1. **General Introduction**

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1.1 INTRODUCTION:

Electrically conducting polymers have become one of the most widely studied materials in recent years. It began with the accidental discovery of the polyacetylene having electrical conductivity comparable with that of metals. Since then various polymers such as polythiophenes, poly-p-phenylenes, polyphenylene sulphide, polycarbazoides, polypththalocyanines and polyquinolines have been studied. Except for polyquinolines, which are n-type and highly unstable, the other polymers derived from heterocyclics are remarkable stable in air over the extended period of time. These conducting polymers have been successfully applied as electrodes in reversible storage batteries, as gas sensors and as electrochromatic devices apart from their use as wire materials.

However, the main disadvantage of these conducting polymers is processibility due to its poor mechanical and physical properties. They are insoluble in most of the organic solvent. One of the method to solve this problem is blending of conducting polymer with ordinary thermoplastic polymer such as polyvinylchloride (PVC), polystyrene, polyethylene, etc. Mechanical blend is also used to prepare a composite. This method is undesirable because the conductivity of conducting polymers decreases due to thermal effect during processing. Thin films can also be prepared in either aqueous or non-aqueous medium using variety of elec-
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trochemical techniques. The conditions during synthesis together with solvents and electrolytes influence the conductivity, mechanical behavior and morphology of materials.

The attractiveness of the polypyrrole conducting polymer system is the base due to several factors such as chemical and thermal stability and high conductivity. But they are insoluble and non-fusible; hence the problem of mechanical properties and processibility arises. To overcome this, modification of the structure by introducing functional group such as ether, long alkyl group at β-site of heterocyclic monomer is one of the approach.

As it was first reported by Gardini et al (1973), pyrrole monomer is very readily polymerized to give a black conducting powder. This chemistry is particularly facile, taking place with a large number of oxidizing agents, resulting a conducting powder have been referred to as pyrrole black for many years. Oxidation of powder with KMnO₄ have been shown to lead predominantly to the 2,5-dicarboxylic acid and this has been interpreted as a evidence that the polymerization leads to a α α’ bonded polymer. Dall’Olio et al (1968) showed that the polymerization can takes place electrochemically as well as chemically. Street et al (1982) examined that, chemically, the pyrrole can be oxidatively polymerized in both
solution and vapor phase. Salmon et al (1982) and Street et al (1982) suggested that, though chemical oxidization usually leads to powders, film can be obtained by allowing the oxidation to takes place at a solid or liquid surface, however these films are of poor quality. The good quality films were first obtained by Kanazawa et al (1980) and Diaz et al (1979) using a modification of the electrochemical technique suggested by Dall'Olio et al (1968). Soon after it was appreciated by Gill et al (1982) that these films consists of polycationic chain of pyrrole, but with the charge counter balance by anion from the electrolyte solution.

1.2 LITERATURE REVIEW:

1.2.1 Synthesis and characterization by FTIR, DTA and TG:

A polymer has synthesized by Rabek et al (1992) in presence of cationic photo-initiators such as iron-arene salts (h- C$_2$H$_5$), Fe (h- arene) under visible or ultra-violet irradiation. They reported the low conductivity and poor electrochemical properties for above polymer.

A blend of polypyrrole and poly (vinyl methyl ketone) (PVMK) have been prepared both by chemically and electrochemically by Wang et al (1999). H-bonding has been verified by IR showed no significant change in conductivity on stretching the blends over 200%. The blends exhibit threshold conductivities near 10% of polypyrrole. TGA shows
that the blends are stable to temperature of 598 K for chemically prepared and 553 K for electrochemically prepared samples.

Saprio et al (1995) disused the significance of two and three-dimensional morphology of electropolymerised polypyrrole-p-toluenesulphonate film. They showed that 2D growth of film directly adjacent to the surface, reverting to 3D dendritic growth as the film thickness increases. Samples of polypyrrole were synthesized under galvanostatic condition. Electrical conductivity varies from $10^{-3}$ to $10^{-1}$ S/cm. Thermal conductivity has been determined between 280 to 335 K from thermal diffusivity, specific heat and density. The results were used to calculate the Lorenz number of polypyrrole, (Lunn et al 1993).

Heo et al (1994) synthesized polypyrrole-p-toluenesulphonate (PPTS) polymers by electrochemical technique. The results of DSC and TGA showed that the weight loss was most rapid in the temperature range 533 to 651 K and maximum values of reaction rate was 0.27 mg/min at 651K. From temperature dependence of electrical conductivity and electron spin resonance, the small polaron hopping is observed in PPTS polymers. Zoppi et al (1994) have prepared polypyrrole and EPOM rubber blends by sorption of pyrrole (vapor phase) in an EPOM matrix containing CuCl$_2$. They measured the electrical conductivity in the range of $10^{-9}$ to $10^{-7}$ S/cm when oxidant particle size was decreased. IR, thermal
analysis and SEM techniques were used for structural characterization. A conducting composite of polypyrrole was prepared via electrochemical method by Selampinar et al (1997). A polyamide is used as the insulating matrix polymer. The characterization has been done by FTIR, TGA, SEM, DSC and pyrolysis reveals that H-bonding exists between two polymers and grafting to certain extent. Kapin et al (1995) studied the morphology chemical structure, electrochemical properties and tensile modulus in polypyrrole films containing 0.1M pyrrole, 0.1M perchlorate. The cyclic holtagramme of films indicates the peaks due to large concentration of bipolarons.

A sample of polypyrrole –p-toluenesulphonate has been prepared by electrochemical polymerization. From the morphology, Sutton et al (1993) proposed that the growth is based on polymerization in the solution followed by a degree of further chain development after precipitation.

The conductivity and also thermal, mechanical and electrochemical properties of PVC- polypyrrole blends were described by Mano et al (1996). These blends were prepared by oxidative chemical polymerization of pyrrole, in the vapor phase in PVC film impregnated with FeCl₃. FTIR, DSC and IR were used for characterization. The mechanical, thermal and conducting behavior shows a dependence on 1) initial concentra-
tion of FeCl$_3$ in the matrix and 2) exposition time of pyrrole vapor. The conductivities of samples varies from $10^{-4}$ to $10^{-1}$ S/cm. Composite of polypyrrole with poly (methyl acrylate) and poly (styrene-co-butyl acrylate) were prepared using FeCl$_3$ impregnated matrix polymer films and dipping them into a solution of polypyrrole in water using a concentration of 67 mol/dm$^3$ and above. FTIR studies do not reveals any H-bonding, the $\equiv$N-H group in polypyrrole and COO group in matrix polymers, (Mandol et al 1996). The polypyrrole-polytetramethylbisphenol composite have prepared by Kalaycioglu et al (1996). A carbonate is used as insulating matrix polymer. Characterization of free standing composite is based on FTIR, IR, measurements and solubility. No evidence of hydrogen bonding in composite has been found. Bhattacharya et al (1996) prepared a TEFLON-FEP (tetrafluoroethylene-hexafluoropyrrole) via $\alpha$- irradiation induced grafting of styrene in octanol medium, subsequent sulphonation of aromatic ring and finally deposition of pyrrole over the sulphonated matrix. Polymerization of pyrrole has been done chemically using different monomer concentration. FTIR spectroscopy was used to confirm the existence of different species. Surface morphology, thermal and mechanical strength, surface resistance have been studied. Chen et al (1998) studied the electrochemical polymerization of N-trimethylesilylethoxymethyl-3-methyl-4-pyrrole carboxilate ethyl ester
electrical conduction in conducting polypyrrole thin films (MPCE-SEM) in presence of pyrrole to give freestanding copolymer film. FTIR and SEM techniques were used for characterization of these films. Conducting polymer graft of pyrrole and poly [(Methyl methacrylate)-co-2 (Pyrrolyl) ethyl methacrylate)] containing 0.7% PEMA have been prepared by potentiostatic anodic polymerization of pyrrole in different electrolytic media. Using FTIR, DSC, TGA, SEM, CV, and elemental analysis made characterizations. The conductivities of the resultants polymers seemed to be in the order of pure polypyrrole prepared under same conditions, (Balci et al 1997). The synthesis of a 1,3-bis (4-fluorobenzoyl)-5-tert-butyl benzene and hexafluor bi-phenol A based poly (arylene ether ketone) (PEK) was made by Selampinar et al (1997). The electrical conductivity of the composite was found to be between 1 to 4 S/cm. Using FTIR, DSC, and TGA, the characterizations of composite were made. Xiaobo Wan et al (1999) measure the large electrical anisotropy in poly-pyrrole thin film with binary solvent consisting of boron trifluoride ethyl ether and additional ethyl ether. They found the highest tensile strength for the film up to 90 MPa.

Coirns et al (1999) have deposited a polypyrrole from aqueous media onto a sub-micrometer sized poly (ethylene glycol)–stabilized polystyrene latex. Deposition experiments were carried out at two different initial concentrations and latex concentration was symmetrically adjusted
in order to control the final polymer loading. They characterized the polymer by TEM and disk centrifuge photosedimentometry (DCP). An electrodeposited polypyrrole film formed on chemically modified hydrogen-terminated silicon surface has been prepared by Vermeir et al (1999). Semiconductor polypyrrole junctions on the native and modified substrates exhibit diode like characteristics, with those on the latter substrate exhibiting higher current densities and better ideality factors. A chemically produced polypyrrole powder doped with the fluro-complexes such as fluro-aluminates, fluro-zirconates, fluro-titanates, and fluorides have studied by Yfantis et al (1999). The samples were synthesized and characterized by four probe conductivity measurements. Results shows that the polypyrrole produced were doped with fluorides and with fluro-metal complexes (Zr, Ti, Al) of different coordination numbers, also, a significant incorporation sulfates originating from the oxidant was determined. The relative concentration of the sulfates and respective fluro-metal complexes is strongly affected by the size of these dopants and much less from their concentration in the solution.

Pionteck et al (1999) have prepared two polypyrrole composites with polypropylene by chemically oxidative reaction of polypyrrole on the surface of polypyrrole particles in suspension, and second by mixing the coated polypyrrole particles with non-coated polypyrrole particles
at room temperature. The processing was done by injection molding exhibits better mechanical properties, anisotropic behavior and electrical conductivity. Feng et al (1999) synthesized electrochemically a polypyrrole/polysulfide conducting composite film in acetonitrile/acetone compound solvent with liquid sulfide rubber as supporting electrolyte. FTIR characterizations suggest that polysulfide counter ions have been incorporated into polypyrrole film during electrochemical polymerization. Electro-activity and electrochemical reversibility have been studied by electrochemical voltammetry. Sezer et al (1999) prepared a polymer composite with N-ethylcarbazole and N-vinylcarbazole by the polymerization with pyrrole both chemically and electrochemically by ceric ammonium nitrate (CAN); the resulting product have been characterized by FTIR, UV spectroscopy and SEM. Goto et al (1999) synthesized the polymer containing benzenoid and quinoid structures of polypyrrole with liquid crystalline subsistent, where phenylcyclohexyl moiety was adopted as a mesogenic core. The polymer exhibits smectic liquid crystalline phase. 2,5-dibromoppy having a liquid crystalline subsistent with a cyclohexyl or bi-phenyl mesogenic core at the N-position was dehalogenatively poly-condensed with Ni, giving soluble and fusible polypyrrole derivatives. IR, NMR, DSC, and XRD investigated the chemical structure, (Kigima et al 1999). Interpenetrating polymer network (IPN)
composite of polypyrrole and polyvinyl acetate (PVAc) were prepared by dipping FeCl$_3$ impregnated PVAc film into solution of pyrrole water. They have found that polyvinylacetate (PVAc) becomes colored due to partial dehydroacetylation and also insoluble due to FeCl$_3$ treatment. DSC studies done by Chakrabarti et al (1999), shows that peaks of PVAc remains unchanged in FeCl$_3$ treated film indicating that dehydroacetylation did not proceed to significant extent. Junhua et al (1999) synthesized a polypyrrole on carbon nanotube using in situ polymerization method and discussed the molecular structure and physical properties. Kalaycioglu et al (2000) synthesized a graft copolymer of Poly (2-(N-pyrrolyl) ethylvinylether) and polypyrrole. The samples were characterized through FTIR, DTA, and DSC to evaluate thermal stability. Coirns et al (1999) examined the surface composition of a series of five polystyrene-polypyrrole composites and three reference materials, the poly (ethylene glycol) (PEG), the uncoated PEG-stabilized polystyrene latex and polypyrrole chloride bulk powder by XPS and SEM. Tae et al (2000) illustrated the carrier scattering time through Drude’s theory and studied the disorder and low mobility of polypyrrole film by opto-electronic beam from low frequency to 2.5 THz.

Iroh et al (2000) have co-deposited Polyaniline and polypyrrole on carbon fibers under potentiostatic conditions. TG and DSC verified
the thermal stability of coating. Characteristic behavior of the sample was deducted from the weight gain plot. Jing et al (2000) prepared composite of polypyrrole with P-dodecylbenzene sulfonic acid sodium salt (NaDS) as a surfactant and dopant. The resultant composite shows a ferromagnetic behavior. FTIR, XRD analysis shows that nano-meter (mn) sized iron oxide particles were responsible for the ferromagnetic behavior of the composite. Chemical deposition of electrically conducting polypyrrole thin films has carried out by Wei et al (2001) on mica and allumina in aqueous solution with and without surfactant. Investigation of films morphology and thickness by atomic force spectroscopy shows a dependence of structure on method of preparation.

Radhakrishnan et al (2001) have deposited a polypyrrole films containing phthalocyanine by electrochemically using solvent system (H₂O with H₂SO₄). FTIR and UV is used for characterization of the films. These films show photochemical response in electrochemical mode increases due to presence of phthalocyanine. Aguilar et al (2001) measured a c and d c conductivity in polypyrrole-poly-oxaphenylene and polypyrrole-poly-oxaphenylene tetrasulphonated tetrasodium metallophthalocyanine composite. The temperature dependence of ac conductivity changes by five times, showing sub-linear dispersive behavior. Temperature dependence dc conductivity gives evidence for a transport mechanism. Hui et al (2001)
have prepared films of 1 wt % polypyrrole, encapsulated latexes at 393 K. They found a clear relation between temperature and stability of films. Madan-Mitra et al (2001) discussed the disorder induced metal-insulator transition in polypyrrole doped with CF$_3$/SO$_3^-$ in an attempt to understand the electrical transport in the vicinity of transition. They observed the special features like plasma resonance and high reflectivity in IR. The surface-enhanced Raman spectroscopy in oxidized polypyrrole shows that the conductivity of polypyrrole is strongly related to and increases with Raman peak intensity of oxidized polypyrrole, (Liu et al 2000). Nicho et al (2000) have prepared a solution of PVAc and polyvinyl alcohol (PVA) with FeCl$_3$. The mixture was coated on substrate and as the solution solvents were evaporated, pyrrole was polymerized in the composite coating. FTIR studies suggest that molecular interaction between the functional groups of the polymer matrices and polypyrrole through the iron salt molecules, which could be the reasons for the good miscibility between the semiconductor and insulator components of coating.

Conductivity relaxation spectra of interpenetrating network conducting composites of polypyrrole and poly (styrene-butyl acrylate)(SBA) have analyzed by Bhattacharya et al (2000). The macroscopic activation energy obtained from coupling model using the strength exponent beta compares favorably with the tunneling energy estimated from the over-
lapping large polaron tunneling model. Chang et al (2000) have prepared a composite of carbon nanotubes and polypyrrole and characterized by SEM, TEM, XRD, and TGA. Okuzaki et al (2000) have synthesized the polypyrrole film containing tetrafluoroborate and measured a tensile stress of 4.8 MPa. Living bi-functional azo-poly-tetra-hydrofuron (azo-PTHF) was terminated with pyrrolyl potassium salt to yield a polymer with electrochemically active functional end groups. This polymer has further used to synthesize poly-tetra-hydrofuron-polystyrene block co-polymer by Oztemiz et al (2000). FTIR, TGA, SEM, DSC, NMR, and GPC characterized the samples. Okuzaki et al (2000) have synthesized the polypyrrole film containing tetrafluoroborate electrochemically and electrically driven motion of the film was investigated. It was found that application of dc voltage brought about reversible contraction of the film in ambient air, where the contraction increased with increasing applied voltage and ambient relative humidity. Lee et al (2001) have prepared the electrochromic film using WO₃, V₂O₅ by sol-gel-spin coating and vacuum evaporation process. Polypyrrole films were prepared by electropolymerization in a polypyrrole solution using acetonitrile and tetra-ethyl-ammonium p-toluenesulphonate. The liquid electrolyte was prepared using LiClO₄, propylene carbonate, poly-methyl-meta-crylate and ethyl acetate. Characterization was done by XRD, DSC, UV techniques. Ramelow
et al (2001) have prepared polypyrrole chemically and electrochemically, using ClO$_4^-$, I$_2$ and P-toluene sulfonic acid and sodium salt as dopants. The samples were characterized by FTIR. Lee et al (2001) have synthesized polypyrrole and metal (AgPd) compound coated on woven polyethylene tetra-phthalate and non-woven polyester fabrics. They found the electromagnetic interference shielding efficiency of polypyrrole/fabric complex in the range of 20-80 dB depending upon the thickness and conductivity. Ustamehmetoglu (2001) developed a new class of dimethyl formamide (DMF) and acetone soluble conducting polypyrrole-kenotic resin co-polymer. The samples were characterized through FTIR and UV spectroscopy. Li et al (2001) described the synthesis of electrochemically conductive nanofibrils derived from pyrrole and aniline using uniform and straight channels of anodic aluminum oxide (AAO) film as template. The chemical polymerization technique for pyrrole and aniline loading is employed and investigated the structure and morphology of co-polymer fibers with IR, TGA SEM and TEM.

Tallman et al (2002) reported the use of electron transfer mediation for the direct electro-deposition of polypyrrole onto Al and onto Al$_2$O$_3$-T$_3$ alloy. SEM, AFM, and XRD and conductivity measurement characterized the samples. A composite of polypyrrole and spinel mixed valance oxide such as CuMnO$_4$ in neutral and alkaline media have synthe-
sized by Cong et al (2002). They found that i) the spinel lattice and the electro-catalytic activity of the oxide remain stable in acidic media, where normally this oxide would be electrochemically reduced, ii) polypyrrole retain its electrical conductivity at cathodic potentials where it would be normally in its insulating reduced state. A polypyrrole and iron oxide nano-composites were prepared by annealing from 373-923 K. These composites were studied using TEM, TG, DTA, and FTIR. After the dissociation of polypyrrole, the phase transition from magnetic to nano-magnetic behavior was observed, (Suri et al 2002).

polypyrrole and polypyrrole -tetra-cynoquinodindimethane (TCNQ) were prepared to see the energy band structure modification and associated change in electrical and opto-electrical properties, (Chakrabarti et al 2002). The temperature dependent electrical conductivity of samples shows higher conductivity at room temperature. Gabrielli et al (2002) have prepared a polypyrrole films by using electrogravimetry. The information about the moment of anions, cations, and solvent during the switching of polypyrrole between oxidation states was obtained. The insertion isotherms and the transfer time constants were obtained. Badani et al (2002) studied the electrochemical polymerization of pyrrole and aniline on some conductive metals such as Fe and Al, used as anodes. Their cyclic voltammetry studies shows that the polymerization mechanism on
Fe or Al appears to be the same as suggested for a noble metal electrodes. Rasika Das et al (2006) have studied HBF₄-polypyrrole blend using FeCl₃ as dopant. They showed that the presence of conjugated π-bond electron system gives broad band in FTIR spectrum of electronically conductive polymer. The broad band in the range 4000-2000 cm⁻¹, which is known as ‘tail of electronic absorption band’ is characteristic of conducting form of polypyrrole. Dallas et al (2007) have studied the synthesis of polypyrrole using Fe(III) as dopant and characterize the sample by gravimetric analysis and FTIR spectroscopy.

1.2.2 AC/DC Conductivity and Dielectric measurements:
Whong et al (1989) detected electrical conductivity up to 5 S/cm in polypyrrole thin film prepared by using FeCl₃ as oxidizing agent.

Electrical conductivity up to 100 S/cm, in a complex synthesized from the exposure of poly (4-vilylpyridines) (P-4VP) with an oxidizing agent such as cupric chloride or ferric chloride to pyrrole and water vapor have determined by Mohammidi et al (1999).

Thin coating of chemically synthesized polypyrrole onto monodisperse silica particles in colloidal silica composite by the insitu deposition showed an electrical conductivity up to 2x10⁻⁵ S/cm, (Armes et al 1991). The electrical conductivity between 6 to 7 S/cm was determined
by Ruckenstein et al (1993), in composites of polypyrrole and poly (alkylmethacrylate). Kelkar et al (1993) have studied the electrical conductivity of nylon-6- polypyrrole composite film with CuCl₂ as dopant and showed that electrical conductivity increases with concentration of dopant. Ribo et al (1993) have prepared a thin film by oxidative chemical polymerization of polypyrrole in vapor phase in PVC film impregnated with FeCl₃, found that the conductivity lies between 10⁻⁴ to 10⁻¹ S/cm. Afterword, Tsutsui et al (1994) determined the electrical conductivity for polypyrrole thin film prepared with various concentration of supporting electrolytes of tetraethylammonium-p-toluenesulphonate which was of the order of 18 to 62 S/cm. Polymer of N- (2-hydroxyethyl) polypyrrole (HEP 1), 2-(N-pyrrolyl) ethyl acetone (PEA, 2) and 2-(N-pyrrolyl) ethyl stearate (3) were synthesized via oxidative polymerization with FeCl₃, 2-(N-pyrrolyl) ethyl acetate (PPEA, 5) and 2-(N-pyrrolyl) ethyl stearate (PPES, 6) were partially soluble in organic solvent and transparent films were cast from solution. The conductivity of about 10⁻⁷ to 10⁻⁵ S/cm was detected depending upon doping of iodine. Structural characterization of composite was made through FTIR, NMR, IR, DSC and GPC techniques (Stanke et al 1995). Truong et al (1995) have studied the conductivity decay Δσ/σ with time and suggested that this decay is due to oxygen diffusion. The film is retarded and affected zones more
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restricted, in a film of polypyrrole with p-toluenesulphont by simplest treatment of sulfuric acid and sodium sulphate.

Li et al (1996) worked out the conductivity and Vis-NIR absorption spectra of polypyrrole films, doped with TsO⁻, ClO₄⁻, NO₃⁻ ions, from room temperature to 473K. They show that the conductivity behavior of polypyrrole film, with increase in temperature, depends up on the nature of counter anions. For polypyrrole film doped with TsO⁻ ions; shows a phase transition at 363 K, over which the conductivity increases with temperature more quickly.

The conductivity increases with decrease of donor number values of solution as shown by Onyang et al (1997), in a polypyrrole film with electrolyte like LiClO₄, Cu(NO₃)₂·2H₂O and TsOH etc.

The vapor of organic solvents like toluene, butanol and ethanol do affect the electrical conductivity of electrochemically-synthesized polypyrrole (Van-de-Leur et al 1999). This property allows the use of polypyrrole in sensors for vapor detection. Chapman et al (1999) studied a set of temperature dependent reflectivity and dc conductivity measurements in a series of PF₆ doped polypyrrole samples, differing only in their synthesis temperature. They showed that observed decrease in the low-energy ac conductivity could be accounted for, by a simple generalization of the heterogeneous disorder model used to explain the dc con-
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ductivity. The report of preparation and characterization of polypyrrole composites with polyvinylidene fluoride (PVDF) and glucose was given by Bhat et al (1999). They have reported that percentage crystallinity of the host polymer decreased, whereas some crystallization of polypyrrole was noticed. Electrical conductivity of the composites was varies in the range of $10^{-8}$ to $10^{-4}$ S/cm. These composites were found to be useful in gas sensors for detection of chlorine and ammonia. Chemical polymerization of pyrrole was carried by Cavallaro (1999) in a reaction calorimeter using FeCl$_3$ or CuCl$_2$ as an oxidant in an acetonitrile medium. The reaction concentration and reaction temperature, which were directly proportional yield by polypyrrole and degree of polymerization was determined along with the electrical conductivity of 0.6 S/cm, having direct relation with the yield of sample and to degree of polymerization. This highest electrical conductivity value was related to polypyrrole fresh synthesized from a 0.017 molar pyrrole solution.

Chakrabarti (1999) have detected the electrical conductivity in polypyrrole synthesized with known normality of oxidizing agent like Fe (SO$_4$)$_2$. He showed that the conductivity increases up to 28 S/cm for 2N normalized oxidizing agent. A graft co-polymer of poly (acrylonitrile-co-pyrrolylmethylstyrene)-g- polypyrrole, (PANPMS-g- polypyrrole) was prepared by Yun et al (2000), and showed that the conductivity of
PANPMS-g- polypyrrole was 100 times higher than that of poly (acrylonitrile-co-chloromethylstyrene)-l- polypyrrole, (PANCMS- polypyrrole) prepared under same condition. Omastova et al (2000) have prepared a composite of poly (methyl methacrylate) and polypyrrole (PMMA) by a chemical oxidation of polypyrrole in PMMA latex medium, resulting in a network like structure of polypyrrole embedded in the insulating polymer matrix. The electrical conductivity of the sample depends upon the concentration of polypyrrole and varies from 10 to 0.01 S/cm. Prissanaroon et al (2000) showed the dependence of specific electrical conductivity with morphology and the effects of using dodecylbenzene sulfonic acid as a dopant on electrical conductivity of polypyrrole films in N₂ atmosphere and SO₂-N₂ mixture. Temperature dependent dc and ac conductivity and thermoelectric power for the conducting nano-composite samples were investigated by combining ferric oxide particles with polypyrrole. The variation of ac conductivity with frequency shows very little change in total conductivity up to a critical frequency, followed by sudden jump with discontinuity and then increases monotonically following a power law. The frequency exponent decreases with temperature as predicted by hopping theory. Above 50 K the ac conductivity increases linearly as predicted by quantum mechanical tunneling model, (Gangopadhyay et al 2000). Polymerization potential, solvent used in
polymerization, modification of polypyrrole with valance Cu and introduction of polyethylene oxide into polypyrrole, increases the conductivity of polypyrrole films and their corresponding stabilities, was suggested by Liu et al (2000). Again the Carbon nano-tube dopant can improve, both the strength and conductivity of polypyrrole (Chen et al 2000). Kalaycioglu et al (2000) also measured the conductivity of polypyrrole / poly (2-(N-pyrrolyl) 2-ethyl (vinyl ether).

Kang et al (2000) showed the electrical conductivity of chemically prepared polypyrrole in aqueous solution was found to be strongly dependent on the preparation technique and polymer additive. Accordingly, the conductivity can be enhanced doubled when preparation technique includes washing treatment with organic solvent and drying under vacuum at elevated temperature to attained maximum removal of water. Jang et al (2001) have measured electrical conductivity at room temperature in polypyrrole -di (2-ethylhexyl) sulphosuccinate sodium salt (NaDEHS) cast from various alcohols.

The conductivity values were found in the range of $10^{-12}$ to $10^{-15}$ S/cm. However the considerable change in the values of the order $10^{-4}$ to $10^{-12}$ at room temperature, using highly soluble organic solvents like m-cresol, THF, acetic acid, chloroform and benzene (Oh et al 2001).

Baozong et al (2001) carried out the surface modification of Poly-
aniline (PAN) films via coating with polypyrrole in an electrochemical cell with organic acid as dopant. The new films have higher conductivity and stability than PAN films.

The result shown by Sutar et al (2001) was the positive magneto-resistance for all the samples, indicating the dominance of electron-electron interaction in the study of temperature dependence of d.c. conductivity and magneto-resistance in polypyrrole sample doped with PF6-polypyrrole-PF6 at various doping level. The estimation of the positive charge carrier mobility and charge carrier concentration in polypyrrole films with Tin-oxide and Au as deposition substrate have made by Valask et al (2001). Electrical properties of polypyrrole-sulfated poly (β-hydroxy-ethers) with sulfated hydroxy group as dopant has been investigated by Kodama et al (2001). Similarly, a thermoelectric property of polypyrrole and Sodium P-toluenesulphonate has measured by Hu et al (2001). They found that thermal the conductivity is of the order of $10^{-2}$ SI units of the film at 423 K.

Eung et al (2001) have prepared the films of polypyrrole with di (2-ethylhexyl) sulphonate as dopant anion. The conductivity was found to be $10^{-3}$ S/cm. TGA and DSC studies showed that the decomposition temperature was limited by the dopant anion. The mixed dopant [di (2-ethylhexyl) sulphonate with molanic acid, 4-sulfophtalic acid and dodecyl-
benzenesulfonic acid, when added to pyrrole, the resulting films became more stretchable and show improved stability and electrical conductivity (255 S/cm). Jing et al. (2001) have detected a good crystallinity in polypyrrole by in situ doping polymerization with 1,5-naphthalenedisulfonic acid as a dopant. Polypyrrole-graft-Poly (β-caprolactone) (ppy-g-PCL) copolymer has synthesized by Mecerreyes et al. (2001) via oxidative co-polymerization of polypyrrole and polypyrrole-end functional macro-monomers. They have carried out co-polymerization in tetra-hydrofuran at 0°C using FeCl₃ as oxidizing and dopant agent. The composite was characterized by FTIR and TGA. They found that electrical conductivity of the nano-composites increases with the amount of polypyrrole in the co-polymer between 10⁻¹ to 10⁻² S/cm and that of 10 S/cm for polypyrrole.

Polypyrrole doped with two dopants has prepared by Lee et al. (2002) with chemical polymerization in aqueous solutions of pyrrole monomer. The solutions contained dode-cylbenzenesulphonnic acid (DBSA) as a dopant, tetraethyl ammonium, tetra-fluoroborate (TEABF₄) as a co-dopant, and ammonium per-sulfonate as an oxidant. The polypyrrole composite (ppy-DBS) co-doped with tetra-fluoroborate were soluble in m-cresol and conditionally soluble in chloroform. The electrical conductivity at room temperature for polypyrrole-DBS-BF is 1.18
S/cm, which is higher than that of polypyrrole doped with DBS (0.04 S/cm). The samples are characterized by FTIR and SEM. The hopping conduction mechanism for soluble polypyrrole-DBS-BF film was suggested. Morales et al (2002) showed that copolymer thin films of polypyrrole-poly-aniline doped with iodine have better conductive properties at lower relative humidity.

Yun et al (2002) have prepared the conducting Poly (methylmethacrylate-co-pyrrolylmethylstyrene) -g- polypyrrole (PMMAPMS-g-polypyrrole) by electrochemical reaction with PMMAPMS and PPY in the electrolyte solution containing lithium perchlorate and a mixture of solvent of acyronitrile and dichloromethane. The electrical conductivity of sample was around 0.1 S/cm. Chemical polymerization of polypyrrole, on a polyester woven fabric, shows high electrical conductivity and low specific volume resistivity (Kim et al 2002).

Polypyrrole films were investigated by Gabrielli et al (2002) using ac electro-gravimetry. Information about the moment of anions, cations and solvents during the switching of polypyrrole between oxidation states was obtained.
1.3 PRESENT POSITION OF RESEARCH WORK IN POLYPYRROLE:

Electrically conducting polypyrrole nanostructures have recently caused a great deal of experiments in the era of physics, chemistry and materials science. Such nanostructures are inherently intriguing chemical systems, and have large technological applications. Many researchers (Mohammadi et al. 1999; Kelkar et al. 1993; Preechatiwong et al. 1996; Yun et al. 2000; Omastova et al. 2000; Jang et al. 2001; Lee et al. 2002; Jong et al. 2001; and Adeloju et al. 2001) have synthesized and characterized the various composite blends or powder, thin films and copolymers with pyrrole (py) such as ppy-poly(4-vinylpyridines) with CuCl$_3$ as oxidizing agent, ppy-nylon-6, ppy-poly(acrylonitrater-pyrrolylmethylstereyrene) copolymer, ppy-di(2ethylhexil)sulfosuccinate sodium salt, ppy doped with two dopants as dedocylbenzenesulfonic acid and tetraethylammonium tetrafluoroborate with ammonium persulfonate as a oxidant, ppy-LiMnO$_4$, ppy-glucose oxide etc.

Recently temperature dependence ac and dc electrical conductivity and thermoelectrical power for conducting nano-composite samples were investigated by Gangopadhay et al. (2000), by combining ferric oxide partiicals with polypyrrole. They showed that, above 50K the ac conductivity increases linearly as predicted by quantum mechanical tunnel-
ing model. A complex composite of polypyrrole was synthesized by Lee et al (2002) with chemical polymerisation and by Yun et al (2002) with electrochemical reaction of pyrrole monomer. Information about the moment of anions, cations and solvents during switching of polypyrrole between oxidation state was reported by Gabrielli et al (2002).


Many research workers have studied the morphology and electrical conductivity of most of polypyrrole composite and thin films, but lesser attention seems to be given to an optical, thermal, dielectric and some other properties of conducting polypyrrole. Therefore we have decided to study the various properties of conducting polypyrrole thin films. The present work reports the study on ac, dc electrical conductivity,
and dielectric behavior, FTIR, DTA, TG and XRD of conducting polypyrrole.

1.4. USE OF POLYPYRROLE IN VARIOUS FIELDS OF INDUSTRIAL AND SCIENTIFIC APPLICATIONS:

The technical application of conductive polymers has been predicted in the 1970s. These applications are largely in the area of energy storage and distribution. Additional applications in electronics, photovoltaic devices and optical devices have also emerges. These applications are based on the characteristics properties of conducting polymers like lightweight, processibility and electronic conductivity. The discovery of electrochemical doping of polyacetylene (Nigrey et al 1979) initiated an idea of applying conducting polymer as battery electrodes. Lewis et al (1999) has determined the true potential at one electrode in two electrode cell while applying a range of potential difference between the two polypyrrole electrodes to give full oxidation and reduction of polypyrrole both in a supporting electrolyte solution and as a component of two electrode solid state device. Jong et al (2001) have developed a LiMnO$_4$ polypyrrole composite cathode for lithium polymer battery. A PEC solar cell based on nano-structured ZnO/dye/ polypyrrole film electrode has fabricated by Hao et al (2000). Its electricity conversion efficiency was 1.3%.
Lemon et al (1999) have been deposited polypyrrole gas sensitive thin films on gold and indium-tin-oxide glass electrodes. It is shown that the crystalline material produced results from the entrapment of packets of electrolytes within the polymer matrix during deposition. The vapor electro-deposited polypyrrole using different counter-ions on both quartz crystal microbalance electrodes and separate inter-digitized microelectrodes can be used as vapour sensor (Cui et al 2000). The ratio of the relative change of resistance to that of frequency on exposure to a vapor was measured and was found to be independent of vapor concentration over wide range. Adeloju et al (2001) have synthesized an ultra-thin polypyrrole-glucose oxide film in supporting electrolyte-free monomer solution potentiometric bio sensing of glucose. Thin films of polypyrrole doped with different counter-ions prepared by in situ polymerization are used for gas sensors with fast response time (De-Souza et al 2001). Hetero-junctions between silicon and polypyrrole doped metal phthalocyanine toluenesulphonate anions have been studied using current-voltage and capacitance-voltage measurements, shows that thermionic current is dominant. Such a composite can be used as gas sensors (Nguyen-Van et al 2001). Thin films of polypyrrole doped with different counter ions and prepared in situ polymerization on conducting glass electrodes, are used for the development of gas sensors. (De Suza et al 2002).
Madden et al (2001) have prepared actuators using polypyrrole. The polypyrrole doped with large anionic detergents have high stability in aqueous systems. Polypyrrole can be reversibly oxidized and reduced electrochemically. The redox change of polypyrrole is accompanied by a change in volume of the polymer. This volume change can be used as a polymer actuator (artificial muscle). (Bay et al 2001). Polypyrrole pipe was electrochemically polymerized in a teflon slender pipe (Kato et al 2001). They found that a polypyrrole film cut from the pipe has anisotropy in conductivity as well as in morphology. This anisotropic polypyrrole film can be used as an actuator. Bay et al (2002) have prepared conducting polymer using polypyrrole and dodecyl benzene sulphonate (DBS). If the pentanol is doped to the synthesis solution in concentration above 2.4 volume % a linear extension of 5.6 % was measured at a constant load of 0.6 MPa. The use of pentanol as co-surfactant during polymerization will be useful for the use of polypyrrole -DBS as active component material in polymer actuators. Benslimane et al (2000) has determined the mechanical work and force densities of polypyrrole, which can be obtained from artificial muscle actuators based on polypyrrole.

Few applications of polypyrrole are reported below.

(a) Silicon polypyrrole junction using organolithium reagent 5-(N-pyrrolyl) pentyllithium. as diode (Kim et al 2000).
(b) A sandwich structure of DBD (1,1'-di-benzyl-4,4-bi-pyridyl dichloride) substituted at a N-position of 2,5 polypyrrole as p-type semiconductor (Roy et al 2002).

(c) Electrochemical superconductor with a specific high capacitance of 268 F (Chi Chang et al 2002)

(d) Electrical stimulation increases the adsorption of serum proteins, specifically, fibronectin, to the electrically conducting polypyrrole, thereby increasing neurite extension (Kotwal et al 2001).

(e) Effectiveness of corrosion protection of an acrylic paint, containing electrically conductive polypyrrole, for magnesium alloy (98.14% Mg and 1.64% Mn) (Truong et al 2000).

(f) Conducting polymer solar cell in tandem that absorb energy from a broader range of solar spectrum have been designed by Kim et al (2007).

1.5. UNCOVERED AREA IN RESEARCH OF POLYPYRROLE:

High performance of hetero-cyclic and aromatic polymers were discovered forty years ago; and these materials are still attractive for their thermo-chemical, electrical and optical properties, also because they offer unlimited possibilities of chemical modifications. For structural materials except for supersonic transport, the trends are not towards very
high thermo-stable performance but rather towards the long-term good thermo-chemical properties in the range of 473K. For such properties the upgrading of industrial poly-condensates like polyamides with low cost heterocyclic groups using reactive processing could be fruitful approach. In an electrical industry, a demand for environmentally friendly enamels is large. Hence the development for new photosensitive formulations without solvent is necessary.

In electronic industries, the dielectric with low dielectric constant and photosensitive precursors are still desperately needed. For the industrial application of polypyrrole in various technological fields, polypyrrole should possess reasonably good conductivity, good mechanical strength as well as processability and stability in ambient temperature. Polypyrrole synthesized chemically or electrochemically do possess high conductivity and environmental stability, but their mechanical properties are not always desirable. In order to improve the mechanical properties of polypyrrole several approaches have been made such as chemically or electrochemically in presence of different counter ions (Wie et al 2001; Madan Mitra et al 2001; Okuzaki et al 2000; Ramelow et al 2001; Sezer et al 1999; Zoppi et al 1994; and Tallman et al 2002) preparation of composites or co-polymers etc, but still the research workers are not satisfied with the mechanical properties of polypyrrole.
It was found that, even though polypyrrole composite possesses good conductivity at ambient temperature, however, the conductivity rapidly declines at elevated temperature. The link between chemical and physical changes of the aged polymer-dopant systems and loss of conductivity has not been established. Nevertheless, there has been empirical success in improving the stability by ion exchange of counter ion dopant.

A variety of work has been carried out in studying the polypyrrole composites. The properties such as XRD, SEM, and DTA are used to determine the morphology of the composites. The properties like ac and dc conductivity, ionic conductivity, hopping distance, activation energy, dimension of conducting areas, adiabatic and non-adiabatic nature of conduction and entropy are highly interesting providing the useful information about structure and conduction mechanism. Various scientists and electronic engineers to gain the new insights into the structure of polypyrrole have studied all these properties. Very little work seems to have been done in optical properties, ac conductivity, ionic conductivity dielectrics, thermal properties and magnetic properties of polypyrrole. It was in the fitness of the things to undertake the unexplored or rather explored areas in polymer research, to study the electrical and thermal properties of polypyrrole.
1.6. PRESENT LINE OF INVESTIGATION:

A detailed literature survey of polypyrrole synthesis reveals that chemical polymerization of pyrrole chosen have, most probably, not been studied. The electrical, dielectric, thermal and physical properties etc. of polypyrrole are very important and are capable of revealing interesting information. These properties are suggestive of giving the information about the internal mechanism, conductivity and some new insights of the polypyrrole. Various techniques are used to study the structure of polymers. Some of them are XRD, FT-IR, DTA, TGA, EXAFS, SEM, and TEM etc. Out of these techniques FT-IR, X-RD, DTA and TGA have been used in present investigation.

FTIR is used to determine the structure and various positions of groups in polypyrrole. Various vibrational frequencies of bonds, stretching and bending of group positions are determined by FTIR.

DTA technique is important to determine the glass transition temperature and also transformation temperature range.

TGA is used to determine the mass loss at different temperature, activation energy and entropy.

XRD technique is important to determine the crystalline or amorphous nature of polymer composite.

The dielectric properties such as complex impedance, dielectric
constant, loss etc. depends on the orientation of polar molecules in solids, which are directly related to the lattice forces, induced displacement of electrons and to a very small extent to the atoms.

In the view of this, a chemical polymerization of pyrrole using polyvinyl acetate as a base and ferric chloride as dopant has been selected for the study.

In the present work, preparation of polypyrrole thin films of various thickness, measurements of dc electrical conductivity (variation with temperature) and hopping conduction, measurements of ac electrical conductivity (variation with frequency and temperature) and measurement of dielectric loss of polypyrrole films have been under investigation. Similarly to understand the structure of polypyrrole, the study of XRD, FTIR, DTA and TGA are incorporated. All these properties are studied with an aim to get some insight into the nature of polypyrrole composites and to understand their general behavior. After studying the various properties of polypyrrole composite, some of the results are expected to yield the information on the conduction process, structure etc.
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