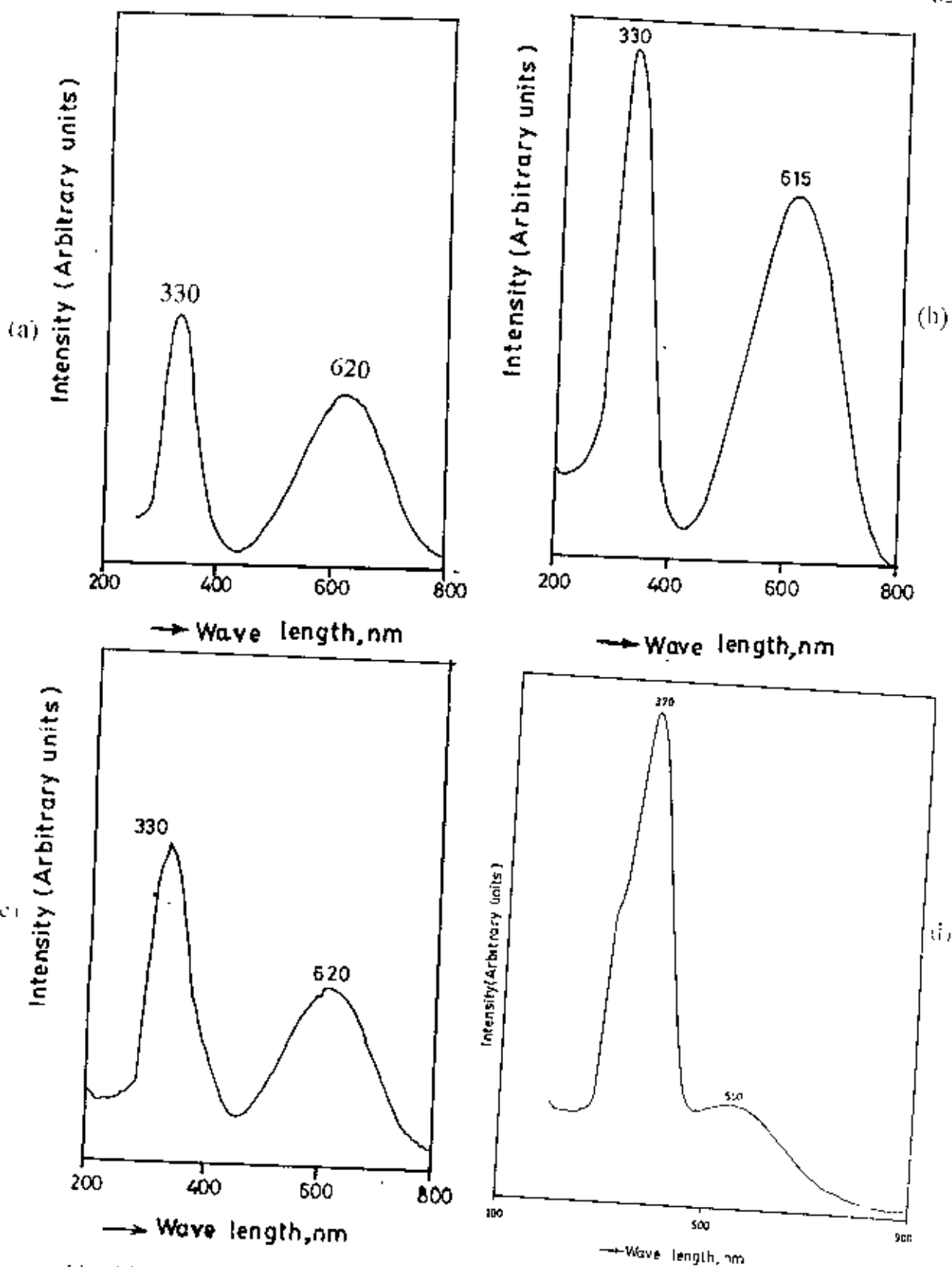
Fig. 4.20 UV-vis spectra of polyaniline deposited at (a) 5°c, (b) 9°c (c) 18°c and (d) 25°c
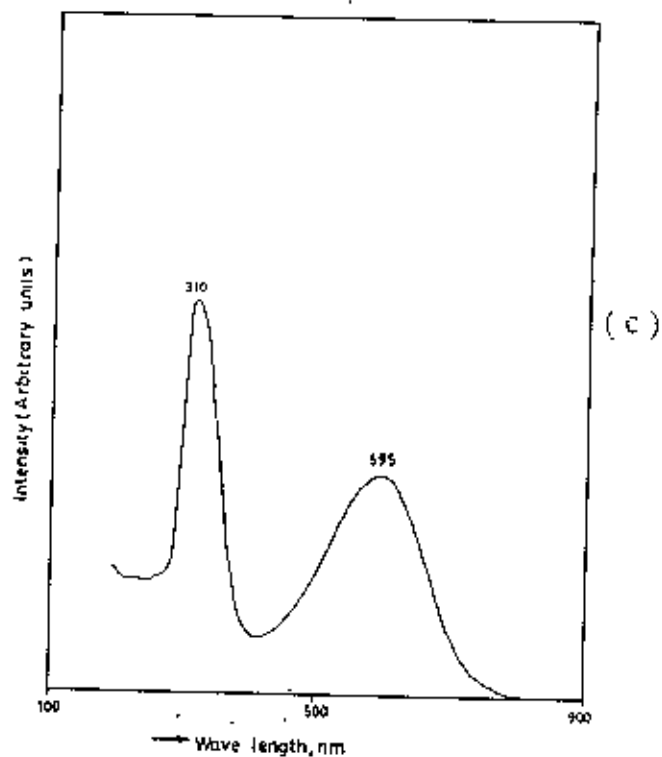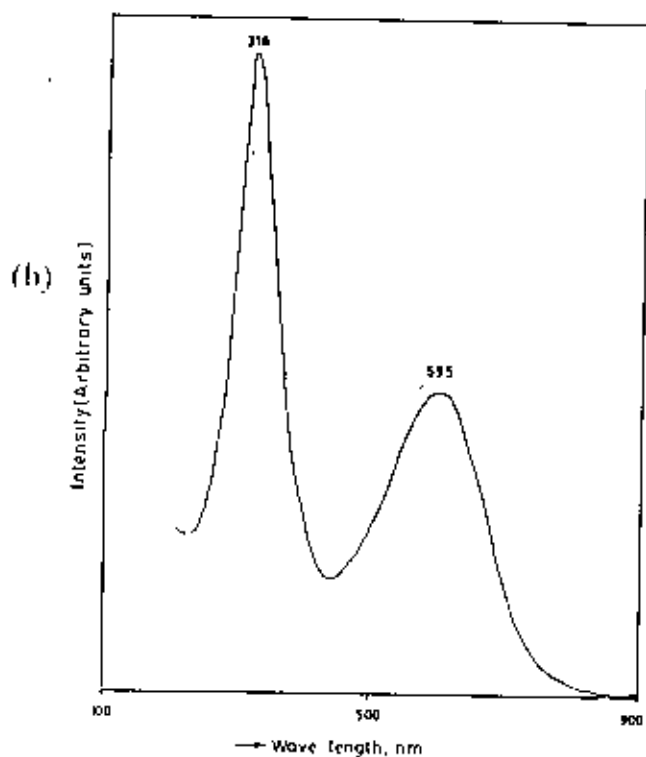(Solution Composition : 20ml/l aniline, 100ml/l H₂SO₄ and current density 10 mA/cm²)

Fig. 4.21 UV-vis spectra of poly o-toluidine deposited at (a) 5mA/cm², (b) 10mA/cm² and (c) 15mA/cm² (Solution Composition : 20ml/l o-toluidine, 100ml/l H₂SO₄ and temperature 25°c)

Fig. 4.22 UV-vis spectra of poly o-toluidine deposited at (a) 5°c, (b) 9°c © 18°c and (d) 25°c (Solution Composition : 20ml/l o-toluidine, 100ml/l H₂SO₄ and current density 10mA/cm²)
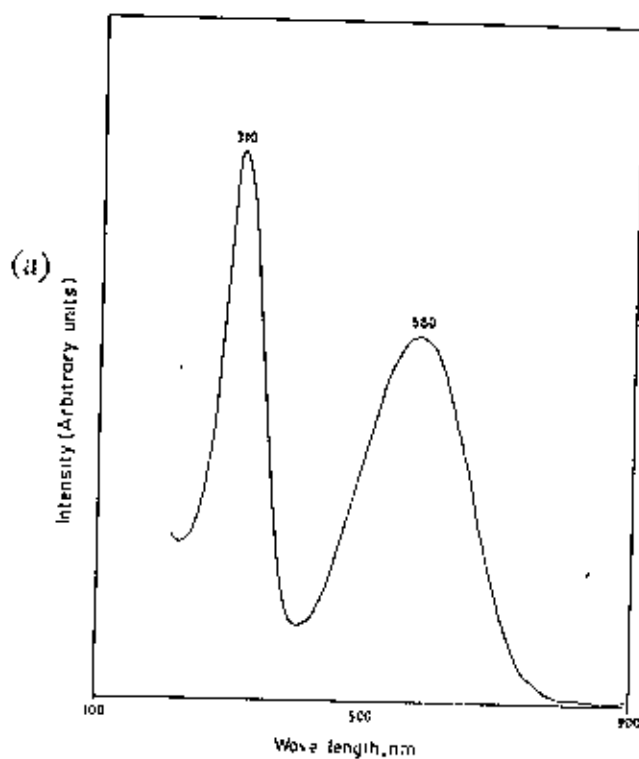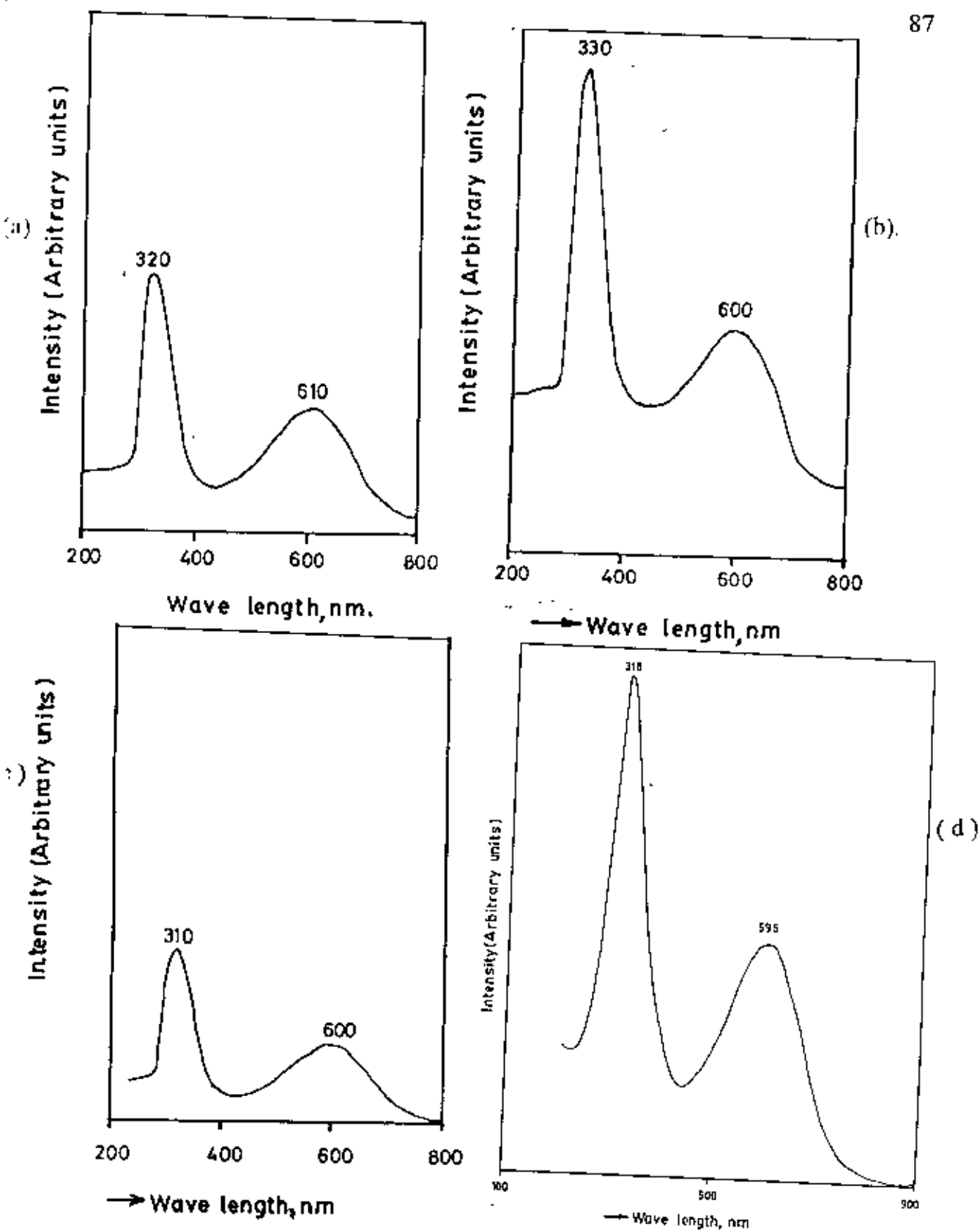
4.5 Infrared spectra :

Infrared spectra have constantly been applied in the determination of structure of molecules. The extensive application of infrared spectroscopy is mainly based on the concept of group vibration. Any structural change like substitution or addition of groups or atoms in a molecule affects the relative mode of vibrations of groups of special interest resulting into,

(i)   Change in band position

(ii)   Change in relative intensities and appearance of new bands

(iii)   Splitting of single peak into two or more peaks.

The infrared spectra of poly o-toluidine and polyaniline deposited under different conditions are given in Fig. 4.23 - 4.30 and peaks assigned to different groups are listed in Table 4(i). Infrared spectra of aromatic ring substituted polyaniline (poly o-toluidine) show the presence of strong absorption at about 840 cm^{-1}. It gives an evidence for 1, 2, 4-substituted aromatic ring. This indicates the bonding in polymer is through 1, 4-position. An absorption band at about 3600 cm^{-1} may corresponds to absorbed water. In the spectra no absorption band is observed at around 3300 cm^{-1}. This indicates the absence of NH in the chain. However there is an absorption band at around 1540 cm^{-1}. These indicates that the polymer chain might consists of -N= sites and may be a fully oxidised doubly charged diprotanated quinoid (diimine) salt. Similar information is also reported by Ginder et al.[201]. The absorption band at around 3000 cm^{-1} may be due to benzene aromatic stretching. There is an absorption band at around 1730 cm^{-1} in the spectra. This may be due to C-O stretching of methyl (-CH$_3$) group. No such band is observed in the case of polyaniline prepared at low current density (5.0 mA/cm^2).

Table 4(i) Characteristic peaks observed in the IR spectra.

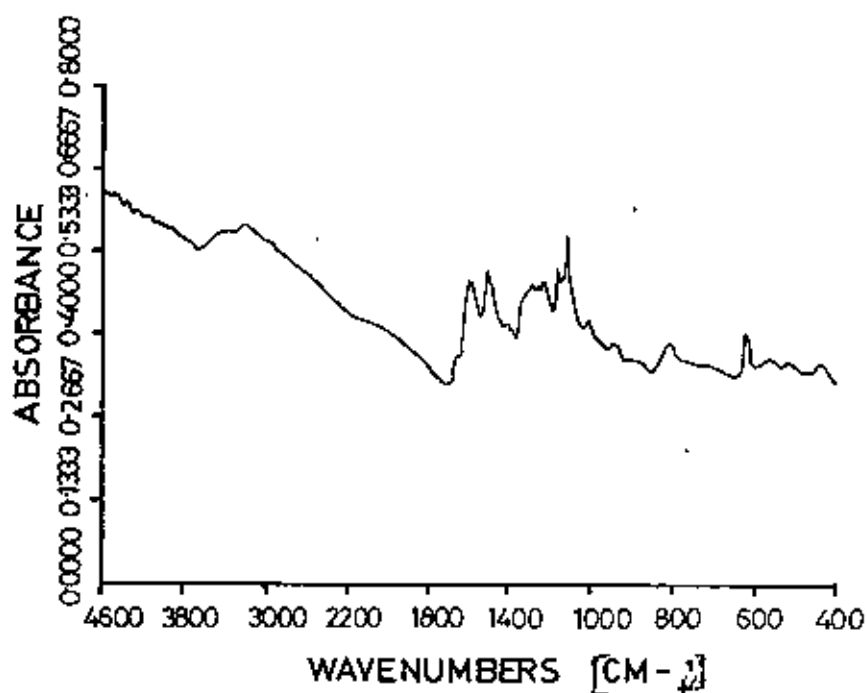| Characteristic bands	Wavenumber (cm^{-1})
Secondary NH (absorbed water)	3600
Aromatic C-H	3000
C-O	1730
C=N-	1540
C-C (aromatic)	1470
δ (CH)	840

Q

Fig. 4.23 Infrared spectra of poly o-toluidine formed at 25°C at a current density of 5 mA/cm². (Bath composition: o-toluidine 20 ml/l, 100ml/l H₂SO₄)

Fig. 4.24 Infrared spectra of poly o-toluidine formed at 25°C at a current density of 10 mA/cm². (Bath composition: o-toluidine 20 ml/l, 100ml/l H₂SO₄)

Fig. 4.25: Infrared spectra of poly o-toluidine formed at 25°C at a current density of 15 mA/cm^2 . (Bath composition: o-toluidine 20 ml/l, 100ml/l H$_2$SO$_4$)

Fig. 4.26.Infrared spectra of poly o-toluidine formed at 5°C at a current density of 10 mA/cm^2 . (Bath composition: o-toluidine 20 ml/l, 100ml/l H$_2$SO$_4$)

Fig. 4.27 Infrared spectra of poly o-toluidine formed at 9°C at a current density of 10 mA/cm². (Bath composition: o-toluidine 20 ml/l, 100ml/l H_2SO_4)

Fig. 4.28 Infrared spectra of poly o-toluidine formed at 18°C at a current density of 10 mA/cm². (Bath composition: o-toluidine 20 ml/l, 100ml/l H_2SO_4)

Fig. 4.29 Infrared spectra of poly o-toluidine formed at 25°C at a current density of 15 mA/cm². (Bath composition: o-toluidine 5 ml/l, 100ml/l H₂SO₄)
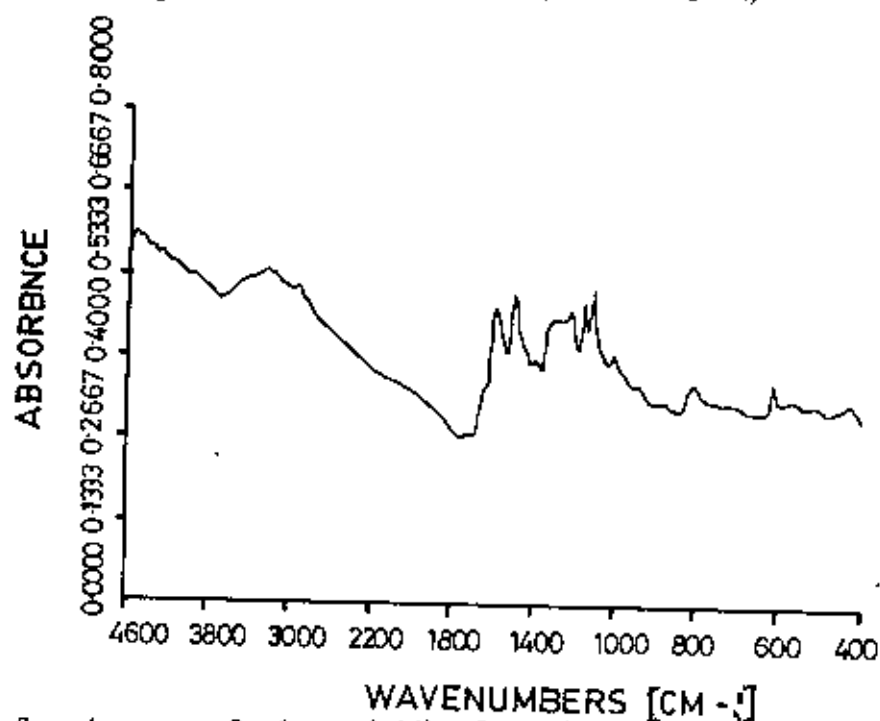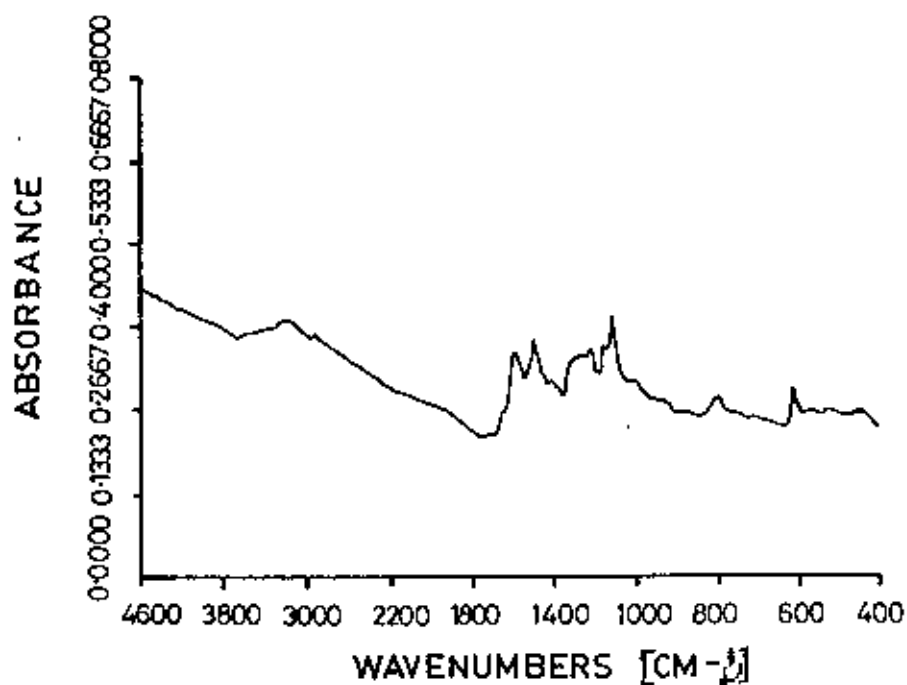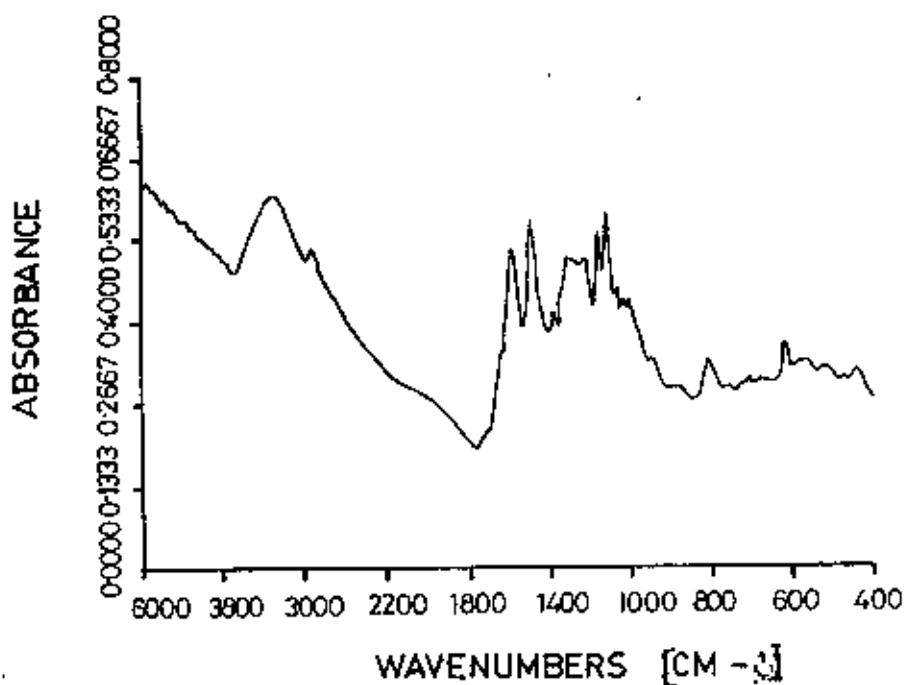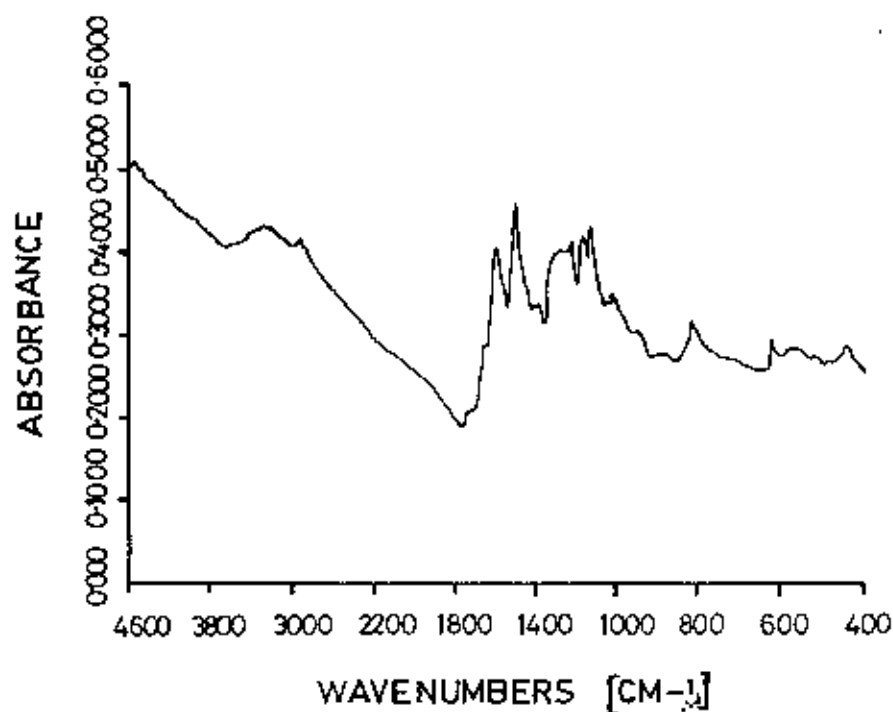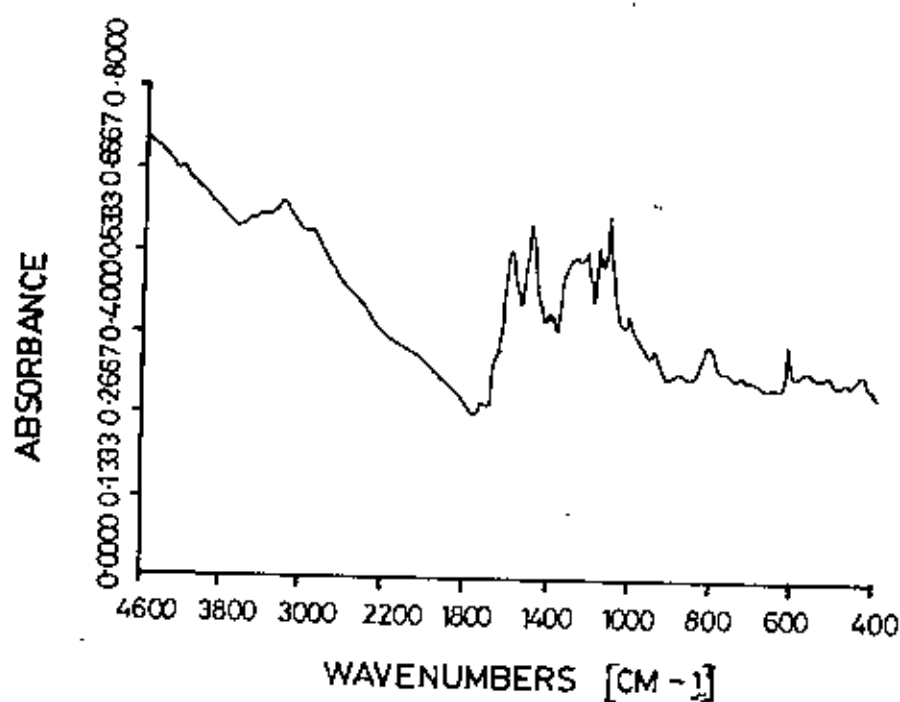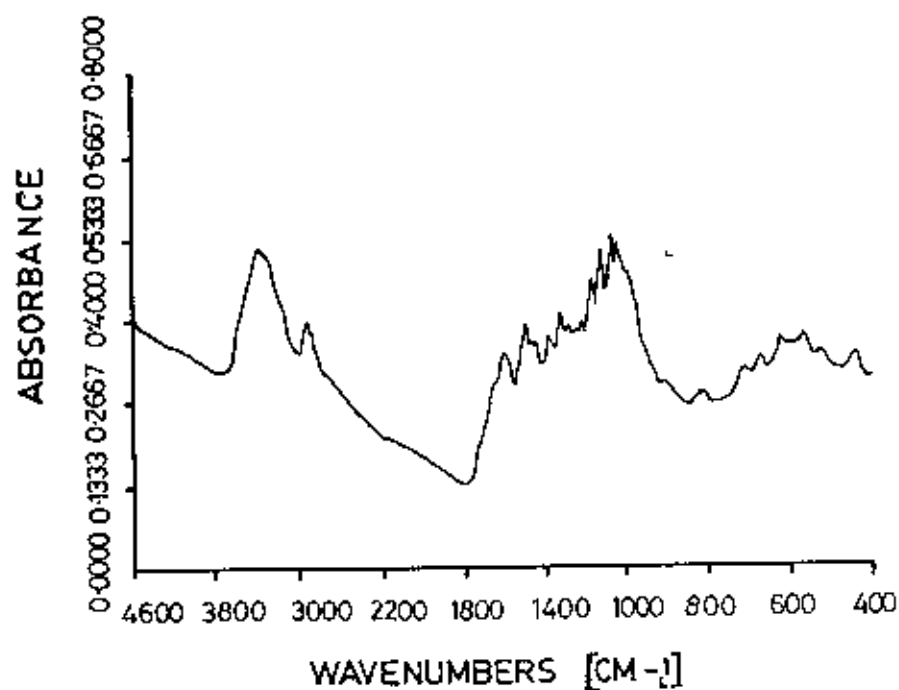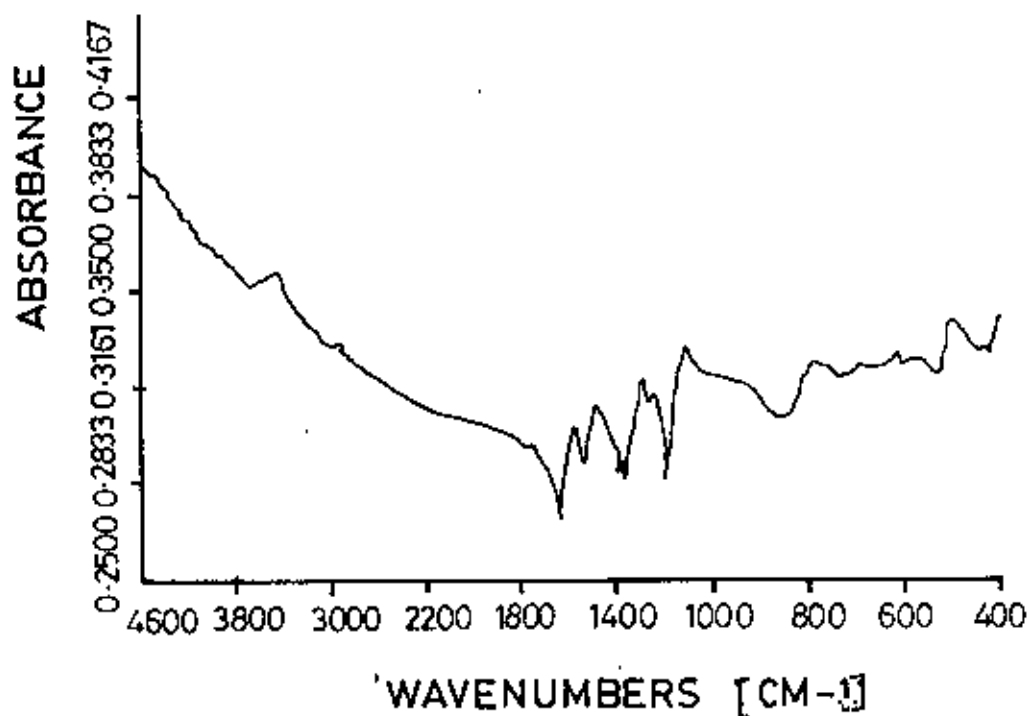

Fig 4.30 Infrared spectra of polyaniline formed at 25°C at a current density 5 mA/cm². (Bath composition: aniline 20 ml/l, 100ml/l H₂SO₄)

4.6   Scanning Electron Microscopy :

Scanning electron microscopy is concerned with the surface structure (morphology) of polymer. It reflects the relationship between adjacent particles and small group of particles[201] . The morphology of polymers depends mainly on the structure of monomer and also on the condition of polymerization. Scanning electron micrographs of polyaniline synthesized at different temperature and current density are shown in Fig. 4.31 and 4.32. It is evident from the scanning electron micrographs that there is a change in morphology of the polyaniline with a change in the condition (temperature and current density) of the synthesis. The Fig. 4.31 shows that the polyaniline prepared at 25°C and at a current density 5 mA/cm^2 exhibits grain like morphology. The average bundle size of the grains of PANI increases with the increase of current density. On other hand, there is a dramatic change in morphology of polyaniline with change in the temperature of synthesis. The grains take microspherical morphology for polyaniline prepared at 25°C temperature, has been changed to a fibrillar one morphology prepared at 9°C. Fig. 4.32 (c) shows that the lower is the temperature of synthesis more prominent is the fibrillar morphology.
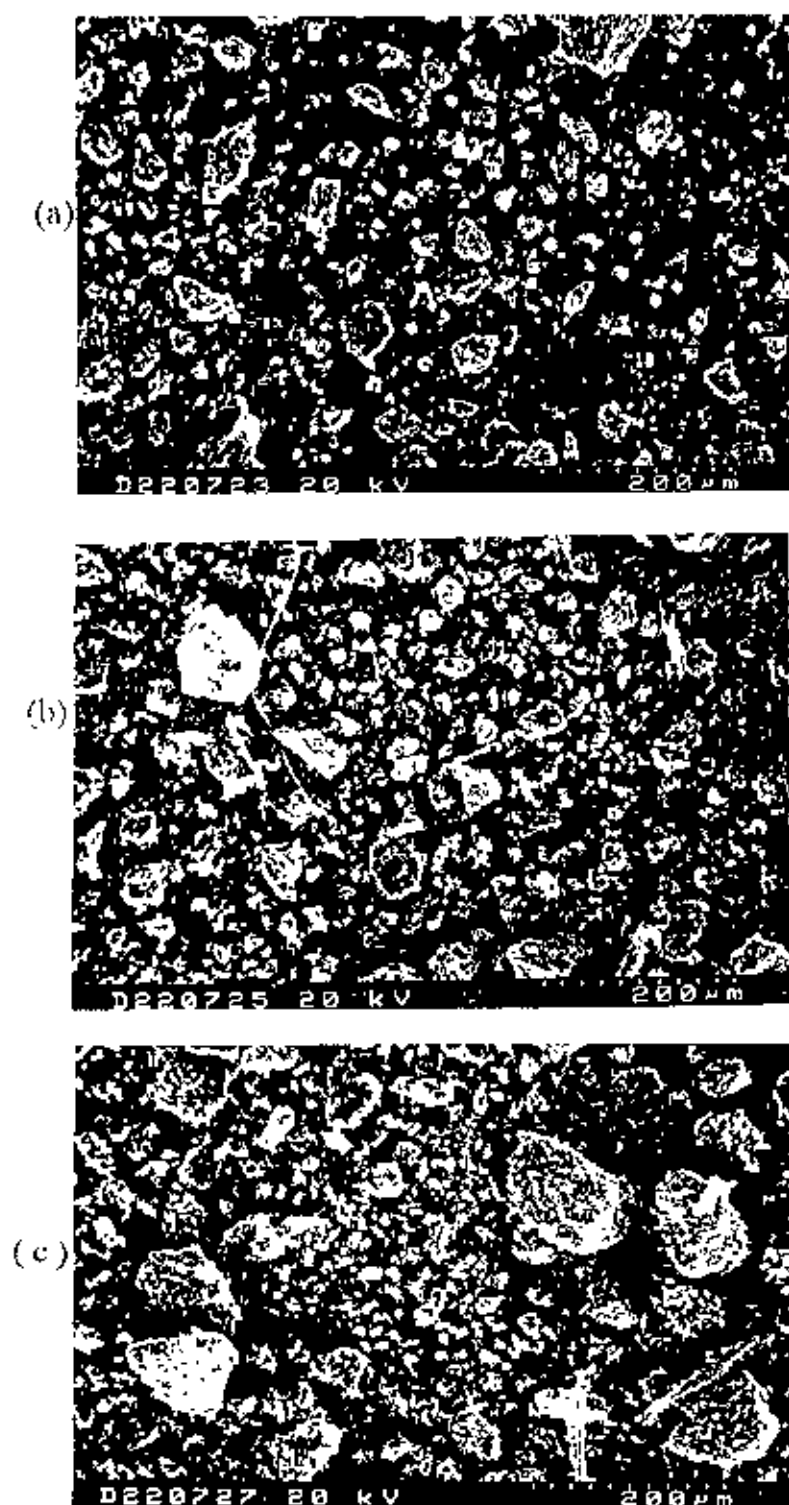
Fig. 4.31 Scanning electron michrograph of polyaniline at (a) 5 mA/cm^2, (b) 10 mA/cm^2, and 15 mA/cm^2. (Solution composition 20 ml/l aniline, 100 ml/l H_2SO_4, temperature 25°c).
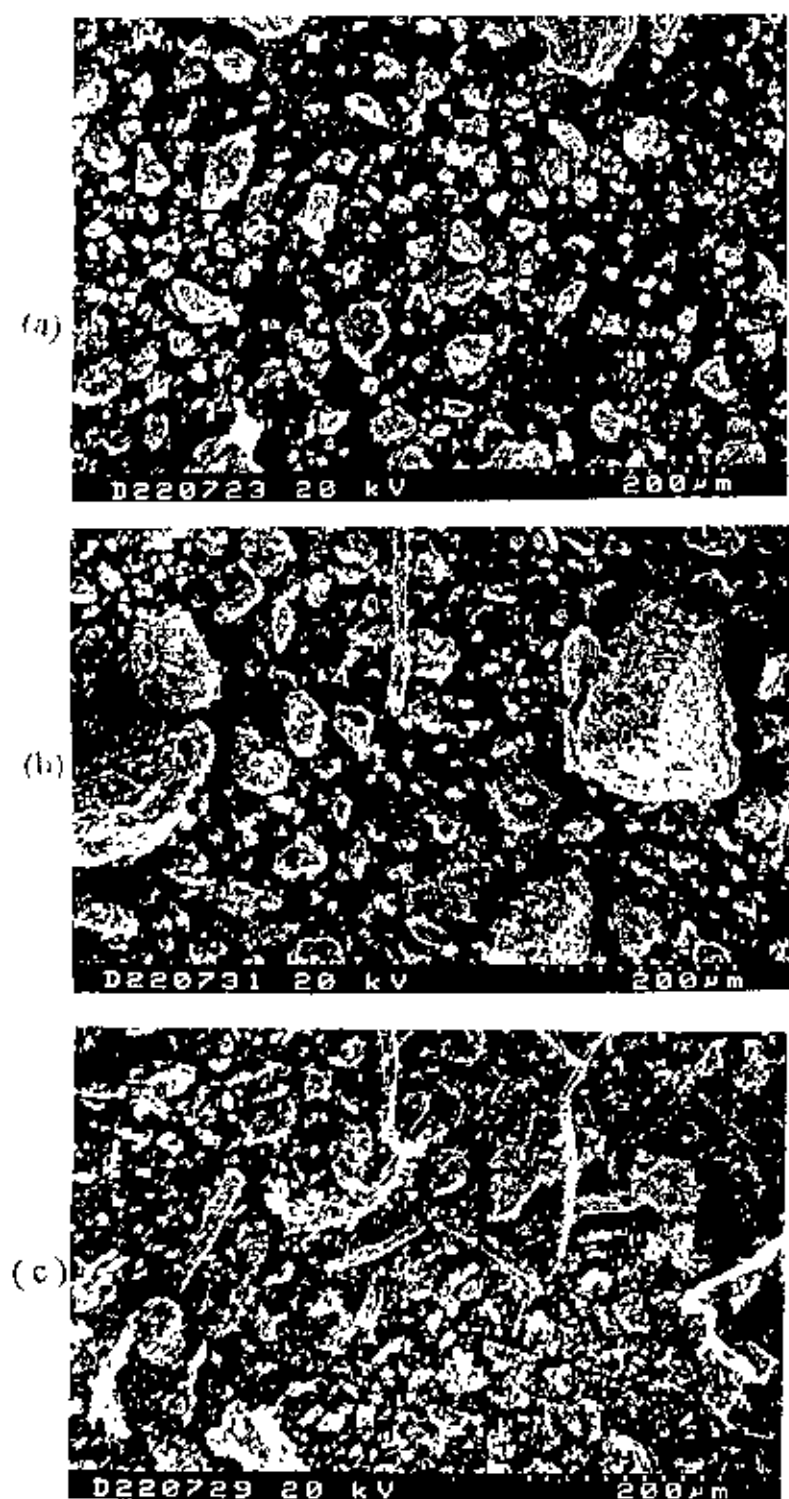
Fig. 4.32 Scanning electron michrograph of polyaniline at (a) 25°c, (b) 18°c and (c) 9°c (Solution composition 20 ml/l aniline, 100 ml/l H_2SO_4, current density 10 mA/cm^2.)

4.7   Elemental Analysis :

Elemental analysis of polyaniline for carbon, hydrogen and nitrogen was done by micro-estimation technique at the Regional Sophisticated Instrumentation Centre, Lucknow-226001 India. The results are given in belowTable 4(j) along with the calculated values. The results given in the Table 4(j) fit with the emperical formula given below :

$$(C_6 H_4NH)_4 .2 HSO_4$$
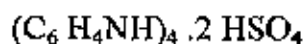
Similar results have been reported by Warhanpand SV.[184]

Table : 4(j) C H and N percentage of polyaniline prepared at 25°C at current density 10 mA/cm^2.

Polymer	Experimental values %			Calculated values %		
	C	H	N	C	H	N
Polyaniline	52.45	3.80	10.53	53.83	3.71	10.46

The emperical formula is based on the following reaction mechanism :

Oxidized polymer.

reduced form.
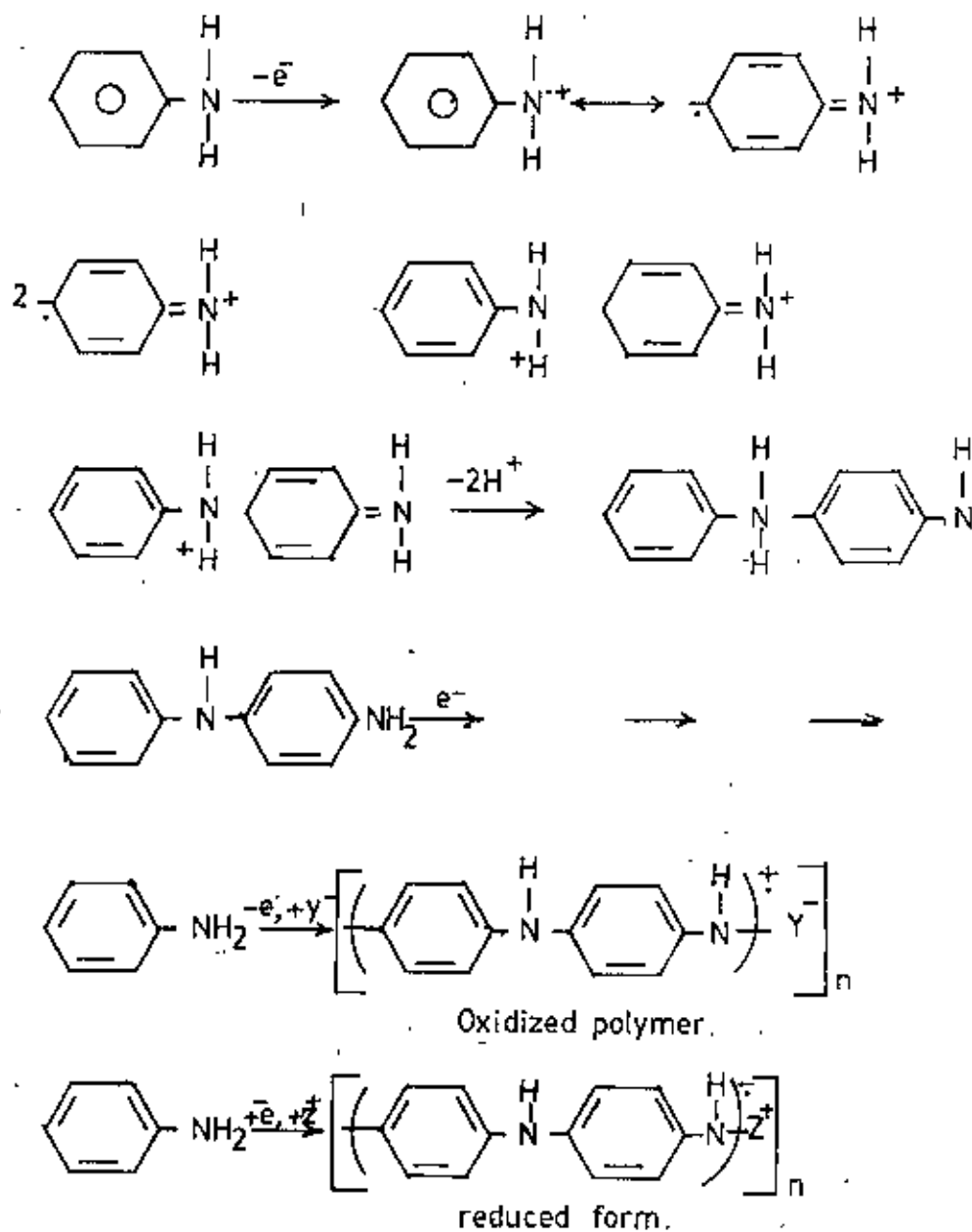
From the results presented in the Table 4(j) it is inferred that one anion is substituted for every two phenyl rings for complete protonation. The discrepancy in the calculated and experimental values is due to different protonation levels. In the calculation complete protonation is assumed but in practice different levels of counterions and protonation level might be occur. The oxidized and protonated forms might have extensive π - conjugation. In the polymer all nitrogen atoms, all C- N bonds and all aromatic rings ($-C_6H_4-$) would be intermediate between benzonoid and quinoid forms. Thus a repeated unit has equal number of oxidized and reduced units.

CHAPTER - 5

SUMMARY AND CONCLUSION

Polyaniline and poly o-toluidine (poly o-methoxy aniline) were prepared both by electrochemical and chemical oxidation at different conditions of temperature, current density and bath composition. The elemental analysis of polyaniline supports the emperical formula of polyaniline as: $(C_6H_4NH)_4 \, 2 \, HSO_4$. The mechanism of polymerisation inferred that one anion (HSO^-_4) is substituted for every two phenyl rings.

The infrared spectra of the aromatic ring substituted polyaniline (poly o-toluidine) show a presence of strong absorption band at around 840 cm^{-1}, which gives an evidence of 1,2,4- substituted aromatic ring. This indicates the bonding in polymer is through 1,4- position of benzene ring. Absorption bands at around 1540 cm^{-1}, 3000 cm^{-1} and at around 1730 indicate the presence of $-N=$, aromatic $-CH-$ and C-O stretching respectively.

Scanning electron microscopy is concerned with the surface structure (morphology) of polymer. The morphology of polymers depends mainly on the sturcture of monomer and also on the condition of polymerisation. From the scanning electron micrograph of polyaniline at 25°C and at a current density 5mA/cm^2 exhibits grain like morphology. The average bundle size of the grains of polyaniline increases with the increase of current density. Also, with the change of temperature their is a dramatic change in morphology of polyaniline. The grains take microspherical morphology for polyaniline prepared at 25°C temperature has

been changed to a fibrillar one when synthesis is carried out at 9°C. As lower is the temperature of the synthesis the more prominent is the fibrillar morphology.

The electrical conductivity of both the polymers (polyaniline and poly o-toluidine) increases with the decrease of temperature. Maximum conductivity is observed at 9°C for both the samples. On further decrease of temperature the conductivity of polyaniline and poly o-toluidine decreases. The highest electrical conductivity is observed in the case of polymer (polyaniline and poly o-toluidine) prepared at the current density 10 mA/cm². Conductivities of polymers synthesized at the lower current density 5 mA/cm² and higher current density 15 mA/cm² were found lower. The lower conjugation of polymer synthesized at lower current density and the amorphous nature of the polymer synthesized at higher current density may be the reasons of these variation in conductivitys values. An optimum current density 10 mA/cm² for polyaniline and poly o-toluidine at which the polymer deposition will be better than at any other values of current density.

The UV-visible spectra of polyaniline and poly o-toluidine show two absorption bands. The band around 280 - 370 nm (4.43 - 3.35 eV) is due to $\pi \rightarrow \pi^*$ transition (from the valence band to conduction band) and a broad band around 500 - 620 nm (2.48 - 2.00 eV) is due to n $\rightarrow \pi^*$ transition. The exciton band is associated with the formation of benzenoid to quinoid ring. The shift in these bands is observed by the change is polymerization conditions such as temperature and current density. Current density 10 mA/cm² shows the smaller band gap energy (370 nm ; 3.35 eV) (i.e. lower energy reqired for $\pi \rightarrow \pi^*$). A lower current density of polymerization 5 mA/cm² the absorption band appears at lower wave length (315 nm). And at higher current density the absorption band also appears at lower wavelength (325 nm) than that of current density 10 mA/cm² (370 nm) polyaniline prepared at 25°C shows the smaller band gap energy (370 nm; 3.35

eV). A hypsochromic shift is observed with the decrease of temperature from 25°C to 18°C. However at a further decrease of temperature no further shift is observed. The absorption band appears always at lower energy in the case of polyaniline than that of poly o-toluidine.

In the X-ray diffraction patterns of polyaniline samples deposited at anodic current densities of 5, 10 and 15 mA/ cm^2 exhibit mainly two peaks which occured at 2θ values in the neighbourhood of 19 and 25°. The peaks are broad and diffused at 5 mA/ cm^2. The peaks become sharper as deposition current density increases. Polyaniline synthesized at higher current densities has higher crystallinity than that synthesized at lower current density. The X-ray diffraction patterns of polyaniline is also influenced by the temperature. X-ray diffraction patterns of poly o-toluidine contain a broad hump around 2θ values of 20-25°. The existance of the broad diffuse peak indicates amorphous nature of poly o-toluidine deposited at room temperature and at current densities ranging from 5 to 15 mA/ cm^2. The diffraction pattern also shows that deposition of poly o-toluidine from a dilute bath yields a more ordered o-toluidine. It is also found that both polyaniline and poly o-toluidine ingeneral lower deposition temperature results in sharper of diffraction peaks suggesting more crystallinity. Although in the case of polyaniline, increased deposition current density increase crystallinity, this is not so evident for poly o-toluidine.

TGA curves of electrochemically synthesized polyaniline under different conditions show an initial mass loss at temperature below 100°C. This is due to the loss of moisture from the sample. After the loss of low molecular mass

moisture, weight decreasing at slow rate up to about 300°C, above which a rapid loss of weight takes place. The degradation of polyaniline was found to follow a single sigmoidal path. The TGA curves of poly o-toluidine exhibit more or less similar behaviour as polyaniline. It is found that both the polyaniline and poly o-toluidine have higher activation energy synthesized at intermediate current density viz. 10 mA/ cm^2. It is further seen that the activation energy of polyaniline is always higher than that of poly o-toluidine. Among the three current densities investigated (5, 10 and 15 mA/ cm^2) the current density of 10 mA/ cm^2 is found to yield highest conductivity in both polyaniline and poly o-toluidine. Band gap energy calculated from UV-visible spectra supports this result. Activation energy calculated from TGA curves further show that polyaniline deposited at 10 mA/ cm^2 possesses the highest thermal stability in air. It is therefore concluded that for the electrodeposition of conducting polymer polyaniline and poly o-toludine there exists an optimum deposition current density at which best results are obtained and this optimum current density is found to be 10 mA/ cm^2 in the present study.

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