İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SYNTHESIS OF SOLUBLE AND CONDUCTING POLYPYRROLE COPOLYMERS

M.Sc. Thesis by

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ÇÖZÜNÜR VE İLETKEN POLİPİROL KOPOLİMERLERİ SENTEZİ

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Date	Name
12/05/2002	Barış Kışkan

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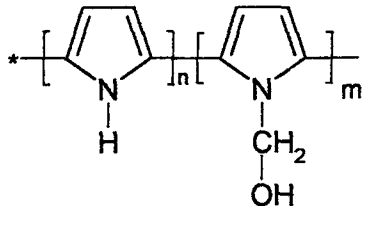
SYNTHESIS OF SOLUBLE AND CONDUCTING POLYPYRROLE COPOLYMERS

SUMMARY

This thesis can be outlined like that; In our research, we have developed soluble and conducting pyrrole copolymers by means of some derivatives of pyrrole.

Briefly, the idea of this research was to synthesize chemically modified pyrroles to obtain solubility when these monomers include to the structure of the polymers chain.

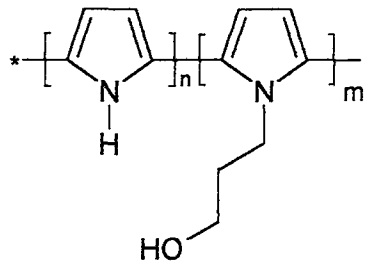
Initially, some pyrrole derivatives were synthesized to create new monomers for copolymerizaiton reactions. As mentioned above, the aim was to obtain soluble and satisfactorily conducting copolymers of pyrrole, which would be processable for some applications. Hence, N-methylol pyrrole synthesized by a published method [1], and synthesized by the modificated way of the same method, which was based on changing the catalist. Then, this pyrrole derivative used in copolymerization reactions (which are chemically oxidative copolymerization reactions by means of $FeCl_3$) with pyrrole, by a hope of obtaining soluble, conducting polymers. The results was not satisfactory for the aim.



(I)

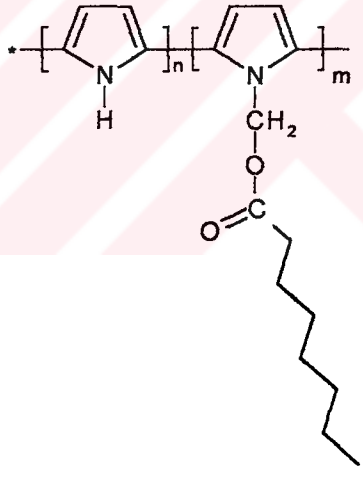
Then another derivative of pyrrole, was synthesized which was N-propylol pyrrole by a published method [2]. This monomer was used in copolymerization reactions with pyrrole to reach the aim, by the same chemically oxidative polymerization method,

which was used for N-methylol pyrrole. The result was not satisfactory, if we discuss their solubility versus conductivity.



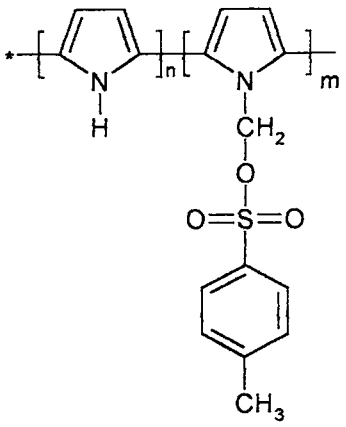
(II)

And another pyrrole derivative synthesized as a monomer by using N-methylol pyrrole as one of the reactant. This monomer was 1-H-pyrrolylmethyl octanoate. Again, copolymerization reactions was accomplished by using chemically oxidative copolymerization method which had a different oxidant compared to the method which was afformentioned above. This different oxidant was Ce(IV) ammonium nitrate. The resulting copolymers were sligltly soluble but not conducting too much.



(III)

In the end, pyrrole derived monomer which was synthesized over N-methylol pyrrole, was used for copolymerization reactions. This monomer was N-methyl-1-pyrrolyl tolune-p-sulphonate. The copolymerization reations carried out by the method which was used for 1-H-pyrrolylmethyl octanoate and pyrrole copolymers. This time, resulting copolymers were relatively soluble. And the conductivities relatively goood. We were able to have ^{1}H-NMR spectrum of one of the copolymer sample.



(IV)

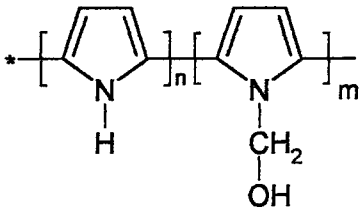
İLETKEN VE ÇÖZÜNÜR POLİPİROL KOPOLİMERLERİ SENTEZİ

ÖZET

Bu teze konu olan çalışmada, bazı pirol türevleri kullanılarak, çözünür ve iletken pirol kopolimerleri geliştirilmiştir.

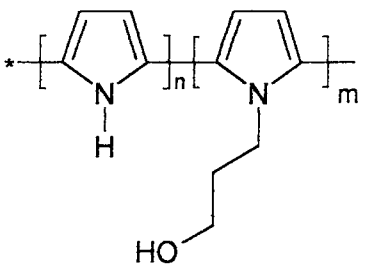
Kısaca, bu çalşmadaki fikir, kimyasal olarak değiştirilmiş, türevlendirilmiş piroller sentezleyerek monomerler yapmak ve bunları kopolimer yapılarına dönüştürmek. Yukarıda değinildiği gibi amaç çözünür ve yeter düzeyde iletkenliğe sahip pirol kopolimerleri elde etmek ve bunların bazı uygulamalar için işlenir olmasını sağlamak. Bunun için önce, bazı yeni pirol türevleri sentezlendi.

Daha önce yayınlanmış bir yöntem kullanarak [1] N-metilol pirol sentezlendi. Bu yöntemin değiştirilmiş hali ile de aynı madde sentezlenebildi, sözedilen değişiklik katlizör değişikliğidir. Sonra bu pirol türevi $FeCl_3$ ile yapılan kimyasal oksidatif kopolimerizasyon tepkimelerinde kullanıldı. Beklenilen çözünür ve iyi iletken polimerdi, fakat sonuç tatmin edici değildi.



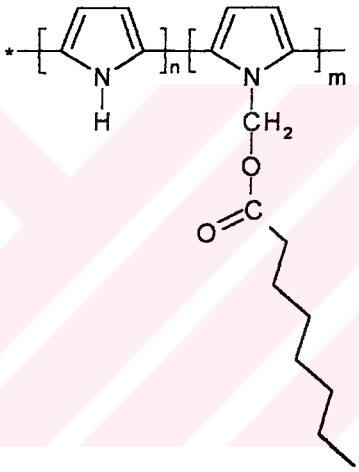
(I)

Böylece, yeni bir pirol türevi sentezlendi, bu türev N-propilol pirol dür. Bu maddenin sentezi de daha önce yayınlanmış bir yöntem ile gerçekleştirildi [2]. Yeni monomer, yukarıdaa anlatılan aynı kimyasal oksidatif kopolimerizasyon yöntemiyle pirol ile kopolimerleştirildi. Sonuçlar, eğer iletkenlik ve çözünürlük değerleri karşılaştırılırsa, yine beklene gibi olmadı.



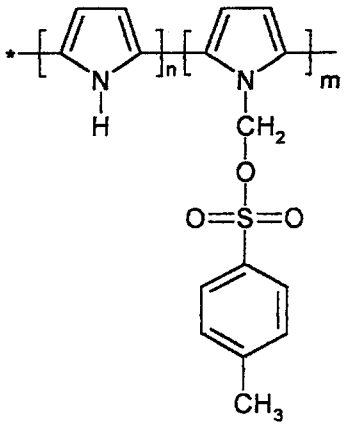
(II)

Yeni bir monomer olarak, N-metilol pirolün başlangıç reaktanı olarak kullanıldığı bir tepkime ile sentezlendi. Bu monomer 1-pirolilmetil oktanoat dır. Ve yine pirol ile kimyasal oksidatif kopolimerizasyon tepkimeleri gerçekleştirildi, bu tepkimelerde $FeCl_3$ yerine Ce(IV) amonyum nitrat kullanıldı. Sonuç kopolimerler az çözünür fakat iyi elektrik iletken değildi.



(III)

Sonunda, bir pirol türevi daha N-metilol pirol üzerinden sentezlendi. Bu monomer N-metil-1-pirolil toluen-p-sülfonat dır. Kimyasal oksidatif kopolimerizasyon tepkimeleri yine Ce(IV) varlığında gerçekleştirildi . Sonuçta iletkenleri göreceli iyi (6 S/cm) ve çözünür polimer ele geçti. Bu kopolimerin ^{1}H-NMR spectrumu elde edildi.



(IV)

1. 1. INTRODUCTION

Most polymers are insulators, with desirable properties such as light weight, processiblity, durability, and low cost. By designing the molecular structures of polymers, chemists have developed new materials that exhibit electrical conductivities comparable to metals while retaining the advantages of polymers. There are three approaches to making conducting materials: pyrolysis to produce a conducting residue (mostly carbon); producing a composite structure from a conducting material and an insulating organic polymer (filled polymers); and making organic conjugated polymers. This thesis addresses the third approach. Generally, these electrically conducting polymers are composed of conjugated polymer chains with π-electrons delocalized along the backbone. In the neutral, or undoped, form the polymers are either insulating or semiconducting. The polymers are converted to the electrically conductive, or doped, from via oxidation or reduction reactions that create delocalized charge carriers. Charge balance is accomplished by incorporating an oppositely charged counter ion into the polymer matrix.

Initially, the drive for research in conducting polymers was the possibility of combining electronic properties with the attractive mechanical properties and processing advantages of polymers. The fist generation of conjugated polymers exhibited insolubility, infusibility, and instability: They could not be processed and were generally, unstable in air. It became evident that the initial expectation of quickly conducting polymers to practical applications may be long. To be potentially useful in electronic applications, a material must be environmentally stable and have excellent electronic and mechanical properties, and it should be solution or melt processable. The delocalized electron structures of π-conjugated polymers that are responsible for their unusual electronic properties tend to yield relatively stiff chains with little flexibility but with relatively strong interchain attractive interaction that makes them insoluble and non-processable.

To place conducting polymers in context, copper has a conductivity of about $5x10^5$ S/ cm (equilavent to per ohm per cm), and polystyrene has a value of $1x10^{-18}$ S/cm. Nylon has a value of 10^{-14} S/cm; Hg, 10^4 S/cm. Typically, undoped conducting

Nylon has a value of 10^{-14} S/cm; Hg, 10^{4} S/cm. Typically, undoped conducting polymers have values comparable to those of other insulating polymers (10^{-12} S/cm), which on doping are increased to 10^{2} S/cm.

For many applications, two distinct ways of processing ICP (inherently conducting polymers) are most frequently used:

1. Mechanical processing of ICP, obtained by chemical synthesis.However, almost all known parent (unmodified) ICP like polyaniline (PANI), polypyrrole (PPy), and polythiophene (PT), have poor mechanical properties, they are insoluble, non-melting, and thus not processible. Therefore, some progress in mechanical processing was achieved by the use of mixtures of ICP with the usual processible polymer materials, as well as by the use of chemically modified ICP.
2. Coating of various materials, including plastics, glass, metals, as well as micro and nanoporous materials, with a thin layer of ICP. Coating of polymer microparticles or latexes with ICP leads in some cases to composite materials that can be further mechanically processed to obtain bulk conducting polymer composites.For many purposes, however, no bulky conduction is required; instead, a thin deposited surface layer of ICP is used.

Spreading of the solution of ICP on the surface of the material, followed by the evaporation of the solvent. Besides the difficulties concerned with the desired uniform coating of material surface with the solution of ICP. the main problem is the insolubility or even poor solubility of many ICP in nearly all solvents of practical interest. During the past years, some progress has been made in the chemical modification of the parent ICP structures to get more soluble polymer derivatives. For example, the introduction of alkyl chain into the 3- position of pyrrole monomer, or of an alkoxy group into the *ortho* position of the aniline monomer, yield upon polimerization the corresponding polymers that are more soluble in some organic solvents, whereas sulfonation of PANI enhances the solubility of the resulting polymer in water. However, the distortion of the molecular structure of ICP occurs upon such chemical modification, leading to a drastic decrease of the electric conductivity of the resulting polymers.

Chemical polymerization, provided with relatively strong chemical oxidants like ammonium peroxydisulfate (APS), ferric ions, permanganate or bichromate anions, or hydrogen peroxide. These oxidants are able to oxidize the monomers in

approciate solution, leading to chemically active cation radicals of the monomers used. The cation radicals thus formed react with monomer molecules, yielding oligomers or insoluble polymers. Chemical polymerization occurs in the bulk of the solution, and the resulting polymers precipitate as insoluble solids. This can be usually achieved by choosing the reaction conditions, like the concentration of the solution components, the concentration ratio of oxidant to monomer, reaction temperature [3]

As it is mentioned above to overcome the main problems for applications of conducting polymers there should be needed solubility of melting properties. The aim of the research which is the subject of this thesis is to obtain soluble and satisfactorily conducting copolymers of pyrrole compared with parent polypyrrole. This was accomplished by using some sort of chemically modified pyrroles.

2.THEORY

2.1 INSULATING POLYMERS

One of the principle applications of polymers is an electrical insulators. Polymers with saturated structures and those with unsaturated groups, in either the backbone 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 levels within the band gap. Typical conductivities and mobilities are 10^{-15} S/cm and 10^{-14} $m^2V^{-1}s^{-1}$ for PE, 10^{-16} S/cm and $10^{-13}m^2s^{-1}$ for poly(tetrafluoroethylene) (PTFE) and 10^{-15} S/cm and $5x10^{-11}$ m^2 V^{-1} s^{-1} for polystyrene (PS). Thus, in add-ittion to a knowledge of the band structure, it is necessary to investigate the motion of carriers and its dependence on sample morphology.

A wide range of quantum chemical methods have been used to calculate the band stru-ctures and densities of electronic state for insulating polymers (4-5). These have been compared with experimental valance-band densities of states determined by X-ray photoelectron spectroscopy (XPS) and UV photoelectro spectroscopy [4,5,6]. XPS has also been used to determine the valance band structure of polymers with pendant groups; here, comprasion with molecular spectra has aided interpretation. The development of reliable theoritical models has allowed XPS to be used for the structural determination.

The mesurment of the electrical properties of higly resistive polymers presents a number of problems. The surface conductivity is often greater tha the bulk value and is increased by absorbed impurities. The latter is also affected by impurities. The presence of localized defect states in the energy gap means that contact with metals is accompanied by charge transfer to the polymer in the absence of an applied field. The triboelectric charge appears to be relatively intensities to sample purity or preparation and even to polymer structure. This indicates that the important defects are structural, with a density that is almost sample indipendent. The work for

function of the metal affects the charge transfer, but large experimental uncertinity renders precise functional fits unreliable.

When charge is injected into polymers by an electric field, the low carrier mobility leads to a space charge near the electrodes and non-linear current voltage charecteristics. These phenomena are of considerable interest in studies of the breakdown of polymeric insulators subjected to high voltages. In practice, this occurs at defects where fields are enhanced and tree like structures occur, which propogate through partial discharges. Guarded needle electrodes have been used for accurate measurment of the injected charge, showing that injection of the energetic carriers is a fast process while subsequent decay in zero field is slow. Space charge in the parallel electrode geometry has been studied using laser generated shock waves, which dispalce the space charge producing a pulse of induced current. In thin films of poly(ethylene terephthalate), the space charge was localized near the electrodes and decayed by the dispersive transport. This is a common feature of carrier transport in polymers and is due to carriers becoming progressively less mobile with time as they encounter deeper traps. The distrubition of trap levels can be probedby thermally stimulated currents. After polarizationof a sample at low temperatures, currents flow whenever thermal excitation leads to detrapping or, for polar polymers, dipole relaxation. For example, in irradiated samples of PTFE fluorine deficient sites have been identified as traps.

The determination of the very low carrier-mobilities encountered in insulating polymer and the results obtained for PE, have been reviewed. Hopping between defect states in PE gives electron and hole mobilities from 10^{-10} to 10^{-15} $m^2V^{-1}s^{-1}$, which are much smaller then es-timated from band-stucture calculations, 0,2-0,6 $m^2V^{-1}s^{-1}$ for electrons and 10^{-2}- 10^{-4} $m^2V^{-1}s^{-1}$ for holes. Experimental differentiation of various types of hopping conductivity is difficult, *e.g.* variable range and multiphonon assisted local hopping both display an $\exp(T/T_o)^{1/4}$ temperature dependence [7].

Through most insulating polymers are not intrinsically ferroelectric, polar materials can be produced by charge injection into insulating poymers Such electreds have been known, studied and utilized for many years. Notable exceptions are poly(vinylidene difluoride) (PVDF) and its copolymers which are ferroelectric. There have been numerous studies of orientation, poling, structure and phase transitions of these polymers. The large piezoelectric effect of PVDF when in the poled state has led to its application in acustic and ultrasonic transducers.

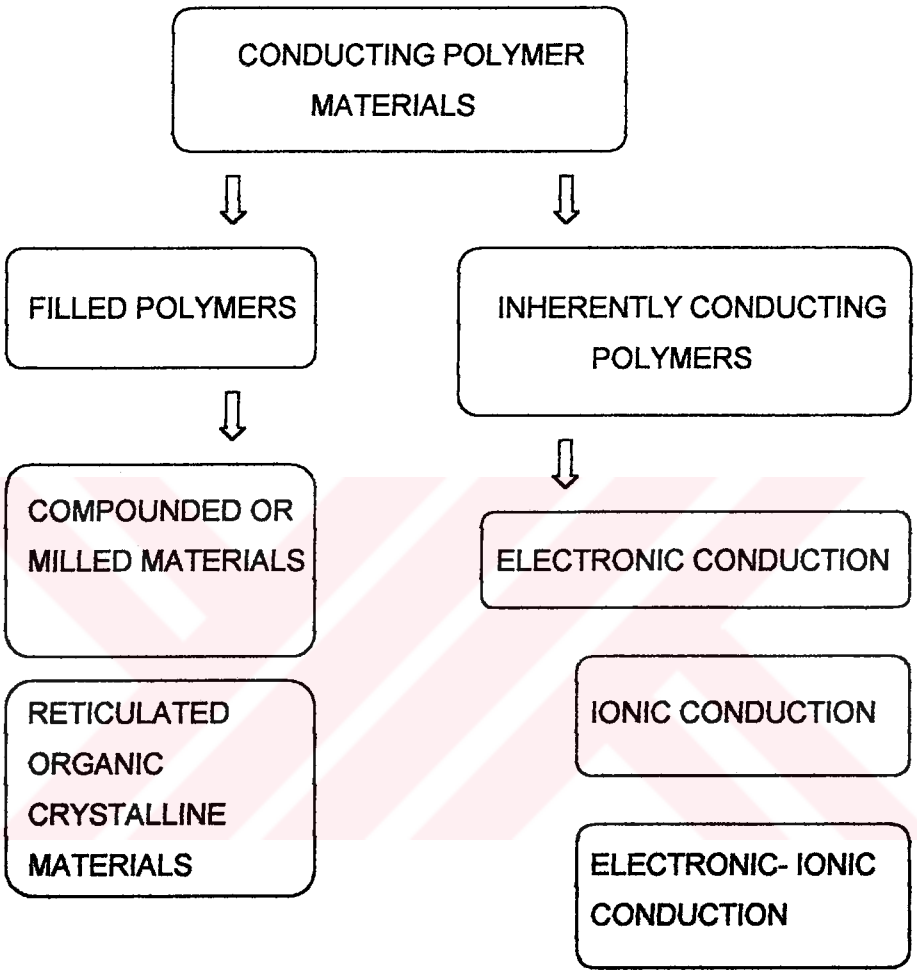
Examinations of the results of AC conductivity measurements shows that the imaginary part of the dielectric function, the dielectric loss factor, is similar over the range 10^{-4} to 10^{5} Hz for many amorphous and partially crystalline polymers. Indeed, it has been argued that there is a 'universal' dielectric responce function that is valid for a wide range of solids. In all cases, the dielectric responce is due to hopping of electrons (or ions) or reorientation of dipoles. These are fast discontinuous processes which provoke a much slower many body responce which screens the charge or dipole . This combination of processes leads, through the Kramers-Kronig relation, to a 'universal' frequency dependence.

Strong electron donors or acceptors can effect charge transfer with insulating polymer and produce some increase in conductivity, *e.g.* from 10^{-15} S/cm to 10^{-12}-10^{-13} S/cm for PS films exposed to iodine. This can be attributed to carrier hopping betweem localized charge transfer sites, *e.g.* the pendant groups. The effect of organic and inorganic impurities is particularly important in polymer films used as insulation and protective layers in semiconductor devices. This has been studied for various poly(ester imide)s by measurment of the residual current in a field effect transistor (FET) coated with impurity doped polymer.

An important application of both insulating and semiconducting polymers is the xerographic process. In this, a photoconductor is charged uniformly by a corona discharge and, on illumination, is selectively discharged to produce the image. A toner, which consist of metallic particles and a polymer, is charged triboelectrically and used to render the image visible prior to its transfer to paper. An effective toner requires optimized triboelectric properties. This has been achieved by the incorporation of conjugated pendant groups, *e.g.* PS and modified PS. The pendant moieties provide molecular orbitals which determine the sign of charge transfer by their position relative to the E_F of the metal. Surface modification can significantly affect triboelectrification, *e.g.* sulfonated PS films show a sharp rise in charge transfer due to the ease of charging the sulfonate groups. Incorporation of counter ions, *e.g.* methylene blue, enables futher control to be exercised over the degree and sign of charge transfer. Futher discussion of topics touched on here can be found in the literature.[8,9]

2.2 GENERAL CLASSIFICATION CONDUCTING POLYMERS

Table 2.1: Schematic classification of conducting polymeric materials



2.3 FILLED POLYMERS

Carbon black, silver, aluminum, and other conducting particulate materials dispered in the form of fibers, flakes, beads, or needles in thermoplastics and thermosets raise the conductivity to a level at which facile charge migration occurs. Filled polymers can be used for electrostatic screening and a variety of charge-disspitation applications. Highly filled materials, with loading particals in excess of 20% w/w, produce high levels of conductivity and in certain cases a positive temperture coefficient of conductivity.[10,11]

Carbon black particals can form chained structures in which interparticale contacts allow currents to be carried. A construction generated by filling the gap between two metallic conductors with a conducting carbon - black matrix can be used as a heating tape. When the matrix is heated , it expands and the number of particle-particle contacts will be reduced and a corresponding increase in the resistivity and reduction will occur in the current carried; hence , heating will cease. A current limited condition is produced and determined by the temperature at which the loss of contacts produced by expansion of the matrix is balanced by the increased conductivity generated by the cooling of th matrix, which increases the contacts. This type of self regulatory or smart structure is used commercially in heating pipes and vessels where spot heating could produce hazardous conditions.

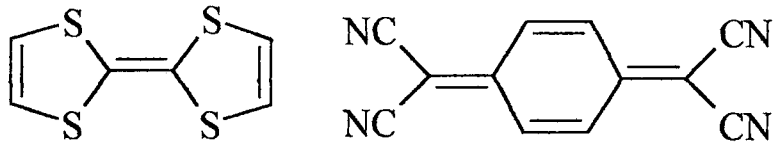
The loading level at which conductivity is imparted to a polymer matrix depends on the shape, size , and distribution of particles. The critical conductivity has little to do with the conductivity of filler, but rather with its size , geometry , and density. For two fillers of equal particle size and shape, the one with the lower density will have a lower critical composition or volume. The higer the aspect ratio, the lower the critical composition: needle shaped materials are better than flakes, which are in turn more effective than spheres. In practice, carbon black, which is constituted from spherical submicrometer particles, will tend to aggregate into chains and increase connductivity. Particle partical contact is not essential if the filler particals are less then 100 nm in diameter, because quantum tunneling effects may well become operative. A number of authoritative publications on carbon black loaded materail exist.[12,13,14]

2.4 RETICULATED ORGANIC CYRSTALLINE MATERIALS

Molecules such as tetrathiafulvene (TTF) and tetracyanoquinodimethane (TCNQ) can be cyrstallized into needle-shaped structures that have a very high intrinsic conductivity [15]. Cyrstals are typically of submillimeter dimensions and are of little practical use. Kryzewski [16] and Berlin [17] grew dentritic structures in polymer matrices that exhibited conductivity levels of 1-10 S/cm at 1-2 % w/w loading levels. The TTF-TCNQ molecules form stacks in which charge transfer between adjacent molecules is assisted by their donor acceptor nature.

A wide range of organic molecules are capable of donor acceptor behavior. The TTF- TCNQ complex dispered in polycarbonate at 1% loading is a light green

transparent solid, making it attractive for applications where conductivity, flexibility, and transparency are all important. These materials had not attracted the attention they deserved until relatively recently. By using similiar concepts, nonlinear optically active polymer films were generated, and this approach is likely to find greater utility in the future for generation of metarials with conductivities in the range of 10 to 10 S/cm.Molecular structures of tetrathiafulvene (TTF) and tetracyanoquinodi methmethane (TCQN) is below.



TTF TCNQ (2.1)

2.5 INHERENTLY CONDUCTING POLYMERS

Inherentely conducting polymers can be divided into three parts:

- Electronically conducting metarials (electronic conductivity is dominant)
- Ionically conducting metarials (ionic conductivity is dominant)
- Mixed conductivity metarials (ionic and electronic processes both play a significant role)

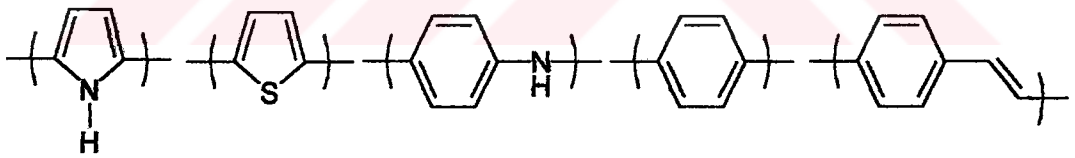
Because of their application in areas such as batteries and smart window technology, ionic conducting materials have been labelled polymeric electrolytes. Polyethylene oxide is the most widely studied of polymer electrolytes. Doped with suitable ionic spieces, it is capable of exihibiting ionic conductivities of the order of 10^{-4} S/cm at room temperature and 10^{-2} S/cm at 100°C. Polymer electrolytes have allowed the devellopment of solid-state devices and form important component in batteries used in heart implants, smart windows, and a range of applications where ionic rather than electronic conductivity is important. Ionically doped polyethylene oxide, polyphospates, and polytungastates all have applications in this area. Conductivity is achieved by migration of ionic dopants in a manner analogous to a

molten electrolyte. A considerable volume of this topic was compiled by Vincent [18].

Electronically conducting materials can be divided into two groups:

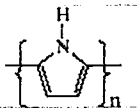
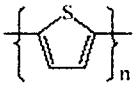
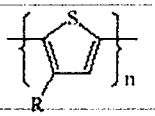
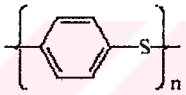
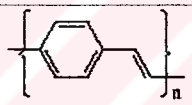
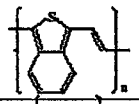
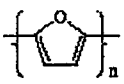
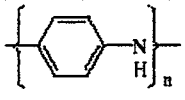
1. Polyacetlene, polypyrrole, polythiophene, polyphthalocyanines, polyphenylvinylene, and polyphenylsulfide are all dominantly electronically conducting and rely on their conjugated structure to facilitate electronic mobility.
2. Polyaniline and one or two related systems behave in a somewhat different manner by exhibiting conductivity that is best described in terms of both ionic and electronic mechanisms.

In both these systems the conductivity is a consequence of a highly conjugated backbone structure that is capable of being doped to yield a high bulk conductivity on doping. See some examples of π conjugated polymers in scheme below and some common organic conducting polymers with their conductivity and doping materials as a chart in Table 2.



(2.2)

Table 2.2: Common organic conducting polymers

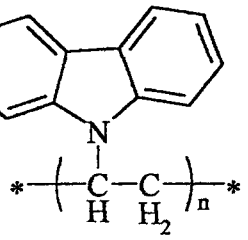
Polymer	Structure	Doping materials	$\Omega^{-1}cm^{-1}$
Polyacetylene	(CH)n	I_2, Br_2, Li, Na, AsF_5	10000
Polypyrrole		BF_4^-, ClO_4^-	500-7500
Polythiophene		BF_4^-, ClO_4^-	1000
Poly(3-alkylthiophene)		BF_4^-, ClO_4^-	1000-10000
Polyphenylene sulfide		AsF_5	500
Polyphenylenevinylene		AsF_5	10000
Polythienylenevinylene		AsF_5	2700
Polyphenylene		AsF_5, Li, Na	1000
Polyisothianaphthene		BF_4^-, ClO_4^-	50
Polyazulene		BF_4^-, ClO_4^-	1
Polyfuran		BF_4^-, ClO_4^-	100
Polyaniline		HCl	200

2.6 SEMICONDUCTING POLYMERS

The boundary between insulators and semiconducting polymers is somewhat arbitrary. However, the latter are distinguished by the photoconductivity they display when exposed to visible wavelenghts. Certain categories of polymers, *e.g.* pyrolyzed and filled polymers, span the semiconductor / metal boundary and are considered seperately. This leaves two distinct classes of semiconducting polymers, those with active pendant groups and those with fully conjugated backbones. Work on these two classes has been largely directed towards different goals and has progressed almost independently.

2.7 CONJUGATED-SIDE-CHAIN POLYMERS

Xerography has driven much of the research into conjugated-side-chain semiconducting polymers. The must studied photoconductor polymer is poly(*N*-vinyl carbazole) (PNVC). PNVC in its pure form is a hole conductor with a dark conductivity of the order of 10^{-14} S/cm. The photoresponce is limited to the absorption profile of the carbazole moiety. Both properties are modified when molecular species are added, so that impurities can mask the intrinsic properties of PNVC, *e.g.* purification leads to lower quantum effiency. Poly(*N*-vinylcarbazole) (PVNC) is showed below.



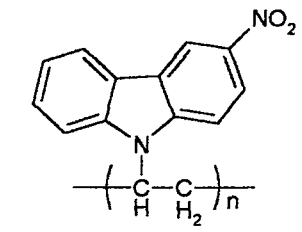
(2.3)

Dye molecules sensitize photoconduction by electron transfer between the exicited state of the dye molecule and PVNC. For weak acceptors which give neutral ground state, *e.g.* 2,4,7-trinitro-9-fluorenone (TNF), photosensitization occurs by direct excitation of electron transfer from the PNVC carbazole group to TNF. A charge-transfer band appears in absorption and photocurrent action spectra and the quantum effiency is high (0.23). Strong acceptors from complexes with ground state charge-transfer and enhanced conductivity, *e.g.* $2x10^{-6}$ S/cm at 77% w/w of I_2. The

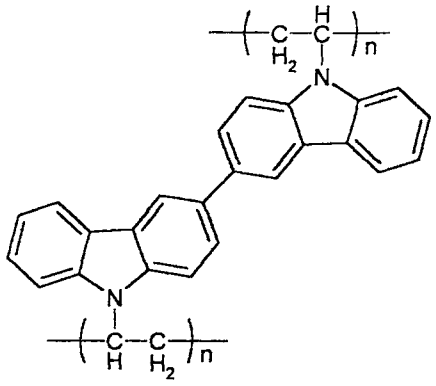
use of both acceptors and dyes is benefical, because the action spectrum contains contributions from dye and charge transfer bands, and degradation due to photochemical reaction is reduced. Coulombic attraction results in the geminate recombination of many electrons and holes. This process was first discussed by Onsager [19] and shows a strong voltage dependence, quantum efficiency increasing with applied field.

Addition to TNF to PNVC gives an increased electron-mobility. Identical behaviour is found for a polyester matrix, indicating electron hopping between TNF molecules. The hole mobility falls by 10^3 for 50% TNF incorporation, as seperation of the carbazole units is increased and charge localizetion occurs. The mobilities are thermally activated and current pulse transits exhibit dispersive transport, both effects being symptomatic of hopping conduction. Apparently, long lifetimes for bound electron hole pairs in PVNC have been explained as an artefact of hopping between sites with Gaussian energy disorder. A detailed discussion of conduction and photoconduction in PVNC can be found in the literature [20].

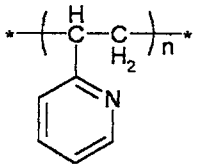
PNVC has been modified chemically to incorporate substituents on the carbazole groups, (fig X). Methylene blue sensitizer can be bonded to sulfonated PNVC. Bonded nitro- and cyano- groups act as acceptors giving rise to enhanced photoconductivity. Antimony pentachloride produces crosslinking of the carbazole groups to form dimeric carbazylium radicals. The conductivity of up to 10^{-5} S/cm has been attributed to electron hopping between the dimer sites. PNVC copolymers with acrylates, methacyrlates and styrene, when sensitized with TNF, are found to give similar photoconductivity to PNVC but with better film properties. Copolymers with mixed carbazole and acceptor pendant groups have been synthesized in order to extend spectral sensitivity, but overall they are less useful than PNVC-acceptor composites. Poly(2-vinylpyridine)s (fig 2.4) and poly(4-vinyl pyridine)s (fig 2.4) have been used as antistatic coatings, as constitiunts of xerographic toners, with PNVC and phthalocynanine dyes as xerographic semiconductors and complexed with iodine for photovoltaic cells and as cathodes for solid-state batteries. Other examples of this class of polymers are poly(*N*-ethyl-2-vinylcarbazole) and related polymers, polyacenapthylene, poly(vinlypyrene), polyindene, poly(vinyl napthalene), poly(vinylanthracene), poly(2-vinylquinoline), *etc.* Some of these polymers are shown in Scheme 2.4.



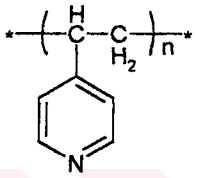
Chemically modified PNVC



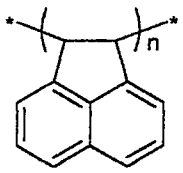
Crosslinked PNVC



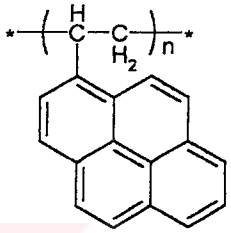
Poly(2-vinylpyridine)



Poly(4-vinylpyridine)



Polyacenapthalene



Poly(vinylpyrene)

(2.4)

2.8 BRIEF STRUCTURAL OVERVIEW OF CONJUGATED POLYMERS

The structures of electronically conductive polymers are characterized by a backbone which each atoms involved in a π-bond (an exception to this is polysilanes which are σ-conjugated systems). Defects and rotations around single bonds in the backbone impart a nonplanaritiy to the polymer and reduce delocalization of the π-electrons. This effect is manifested as a blue shift in the absorption spectrum of the conjugated polymer when heated.[21]

Defect free conjugated polymers can be considered as a one dimensional system with one electron per carbon atom. The typical energy gap between the conduction and valance ba-nds is 1 to 3 eV. Since it is highly unlikely that exitation of carriers would occur across a gap of 2 eV, these systems would be insulators or, at best, semiconductors. It has been shown that the conductivity of semiconducting polymers becomes metallic if they are doped with strong oxidizing or reducing agents. Introduction of dopants gives rise to strong electron-phonon interactions,

leading to new quasiparticals: solitons, polarons, and bipolarons. The electrical conductivity of conducting polymers result from these mobile charge carriers [22].

From the point of view of metallic conduction, conducting polymers are not comparable to inorganics. The superiority of conducting polymers over their inorganic counterparts resides in their structural versatility, flexibility, and processibility. Ironically, one of the most challenging problems of conducting polymers technology is processibility. The presence of strong inter-chain electron transfer interactions, a desirable property for electronic conduction, makes them, nevertheless, frequently insoluble and infusible.

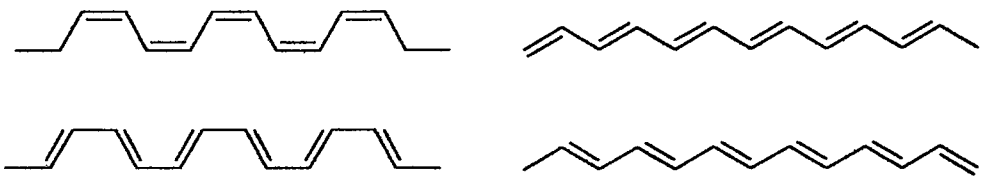
2.9 THEORY OF INHERENTLY CONDUCTING POLYMERS

Polyacetylene (PA) is the simplest conducting organic material, and central to understanding conductivity in organic polymers is the soliton model. This mathematical description of energy levels in conducting polymers can be applied with suitable modification to any system in which the backbone forms an extended conjugated structure. [23]

In the case of polyaniline it is necessary to consider the role of proton migration; however, even in this case the underlying concepts of the soliton model are still correct.

PA is the simplest conjugated polymer conductor, and each unit has three of its four valence electrons in carbon sp^2 hybridized orbitals: Two generate σ-bonds and form the 1-D lattice, and the third is used to form a bond with hydrogen [13,25]. The remaining π-electron forms the conjugated structure that is prerequisite of organic conductors. PA can exist in cis or trans isomeric structures, and these structures heva nondegenerate energy levels and different conductivities. (Scheme 2.5)

Cis- trans-



(2.5)

Pristine films of PA will contain a mixture of the less conducting cis and the more conducting trans forms [26]. The trans form is the thermodynamically more stable structure, and isomerization is achieved by doping the films by using either gaseous diffusion or electrochemical techniques. p-$[(D^+)_y(CH)]_x$ or n-$[(A^-)_y(CH)]_x$ typmaterial can be obtained depending on whether A and D dopants are acceptor or donor molecules. Semiconducting properties are achieved at approximately 1% dopant levels; higher levels lead to metallic conductivity [27]. Doping may increase the conductivity by as many as 10 orders of magnitude, and understanding this process is fundemental to the development of more effective conducting polymers.

2.10 SOLITON RELATED MODELS

Conductivity in conjugated polymers relies on the generation of accesible levels within the band gap, formed by delocalized bonding and antibonding electron sites and associated with conformationally excited states. PA is a board-band quasi 1-D semiconductor with an overall band width (W) associated with electronic motion along the chain. The value of W can be estimated from tight-binding theory by eq 2.1, wheze z is the number of nearest neighbors and t_o is the intercarbon transfer energy for an electron.

$$W = 2zt_o \qquad (2.1)$$

The t_o parameter was obtained from spectroscopic studies and has a value of 2-2,5 eV, indicating that W is approximately 9-10 eV. However, because of the effects of the bond alternation, trans $-(CH)_x$ is a semiconductor with a band gap of about 1,5 eV. The ability of stable trans $-(CH)_x$ to sustain free stable soliton as natural nonlinear excitation leads to the importance of PA as a prototype conducting polymer.

In an idealized PA structure, all the C-C bonds would be identical; however, as a consequence of the Peierals instability (see figure 2.1), pairs of CH groups move toward each other to form alternating shorter (pseudo-double) and longer (pseudo-single) bonds. The resulting lowering of the energy and creation of an energy gap at the Fermi level allows conductivity to be achieved. This process can

be described theoretically in term of changes in the resonance integrals associated with the π-σ^* excitation and generation of an energy gap. The gap (Φ) seperates the highest occupied and lowest unoccupied molecular orbital states and corresponds to a difference in the transfer (resonance) integrals for the single and double bonds. Change in the bond structure from cis to trans leads to change in the electron distribution and energy gap seperation.

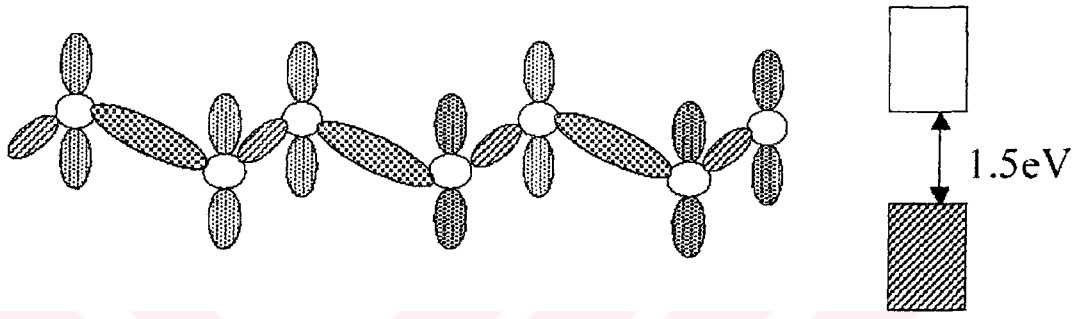


Figure 2.1: Peierals instability

For the trans structure, the two forms are isoenergetic, and both forms are thermodynamically stable and degenerate. The cis forms are non isoenergetic. The cis-transoid has a lower energy than the trans transoid form; therefore, only the lower energy form is thermodynamically stable, and the ground state is nondegenerate. X-ray studies [28] of the trans form have confirmed the effects of the Peierels instability. The basic cyrstal structure conforms to a $P2_1/n$ space group, where a =0,425 nm, b=0.737 nm, c= 0,246nm, and β= 91,5 (where β is the angle of the unit cell, which contains two chains). The instability leads to a distortion of the a-c plane of approximately 0,003nm, which is sufficent to break the symmetry and generate an energy gap.

Theoretically, the energy gap is given by eq 2.2

$$\Phi = 8\beta U_o \qquad (2.2)$$

Where β is the electron-phonon coupling constant describing the modulation of the π electron transfer integral, and U_0 is the energy distortion resulting from changes by the Peierels instability.

Analysis of optical absorption spectra indicates that Φ is between 1,6 and 1,8 eV. Substitution of this value in eq 2 yields a value of 7,1 eV for V the electron-phonon coupling constant (β). Good agreement between measured [29] and predicted [30] energy gaps implies that effective electron electron interactions is relatively weak and does not dominate the conduction process. The degenerate ground state is trans- PA leads to the possibility of stable phase domains and the presence of domain walls within the material. As the temperature is raised, a cis-$(CH)_x$ chain begins to isomerize, but because each carbon is identical, the isomerization will commence randomly along the chain. The ground state is degenerate, different phases will be produced at random, and where they meet a nonlinear topological excitation, a soliton will occur. (figure 2.2)

These solitons give rise to localized states in the center of the band gap. The nature of these sites and their interactions with other soliton sites are strongly dependent on the accupancy of these localized states. The soliton is negative and has a spin of ½ when the state is singly occupied. If the state becomes unoccupied or doubly occupied, the soliton has no spin.Theoritical studies [31] indicated that two neutral solitons simply combine and live no deformation, two identically charged solitons will tend to repel each other, but a charged and neutral soliton will be stable when in close promixty. This neutral charged soliton pair is called an antisoliton pair, or a polaron. The presence of a polaron generates two states in the band gap (a bonding and nonbonding state) that are spaced equally on either side of the Fermi level. (Fig 2.2). Analysis of the spatial distribution of these structures suggest that the soliton is spread over about 15 CH units and involves a slow variation in both bond length and charge. Whereas the point location on the chain is arbitrary, the motion of the soliton observed by external nuclear double resonance involves two discrete states. The two states (Fig 2.2) have different charge locations and result in the soliton being distributed over different lengths of chain segment. The moving soliton may be treated rather like a particle that has a kinetic mass of m_g given by equation 3, where M_{CH} is the mass of the C-H fragment, U_o^2 is a potential function, l is the half width of the soliton wave function in units of the primary C-C chain. (found theoretically to be about 7 units), and a is the primary bond length.

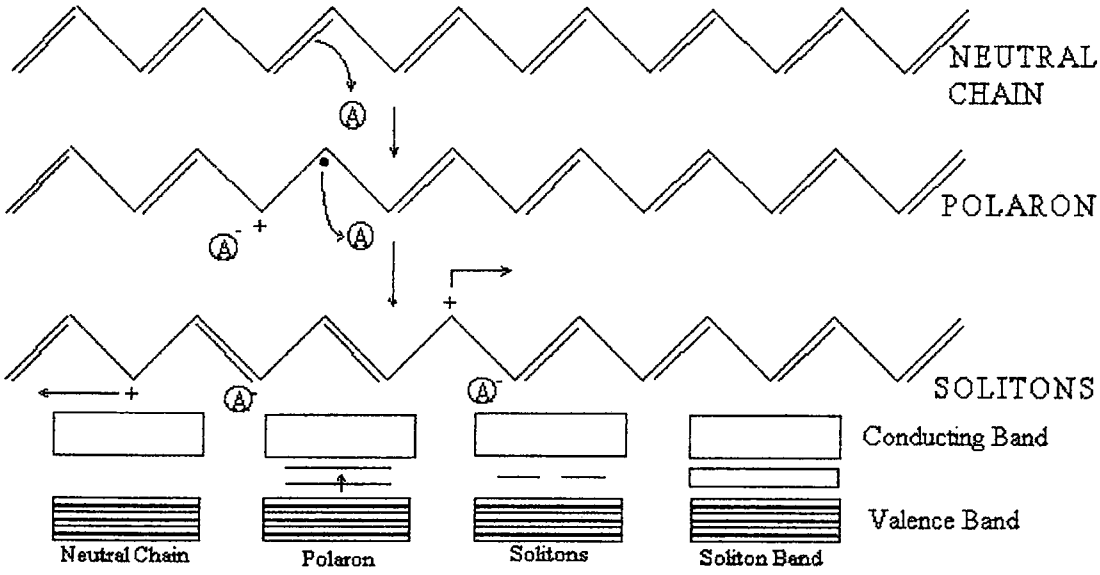


Figure 2.2 : Bonding distribution of in a soliton in polyacetylene. Energy levels of the soliton and polaron.

As a comprasion we can see electtrically insulating polymer such as polyethylene and unsatureted conjugated polymer (continous π system) as polyacetylene. (see figure 2.3 and 2.4)

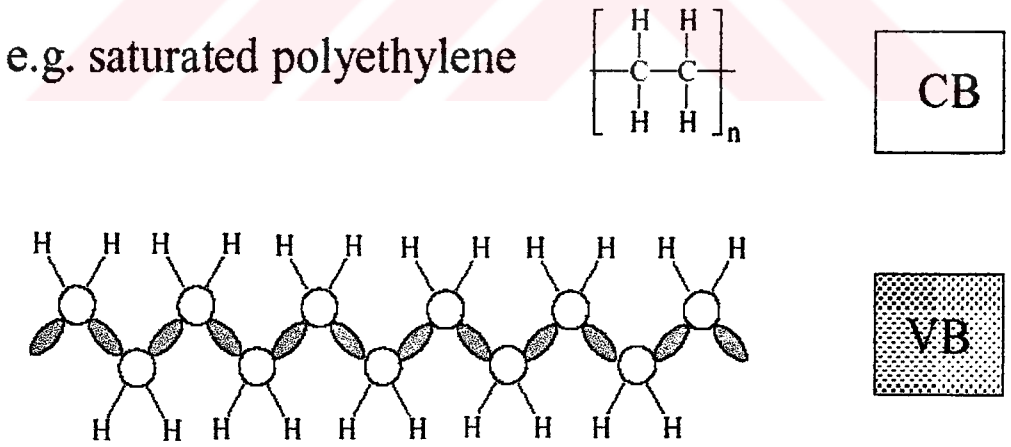


Figure 2. 3 : Saturated polyethylene and its orbital structure.

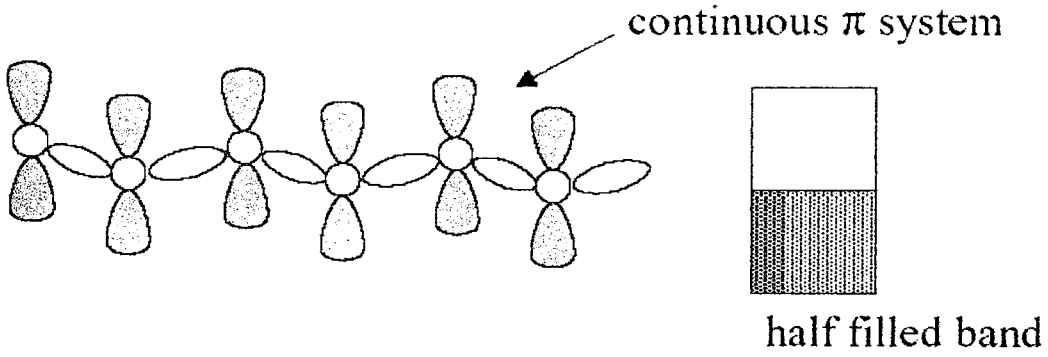


Figure 2.4: Unsaturated polymer and its orbital structure.

$$m_g = M_{CH}U_o^2/al \qquad (2.3)$$

When an anion or cation was brought close to the PA chain, it was originally expected to generate a charged soliton of the opposite sign on the chain. This simplistic approach did'nt account for the generation of the alternate phase. It is now widely believed that at low doping levels, when the centers are widely seperated, polarons are genrated on the chain. As the concentration increased the polarons begin to interact, allowing annihilation of two neutral soliton and the liberation of two charged solitons. These two charged solitons move apart and give free solitons on the chain (Fig 2.5). This hypothesis is supported by electron spin resonance data Which indicate that at low doping levels the spin of the charge carries can be detected, but as doping concentration rises the number of spin carriers fall although the conductivity rises. Therefore, the dopant plays not only a role in the generation of the solitons but also in interchain charge migration.

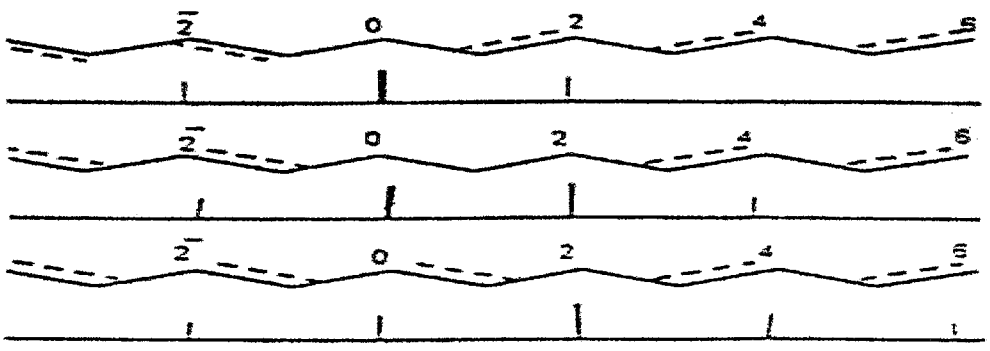


Figure 2.5: Change of electron distrubition with motion of soliton down the polymer.

The doping behavior of the system depends on the relative magnitute of the energy required to add an electron or hole, or gap (Φ), and the energy (E_s) required for creation of the distortion. If $\Phi < E_s$, charge-transfer doping will occur by creating free bond excitations; if $\Phi > E_s$, then distortion formation would be favored. The continuum model yields eq 2.4.

$$E_s = 2\Phi/\pi \qquad (2.4)$$

That fact that $E_s<\Phi$ ensures that topological distortions are the primary electronic exittations of the *trans*-$(CH)_x$ lattice. The topological nature of these defects makes them very different from the states involved in conduction in conventional 3-D semiconductors. The soliton mid-gap state is generated with no dependence on the nature of the dopant, although there is evidence from external nuclear double resonance measurments that the half width of the soliton wave function is dependent on the nature of the dopant and may be as long as 46 units at 4,2 K for an ReF_6^- anion [32].

The process by which charge is transmitted in PA was initially believed to be dominated by solitons, but studies have shown temperature (T) dependencies of the form $T^{-1/4}$. These dependencies are consistent with the Mott random range hopping model. These results are not consistent with the soliton dominated hypothesis. Kivelson [33] suggested that at low doping levels phonon assisted hopping between soliton band states is the predominant mechanism, whereas at higher doping levels soliton transport along the chain is more important. Pulsed photoconductivity measurments on *trans*-$(CH)_x$ suggest a carrier lifetime of <3 ns and conclude that if solitons do exist, they are merely short lifetime fluctuations of the chain order.

Other optical and photoconductivity data, however, are interpreted as supporting the proposed soliton model. Calculations based on photoexcitation of an electron-hole pair suggest that it evolves into a soliton antisoliton pair in a time of the order of the reciprocal of the optical photon frequency. Sethna and Kivelson [34] suggested that photon energies less than the Peiers gap can give rise to the direct production of soliton-antisoliton pair via a standart dipole electronic transition accompanied by a highly nonlinear lattice motion associated with fluctuation of the chain. This progress gives rise to photoconduction at energies smaller than the band gap; indeed, the treshold for *trans*-$(CH)_x$ normally lies at about 1eV. Free carrier generation efficency

rises exponentially above this treshold and then changes to a slow increase with the onset of direct gap transitions.In the case of the *cis*-$(CH)_x$ the lack of ground state degeneracy means that the soliton pairs are inherently highly unstable and recombine rapidly.

A pair of kinks would require a total energy of E_{tot}, given by eq 5, where E_s is the energy for creation of a single soliton, n is the number of CH units separating the two kinks, and E_o is the energy difference between cis-transoid and trans-cisoid cofigurations, which is expected to be a small fraction of the full gap. [$2\Delta = 2.0$ eV in *cis*-$(CH)_x$].

$$E_{tot} = 2E_s + n\Delta E_o \qquad (2.5)$$

As a consequence, two solitons would be confined or bound into a polaron-like entity. the farther apart the greater the energy. As a result, solitın photogeneration does not make a significant contribution to the photoconduction; indeed, there is little generation of free carriers even for photon energies 1 eV greater than the band gap, because the photoexcited carriers are con-fined by carrier site interactions. These photoconduction properties are consistent with the observed luminesence in the respective systems. In *cis*-$(CH)_x$, a relatively luminesence structure peaking at 1,9 eV near the interbond absorption edge, together with anumber of multiple Raman lines, is observed, a result consistent with the confinement of photogenerated carriers by interaction with the site. Furhter, the luminesence turns on sharply for excitation energies greater than 2.05 eV and impli-es a Stokes shift of about 0.15 eV. In *trans*-$(CH)_x$, there is the complete absence of any hard edge luminesence, even at the lowest temperature.This absence is consistent with the generation and seperation of the soliton-antisoliton pairs.

2.11 DOPING AND HIGH CONDUCTIVITY POLYMERS

Semiconducting and metallic properties are only achieved when PA is doped with donor or acceptor materials. A wide range of materials have been used as doping agents. Transition metal halides such as $TiCl_4$, $ZrCl_4$, $HfCl_4$, $NbCl_5$, $TaCl_5$, $TaBr_5$, TaI_5, $MoCl_5$, and WCl_3 and also nontransition metal halides such as $TeCl_4$, $TeBr_4$, TeI_4, $SnCl_4$, and SnI_4 all acts as dopants . In the initial studies, iodine, bromine, and AsF_5 were used as dopants, and maximum conductivity in the *trans*-PA was higher

than in *cis*-PA. The efficency of doping is observed to be a function of solvent. Doping in a good solvent indicates that the conductivity is indepe-ndent of the metal halide but is a function of the ratio of dopant to CH units. At a mole ratio of 0.1:1, the conductivity is 10^3 S/cm. Mössbauer spectroscopy and extended X-ray absorption fine structure (EXAFS) studies of $FeCl_3$ indicated that on doping:

$$2FeCl_3 + e^- \longrightarrow FeCl_4^- + FeCl_2 \qquad (2.6)$$

Several structural factors may influence the electronic properties; the ideal PA cyrstal has the chains ordered periodically. This periodicity is perturbated or destroyed on a molecular scale by stacking faults, dislocation vacancies in dopant occupation, chain defects associated with chain ends, irregularities in backbone conformation, and substitution (Fig 2.6). Doping in PA is assumed to occur randomly; however, clustering is favored because it minimizes the strain energy associated with insertion into the matrix. Iodine is isovolumetric with the CH unit, and insertion of a column of iodine requries less energy than a random distribution of dopant, as indicated by X-ray studies.

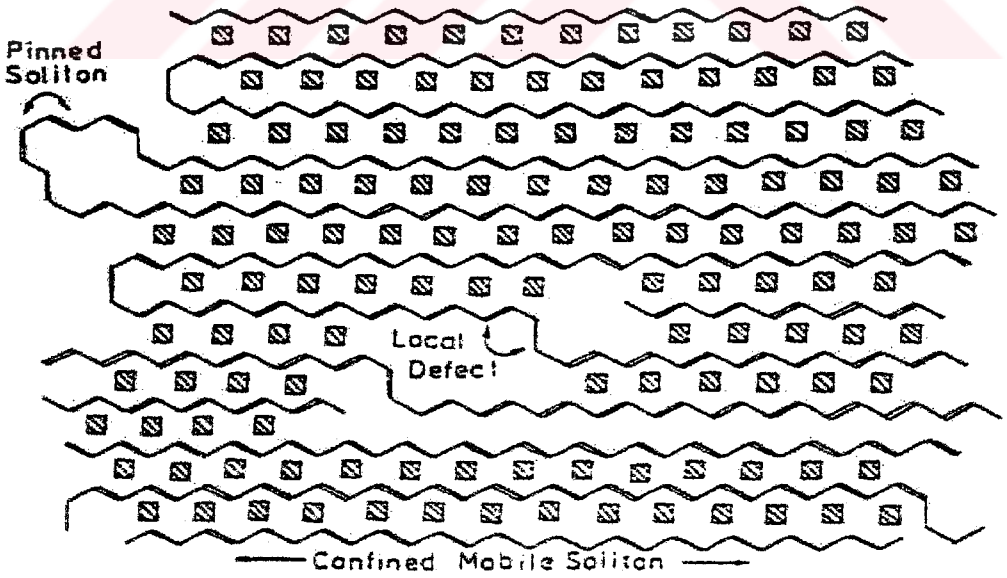


Figure 2.6: Defect structure of polyacetylene: pinned soliton, local defect, and confined mobile soliton.

The temperature and field dependence of the electrical conductivity and dielectric constant is reproduced if dopant is assumed to be in the form of sheets that are 1.27-nm thick and are intercalated layers. Maximum conduction is obtained when the structure consists of alternating layers of PA chains; lower conductivities arise when the conducting layers are interspersed with undoped PA chains. PA chains not constrained into crystalline regions are susceptible to chemical reaction.

Extensive spectroscopic studies including time-resolved ESR (spin echo and saturation recovery) and NMR (magic-angle spinning sample, cross-polaziration, and magic-angle spin echo) experiments identified three different types of defect structures, mobile spins (neutral solitons), fixed distributed spins (pinned solitons or polarons), and chain defects (see Fig 2.6). The oxidation occurs predominantly in the amorphous regions and can be associated with the accessible pinned solitons Local defects will lead to a lowering of the crystalline perfections,and within the highly ordered regions, percolation of oxygen is assumed to be very low. In fig. 7 unique dopping curve can be seen also.

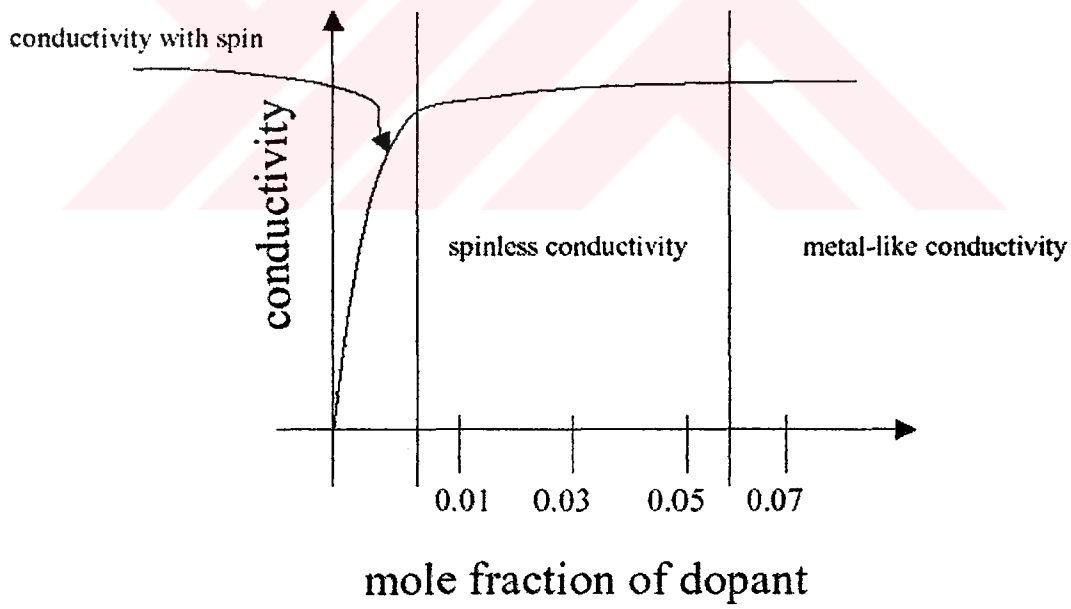


Figure 2.7 : Unique dopping curve.

2.12 ENVIRONMENTAL SUSCEPTIBILTY

Oxygen is capable of acting as a dopant at low concentrations and leads to an increase in the conductivity. This initial doping is also observed to be reversible and

indicates that no chemical reaction has occured [35] (Fig 2.8). However, further increase in oxygen content has the reverse effect of lowering the conductivity. Oxygen reacts with localized states in the amorphous regions to form highly reactive peroxides and leads to the generation of furan or related structures. The intrinsic reactivity with oxygen has caused many device applications to fail in the final product stage. However, Naarman (personal communication) developed a method of synthesis for PA that produces a maerial on doping with iodine. This material has a conductivity about half that of copper, is stable in air for several weeks, and has an initial conductivity of $147x10^3$ S/cm. These conductivities are much higher than those that were obtained previously, typically 200 S/cm. The BASF material is more crystalline than that produced by the alternative methods and contains less than 1% of sp^3-hybridized carbon defects. The improved stability of the polymer composite is associated with its low amorphous content. These highly crystalline materials are difficult to process and are somewhat of academic interest, but they indicate that PA story is far from being complete.

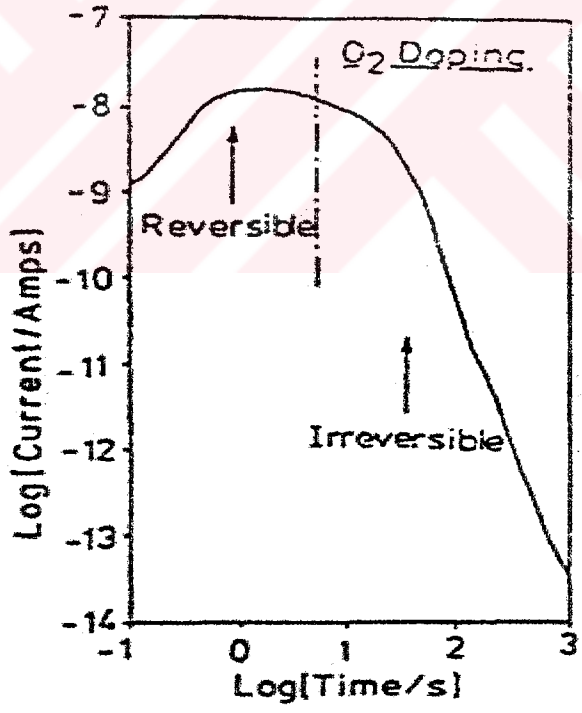


Figure 2.8: Effect of O_2 doping on the conductivity of polyacetylene

.2.13 MECHANISM OF CHARGE MIGRATION

A detailed analysis to the conclusion that the intersoliton-hopping model is the best representation of the process that occur. The charged defect migration process at low doping levels is controlled by the concentration of the dopant. The population of the free charges is mainly governed by the interaction energy (E_{ip}) of the ionized dopant injected charge ion pair.

The conductivity (σ_{cm} based on charge migration) can be described by eq 6, where D_{ch} is the diffusion coefficent of the charge defects, k is the Boltzmann constant, T is temperature (K), e is the electron charge, n is number of charge defects introduced per chain by each dopant (n<1), x is number of possible states corresponding to E_{ip},and N_a is the density of carbon atoms

$$\Sigma_{cm} = e^2/ kT \, . \, N_a D_{ch} \, .(\, 1\text{-}n/n \,) \, x \, \exp(\, -E_{ip}/kT \,) \qquad (2.6)$$

In the absence of disorder, the diffusion coefficent of the charge defects (D_{ch}) may be approximated by the difusion constant of the neutral radicals (D_{neut}), which may in turn be estimated from the expression of a 1-D Brownian motion of domain walls in contact with thermal phonons. Calculations lead to $D_{neut} \approx 2x\ 10^{-2}$ cm^2/s. If a_c is the latttice constant, this diffusion coefficent corresponds to to diffusion rate D_n/a_c^2 equal to 10^{14} s^{-1} . This value is in good agreement with the NMR relaxation result of $4x10^{14}$ s^{-1}. The thermoelectric power (T_{cm}) is given by eq 2.7.

$$T_{cm} = e/k \, [\, E_{ip}/ \, kT \; + \; \ln \; (\, 1\text{-}n \,)x \, / \, n \, T \,] \qquad (2.7)$$

In the process involving charge transfer between neighboring chains (inter-soliton hoping), the energy necessary for electron hoping depends on whether a dopant molecule is near the neutral radical defect. If so, the hoping energy is lowered considerably. The corresponding expression for the conductivity is given by eq 8, where Y_n and Y_{ch} are, respectively, the molar concentration of neutral and charged defects, N is the number of carbon atoms per conjugated squence, and $W_{ih}(T)/N$ is a frequency proportional to the fraction of time that the defects are situated within kT of each other.

$$\sigma_{in} = 0.45 \left(c^2 W_{ih}(T)\, \psi_d\, Y_n Y_{ch} \right) / \left(kTN\ d_0^2 \left(Y_n + Y_{ch}\right) \exp 2{,}78 d_0 / \psi_d \right) \quad (2.8)$$

Where σ_{in} is intrinsic conductivity, and c is velocity of light. The exponential factor reflects the electronic overlap between two defects separated by the mean distance between the dopant molecules (d_o) (eq 2.9).

$$[\text{dopant}] = \left(4/3\ \pi d_o^3 \right)^{-1} \quad (2.9)$$

The ψ_d variable is the 3-D averaged electronic decaylength according to eq 2.10, where $\psi_{d=}$ and $\psi_{d\perp}$ are, respectively, the parallel and perpendicular resonance integrals.

$$d_o = \left(\psi_{d=} \psi_d^2{}_{\perp} \right)^{1/3} \quad (2.10)$$

At every hop, a spin and charge are transported in opposite directions. Minimization of the ion-pair binding energy (E_{ip}) is achieved by increasing the local dielectric constant near the doping molecule or the distance between the dopant and the charge carrier. A maximum conductivity increase of 10^4 is observed at low sodium doping levels; an estimation of E_{ip} is possible from eq 11, leading to a value of 0,23 eV, which is a lower limit for the ion-pair binding energy [66,68].

$$\exp \left(- E_{ip}/kT \right) = \sigma_{unsolvated} / \sigma_{solvated} = 10^{-4} \quad (2.11)$$

Where $\sigma_{unsolvated}$ and $\sigma_{solvated}$ are conductivities of unsolvated and solvated ions, respectively.

2.14 ELECTRONIC CHARACTERISTICS

Conjugated polymers in their pure undoped state are electrical insulators. The conductivity of *cis*-PA is 10^{-9} S/cm and increases to 10^{-5} S/cm on isomerization to the trans form.The conductivity (σ) is proportional to the product of the free carrier

(n) and carrier mobility (μ) according to eq 12, where e is the unit electronic charge ($1{,}6 \times 10^{-19}$)

$$\sigma = en\mu \qquad (2.12)$$

For intrinsic conductivity, the carrier concentration decreases exponentially with increasing band gap and is very low at normal temperatures. Doping of conjugated polymers generates high conductivity primarily by increasing the carrier concentration. The term doping is misleading, because the concentrations used are exponentially high compared with those in inorganic semicoductors, where levels of parts per million are used. In organic systems the dopant can constitute 50% of the weight, and a more appropriate description for these materials might be charge-transfer complexes rather than doped polymers.

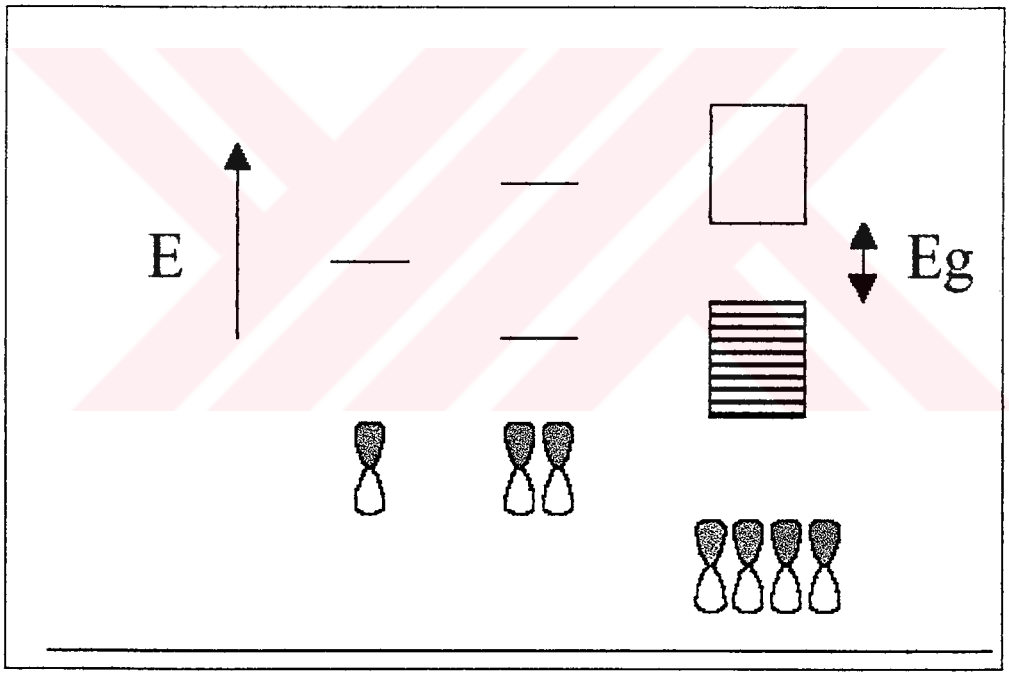


Figure 29a: classic band orbital picture

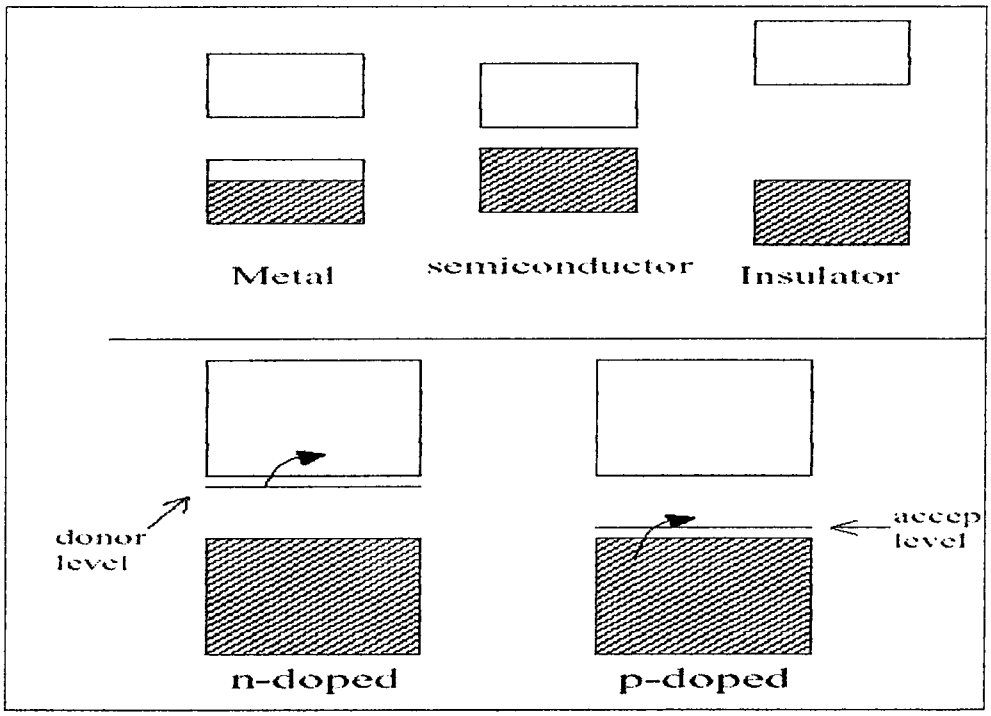


Figure 2.9b: Comprasion of classic band picture to delocalized system

2.15 MEASURMENT OF CONDUCTIVITY

In literature a variety of units is used to describe th efficency of charge transport in an ICP sample. In principle, there are two different quataties that can described this efficency. One can either talk about the conductivity or resistivity of an ICP. The choice between these two is arbitrary because they are linked by definition, the conductivity is defined as the reciprocal resistivity. The unit of the conductance, the reciprocal Ohm (O^{-1}), is usually called Siemens (S).

When refering to the resistivity of an ICP, often the *volume resistivity* or *intrinsic resistivity* $?_v$ is used. The S.I unit of the intrinsic resistivity is Ohm.m, but in literature this resistivity is usually given in Ohm.cm. The intrinsic resistivity is defined as the resistance between opposite faces of a unit cube. To characterize the current flow over a surface, the *surface resistivity* $?_s$ is often used. The surface resistivity is often used to characterize current flow over a film surface and is defined as the resistance between opposite edges of an unit square. The surface resistivity is independent of the size of the square and its units is simply the Ohm (O), but for sake of clarity

usually Ohm per square (O/?) is listed. The relation between the surface resistivity and the intrinsic resistivity is given an equation 13, where *d* is the layer thickness.

$$\rho_s = \rho_v / d \qquad (2.13)$$

Thus the surface resistivity is not amaterial property, but only a property of a specific specimen.Therefore it is necessary to list the value of the surface resistivity always combined with the thickness of the film or a property that is related to the film thickness, like transparency.

The main problem in accurate measurment of a low resistivity is one of contact resistance between the measurment electrodes and the specimen. A method to deal with contact resistance is to use a so called 4-point-probe method. In case the contact resistance is one of the same order of magnitude as the input resistance of the voltmeter, contact resistance may be reduced by depositing the metal electrodes directly onto the surface either by vacuum deposition or by using a conducting (silver) paint. An illustration of 4-point-probe method is given in figure 2.10

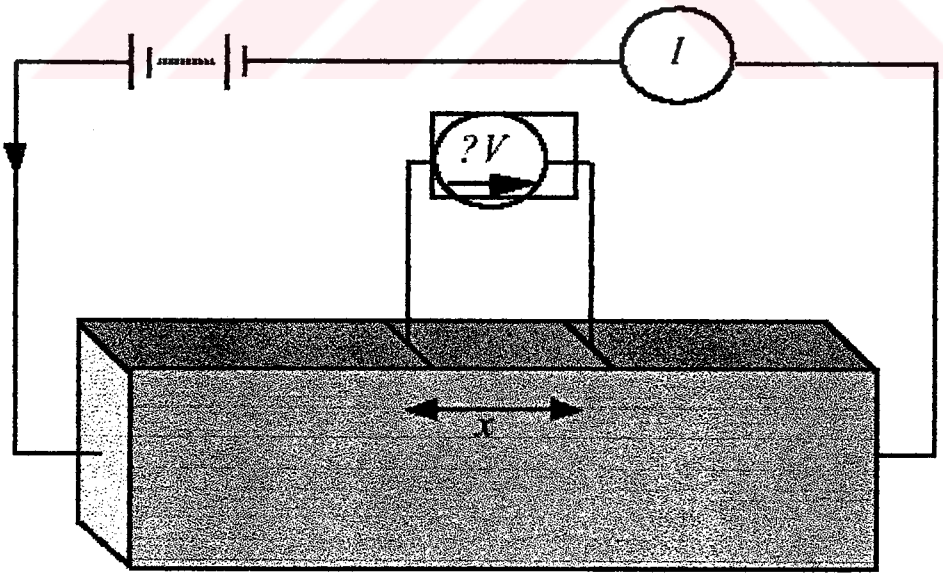


Figure 2.10: Circuit diagram for a 4-point-probe resistivity measurment

The intrinsic resistivity of the specimen can be calculated using equation

$$\rho_v = \frac{I/A}{\Delta V/x} \qquad (2.14)$$

Where I is the current (A), A is the cross sectional area (m^2), ΔV is potential drop across the two inner electrodes, and , and x is the seperation between the two inner electrodes.

For practical, reproducible measurements of the intrinsic resistivity, special setups have been developed for the four-point-probe method. One of the most practical setups is shown in figure 2.11

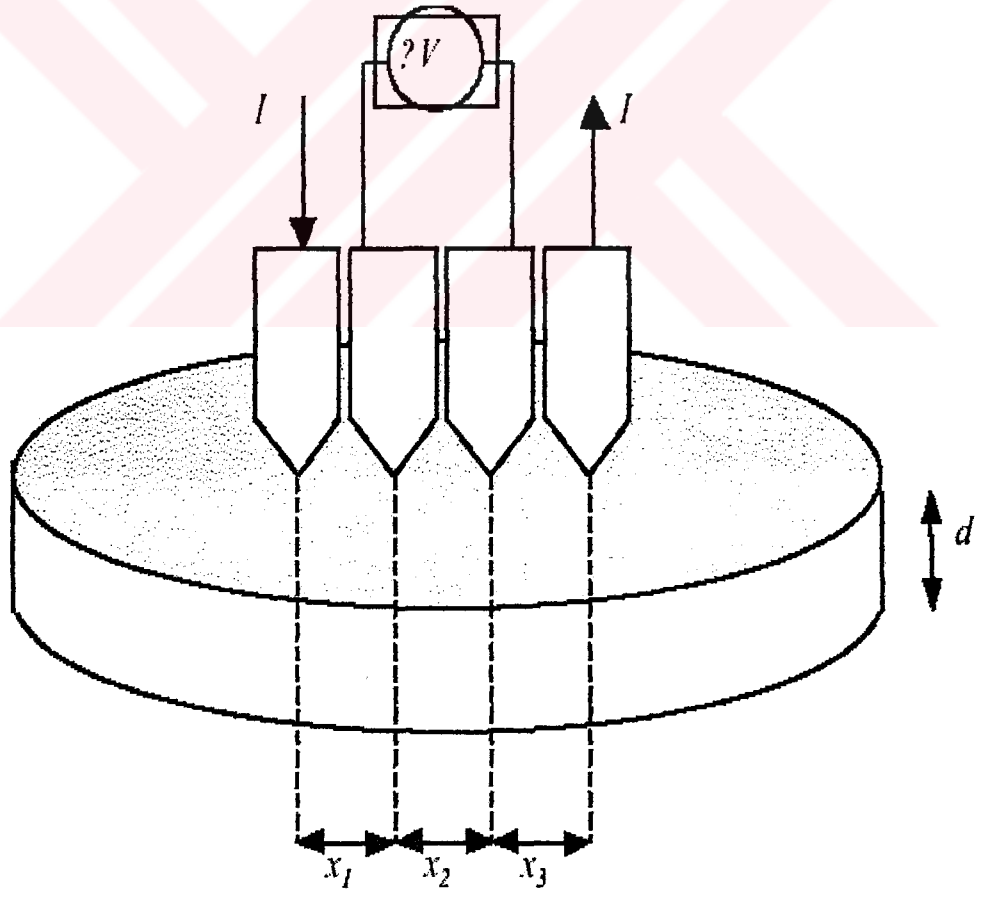


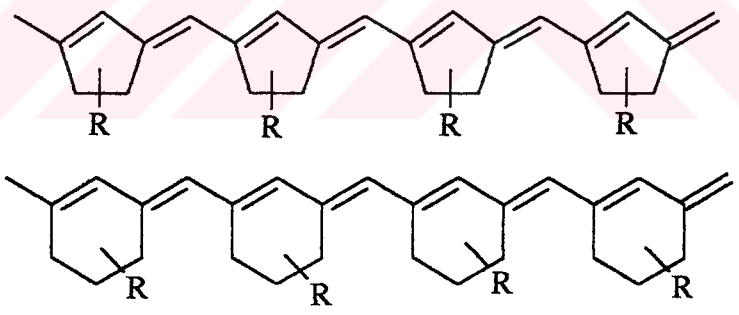
Figure 2.11: Schematic presentation of an intrinsic resistivity measurment with a four-point-probe.

Provided that (i) the thickness *d* of the specimen is much smaller than the distances $x_{1,2,3}$ between the elctrodes, (ii), the electrodes have an equispaced distance ($x_1 = x_2 = x_3$), (iii) the specimen is placed on a non-conducting surface, (iv) the contact-diameter of the electrodes, and (v) the distance between the electrodes and specimen-boundary is large compared to the distance between the electrodes, the intrinsic conductivity of the material can be calculated using equation 2.3

$$\rho_v = \frac{\Delta V \times \pi \times d}{I \times \ln 2} \qquad (2.15)$$

2.16 OTHER CONDUCTING POLYMERS

In the 1980s it became apparent that the essential feauture for conduction in organic polymers was the existence of an extended conjugated structure capable of being doped. In principle, any of the structures shown in scheme (2.6) could exhibit conductivity.



(2.6)

Kossmehl [36] indicated in a review the range of chemistry that can be encompassed by this simple concept, and the number of possible runs into the thousands. Selection between different systems relies on the identification of a design philosophy that needs to identify the critical parameters for a particular system and balance these with other factors. For instance, many of these systems are important because of their potential nonlinear optical properties. In the case, optical clarity is an important factor in the total design.

2.17 PYRROLE-BASED POLYMERS

The attractiveness of the polypyrrole systems stems from several factors. Although initially the most important factor was undoubtedly the chemcal and thermal stability of these polyners relative to $(SN)_x$ and $(CH)_x$, the ease of preparation was also appealing. Key too was the ready ability to preparare derivatives which had a range of conductivities, a stituation which contrasted with the attempts to prepare such derivativies of $(SN)_x$. Futher encouraging features of the pyrrole systems were the degrees of freedom available to modify the electrical and physical properties by resorting to derivativies, copolymers, or particular anions in order to achieve any desired matrix of polymere properties. All these attributes encourged us to believe that the effort to understand these somewhat interactable polymers would be worthwhile.

2.18 STRUCTURE OF POLYPYRROLE

All forms of polypyrrole reported so far are extremely poorly crystalline, which means that much of our knowledge of the structure of these systems is obtained from a variety of indirect measurments. The demostration that the pyrrole blacks were primarily bonded via the α,α'- carbons, coupled with the fact that blocking α-positions sems to prevent the electrochemical polymerization pyrroles, led to the conclusion that the electrochemically prepared films were also bonded in this fashion. In the case of polymers derived from unsustituted pyrroles, it has been shown by magic angle spinning ^{13}C-NMR and IR techniques that, though this assumption is largely true, there is also some involvement of the β-carbons in the chain bonding which could cause some crosslinking of the polymer. Blocking both the β-positions with a methyl group eliminates the possibility of other than α,α-bonding. As would be expected, this leads to a much more ordered chain and results in a significant increase in the crystallographic order of the chains. This increased order reflects itself not only electron diffraction data, but in all the techniques have been used to study these materials, for example , UPS, NMR, and electron paramagnetic resonance. The coulometry and properties of these two pyrrole polymers are so similar, including the electron diffraction data and the XPS data shown in figure 2.12, that it seems that both polymers must have basically the same chain structure, although the unsustituted pyrrole will clearly show the effects of disorder related to the partial involvement of the β-carbons in ring-ring bonding. Assuming a completely α,α-bonded polymer, a planar cyclic structure with all the

pyrrole nitrogens pointed to the center would require 10 pyrrole molecules to complete the ring. It has been suggested that the structure of polypyrrole is analogous to the ring structure of the porphyrins or phthalocyanines. This would require considerable chemistry to take place to provide the NH or CH linkages between the pyrrole moieties necessary to form a planar ring from only four pyrrole rings.

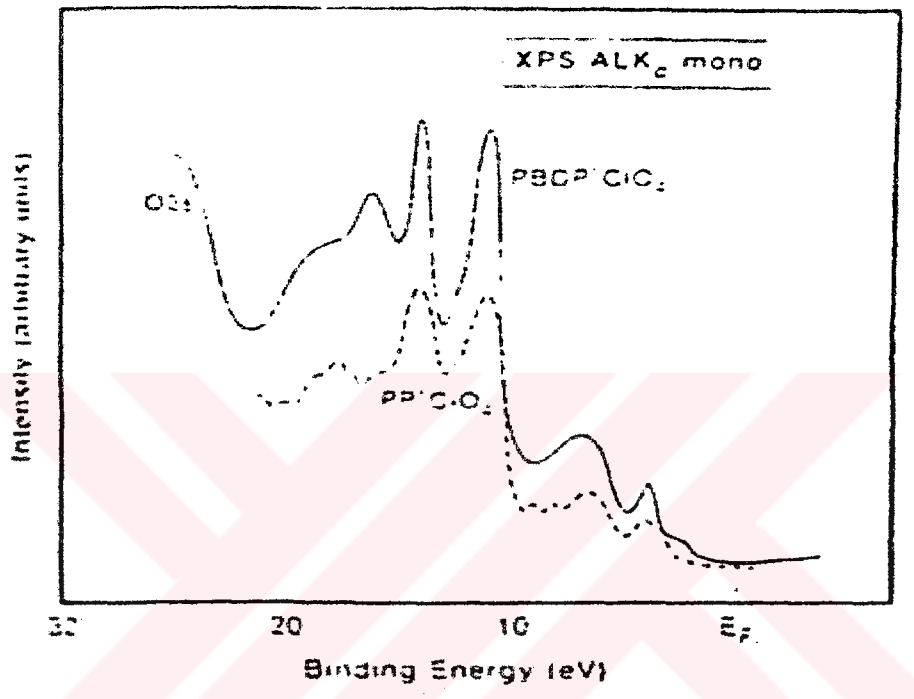


Figure 2.12: Comprasion of the XPS spectra of polypyrrole perchlorate and poly-β,β'-dimethylpyrrole.

Alternatively, one could consider a spiral arrangement; however, a linear, completely planar, exclusively α,α-bonded chain in which the orientation of the pyrrole molecules alternate, as shown in figure 2.13, is the best model for the ideal structure of polypyrrole. The dimensions are those experimentially determined for the center ring of pyrrole trimer. Using this model chain structure, Geiss et al. (37) heve been able to fit the electron diffraction data for neutral polypyrrole exposed to oxygen to a monoclinic structure derived from the planar arrangement of chains shown in figure 14, in which the planes are seperated by a distance of 3.41 A° similar to that observed for the basal spacing in graphite (3.36 A°).

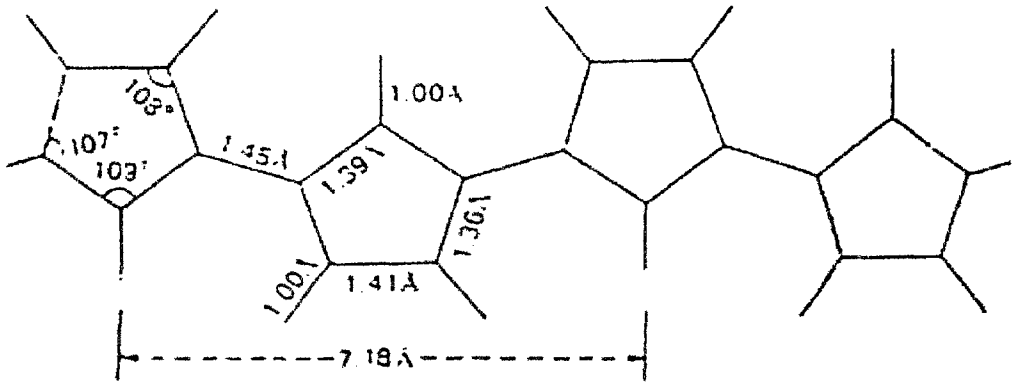


Figure 2.13: Proposed chain structure of neutral polypyrrole.

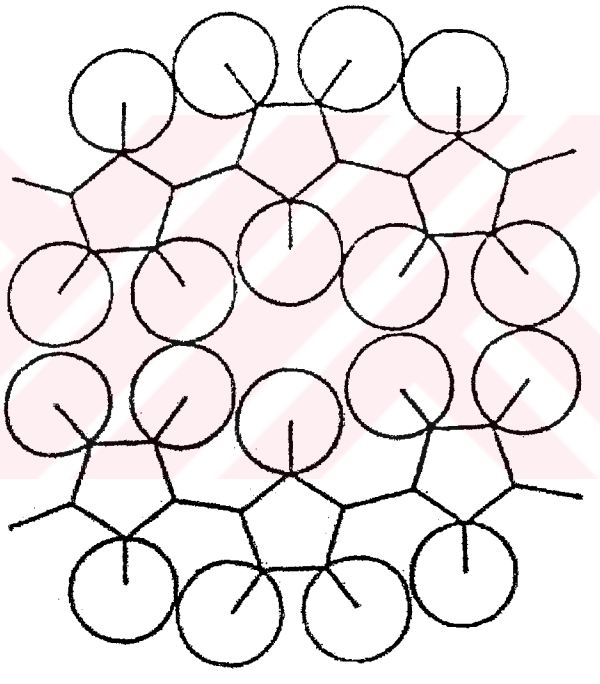


Figure 2.14: Planar arrangement of polypyrrole chains proposed monoclinic structure of polypyrrole after exposure to oxygen.

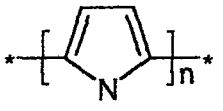
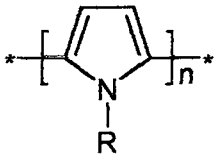
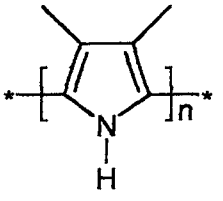
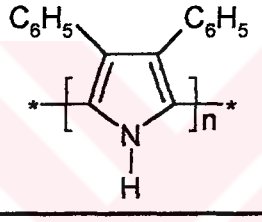
In the case of the β,β-dimethylpyrrole polymer, this separation increases to 3.65 A° because the methyl groups now determine this separation. The electron diffraction studies indicate that the chains lie flat in the plane of the film. The diffraction patterns of poly(β,β-dimethylpyrrole) show that within the plane of the films the chains are oriented parallel to one another, whereas in polypyrrole itself the alignment of the chains within the film planeis random. Though this structure fits the

limited diffraction data available, it must be emphasized that it is not a unique structure. More crystalline films or better structural techniques will be necssary to establish the correctness of the proposed structure. However, strong evidence for the assumed planar chain geometry has now been obtained from an X-ray determination of the structure of pyrrole dimer and trimer . Both these molecules are linear and planar, with an alternating arrangement of the pyrrole rings. In the dimer the pyrroles are stacked on the top of one another in parallel chains. A similar situation arises for the trimer, except that adjacent molecules in the chain are not in the same plane.

2.19 CONDUCTING POLYMERS DERIVED FROM SUBSTITUTED PYRROLES

One of the attractive features of the pyrrole system is the ability to readily prepare a number of functionalized polymers by polymerization of the appropriate pyrrole monomer. This contrasts favorably with the case of $(SN)_x$, for which the only derivatives are those obtained by halogenation, and this despite all the effort that went into the synthesis of other derivatives. Table 3 shows the types of pyrrole derivatives which have been prepared. Without exceptions, all such polymers have conductivities at least four orders of magnitude less than the parent polymer. It can be taken the advantage of thid to control conductivity by preparing copolymer films of pyrrole and N-methylpyrrole with intermediate conductivities. In some papers it was speculated that this loss of conductivity was the result of lack of planarity in N-substituted polymers. Now it is confirmed that speculation by X-ray studies of the tetramer of N-methylpyrrole which show that the N-methyl cause the tetramer to become grossly nonplanar [38]. Although, the structure of the tetramer does not have to be the same as the poly(N-methylpyrrole) chain, examination of the geometry indicates that the presence of the methyl group on the nitrogen precludes a planar chain.

Table 2.3: The types of pyrrole derivatives

Monomer	Conductivity $\Omega^{-1}cm^{-1}$
	40
	10^{-3}
	10
	10^{-3}

Calculations ionization potential and bandwidth for a planar poly(N-methylpyrrole) chain gave very poor agreement with experiment, suggesting that the assumption of a planar chain is incorrect. Thus it seems most likely that the low conductivity of all N-substituted polymers, relative to the parent polypyrrole, is due to this loss of planarity. Although the crystal structure of the dimer of β,β'-dimethylpyrrole shows it too is nonplanar, model show that a methyl group in one or both of the β-position does not necessarily prevent chain planarity, and the high conductivities measured for these polymers imply that they are in fact essentially planar. However, it should be pointed out that the redox potential of poly(β,β'-dimethylpyrrole) is slightly more positive than polypyrrole itself, whereas the reverse would be expeced on account of the N-methyl groups. This effect could indicate some deviation from planarity in the substituted polymer. On the other hand, large bulky phenyl groups in the β-positions clearly lead to loss of planarity and result in the same low conductivity observed for nonplanar poly(N-methylpyrrole). It has been proposed that the high conductivity associated with the parent polymer was relatd to the presence of the hydrogen on the nitrogen. The low conductivity of β,β'-diphenyl polymer seems to show that the presence of an unsubtituted nitrogen is not sufficent to convey high conductivity to the polymer. However, some very interesting results have shown that treating

polypyrrole tetrafluoroborate with NaOH lowers its conductvity by four orders of magnitude. It had previously been shown that ammonia vapor lowered the conductivity of polypyrrole films by an order of magnitude, and that the original conductivity could be restored by pumping off the ammonia. It was shown that initial conductivity of the NaOH treated films can be restored by the exposure to acid, and they interpreted thier results in terms of the deprotonation and reprotonation of the pyrrole nitrogen. In the deprotonated state the polymer is poorly conducting. As the insulating form of polypyrrole produced by the electrochemical reduction has been shown by IR to contain NH groups, it would appear that there may be more than one mechanism of modifying the conductivity of pyrrole.

2.20 CHARGE CARRIERS IN POLYPYRROLE

Intrinsically, conducting polymers can be prepared via chemical or electrochemical polymerization, as afformentioned in above sections. In this reaction a conjugated monomer is polymerized and charge carriers generated via doping. The doping process is an oxidation or reduction reaction in which electrons are transfered away from or to the polymer chain, respectively.

The mechanism of charge transport in polypyrrole can be described as follows in figure 2.15. The general structure of polypyrroleis an alternating sequence of single and double bonds. Most ICPs, however, possess a nondegenerate ground state with a prefered sense of bond alternation. Polypyrrole is an example of nondegenerate ground state polymer that possess an aromatic configuration with long bonds between the rings and an aromatic structure within the ring. The other sense of bond alternation, the so-called quinoid configuration is characterized by shortened bonds between rings and quinoid rings. Figure 2.15: The quinoid geometry can be considered as an excited state configuration of the aromatic structure.

Oxidation of a nondegenerate ground state polymer such as polypyrole has a somewhat different result than PA. The positive charge and unpaired electron of the initially formed cation radical cannot move independently. The structural motif of the chain segment between the positive charge and the unpaired electron is that of quinoid configuration, which is higher in energy and confines the charge and spin density to a single self-localized structural deformation that is mobile along the chain (figure 15). In condensed-matter physics such a cation radical with an associated

lattice deformation is called a polaron and carriers a spin (S=1/2). Detailed explanations was made about charge carriers in upper sections.

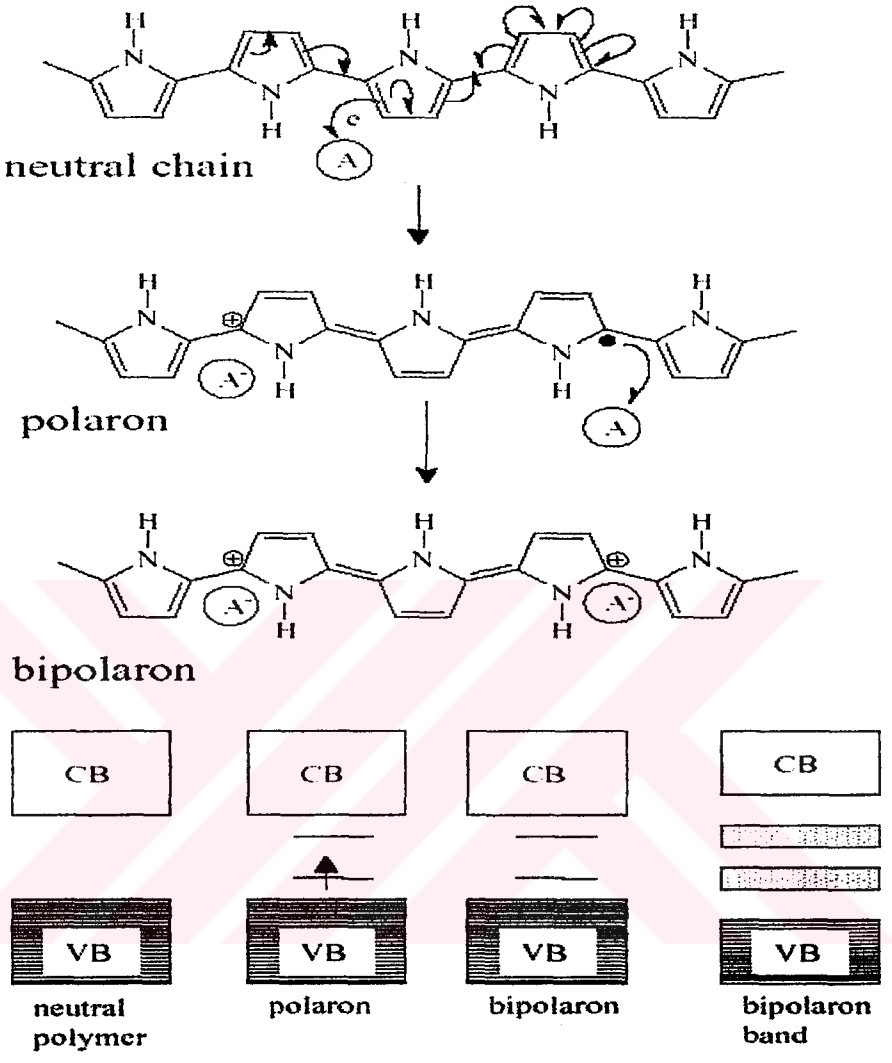


Figure 2.15: polarons and bipolarons in oxidized polypyrrole

2.21 SYNTHESIS OF ELECTRICALLY CONDUCTING POLYMERS

Conducting polymers are prepared either directly, by electro- or oxidative polymerization, or are polymerized and then oxized chemically or electrochemically. The different preperations have been driven by the desire to examine many different types of polymers and to create polymers that are soluble in water and common organic solvents and are processable in various forms. Other goals include novel structures, easier synthesis, and stability both in conducting and non-conducting states.

Among well-known conducting polymers, polyacetylene and poly(phenylene vinylene) are synthesized almost exclusively by chemical polymerization or from precursor route. Polyheterocycles such as polythiophene or polypyrrole are synthesized by both chemical and electrochemical polymerization.

2.22 ELECTROCHEMICAL SYNTHESIS OF POLYPYRROLE

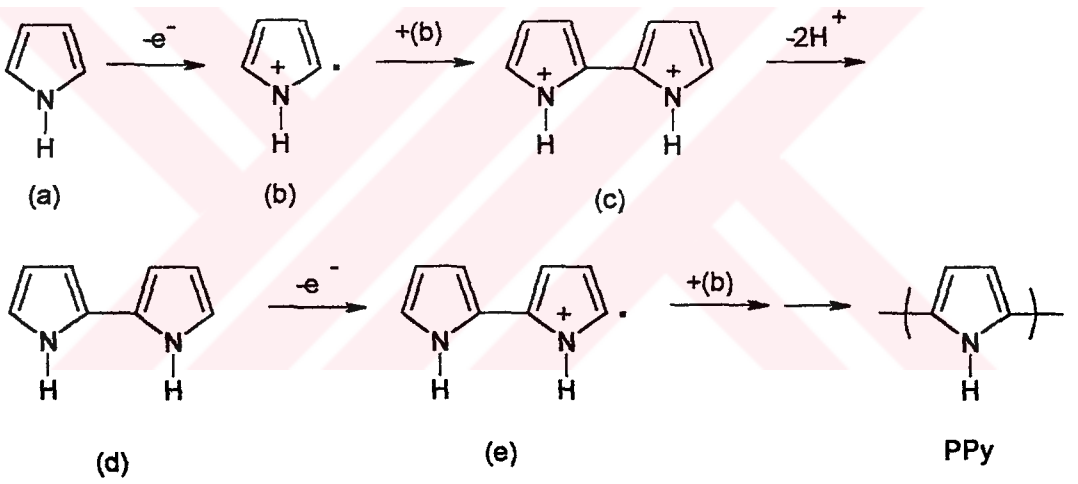
This method of synthesis produces films that are doped simultaneously. A wide range of electrolytes have been used, including quarternary ammonium salts, R_4NX, where R= alkyl or aryl, and X= Cl^-, Br^-, I^-, ClO_4^-, BF_4^-, PF_6^-. Also, metal salts, MX, were used, where M=Li^+, Na^+, ans As^+, and X= BF_4^-, ClO_4^-, PF_6^-, $CF_3SO_3^-$, AsF_6^-, and $CH_3C_6H_4SO_3^-$. The advantages of the electrochemical polymerization of conducting polymers are as follows.

1. Reactions are carried out at room temperature.
2. Thickness of the films can be controlled by adjusting either the potential or current.
3. Polymer films are formed directly at the electrode surface.
4. It is possible toproduce homogenous films.
5. The salts provide conductivity and allow incorporation of anion into the matrix.
6. It is possible to obtain copolymers and graft copolymers.

Polypyrrole electrochemically doped has been the subject of extensive study over the last decade. Much of the early research was concerned with attempts to resolve the apparent variability of the values of the conductvity that were possible. More recently, better understanding of various factors influencing the synthesis has led to concern over the extent to which the simple chemistry of the polymer adequately describes the real situation. Even when the polymer structure is well defined the problem of location and nature of the doping species is important. As with other conducting polymers, morphological variations have profound effect on the conductivity developed in the material.

2.23 CHEMICAL POLYMERIZATOIN OF ICP

Many well-known chemical oxidants are able to oxidize monomers like aniline or pyrrole, yielding highly active intermediate species like their cation radicals, thus initiating the polymerization process. Once formed, intermediate species react with solution monomer molecules, yielding dimers, oligomers, and polymers as end products of oxidative polymerization. Scheme 2.7 shows schematically the process of polymerization of pyrrole. A neutral molecule of pyrrole monomer (a) yields upon its oxidation cation radical species (b), that can recombine, yielding consecutively a dication of bipyrrole (c), and, after its disproportionation, a neutral bipyrrole molecule (d). The latter can undergo further oxidation (e), deprotanation and recombination steps, leading to PPy as the end product of oxidative polymerization.



(2.7)

The formation of intermediate species such as cation radicals has been evidenced in many works dealing with the polymerization of some monomers. Figure 16 shows UV-VIS spectra for electro-oxidation of *N*-ethylaniline, provided in an acidic solution of this monomer at indium doped tin oxide (ITO) transparent electrode. After application of a suitable electrode potential, two absorbance bands appear in the spectrum, and a continous growth of their intensities is observed during electrolysis. After interruption of electrolysis, the band at ca. 450 nm decreases gradually and disappears in afew minutes, indicating clearly its origin from intermediate species, formed during electrolysis. At the same time, the band at ca 740 nm continues to grow to some extent, indicating its origin from an end product of electro oxidation.

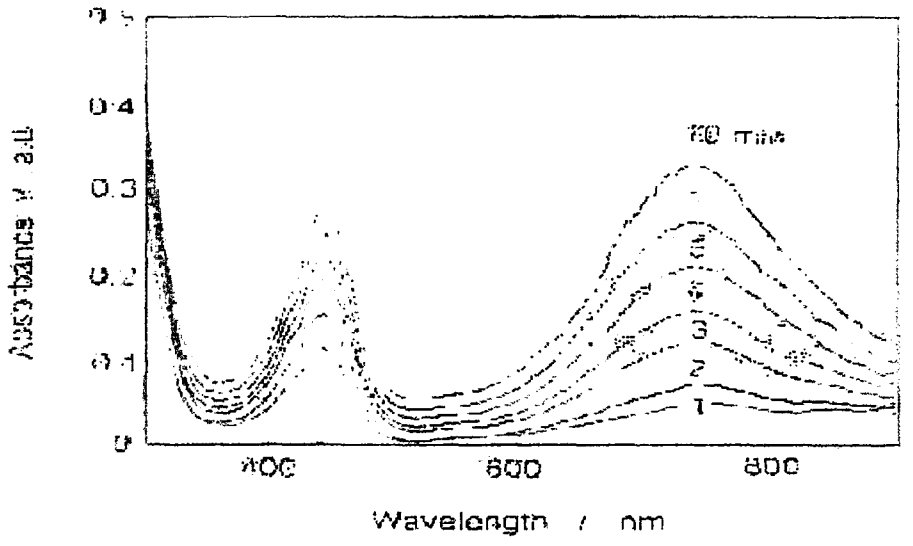
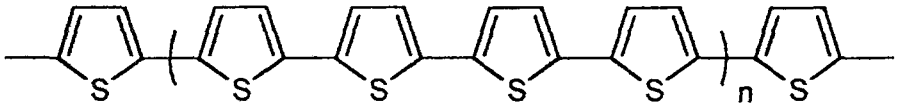


Figure 2.16: UV-VIS absorbance spectra, obtained at transparent ITO glass electrode in a solution of 0,5M H_2SO_4 containing 25 mM of N-methylaniline, by applying the electrode potential of 0.1 V vs. NHE, as recorded at different time moments (as indicated, in minutes.)

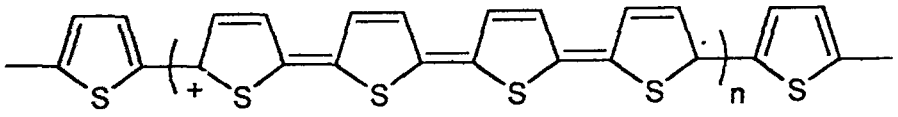
The process of chemical oxidative polymerization is usually followed by visible changes in the color of the polymerization solution. An initially colorless solution turns, after a definite time, blue and dark blue, indicating that dimers and oligomers are to be formed. Some time later, the precipitation of a dark blue or black solid polymer is observed. In most cases, the chemical polymerization possesses a well defined autocatalytic character, *e.g.* rapid coloration and polymerization proceeds after a definite induction period. The rate of the process depends upon many variables, such as the nature of the oxidant used, and the concentration of reactants. Usually, most of the ICP formed by the chemical polymerization precipitates after the reaction is completed. However, a part of the ICP can spontanously deposit as a thin layer on various substrates present in a reaction medium.

Many ICP can exist in a variety of redox forms ; However, the electric conductivity is assigned usually to only one of them. For example, the withdrawal of one electron from the PT molecule (scheme 2.8 a), followed by its doping with a solution anion, leads to its conducting half-oxidized polaronic state (scheme 2.8 b), whereas the loss of the second electron leads to oxidized bipolaronic form (scheme 2.8 c). On an electrochemical potential scale, the regions of the existence of different redox

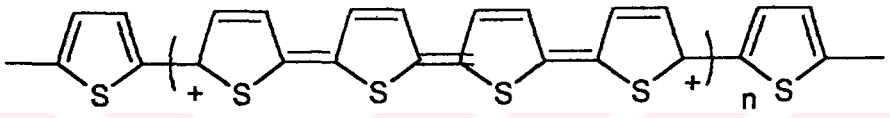
an electrochemical potential scale, the regions of the existence of different redox forms depend greatly on the nature of ICP, the acidity f the solution, and other variables.



(a)



(b)



(c) (2.8)

2.24 SOLUBILITY

2.24.1 Physical Origin of The Solubility

Conducting polymers are basically different from the other conventional organic polymers. The exact mechanism for the aggregation of doped conducting polymers in solution is as yet uncertain. Two possible causes for this aggregation are the increase in rigidity of the polymer chains on doping and the increased polar interactions between the polymeric chains. An increase in the electron density in the region between monomer units (mainly the double-bond structure) implies an increase of the chain stiffness and thus the rigidity. Rigidity can also be explained by the measure of statistical length (measured by the small angle neutron scattering technique) (eq 2.16).

$$b = 2a/1 - \langle\cos\Phi\rangle \qquad (2.16)$$

The statistical length *b* is a measure of the angular corelation along the polymer. It is very consistent with the degrees of double-bond character between monomer units in the system. The higher the statistical length value is, the greater is the rigidity. Statistical lenght *b* can be calculated from the expression where *a* is the monomer unit length, and θ is the angular deviation between neighboring monomer units.

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad (2.17)$$

The effect of chain rigidity can be understood by considering a simple thermodynamic description of the dissolution of an amorphous polymer: where ΔG_m, ΔH_m, and ΔS_m are the change in free energy, enthalpy, and entropy on dissolution, respectively, and T is the absolute temperature. The magnitude of ΔS_m is always positive due to the increased configurational freedom of the polymer solution. For undoped polymer, ΔG_m is negative since dissolution occurs. On doping it becomes more extended as a result of electron delocalization. This means that ΔS_m is smaller than in the case of the neutral polymer. Consequently, ΔG_m increases and may become positive on doping, signaling that aggregation is favored over dissolution.

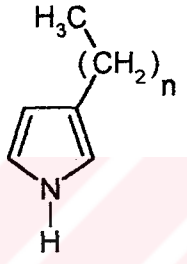
In addition, if a weak attractive interaction exists between macromolecules, a more rigid chain is sterically more favorable for aggregation as it allows multiple associations between successive repeat units along sections of the polymer chain that have been aligned. Also, the interaction forces between solvents and doped polymer chains play an important role in solubilization. Introducing polar groups to the dopant structure should increase the interaction forces between dopants and the polar solvents, but may also lead to increase of intermolecular forces. Certain selected dopants may result in stronger forces between polymer and solvent, rather than polymer-polymer interactions rendering the doped salts more soluble.

2.24.2 Polypyrrole

Due to the presence of nitrogen heteroatom in pyrrole (five member ring), its chemistry is different from that of acetylene. Polypyrrole obtained chemically under the action of $FeCl_3$, $SbCl_5$, H_2O_2, $Cu(ClO_4)_2$, and the like or electrochemically is a nonthermoplastic polymer insoluble in organic and inorganic solvents.

To sort out the problem of solubility, the chemist's primary intention is to introduce substituents onto the polymeric chains to inhibit the degree of cross-linking, producing short-chain polymers that can solubilize more easily. Actually, the oxidation potential varies with the monomer, in agreement with the substituents, and thus the stereoregularity varies. The presence of substituted chains in the pyrrole ring provides the polymers with an interesting solubility without affecting their electrical performance in relation to the parent PPy.

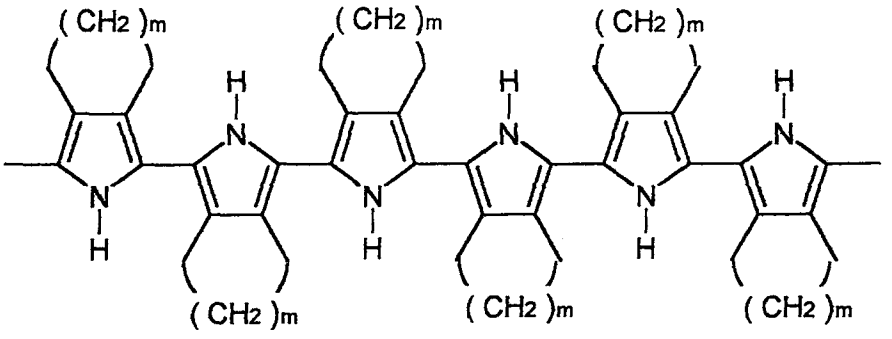
It have successfully polymerized a variety of 3-alkyl pyrroles (Scheme 2.9) by electrochemical polymerization. The monomer was synthesized



n: 1,5,7,9,11,14,17 (2.9)

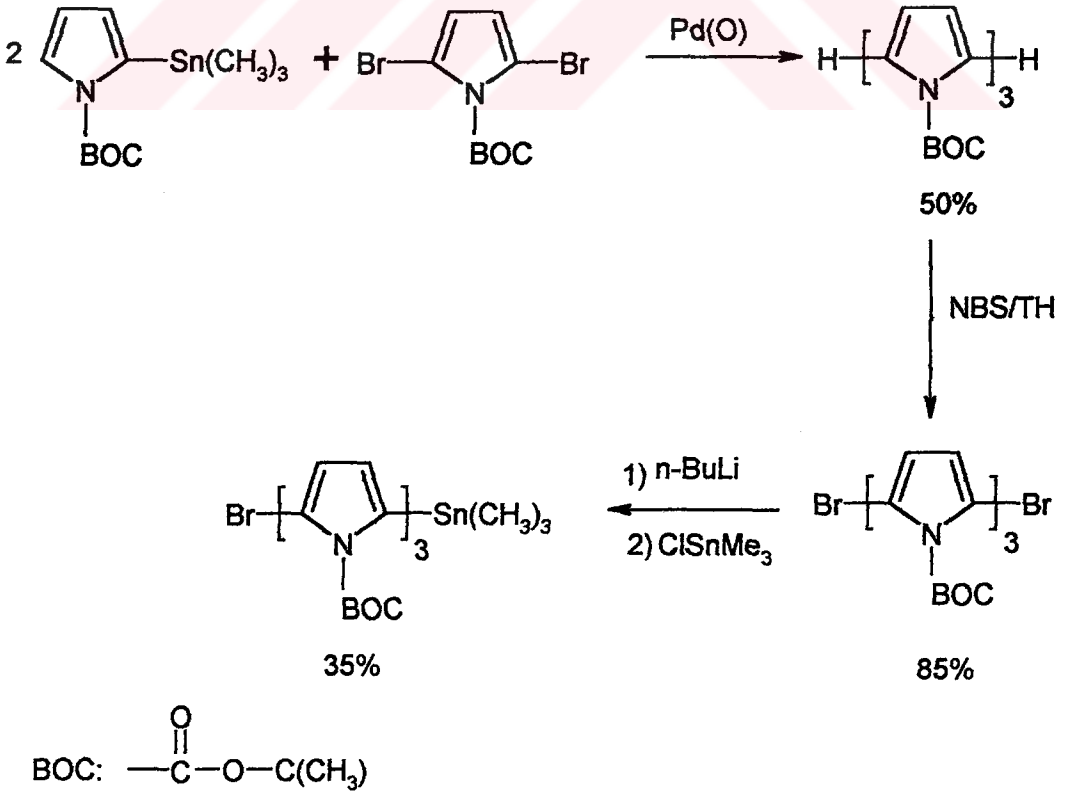
by acylation of 1-tosyl pyrrole, saponification of the tosyl protecting group, followed by reduction of the obtained ketone with a complex hydride with 45–70% overall yield. Neutral poly(3-alkyl pyrrole)s are soluble in common organic solvents like chloroform, THF, or ortho-dichlorobenzenes. The solutions are stable when kept under argon, but oxidize rapidly in air, with precipitation of a black degraded solid. Neutral poly(3-alkyl pyrrole)s are, like neutral PPy itself, very sensitive to oxygen. Poly(3-alkyl pyrrole)s can also be obtained by chemical oxidation of 3-alkyl pyrroles by Fe(III). The resulting polymers have a film-forming property and are soluble in solvents like chloroform or ortho-dichlorobenzene in the oxidized states.3,4-Dimethyl pyrrole and 2,3,4-trimethyl pyrroles were electropolymerized in acetonitrile using a number of different counterions (tetrafluroborate, perchlorate, toluene sulfonate, and dodecyl benzene sulfonate). On substitution, the oxidation potential decreases (3,4-dimethyl pyrrole 0.35 V compared to pyrrole 0.8 V). Due to the presence of alkyl substituents, the cross-linking is hindered, and the polymer dissolves. Another interesting compound is poly(3,4-cycloalkyl pyrrole (Scheme 2.9), in which adjacent

pyrrole moeities are not arranged planarly, but have to be tilted against each other for steric reasons.



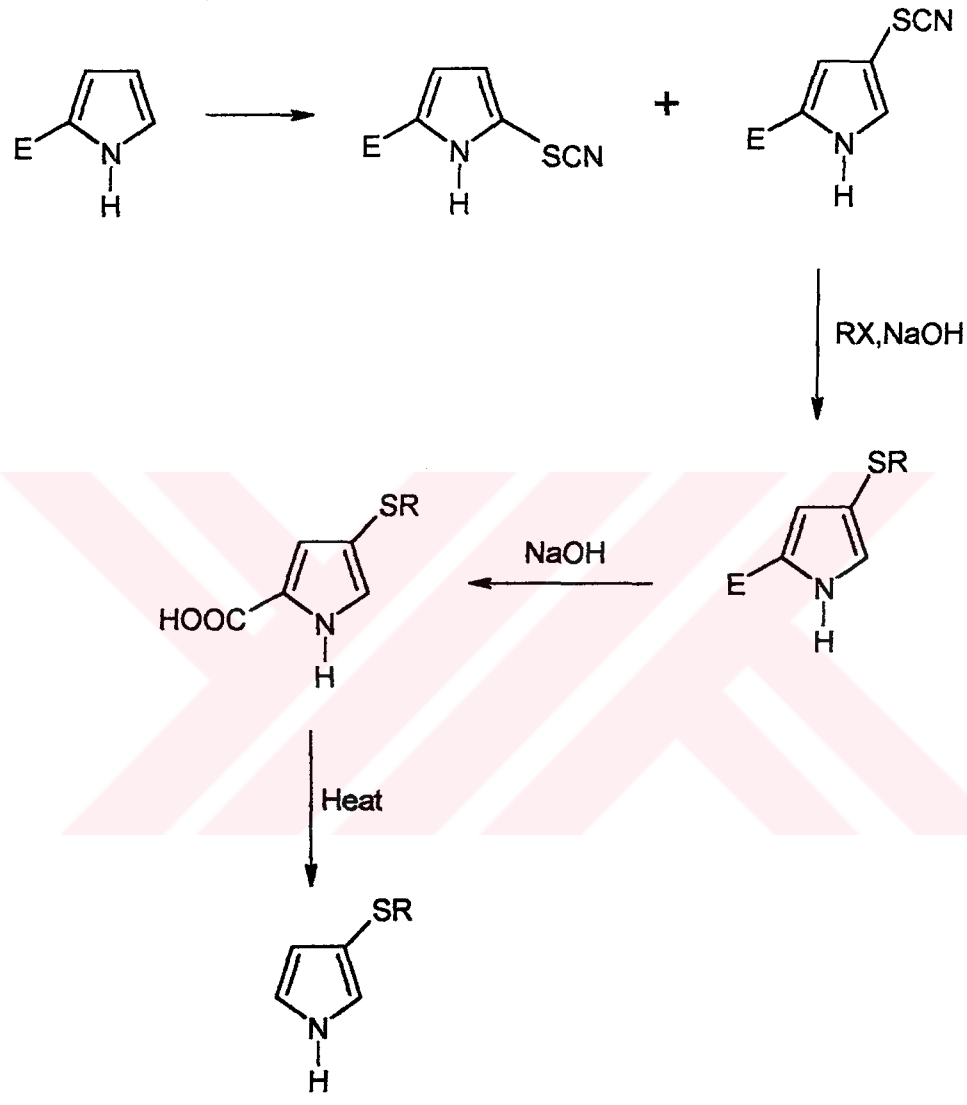
(2.10)

Therefore, the individual PPy backbones are surrounded by a cylinder of methylene groups. Structural defects like α-β couplings are always present in the materials synthesized according to the methods described normally. The failure to produce perfectly 2,5-linked PPy has been overcome by using organometallic polymerization techniques. Pyrroles with a tert-butoxy carbonyl (BOC) protecting group at nitrogen, polymerized via a Stille coupling, yielded a soluble nonplanar precursor polymer that was deprotected by thermal treatment.



(2.11)

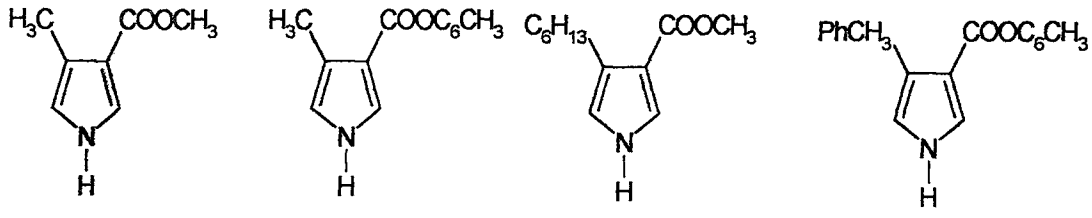
The polymerization reaction is depicted in considering the modification of pyrrole monomer, it was synthesized 3-alkyl thiopyrroles with a variable chain length. The preparative method is outlined in Scheme 2.11



(2.12)

For β-substituted oxidized pyrroles with short or long alkyl chains, slight solubility occurs either in dimethylsulfoxide (DMSO), DMF, or chloroform. For the lower members of the series (*R* = $-CH_3$, $-C_2H_5$, and $-C_4H_9$), the film forming process is slower, and in every case the electrode is covered with a dark deposit. The fact that the solution in the vicinity of the electrode is deep blue suggests that some dissolution, probably of lower oligomers, is taking place. This phenomenon is particularly evident for the lower members, and the above interpretation is confirmed by the lower yields of the deposited polymers.

It was reported the solubility of undoped PPy derivatives synthesized from pyrrole monomers substituted in the 3 and 4 positions by the alkyl and ester groups (Scheme 2.13)



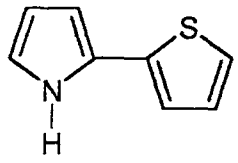
(a) (b) (c) (d)

(2.13)

The monomers are simply dissolved in diethyl ether with anhydrous ferric chloride, and the polymerization occurs slowly, with formation of a substituted PPy film, which is in its reduced state while the solvent is evaporated. After synthesis, the films can be doped chemically with classical oxidizers like iodine vapor. Here, ferric chloride is a good polymerizing agent, although it does not have a high enough potential in etheral solution to oxidize the polymer, unlike gaseous iodine. The oxidation potentials of the substituted PPy are higher than those of PPy itself, probably because of the electron-withdrawing character of the ester group, which raises the potential.

The solubility of the substituted PPy films depends on interfacial tension and on the acceptor number E_T of the solvent. The substituted PPy were soluble in solvents for which the surface tension $\gamma > 3.5$ and $E_T < 0.44$. However, exceptions can be found like *N*-methyl pyyrolidone ($\gamma \geq 4.05$), which is a good solvent for PPy, and methanol, which, despite having a low γ and E_T, does not solubilize the polymers. Specific interactions exist between each solvent and each polymer, probably due to the fact that these PPy are substituted on one side by the nonpolar alkyl groups and on the other side by very polar ester groups. This leads to difficulties in predicting the value of global interaction with a given solvent because of the specific solvation of different groups. Another interesting way to prepare soluble undoped polymer is from the thienyl pyrrole monomer Normally, electrocopolymerization of pyrrole and thiophene is difficult due to their large difference in oxidation potential. The beauty of this polymer is the presence of alternating copolymer units of pyrrole and thiophene. The

pyrrole unit donates electrons to the thiophene unit in PTP (polythienyl pyrrole), leading to a large difference of the electronic structure of PTP from that of PPy and polythiophene. Scheme 2.13.



(2.14)

Apart from the substitution, it was reported that, using stable radical cations, the prepared polymers can be made soluble. Actually, *p*-substituted triphenylamines (mild one electron oxidant) can stop the polymerization process at the stage of lower molecular mass and reduce the likelihood of the cross links of PPy chains, which would promote the solubility of the polymer. It was possible to synthesize PPy, which is soluble in organic solvents like acetonitrile, by polymerizing pyrrole in the presence of chemically or electrochemically generated radical cations of p-substituted triphenylamines $(XC_6H_4)_3N^+A^-$ where $x = OCH_3$, $A^- = SbCl_6^-$ (I); $x = CH_3$, $A^- = SbCl_6^-$ (II); x = Br, $A^- = SbCl_6^-$ (III); and $x = OCH_3$, $A^- = BF_4^-$ (IV).A typical synthetic method involving radical cation (I) was as follows: the radical cationic solution (1.7×10^{-3} M in 10 ml acetonitrile) was added to the pyrrole solution (8.3×10^{-1} M in 15 ml acetonitrile) at 25°C under argon flow. The authors were able to isolate three fractions of polymeric products and the triphenylamine after complete polymerization. The three fractions were insoluble fractions (50% aggregate weight of the isolated polymer), soluble in acetonitrile polymer (48%), and a small amount of polymer soluble in benzene and acetonitrile. The resulting polymeric fraction was found to be paramagnetic, the ESR spectra of their solid samples represent singlets, and the line width increases in going from insoluble to soluble fractions in acetonitrile. The conductivity of the isolated insoluble fraction was found to be much greater than that of the soluble fraction. The solubility of the resulting polymer decreases with increasing oxidizing capacity of the radical cation in the order I < II < III. This decrease was caused by increasing molecular weight of the polymer and a number of cross links of the polymeric chains.

The other technique to make the polymer soluble is counterion induced processibility. The concept of counterion induced processibility of conducting polyaniline, which consists of doping polyaniline with functionalized protonic acids, thus rendering the polymer conducting and soluble. The functionalized counterion

provides solubility of the doped polymer backbone, allowing solution processing. Following this technique, soluble PPy synthesized chemically using ammonium persulfate as an oxidant and dodecyl benzene sulfonate and naphthalene sulfonate as the dopant. The solubility depends greatly on the molecular weight of PPy. There is a critical concentration range of the oxidant at a given polymerization temperature to obtain soluble PPy. Soluble PPy seems to have a high concentration of free radicals, which are very stable in air, but different from the free radicals generated by polymerization initiators. The solubility depends on oxidant/monomer (O/M) and dopant/monomer (D/M) molar ratio. When O/M is less than 0.2 and D/M is less than 1.0, the PPy obtained was partially soluble in *m*-cresol or *N*-methyl-2-pyrrolidone (NMP). Its solubility decreases as the increase of O/M. When the O/M ratio was greater than 0.2, the polymer obtained was totally insoluble in any solvent. Homogeneous solutions prepared from the solvents (*m*-cresol, chloroform, DMSO, NMP, etc.) show different behaviors in the near-infrared (NIR) region that depend on the solvent used.

In Fig. 2.17 a ultraviolet-visible (UV-Vis)/NIR spectra of PPy-DBSA (dodecyl benzene sulfonic acid) solution are shown that vary with the solvent used and can be categorized into three groups depending on the absorption intensity in the NIR region. In a relatively nonpolar solvent such as chloroform, the absorbance is higher than that of the solutions in benzyl alcohol, *m*-cresol, or polar solvents. This behavior may be attributed to the micelle formation of DBSA and solvent interactions with the PPy backbone. Since DBSA has a long alkyl group, the doped regions of the PPy backbone are easily screened in chloroform; PPy has a loosened coil conformation so that the charge carriers easily move along the chain, and higher absorbance is observed. In polar solvent such as NMP and DMSO, the solvent molecules are able to approach the doped regions, and the micelles around PPy are somewhat perturbed. Hence, the positively charged region of PPy may be exposed, and the negative charge may be shared with the other part of the polymer; therefore, the PPy conformation is more likely a relatively collapsed coil due to the intrachain charge-sharing interaction. For benzyl alcohol and *m*-cresol solvent, the aromatic interaction between the solvent and the PPy backbone somewhat moderates the DBSA interaction with PPy. With NSA (naphthalene sulfonic acid) (Fig 2.17b), the aromatic interaction of dopant overwhelms the solvent interaction, so the solvent effect is relatively weak.

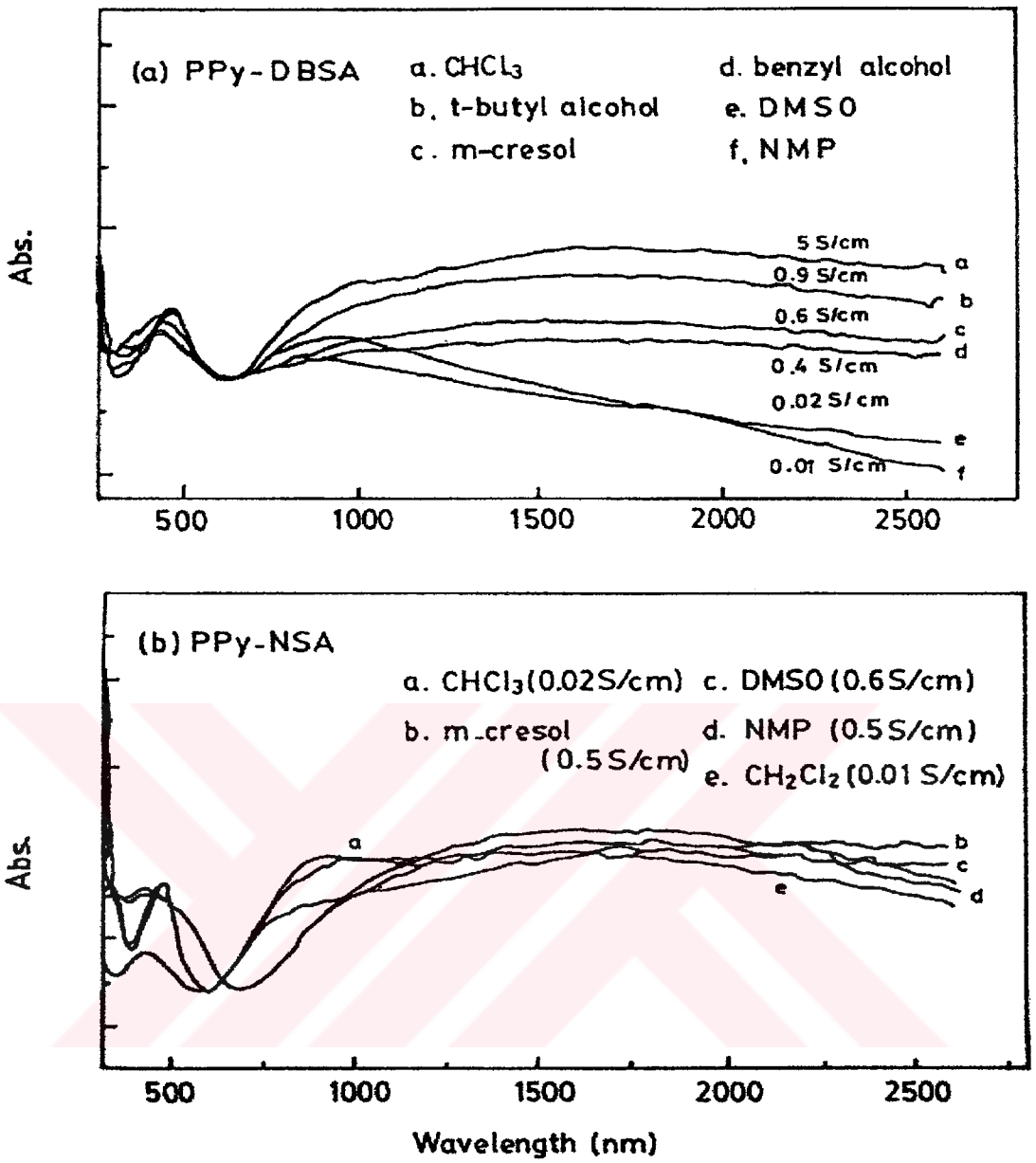


Figure. 2.17. UV-Vis/NIR spectra of (a) PPy-DBSA solution; (b) PPy-NSA solution in various solvent

Recently, it was introduced an extension of this so called counterion induced processibility of conducting polymers concept from acid doping oxidative doping: acid-assisted oxidative doping and solubilization. This principle is schematically outlined below. Hydrogen peroxide is chosen as the oxidant, [Polymer] represents a repeating unit of the conjugated polymer, and *HX* symbolizes the protonic acid. The deprotonated acid serves as a counterion (although the polymer is being oxidized), providing solubility in the case of well chosen functionalized counterion. The mechanism is based on acid-assisted oxidative polymerization, immediately

followed by the oxidative doping using hydrogen peroxide in both steps as the oxidant and yielding only water as a side product. The functionalized deprotonated acid (e.g., camphor sulfonate) serves as a counterion to provide solubility of the polymeric complex. The PPY-camphorsulfonate complexes can be fully dissolved in organic solvents.

Overall, (a+b)

$$([\text{Polymer}] \rightarrow [\text{Polymer}]^{+} + e)*n \; (HX \rightarrow H^{+} + X^{-})$$

$$* \; n \; (H_2O_2 + 2H^{+} + 2e \rightarrow 2H_2O)$$

$$* \; n/2 \qquad \text{or } [\text{Polymer}]*nHX* \; n + H_2O_2$$

$$* \; n/2 \rightarrow [\text{Polymer}^{+}X^{-}]*n + H_2O* \; n \qquad \text{(a)}$$

$$[\text{Monomer}]*m*n \rightarrow [\text{Polymer}]* \; n + (2H^{+} + 2e)$$

$$*m*n \; (H_2O_2 + 2H^{+} + 2e \rightarrow 2H_2O)*m* \; n \qquad \text{(b)}$$

Overall, (a+b)

$$[\text{Monomer}]*m*n + H_2O_2*(m*n + n/2) + HX*n \rightarrow$$

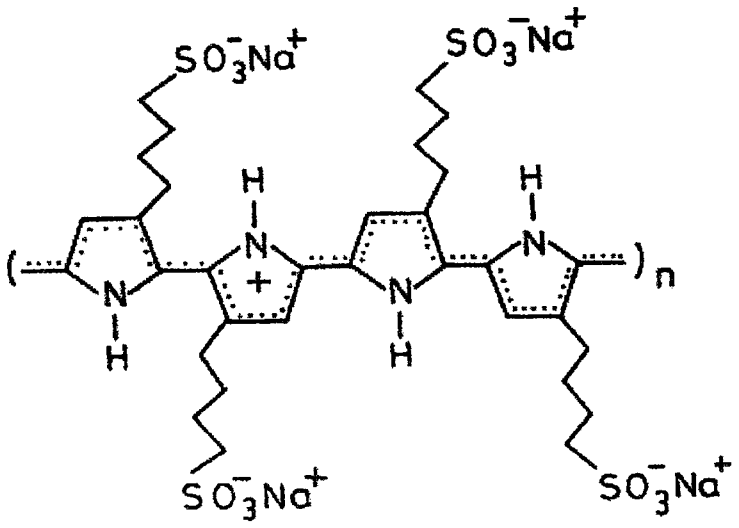
$$[\text{Polymer}^{+}X^{-}]*n + H_2O* \; (2m*n + n)$$

Figure 2.18: Acid-assisted oxidative doping (and solubilization) of conjugated polymers

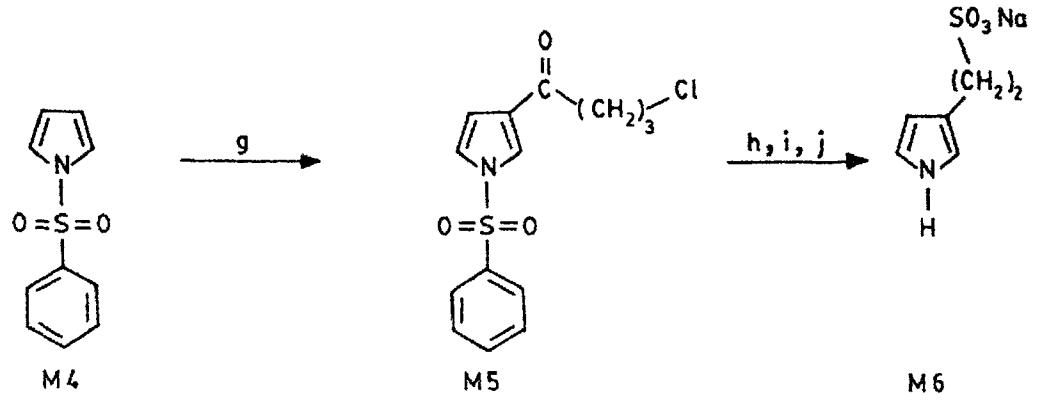
Acid assisted oxidative doping (and solubilization) of conjugated polymers is shown in (a) above and (b) is an overall extension of (a) that results in acid-assisted oxidative polymerization doping and solubilization of conjugated polymers. A new class of water-soluble PPy was developed. It was accomplished by oxidative matrix polymerization of pyrrole monomer with Ce(IV) in the presence of poly(acrylic acid) (PAA), poly(vinyl pyrrolidone) (PVP), and copolymers of vinyl pyrrolidone (VP) with acrylic acid (AA) [VP/AA:25/75 $(CP)_1$, 50/50 $(CP)_2$, 75/25 $(CP)_3$]. Polymers and PPy fragments interact, including oppositely charged fragments of components, and formation of chelate units occurs with Ce(III) ions because of the electrostatic interaction of PAA and polyvinylpyridine and that of PAA and polyacrylamide. The possibility of quarternization of nitrogen at the pyrrole ring is always high, so PAA and PPy may interact, including the PAA-Ce(III)-PPy ternary complex side, depending on the Ce(IV) concentration. Accumulation of oligomers on the polymer matrix was observed from the viscosity and spectroscopic results (wavelength

shifts). The possibility of complex formation was increased in the presence of macromolecule, with a higher density of regularly arranged interacting AA and VP groups. The driving force of complexation is the electrostatic interactions (salt and ion-coordination bands) of components. The interaction of vinyl pyridine and acrylic acid in copolymers by the formation of intramolecular salts provides the compacting of copolymer chains in reaction conditions, which in turn changes the character of polymerization of pyrrole. Because of this, in the mixture of $(CP)_1$ and $(CP)_2$ formation of soluble reaction products is not observed. Inclusion of cerium ions in interpolymer complexes increased the hydrophobicity of these particles and helped precipitation. Among the investigated (CP) systems, only in the case of $(CP)_3$ soluble products were observed. The free sections of formed interpolymer complexes that contain mainly VP fragments of copolymers form less-stable complexes with metal ions, and this may cause the solubility of the ternary mixture (CP_3-Py-Ce).

Self-doping of PPy is another method for preparing water soluble polymers. Self-doping is attributed to the conducting polymers in which the dopant anion is a part of the polymer matrix. The self doping technique was used as early as 1987. The approach to self-doping of polymers was based on monomers that are easier to polymerize electrochemically. The authors have used two monomers (3-propyl potassium sulfonate-2,2'-5,5'-terthienyl pyrrole and 3-butyl sodium sulfonate-pyrrole) for the preparation of the soluble polymers (Scheme 2.15) The substituted pyrrole monomer was synthesized using the following scheme (Scheme 2.16)



(2.15)



g.$ClCO(CH_2)_3Cl.AlCl_3$ h.Zn(Hg) HCl i Na_2SO_3 Bu_2NBr. NaI. EtOH. water j.NaOH

(2.16)

2.25 PROCESSIBILITY

Conjugated polymers may be made by a variety of techniques, including cationic, anionic, radical chain growth, coordination polymerization, step growth polymerization or electrochemical polymerization. Electrochemical polymerization occurs by suitable monomers which are electrochemically oxidized to create an active monomeric and dimeric species which react to form a conjugated polymer backbone. The main problem with electrically conductive plastics stems from the very property that gives it its conductivity, namely the conjugated backbone. This causes many such polymers to be intractable, insoluble films or powders that cannot melt. There are two main strategies to overcoming these problems. There are to either modify the polymer so that it may be more easily processed, or to manufacture the polymer in its desired shape and form. There are, at this time, four main methods used to achieve these aims.

The first method is to manufacture a malleable polymer that can be easily converted into a conjugated polymer. This is done when the initial polymer is in the desired form and then, after conversion, is treated so that it becomes a conductor. The treatment used is most often thermal treatment. The precursor polymer used is often made to produce highly aligned polymer chain which are retained upon conversion. These are used for highly orientated thin films and fibres. Such films and fibres are highly anisotropic, with maximum conductivity along the stretch direction. The second method is the synthesis of copolymers or derivatives of a parent

conjugated polymer with more desirable properties. This method is the more traditional one for making improvements to a polymer. What is done is to try to modify the structure of the polymer to increase its processibility without compromising its conductivity or its optical properties. All attempts to do this on polyacetylene have failed as they always significantly reduced its conductivity. However, such attempts on polythiophenes and polypyrroles proved more fruitful. The hydrogen on carbon 3 on the thiophene or the pyrrole ring was replaced with an alkyl group with at least four carbon atoms in it. The resulting polymer, when doped, has a comparable conductivity to its parent polymer whilst be able to melt and it is soluble. A water soluble version of these polymers has been produced by placing carboxylic acid group or sulphonic acid group on the alkyl chains. If sulphonic acid group groups are used along with built in ionizable groups. then such system can maintain charge neutrality in its oxidized state and so they effectively dope themselves. Such polymers are referred to as "self-doped" polymers. One of the most highly conductive derivative of polythiophene is made by replacing the hydrogen on carbon three with a $-CH_2-O-CH_2CH_2-O-CH_2CH_2-O-CH_3$. This is soluble and reaches a conductivity of about 1000 S cm^{-1} upon doping.

The third method is to grow the polymer into its desired shape and form. An insulating polymer impregnated with a catalyst system is fabricated into its desired form. This is then exposed to the monomer, usually a gas or a vapour. The monomer then polymerizes on the surface of the insulating plastic producing a thin film or a fibre. This is then doped in the usual manner. A variation of this technique is electrochemical polymerization with the conducting polymer being deposited on an electrode either the polymerization stage or before the electrochemical polymerization. This cast may be used for further processing of the conducting polymer. For instance, by stretching aligned bends of polyacetylene/polybutadiene the conductivity increase 10 fold, due to the higher state of order produced by this deformation.

The final method is the use of Langmuir-Blodgett trough to manipulate the surface active molecules into a highly ordered thin films whose structure and thickness which are controllable at the molecular layer. Amphiphilic molecules with hydrophilic and hydrophobic groups produces monolayers at the air-water surface interface of a Langmuir-Blodgett trough. This is then transferred to a substrate creating a multilayer structure comprised of molecular stacks which are normal about 2.5 nm thick. This is a development from the creation of insulating films by the same

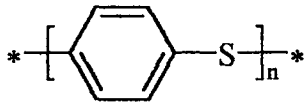
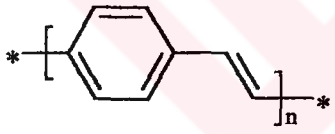
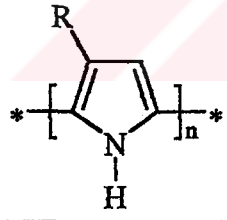
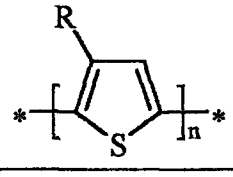
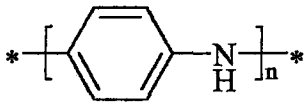
technique. The main advantage of this technique is its unique ability to allow control over the molecular architecture of the conducting films produced. It can be used to create complex multilayer structures of functionally different molecular layers as determined by the chemist. By producing alternating layers of conductor and insulator it is possible to produce highly anisotropic film which is conducting within the plane of the film, but insulating across it.

2.25 STABILITY

There are two distinct types of stability. Extrinsic stability is related to vulnerability to external environmental agent such as oxygen, water, peroxides. This is determined by the polymers susceptibility of charged sites to attack by nucleophiles, electrophiles and free radicals. If a conducting polymer is extrinsic unstable then it must be protected by a stable coating.

Many conducting polymers, however, degrade over time even in dry, oxygen free environment. This intrinsic instability is thermodynamic in origin. It is likely to be cause by irreversible chemical reaction between charged sites of polymer and either the dopant counter ion or the p-system of an adjacent neutral chain, which produces an sp^3 carbon, breaking the conjugation. Intrinsic instability can also come from a thermally driven mechanism which causes the polymer to lose its dopant. This happens when the charge sites become unstable due to conformational changes in the polymer backbone. This has been observed in alkyl substituted polythiophenes

Table 2.4: Processing attributes of common conducting polymers

POLYMER	CONDUCTIVITY ($W^{-1}cm^{-1}$)	STABILITY (doped state)	PROCESSING POSSIBILITIES
Polyacetylene CH=CH	10^3 - 10^5	poor	limited
Polyphenylene 	1000	poor	limited
PPS 	100	poor	excellent
PPV 	1000	poor	limited
Polypyrroles 	100	good	good
Polythiophenes 	100	good	excellent
Polyaniline 	10	good	good

2.26 APPLICATIONS

The extended p-systems of conjugated polymer are highly susceptible to chemical or electrochemical oxidation or reduction. These alter the electrical and optical properties of the polymer, and by controlling this oxidation and reduction, it is possible to precisely control these properties. Since these reactions are often reversible, it is possible to systematically control the electrical and optical properties with a great deal of precision. It is even possible to switch from a conducting state to an insulating state.

There are two main groups of applications for these polymers. The first group utilizes their conductivity as its main property. The second group utilizes this electroactivity. They are shown below

Table 2.5 : two main groups of applications for conducting polymers

Group 1	Group 2
Electrostatic materials.	Molecular electronics
Conducting adhesives	Electrical displays
Electromagnetic shielding	Chemical and biochemical sensors
Printed circuit boards	Rechagable batteries and solid
Artifical nerves	electrolytes.
Antistatic clothing	Drug release systems
Thermal sensors	Optical computers
Piezoceramics	Ion exchange membranes
Active electronics	Electromechanical actutators
Swithes	'Smart' structures
Aircraft structures	

3. EXPERİMENTAL SECTION

3.1 MATERIALS

Pyrrole (Py), acetonitrile,$FeCl_3.6H_2O$, Octanoil chloride, DMSO, 2,5-dimethoxy tetrahydrofuran, 3-amino-1-propanol, and formaldehyde were purchased from Merck and used without futher purification. DMF, from Carlo Erba, Pyridine and Ceric (IV) ammonium nitrate from AnalaR, THF from Riedel de Häen, Tosyl Chloride from Fluka. CH_2Cl_2 and aceton were distilled before usage.

3.2 ANALYSES

Inrared (IR) spectra were recorded on a JASCO FTIR 5300 fourier transform infrared spectrometer.

^1H- NMR spectra on a Bruker AC (250 MHz).

Electrical conductivities of the solid products were measured by using four point probe technique and WTW micro processor type conductometer.

And UV-VIS were recorded on a Shimadzu 164 A Recording Spectrophotometer.

3.3 CONDUCTIVITY MEASURMENTS

To measure the electrical conductivity of precipitates, compact thin pellets were prepared under 8-10 tons/cm^2 pressure. A typical sample diameters were 13mm at a thickness of 0.8 mm. Conductivity measurments of polymers were performed by the four probe technique and calculated from the following equation:

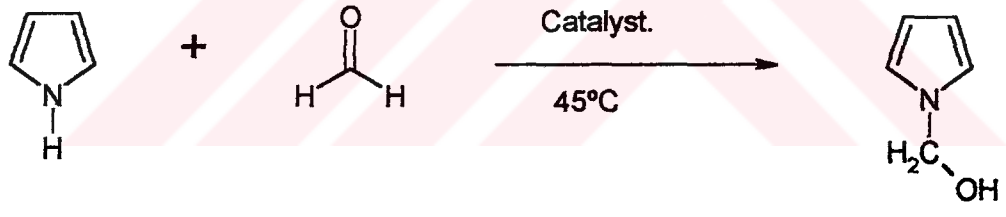
$$\sigma = V^{-1} I (\ln 2/ \pi d_n)$$

Where V is the potential in volts, I is the current in amperes, and d_n is the thickness of the samples in centimeters.

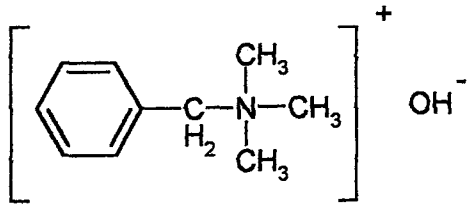
3.4 SYNTHESIS OF 1-(HYDROXYMETHYL)PYRROLE

Method 1 : Anhydrous potassium carbonate 0,2 gram was added to 15 gram (0,45 mol) of anhydrous paraformaldehyde and 34,5 gram (0,51mol) pyrrole. The mixture was cooled in a nitrogen atmosphered and light prevented flask until paraformaldehyde dissolved in pyrrole and the reaction became exothermic. After dissolving, the mixture was heated to 45° C and, stirred for four hours. Red-brown liquid was obtained as a crude product. This product distilled under vacuum and the desired pure N-methylol pyrrole obtaind as a result [1]. The structure was proved by means of ^{1}H-NMR and FT-IR. Which those spectrums are in the addition part.

Method 2: 0,1 ml benzyl(N,N,N-trimethyl)ammonium hydroxide was added to 6 gram of anhydrous paraformaldehyde and 14,2 ml pyrrole . The mixture was cooled in a nitrogen atmosphered and light prevented system, until paraformaldehyde dissolved in pyrrole. The reaction became exothermic during this process. After dissolving the mixture was heated to 45°C and, stirred under nitrogen blanket for four hours. Distillation was needed for purification. The reaction figured in scheme 3.1



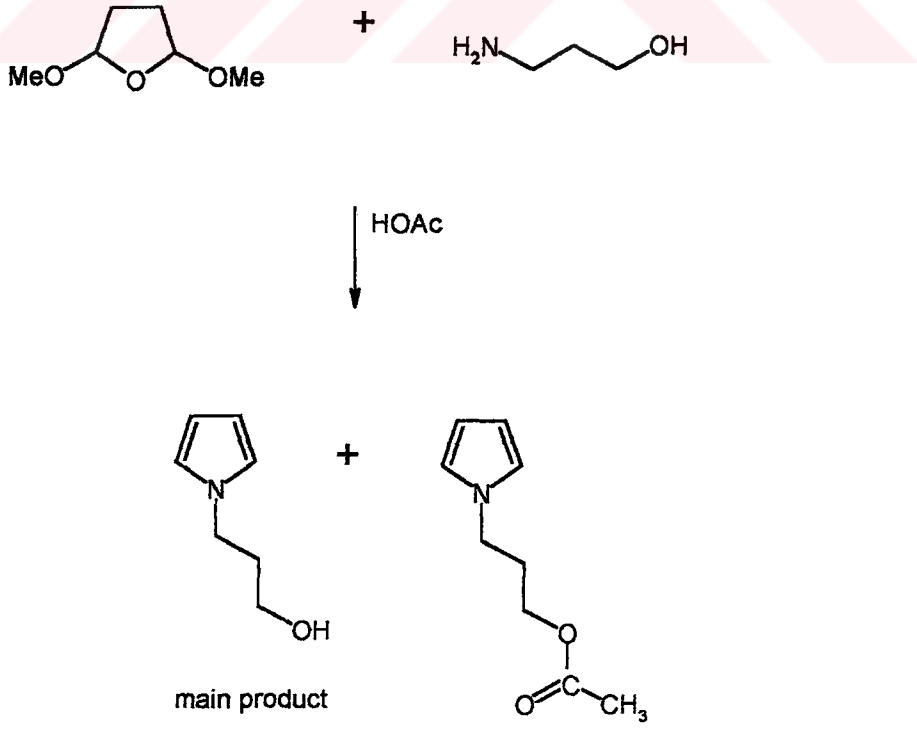
Catalyst: 1. K_2CO_3

2. 

benzyl(N,N,N-trimethyl)ammonium hydroxide (3.1)

3.5 SYNTHESIS OF 1-(3-HYDROXYPROPYL)PYRROLE

3-amino-1-propanol (5,72ml) was added with efficient aggitation to glacial acetic acid (11,34 gr), cooled in an ice- salt mixture at a rate such that the temperature was maintained at 15-25 °C. When the addition was completed, 2,5-dimethoxytetrahydrofuran (2,95 ml) was added in one portion, the raction vessel was removed from the cooling bath and set up for downward distillation. The reaction flask was placed in an oil bath and the temperature was raised 100-120 °C, at which point of ditillation of a liquid commenced. After 1,5 hour at this temperature some distillate had been collected. The residual liquid in the reaction vessel was cooled to room temperature, it was diluted with water, and extracted with CH_2Cl_2. The extract was washed successively with saturated aquous solutions of NaCl and Na_2CO_3, it was dried with $MgSO_4$, and then the solvent removed in vacuo. The residue, which consisted mainly of the desired alcohol (1-(3- hydroxypropyl)pyrrole) and a lesser amount of the corresponding acetate [fig 1], was dissolved in methanol, 20 wt. % NaOH (50ml) was added, and the solution was left at room temperature for one hour. The solution was poured into saturated NaCl solution (60ml), the product was extracted into CH_2Cl_2, and the extract was dried with $MgSO_4$. The solvent was removed in vacuo leaving an oil. Which was spectroscopially identified by ^{1}H-NMR and FT-IR. [2] The reaction is shown in scheme 3.2.

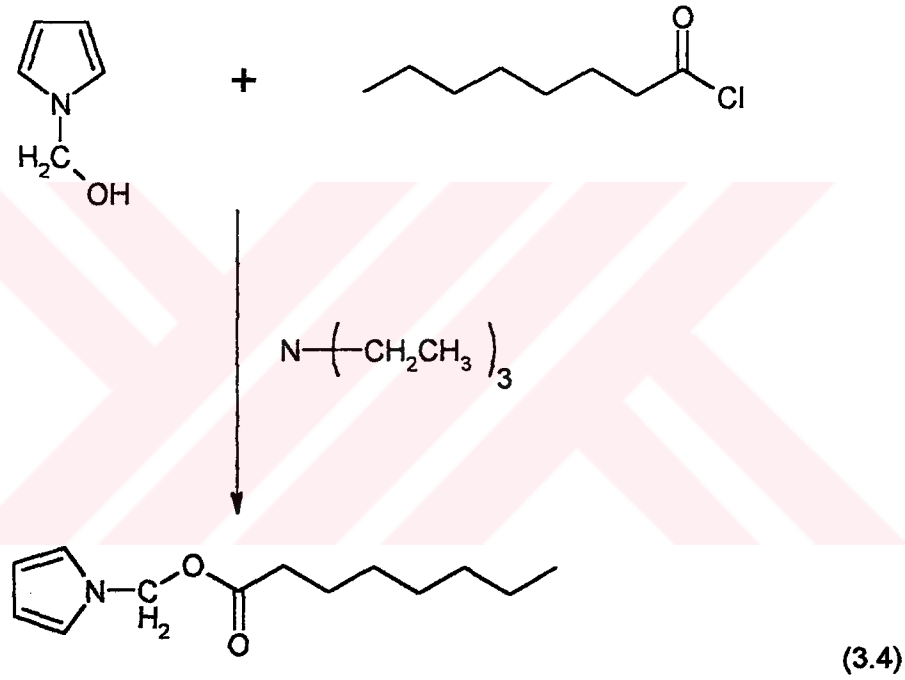


main product

by-product (3.2)

3.6 SYNTHESIS OF 1-PYRROLYLMETHYL OCTANOATE

In a 50 ml two necked flask with a magnetic stirer, and a thermometer, 1-(hydroxy mehyl)pyrrole (0,69 g), triethylmine (1ml), and dichloromethane (5ml) was placed and cooled at 0°C with aggitation. Octanoil chloride (1,15 g) was added by portions in thirty minutes not to rise the temperature above 20 °C. After one hour, the readtion vessel was cooled to –25-30°C for one day. The mixture filtered. Colorless crystals seperated from the product which are octanoic acid salts. The solvent was removed and the residual liquid was mainly consist of the desired product. The structure of the 1-H-pyrrolylmethyl octanoate was proved spectroscopially by ^{1}H-NMR and FT-IR. The reaction is shown in scheme 3.3

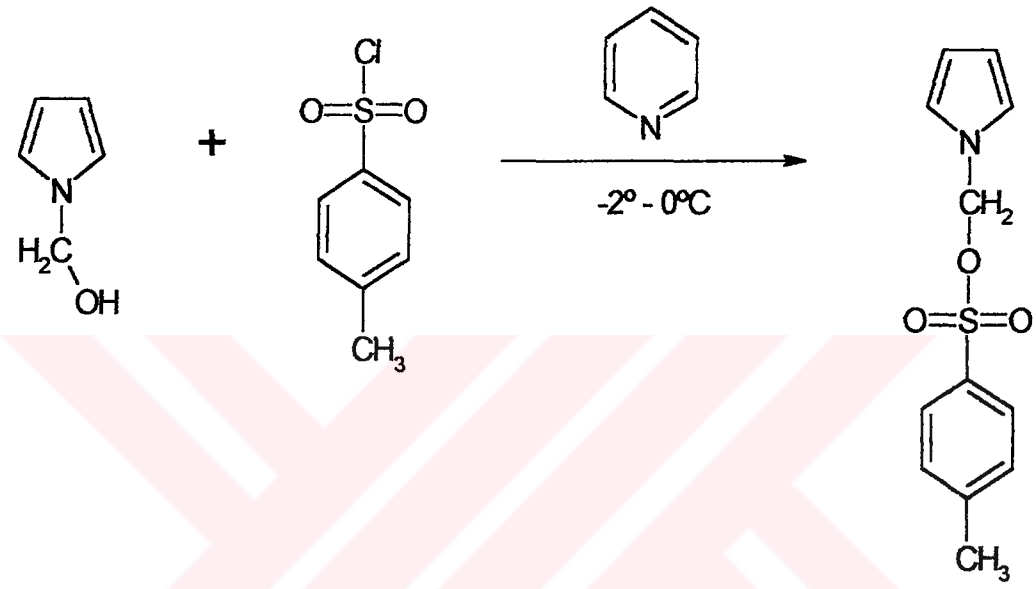


(3.4)

3.6 SYNTHESIS OF N-METHYL-1-PYRROLYL TOLUENE-p-SULPHONATE

In a 100ml three-neckhed flask, equipped with a magnetic stirer, a thermometer and nitrogen inlet apparatus (to provide nitrogen atmosphere during the reaction), 6 gram (0,062 mol) N-methylolpyrrole, and anhydrous 20,2 ml(0,25 mol) pyridine was placed. The flask was surrounded by a bath sufficiently cold to lower the temperature of the mixture to around –2°C. Toluene-p-sulphonyl chloride (0,070 mol) was added to the flask in portions, or at such a rate that temperature did not rise above 20°C. The mixtured was stired for one hour at a temperature below 20°C, then it was diluted with water of hydrochloric acid in 150 ml of ice-water (caution:

concentrated acid solution might cause polymerization). The solution was extracted with dichoromethane (6x20ml) and the extract was washed with an aqueous solution of hydrochloric acid many times to neuttralize pyridine from the prduct. After drying on $MgSO_4$ and evaporation of the solvent, N-methyl-1-pyrrolyl tolune-p-sulphonate was obtained as an orange oil, which the structure was proved by ^{1}H-NMR and FT-IR spectroscopy techniques.



3.8 PREPARATION OF 1-(HYDROXYMETHYL)PYRROLE AND PYRROLE COPOLYMERS

Copolymers were prepared via oxidative copolymerization of pyrrole and 1-(hydroxymethyl) pyrrole. In a classical experiment, pyrrole and monomer were seperately dissolved in acetonitrile. And $FeCl_3.6H_2O$ solution in CH_3CN (equivalent with respect to pyrrole total units) was added under stirring. After 1h the polymerization was halted and black precipitate was filtered, washed with acetonitrile and water [39].

3.9 PREPARATION OF 1-(3-HYDROXYPROPYL)PYRROLE AND PYRROLE COPOLYMERS

Copolymers were prepared by the method used in part 3.7

3.10 PREPARATION OF *1H* –1-PYRROLYLMETHYL 4-METHYL-1-BENZENE SULFONATE AND PYRROLE COPOLYMERS

In a common experiment , oxidative copolymerization accomplished by the method which was afformentioned in 3.7 instead of $FeCl_3.6H_2O$, ceric(IV) ammonium nitrate solution in CH_3CN was used as an oxidant.

3.10 PREPARATION OF 1-H-PYRROLYLMETHYL OCTANOATE AND PYRROLE COPOLYMERS

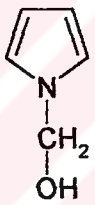
The method used for oxidative copolymerization is as same as the method used above

4. RESULTS AND DISCUSSIONS

Solid state conductivities and solubilities of the various pyrrole substituted copolymers at room temperature are listed in Tables I, II, III, and IV. The tables which include the effect of $FeCl_3$, Ceric (IV) ammonium nitrate, and Pyrrole concentrations are listed below, respectively.

4.1 1-(HYDROXYMETHYL)PYRROLE

1-(hydroxymethyl)pyrrole or N-methylol pyrrole molecular structure is shown below in scheme 3.1



(4.1)

FTIR spectrum of this molecule has obtained, and the O-H streching vibration band can be seen from the spectrum around 3381 cm^{-1} region. Aromatic C-H strechting vibration bands are around the region 3117 cm^{-1}. C-O streching vibration band which indicates primary alcohol is around 1026 cm^{-1}.

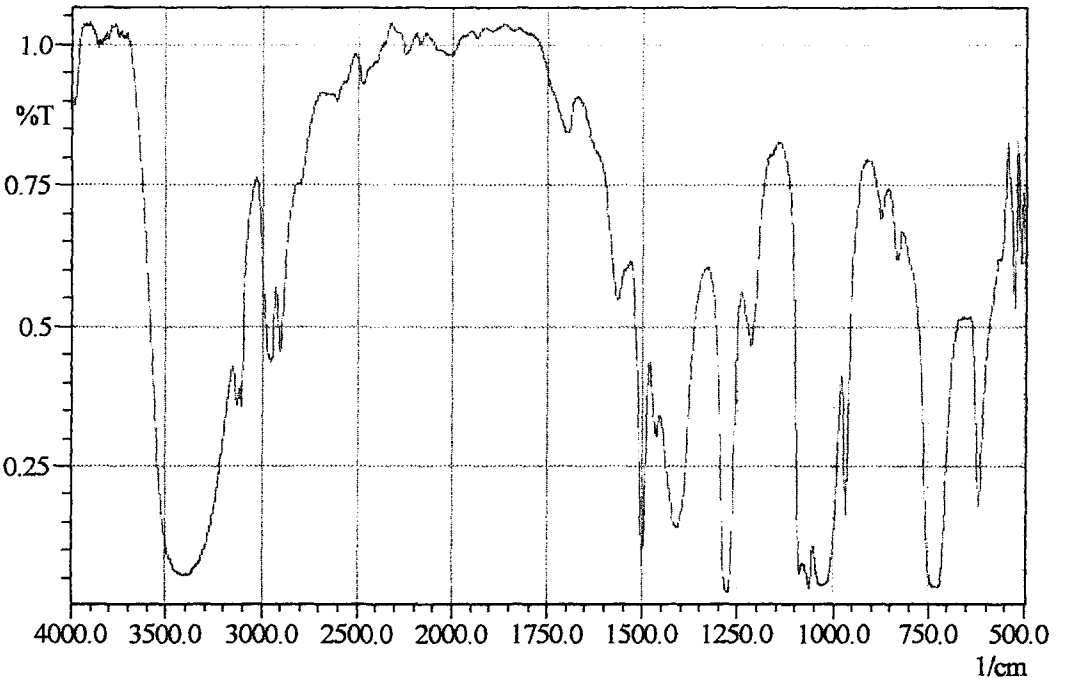


Figure 4.1 FTIR spectrum of N-methylol pyrrole

In figure 4.2 there is the proton NMR spectrum of the N-methylol pyrrole is present in the spectrum a, 3.81 ppm ; b, 5.15ppm; c, 6.24ppm; d, 6.73ppm.

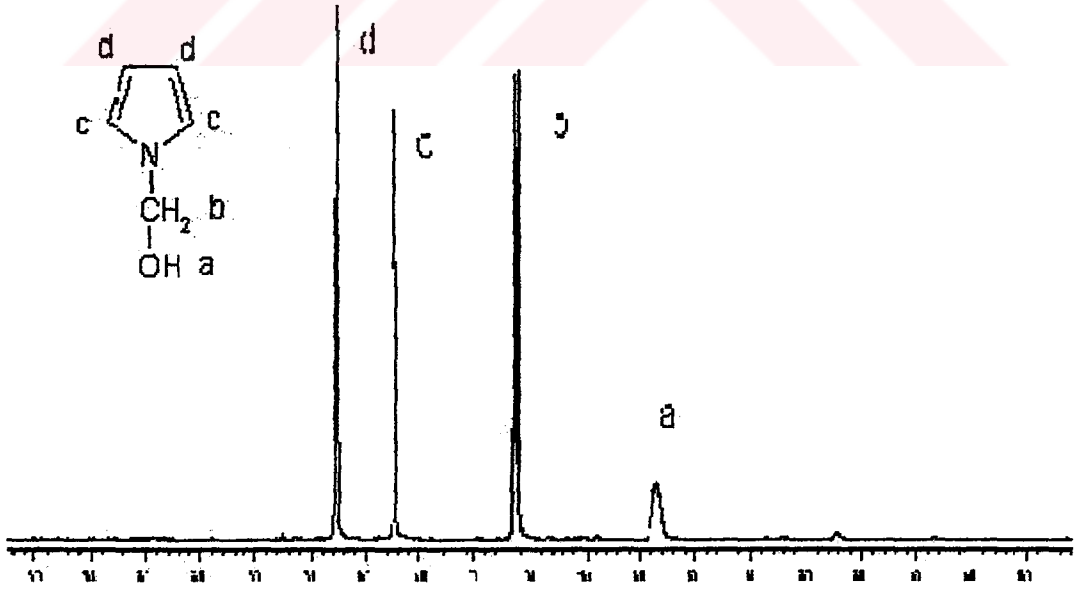


Fig 4.2: ^{1}H-NMR spectrum of N-methylol pyrrole

4.2 1-(HYDROXYMETHYL)PYRROLE AND PYRROLE COPOLYMERS

By means of chemical polymerization, provided with the use of $FeCl_3$ oxidant, pyrrole and N-methylol pyrrole was polymerized. The effect of pyrrole, N-methylol pyrrole, $FeCl_3$ on the conductivity and solubility were investigated. The results are listed in table I. And FTIR spectrum are shown below.

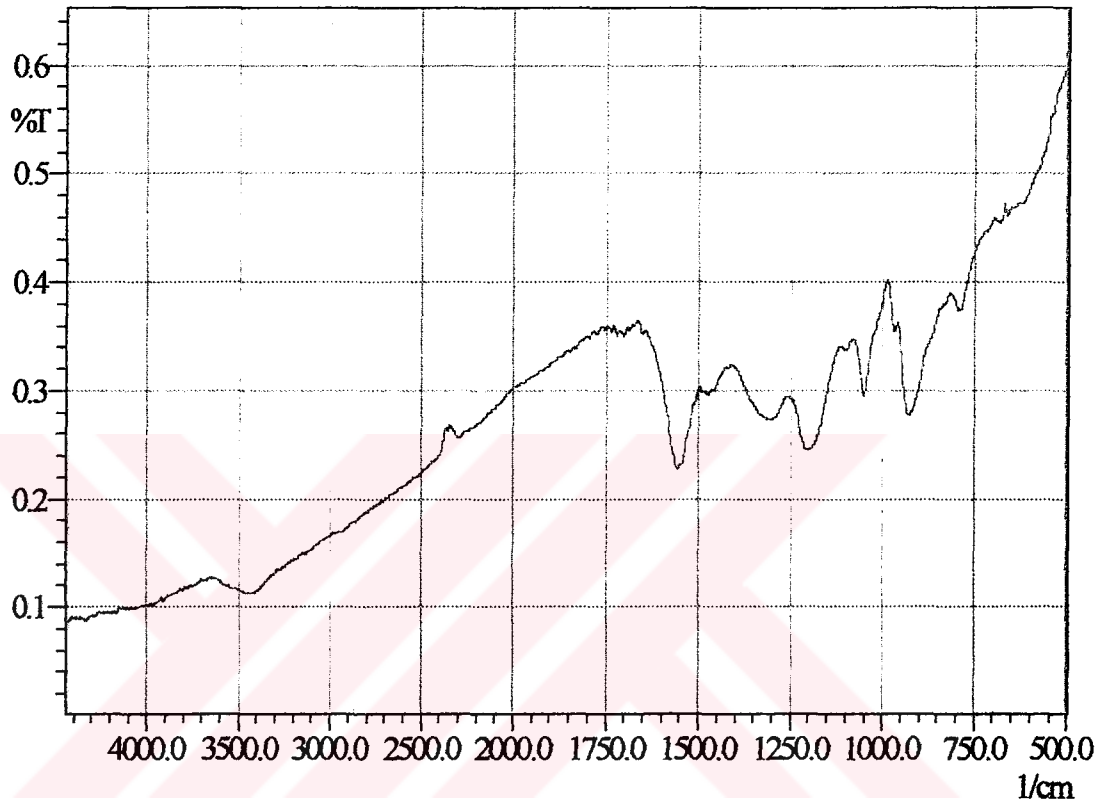


Figure 4.3: FTIR spectra of N-methylolpyrrole and pyrrole copolymer.

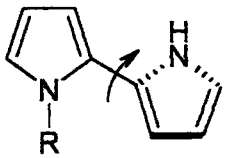
FTIR spectrum of N-methylol pyrrole-pyrrole copolymer showed bands at around 1560 cm^{-1} due to aromatic pyrrole ring vibration. The band at 1050 cm^{-1} due to C-O streching vibrations. Or this can be attributed to N-H bending of pyrrole, which generally occurs around 1074 cm^{-1}.

Table 4.1: Conductivities and solubility data of N-methylolpyrrole and pyrrole copolymers

[Py]	[Np]	[Fe]	Cond.(s/cm)	DMSO	THF	Aceton
0,150	0,151	0,187	10^{-6}	İnsoluble	İnsoluble	İnsoluble
0,150	$1{,}9.10^{-3}$	0,187	0,2	İnsoluble	İnsoluble	İnsoluble
0,327	0,075	0,475	10^{-4}	İnsoluble	İnsoluble	İnsoluble
0,654	0,075	0,950	10^{-3}	İnsoluble	İnsoluble	İnsoluble

[Py] ; Pyrrole concetration [Np]; N-methylol pyrrole concentration [Fe]; $FeCl_3.6H_2O$ concentration. Cond; Siemens/cm

The effect of pyrrole concentration on the conductivity was examined for different concentrtions of pyrrole, which is shown in table I. İt is seen that, the conductivities increases with respect to the pyrrole concentration,(see Table 4.1) of course this result is expectable. And we also see that the conductivities of these copolymers are not high enough (10^{-4} S/cm), if it is compared with polypyrrole 3,75 S/cm. Distortion of the planarity of the quinoide structures of the polymer causes a decrease on the conductivities. And unsurprisingly, the N-methylol pyrrole monomers which are included to the polymer chain distort the planarity (scheme 4.2).



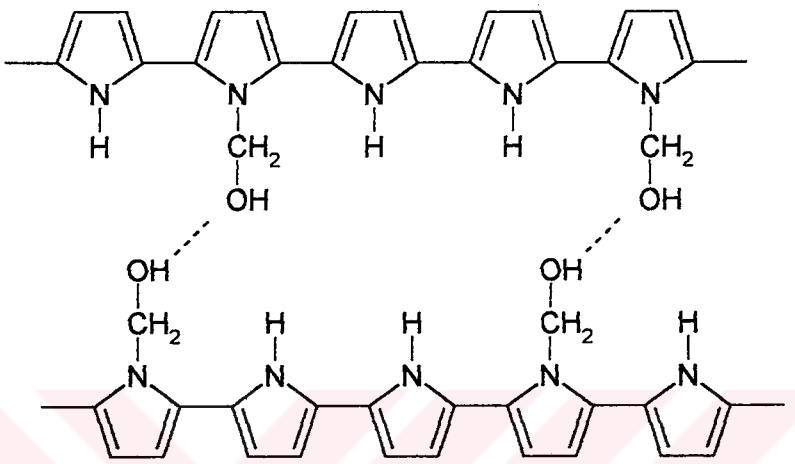
R : —C—OH
H_2

(4.2)

But the intent of usage of N-methylol pyrrole monomer is to provide solubility to the polymer structures. As it is seen in Table I, all the samples are insoluble. There can be several reasons of the insolubility. The first and general reason is the cross-linkings which are observed in many pyrrole polymers reported before and the increase in rigidity of the polymer chains plus increased polar interactions between

the polymeric chains. An increase in the electron delocalization of the polymer chain implies an increase of the chain stiffness and thus the rigidity.

An additional reason for these particular copolymers which is afformentioned generally, as mentioned above, is may be, due to the strong hydrogen bondings between the polymer chains scheme 4.3



(4.3)

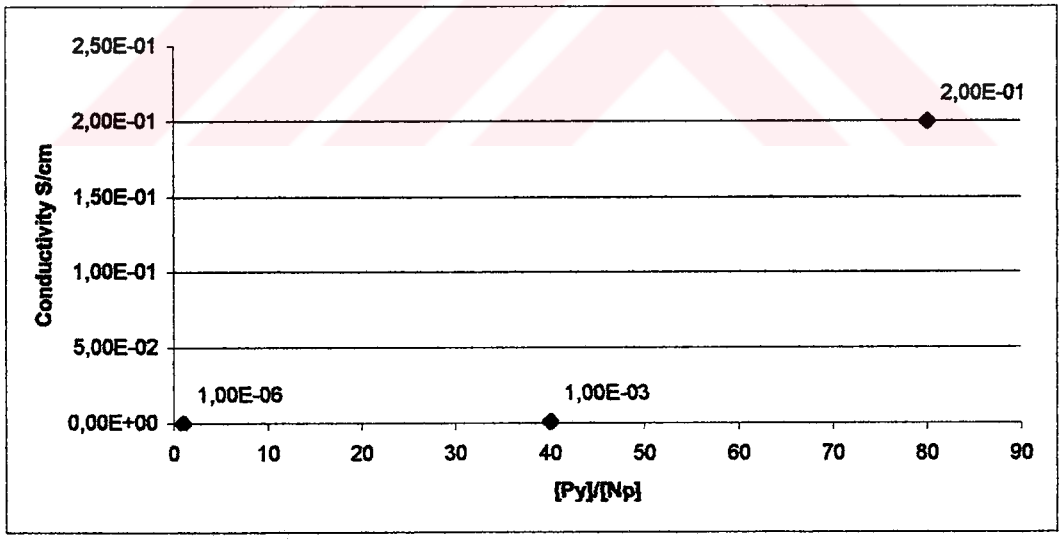
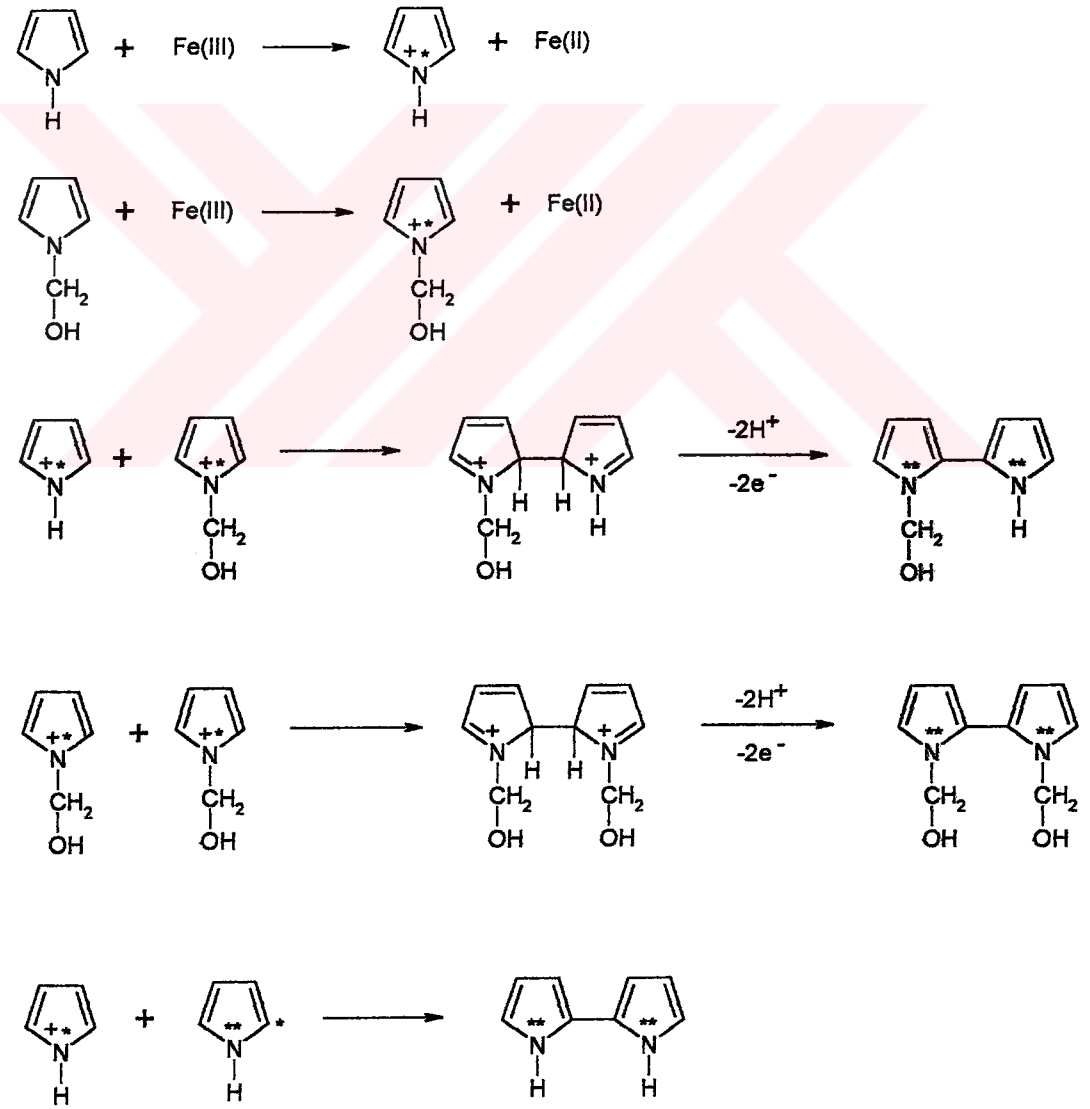


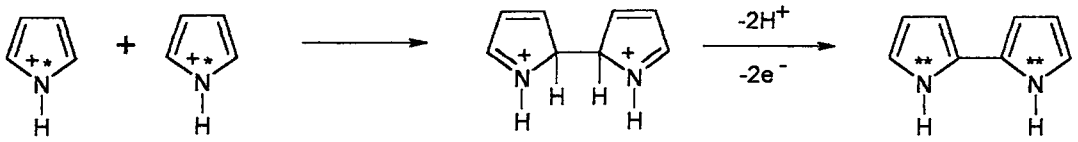
Figure 4.4: The effect of the ratio of pyrrole concentration to N-methylol pyrrole concentration on the conductivity.

4.2.1 MECHANISM

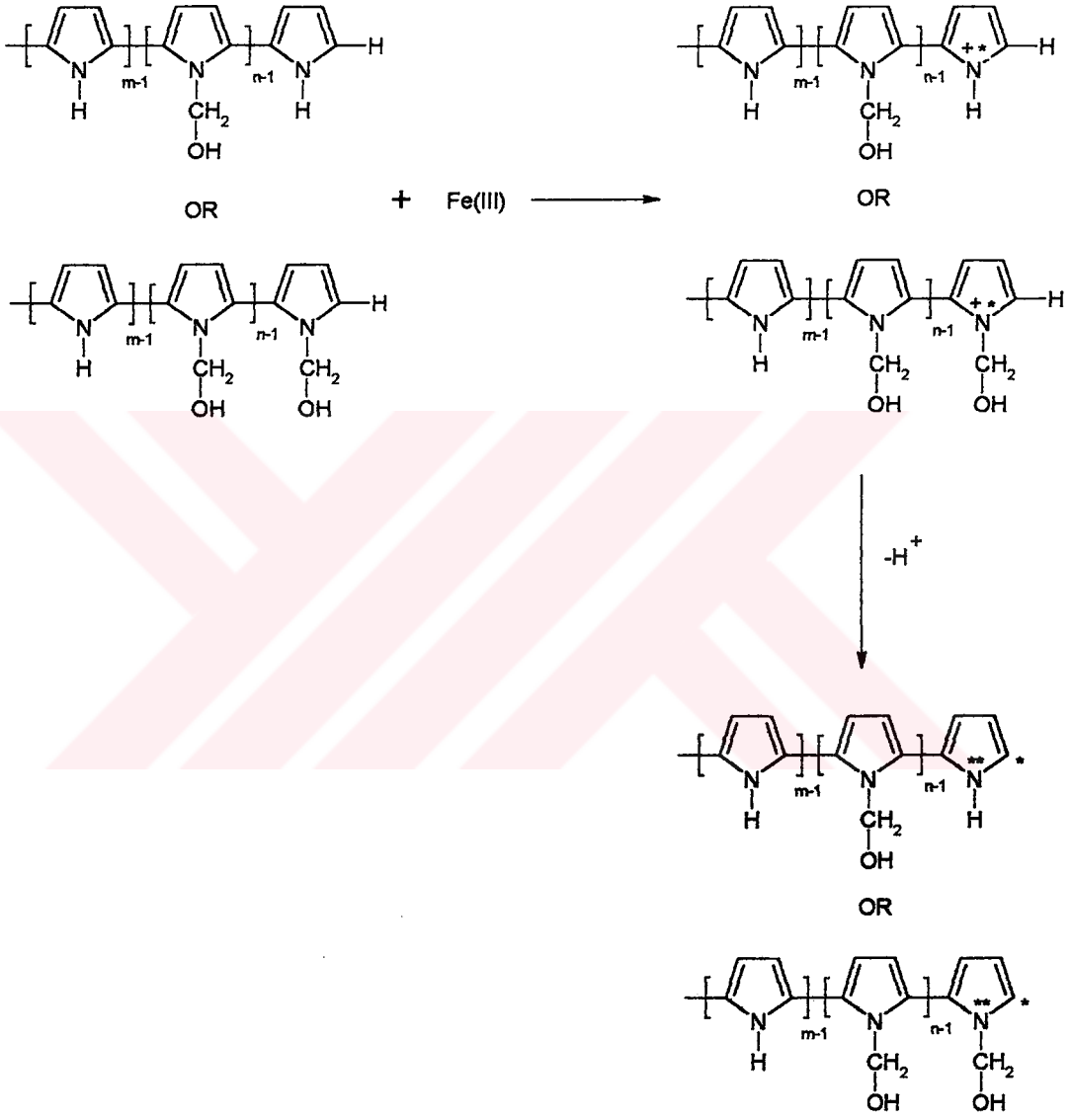
Polymerization in solution proceeds via oxidation of pyrrole by Fe(III) to produce radical that dimerize with expulsion of protons. The second mechanistic possibility in the inititation step is the proton loss of the radical cation to form radical that attacks another pyrrole molecule and polypyrrole chain continous to grow as long as pyrrole and Fe(III) are available. In the presence of N-methylol pyrrole, Fe(III) also attacks N-methylol pyrrole and produces radical. Oxidation of pyrrole and N-methylol pyrrole by Fe(III) starts simultaneously and copolymer probably forms by combination reaction between growing polypyrrole and N-methylol pyrrole radicals.(Scheme 4.4)

Initiation:

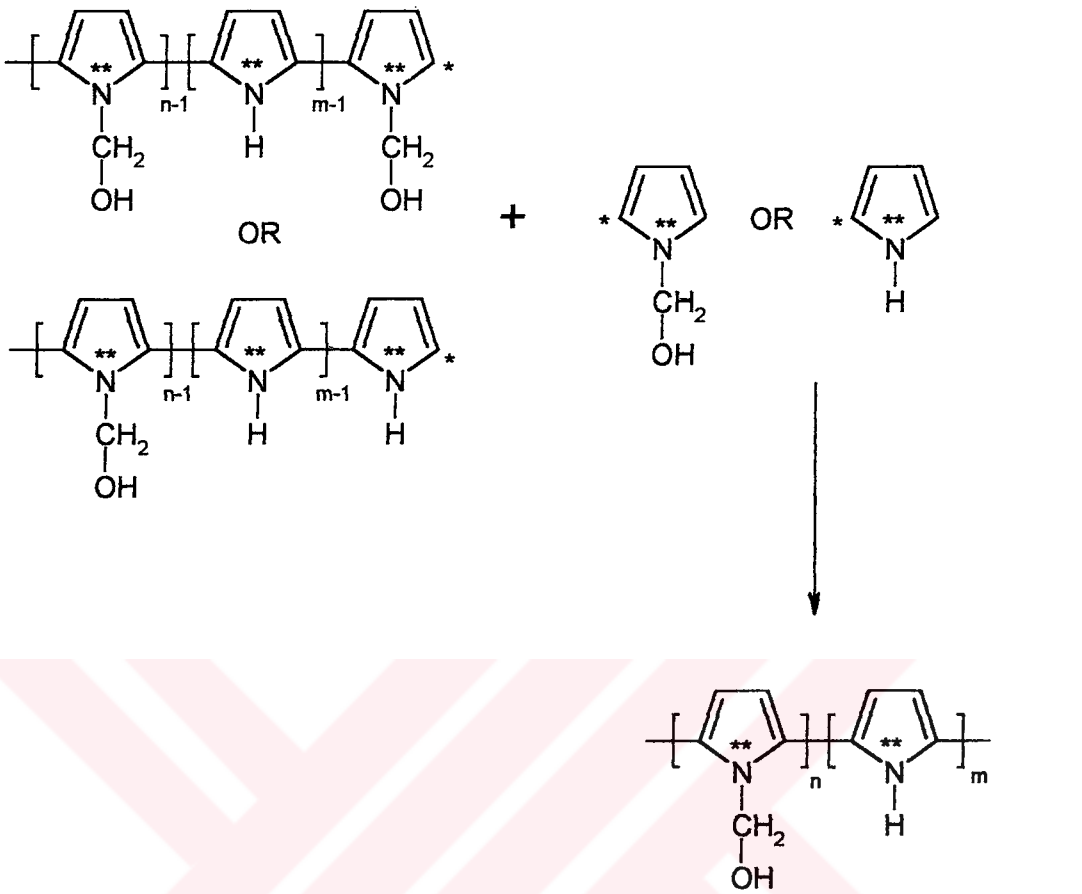




Propogation:



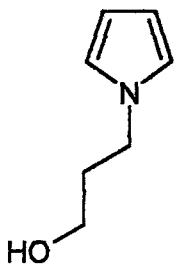
Termination:



(4.4)

4.3 1-(3-HYDROXYPROPYL)PYRROLE

Scheme 2.5 shows the structure of 1-(3-hydroxypropyl)pyrrole or N-propylol pyrrole



(4.5)

FTIR and ^{1}H-NMR spectra of 1-(3-hydroxypropyl)pyrrole is shown below.The O-H streching vibration band easily can be seen from the spectrum around 3390 cm^{-1} region. Aromatic C-H strechting vibration bands are around the region 3110 cm^{-1}. C-O streching vibration band which indicates primary alcohol is around 1055 cm^{-1} .

C=N vibraiton band is around 1542 cm^{-1} which is a proof of pyrrole ring in the structure.

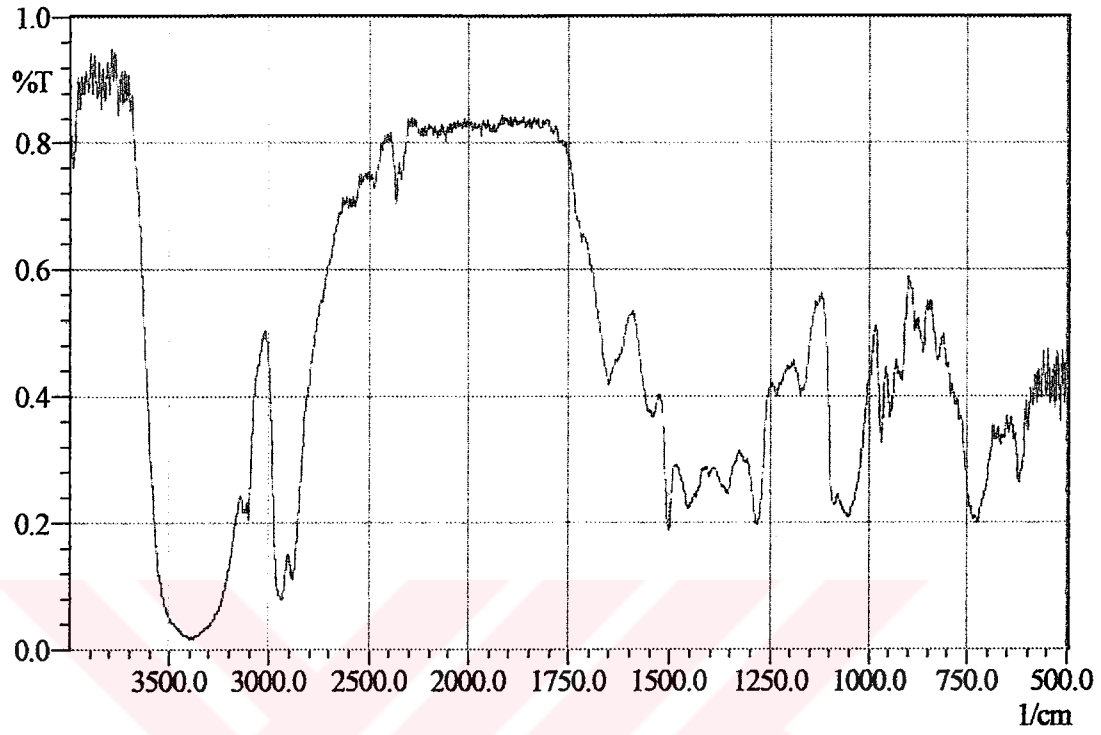
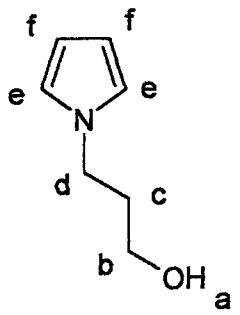


Figure 4.5: FTIR spectrum of 1-(3-hydroxypropyl)pyrrole.

Below, the proton NMR spectrum of 1-(3-hydroxypropyl)pyrrole is shown below, Scheme 4.6 indicates the protons in the spectrum



(4.6)

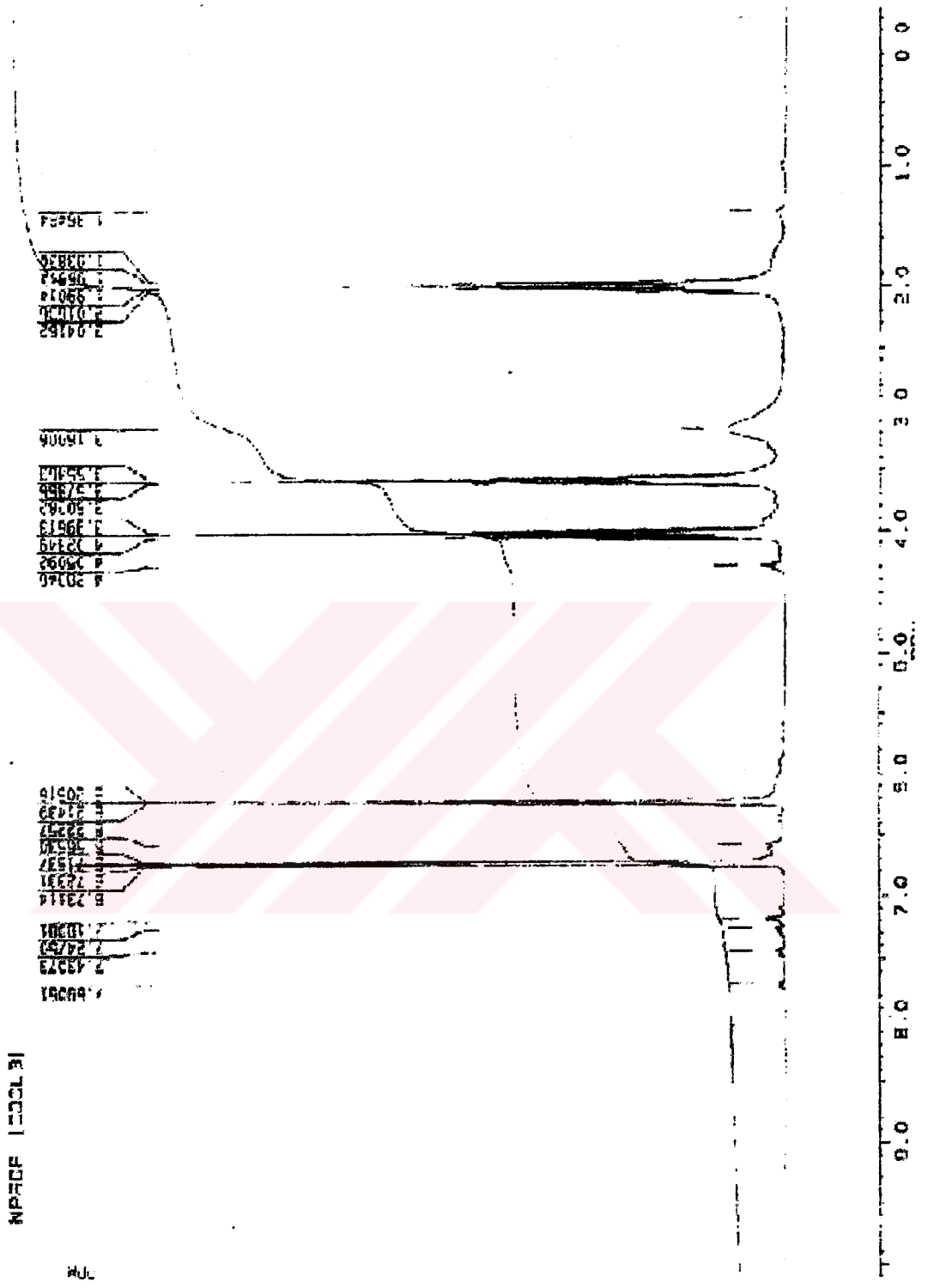


Figure 4.6: ^{1}H-NMR spectrum of 1-(3-hydroxypropyl)pyrrole. The spectrum obtained on 250 MHz device and the solvent was $CDCl_3$.

4.4 1-(3-HYDROXYPROPYL)PYRROLE AND PYRROLE COPOLYMERS

1-(3-hydroxypropyl)pyrrole was polymerized chemically with the use of $FeCl_3$ oxidant. FTIR spectrum of the copolymer was obtained and the effect of pyrrole on the conductivity, solubility was investigated. The results are listed below in table III: (conductivities and solubility data)

According to the FTIR spectrum of 1-(3-hydroxypropyl)pyrrole-pyrrole copolymer, there is a band around 3400 cm^{-1} region can be marked as O-H streching vibraiton. And also the band at 1030 cm^{-1} can be refered as C-O streching vibration. The bands which are 1386 cm^{-1}, 1421 cm^{-1}, 1458 cm^{-1}, and 1543cm^{-1} can be indicated as the results of vibrations of the pyrrole ring.

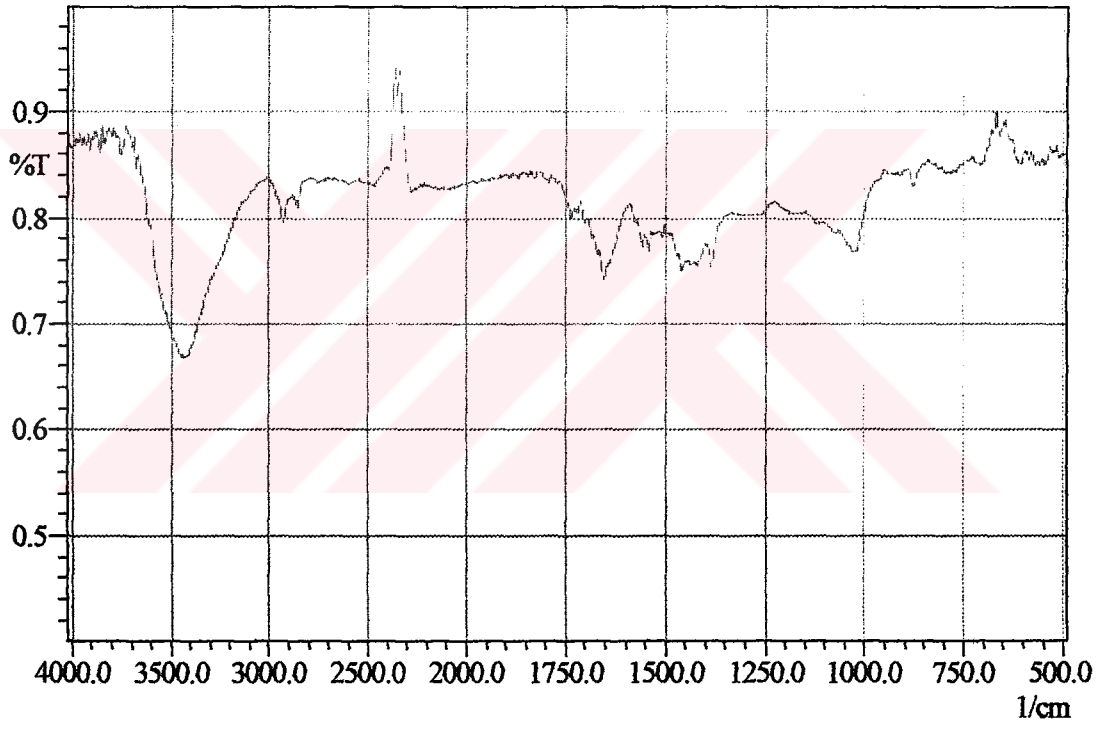


Figure 4.7: FTIR spectrum of 1-(3-hydroxypropyl)pyrrole-pyrrole copolymer

4.4.1 Role of Pyrrole Concentration.

Table 4.2: Conductivities, solubility properties of 1-(3-hydroxypropyl)pyrrole and pyrrole copolymers

Sample	[Py]	[NproP]	[Fe(III)]	Cond. (S/cm)	Solubility in DMSO
1	0,02	0,02	0,04	No precipitate	----------
2	0,06	0,02	0,08	$2x10^{-4}$	insoluble
3	0,1	0,02	0,12	$3x10^{-3}$	insoluble
4	0,2	0,02	0,22	17,9	insoluble

[Py]: indicates pyrrole concentration, [NproP] is the 1-(3-hydroxypropyl)pyrrole concentration and [Fe(III)] is the $FeCl_3$ concentration.

The effect of pyrrole concentration on the conductivities, solubility properties was researched in this study. This was done by keeping the 1-(3-hydroxypropyl)pyrrole concentration constant and varying the pyrrole concentration.

As it is seen in Table 6, with the increase of pyrrole concentration, the conductivities increases (see figure 4.8) . Because as afformentioned in section 4.2 inclusion of more pyrrole to the polymer backbone increases the stiffness and the rigidity of the polymer chain. As far as it is known from the theory, planarity , stiffness and rigidity increases the conductivity. In contrast, inclusion of more 1-(3-hydroxypropyl)pyrrole to the polymer backbone decreases the conductivity, this situation can be explained as the lack of planarity and the rigidity of the polymer backbone because of the bulky group which is attached to the pyrrole ring.

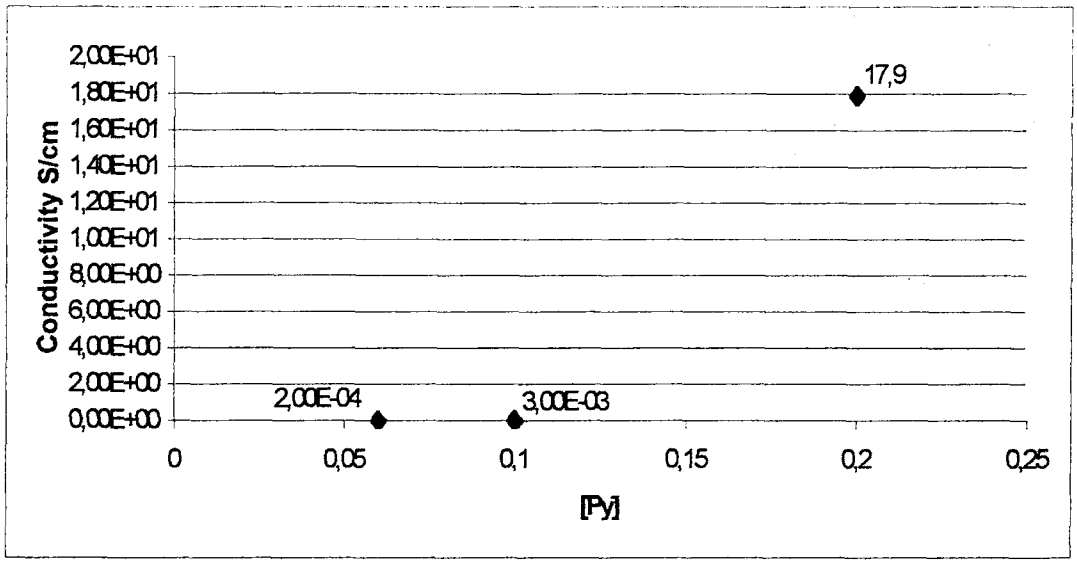


Figure 4.8: Grafic of pyrrole concentration versus conductivity.

4.4.2 SOLUBILITY

The synthesis of 1-(3-hydroxypropyl)pyrrole and pyrrole copolymers of a parent conjugated polypyrrole with more desirable properties was tried. But these copolymers has not got sufficient conductivities and solubilities.

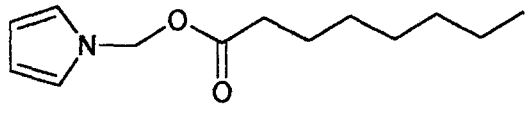
The reasons of beeing unsoluble are the cross-linkings, hydrogen bondings which is explained in section 4.2 for N-methylol pyrrole derivative, and polar interactions between the polymeric chains. It is understood that the alkyl spacer between the –OH group and pyrrole ring does not provide solubility.

4.4.3 MECHANISM

The mechanism is the as same as the mechaism shown in section 4.1, except monomer difference.

4.5 1-H-PYRROLYLMETHYL OCTANOATE

Scheme 4.7 demonstrates the structure of 1-H-pyrrolylmethyl octanoate



(4.7)

FTIR and ^{1}H-NMR spectra of 1-H-pyrrolylmethyl octanoate is shown below.

An intensive C-H streching band around 2937 cm^{-1} and C=O streching band around 1747 cm^{-1} improves the octanoat ester. The bands at 1381, 1415, 1456, 1496, and 1560 cm^{-1} may be attributed to the ring vibrations of the pyrrole. And 1087 cm^{-1} might be marked as N-H bending vibrations, 1153 cm^{-1} should be the C-O streching vibration of the ester.

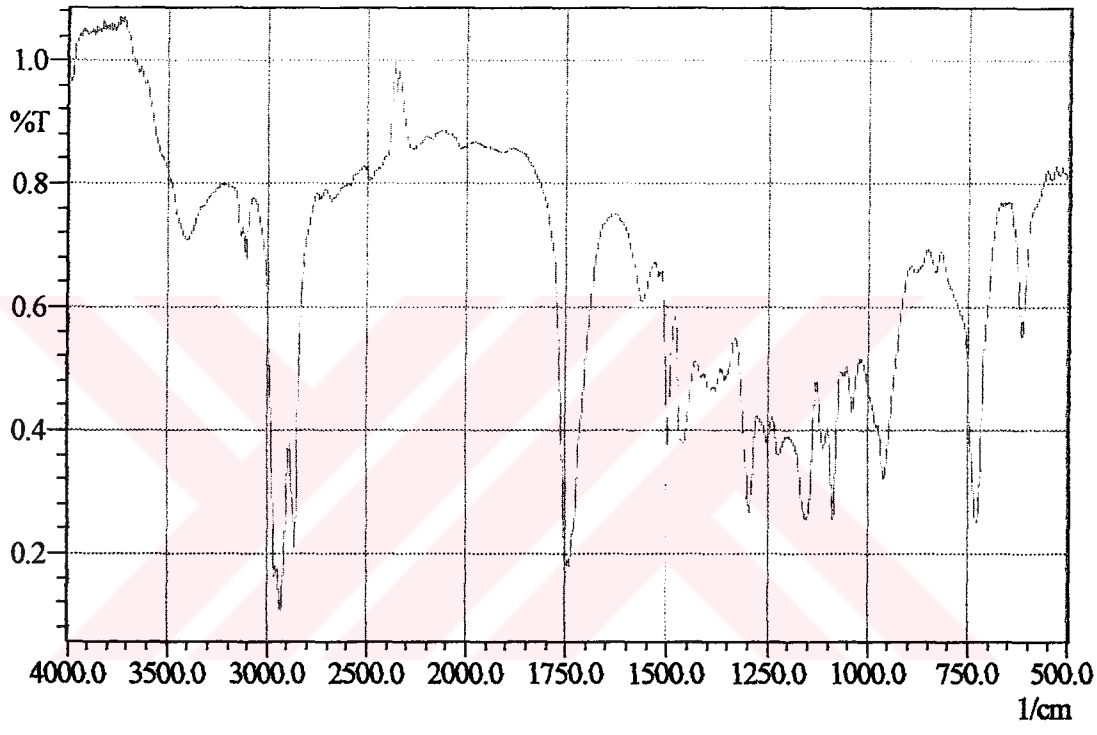
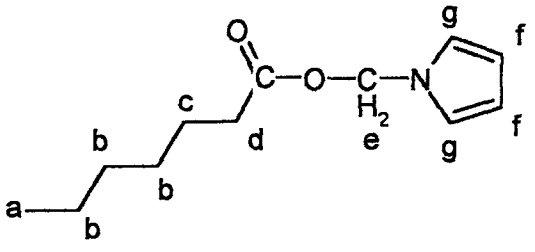


Figure 4.9 : The FTIR spectrum of 1-H-pyrrolylmethyl octanoate

The protons are marked on the ^{1}H-NMR spectrum and on the molecular structure of 1-H-pyrrolylmethyl octanoate at scheme



(4.8)

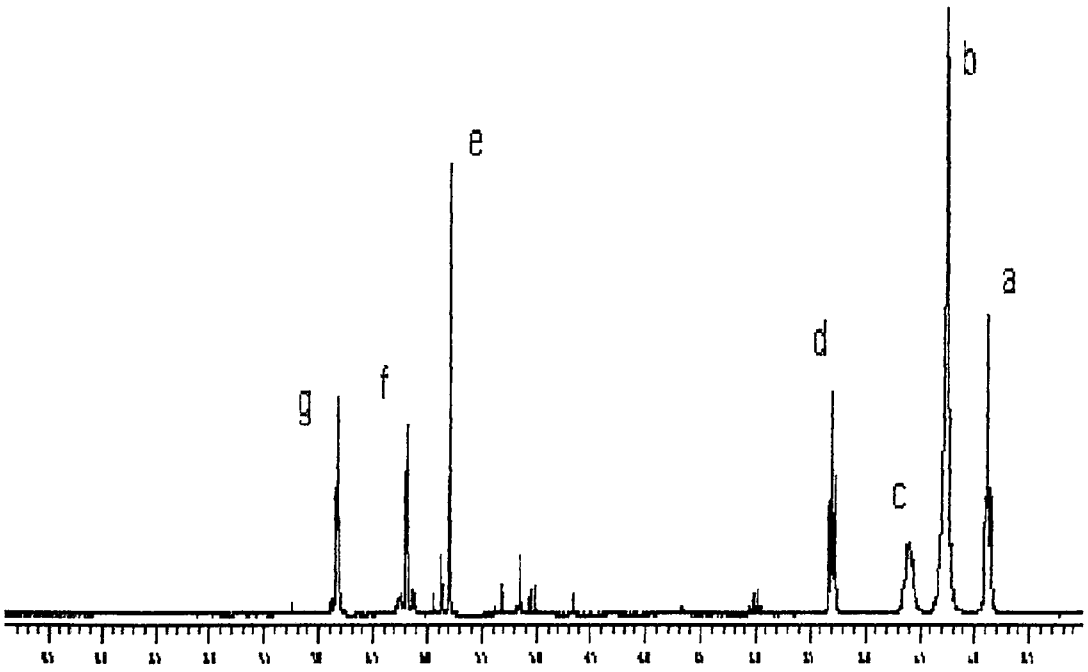


Figure 4.10: ^{1}H-NMR spectra of 1-H-pyrrolylmethyl octanoate

4.6 1-H-PYRROLYLMETHYL OCTANOATE AND PYRROLE COPOLYMERS

With the use of ceric (IV) ammonium nitrate 1-H-pyrrolylmethyl octanoate and pyrrole was oxidatively polymerized The effect of various CAN and pyrrole concentrations on the conductivity and solubility was examined. The results are listed in Table III. Also FTIR spectrum of the copolymer is shown below.

When spectrum of the copolymer is interpeted the band (1383 cm^{-1}) can be seen which is the result of NO_3^- and copolymer interactions. In the spectrum the lack of C=O streching vibration band might be due to the complex formation of pyrrole-Ce(III)- 1-H-pyrrolylmethyl octanoate

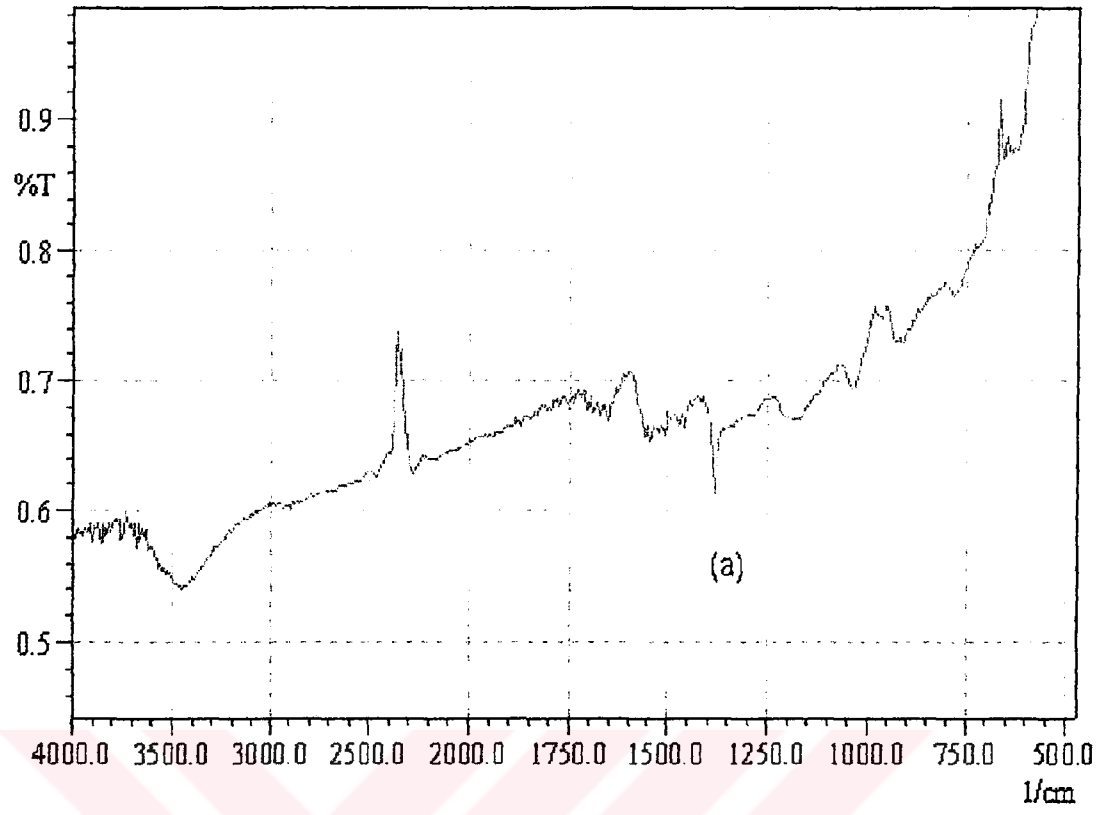


Figure 4.11: FTIR spectrum of 1-H-pyrrolylmethyl octanoate and pyrrole copolymer

Table 4.3 : Conductivity and solubility data of 1-H-pyrrolylmethyl octanoate and pyrrole copolymers. [OctaNp] is 1-H-pyrrolylmethyl octanoate concentration.

	[Py]	[OctaNp]	[CAN]	Cond.(s/cm)	Solubility in DMF
Sample 1	0,225	0,045	0,270	10^{-4}	Slightly Slb
Sample 2	0,315	0,045	0,360	$6x10^{-5}$	Slightly Slb
Sample 3	0,450	0,045	0,495	$1,7x10^{-6}$	Slightly Slb

4.6.1 Role of Pyrrole and CAN Concentration

Increase in pyrrole concentration with CAN decreases the conductivity (See figure 4.12). Although, pyrrole concentration was increased the conductivites was degreased see figure 4.13). Hence, it is seen that changing pyrrole concentration is not the main effect in solubility and conductivity for tis copolymers according to these serial experimental results. It can be made such a commentary that increase in CAN consentration leads to emerge short polymer chains which are not satisfactorily conductive but slightly soluble. Short polymer chains and large deviation from the planarity of polymer structure due to the bulky group which is attached on the nitrogen of pyrrole decrases the conductivity drastically. If it is deduced that 1-H-pyrrolylmethyl octanoate oxidation potential is les then pyrrole, increasing the molarity of oxidant will give chance to 1-H-pyrrolylmethyl octanoate monomers to include into the polymer structure as many as pyrroles. This should be an additional effect on the solubility.

The solubilities are slightly this means there are insoluble parts in the structure which are mostly related to the cross-linkings. Beacuse increased CAN concentrations can lead to progress polymerization from β,β' positions of the pyrrole ring. And the effect of rigidity and polar – polar interactions of polypyrrole can be still a explanation for insoluble parts.

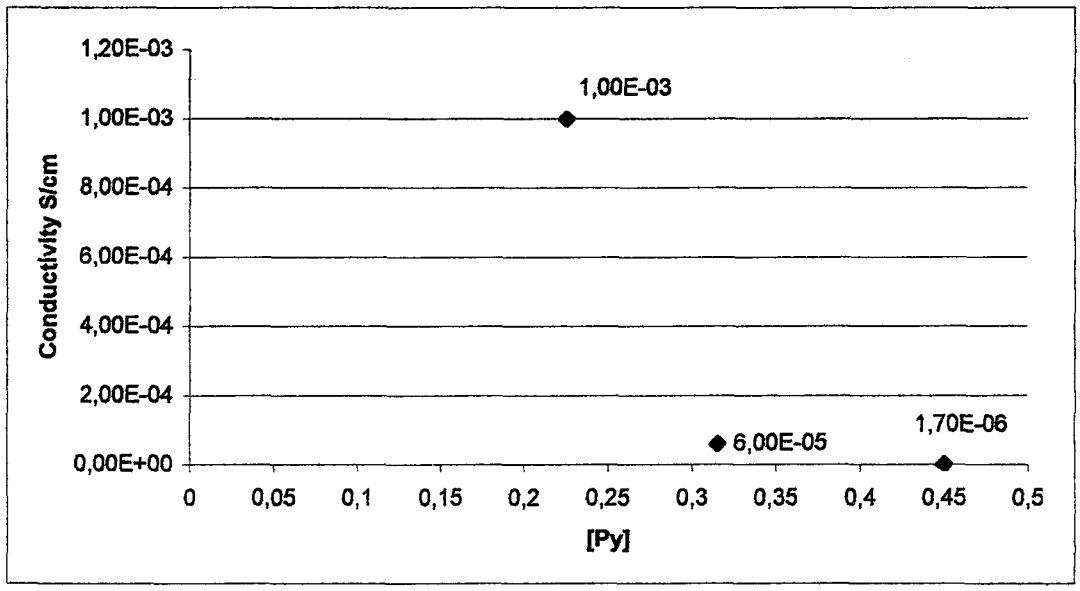


Figure 4.12: Pyrrole concentration versus conductivity

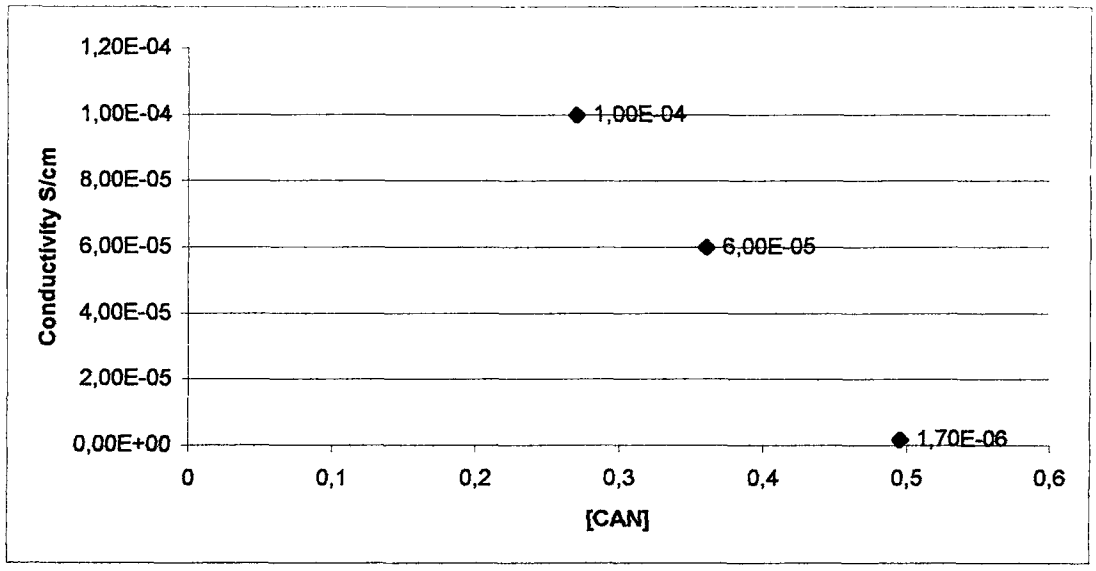


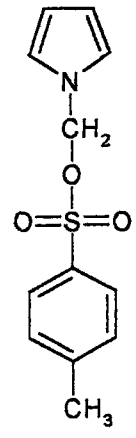
Figure 4.13: CAN concentariton versus conductivity.

4.6.2 Mechanism

The mechanism is the as same as the mechaism shown in section 4.1, except monomer difference.

4.7 *1H* –1-PYRROLYLMETHYL 4-METHYL-1-BENZENE SULFONATE

In scheme 4.9 The structure of 1*H*-1-pyrrolylmethyl 4-methyl-1-benzenesulfonate is demonstrated.



(4.9)

FTIR and ^{1}H-NMR spectra of 1-H-pyrrolylmethyl octanoate is shown below.

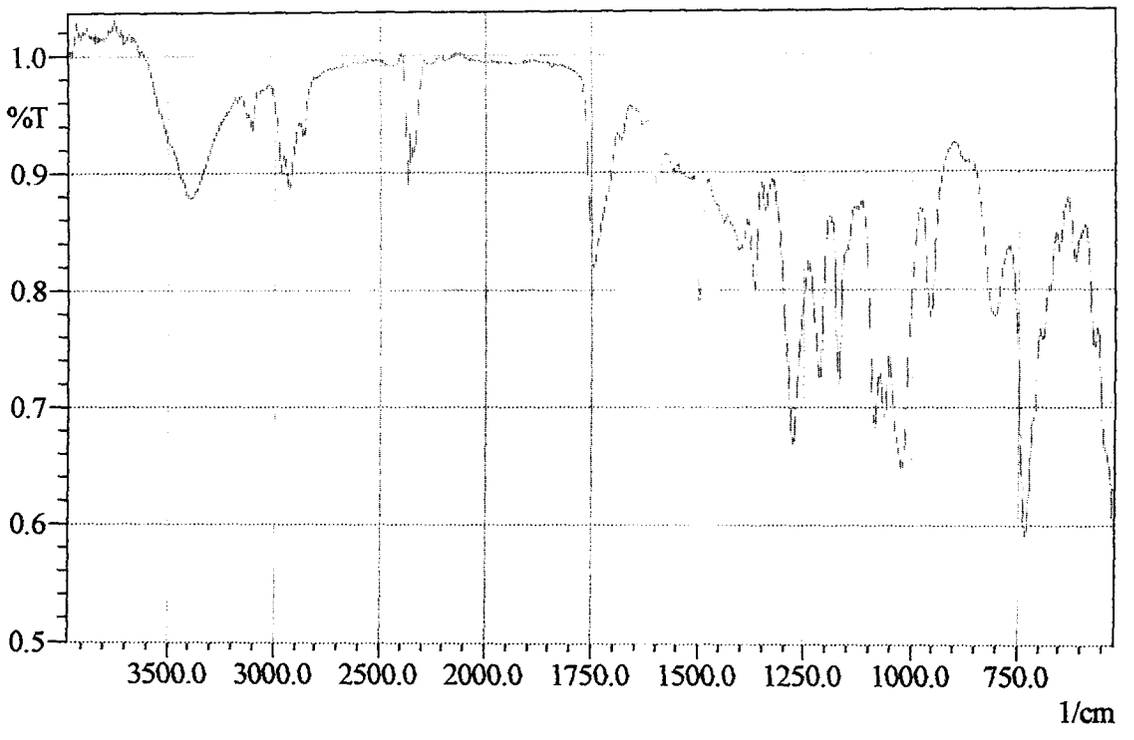


Figure 4.14: The FTIR spectrum of 1-H-pyrrolylmethyl octanoate

At the region 3100 cm^{-1} it can be easily recognized the aromacity, the C-H streching of aromatic structure. 1168 and 1367 cm^{-1} these two bands can improve SO_2 vibrations.

4.8 *1H* –1-PYRROLYLMETHYL 4-METHYL-1-BENZENE SULFONATE AND PYRROLE COPOLYMERS

1*H*-1-pyrrolylmethyl 4-methyl-1-benzenesulfonate, and pyrrole was chemically polymerized by means of CAN. The effect of various CAN and pyrrole concentrations on the conductivity and solubility was investigated. The results are listed in Table III. Also FTIR spectrum of the copolymer is shown below.

The FTIR spectrum of copolymer indicates Ce(III) and NO_3^- ligands incorporated into the polymer. (fig 4.6 , (a) and (b))

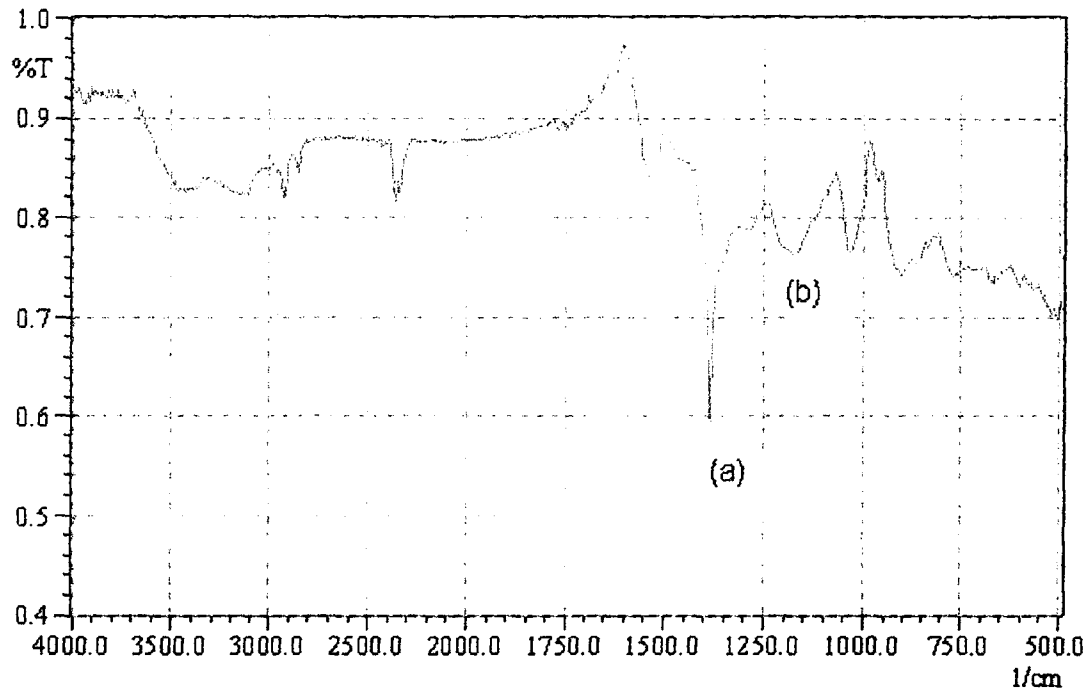


Figure 4.15:FTIR Spectra of Polypyrrole–1*H*-1-pyrrolylmethyl 4-methyl-1-benzene sulfonate copolymer

Table 4.4: Conductivities and solubility data of 1*H*-1-pyrrolylmethyl 4-methyl-1-benzenesulfonate, and pyrrole copolymers 1*H*-1-pyrrolylmethyl 4-methyl-1-benzenesulfonate concentration is constant and 0.02 M.s

Sample	[Py]	[CAN]	Con.(S/cm)	DMF	DMSO	Yield
1	0,05	0,07	$4x10^{-3}$	sl soluble	sl soluble	% 9.4
2	0,1	0,12	6	soluble	soluble	%14
3	0,2	0,22	10^{-2}	soluble	soluble	%47
4	0,1	0,06	6	insoluble	insoluble	
5	0,1	0,24	$5x10^{-5}$	soluble	soluble	

4.8.1 Role of Pyrrole and CAN concentration

The effect of pyrrole concentration on the yields, conductivity, and solubility was examined for different concentrations of pyrrole (figure 16), conductivity values of precipitates increased by increasing pyrrole concentration up to 0,1 M. After which value they decrease (Figure 4.16).

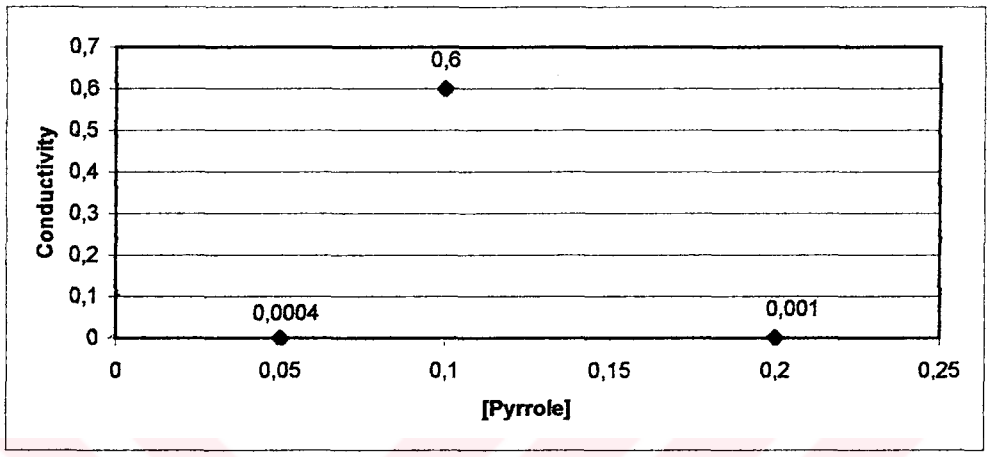


Figure 4.16: The effect of pyrrole concentration on the conductivity

Experimental samples 2, and 4 show that, as it is shown in table II. Sample 2 has got more solubility compared to sample 4. Here, the different CAN concentrations affects the solubilities, less concentrated CAN creates long copolymer backbone, and actually, the oxidation potential varies with the monomer, in agreement with the substituents, and thus the stereoregularity varies. We can think that the oxidation potential of pyrrole is may be less than the oxidation potential of 1*H*-1-pyrrolylmethyl 4-methyl-1-benzenesulfonate, so in less concentrated CAN solutions pyrroles can consume CAN much more than 1-pyrrolylmethyl 4-methyl-1-benzenesulfonate. Hence, the monomer which provides solubility to the copolymer can not join into the structure easily.

Conductivities of samples 1,and 3 are affected significantly by CAN concentration. The relationship between conductivity and CAN concentration is given in figure 17. This also supports the idea that the samples which were obtained by high CAN concentrations, includes more 1*H*-1-pyrrolylmethyl 4-methyl-1-benzenesulfonate monomers in the copolymer chain.

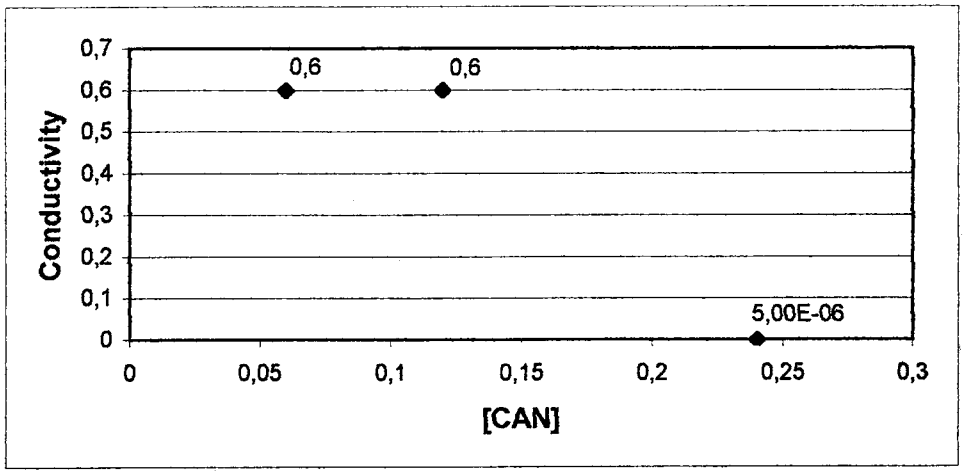


Figure 4.17: The relationship between conductivity and CAN concentration

The relationship between the CAN and pyrrole concentration and the yield of samples 1, 2, and 3 is given in figure 4.18, and 4.19.

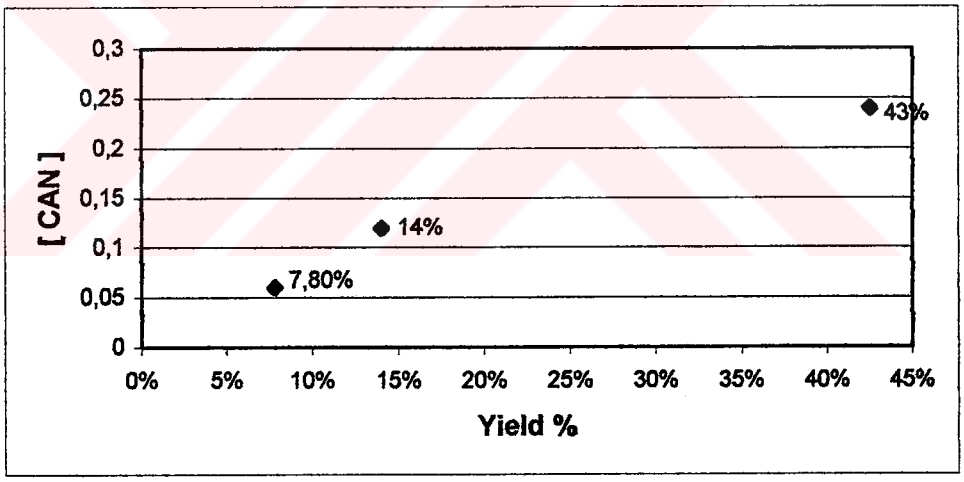


Figure 4.18: The relationship between the CAN and the yields

Yields increase by increasing pyrrole and CAN concentrations, respectively. See figures 4.18 and 4.19. This shows that, despite high pyrrole concentrations, the possibility of 1-pyrrolylmethyl 4-methyl-1-benzenesulfonate inclusion into the copolymer chain, increases by means of CAN quantity in the reaction mixture.

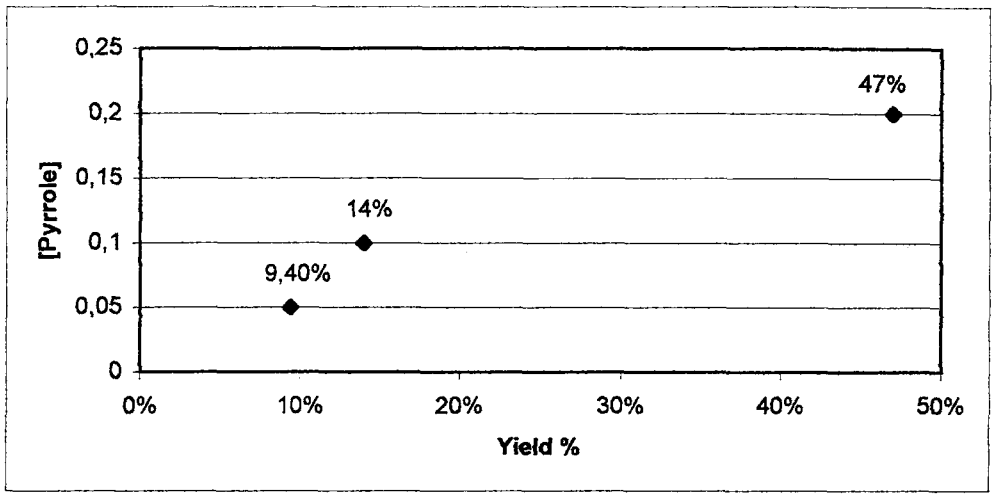


Figure 4.19: The relationship between the pyrrole concentration and the yield

From these results, we can understand that CAN concentration directly effects the solubility and conductivity much more than the pyrrole concentration. High concentarions of CAN results in more soluble and generally less conductive polymers.

4.8.2 UV-Visible results of 1-pyrrolylmethyl 4-methyl-1-benzenesulfonate – CAN – Pyrrole mixture.

The copolymerization reaction of pyrrole and 1-pyrrolylmethyl 4-methyl-1-benzenesulfonate with CAN was investigated by following the absorption of soluble oxidized product. Example of such absorbances are given in the previous figures.

The shift in the absorbance of 1-pyrrolylmethyl 4-methyl-1-benzenesulfonate (PyBS) figure 4.20, compared against that of the 1-pyrrolylmethyl 4-methyl-1-benzenesulfonate – CAN mixture figure 4.21, indicates the interaction of PyBs with Ce(IV). Because the the PyBS, pyrrole, and CAN alone do not have any absorbance at 330 nm and 415 nm. See figures 4.20,4.21,4.23,4.24. The small peak at 580 nm may be attributed to the oligomeric products of the reaction see figure 4.24.

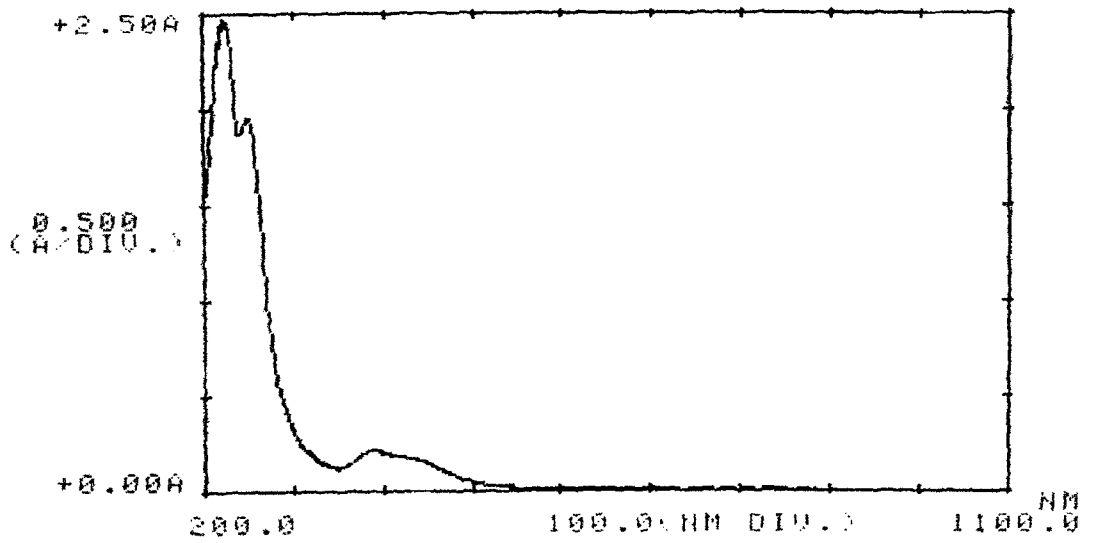


Figure 4.20: 1-pyrrolymethyl 4-methyl-1-benzenesulfonate in DMF alone.

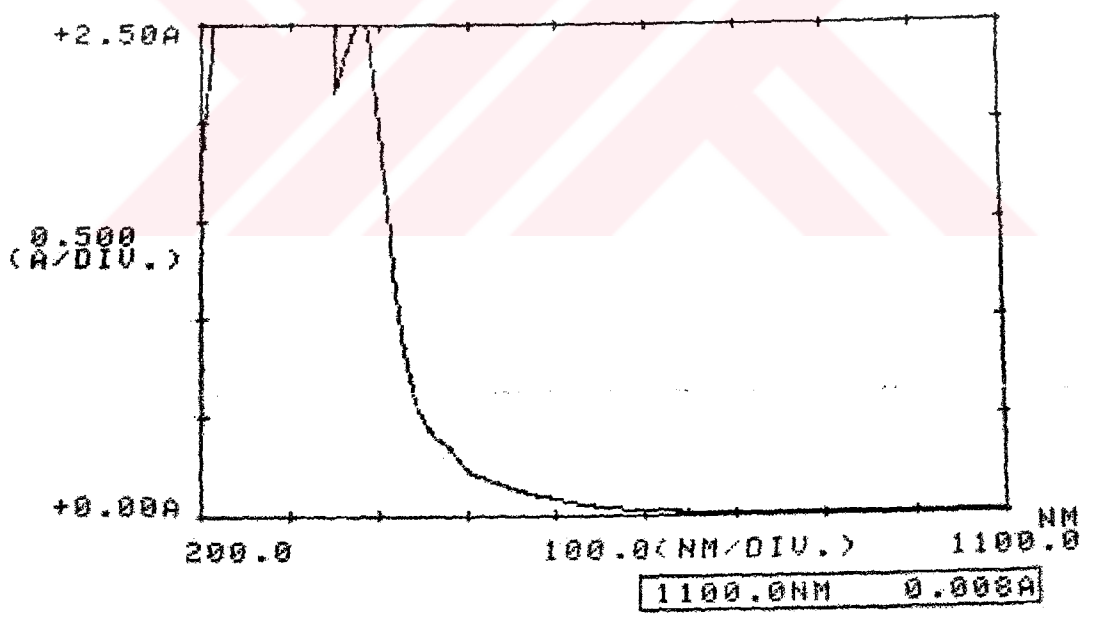


Figure 4.21: 1-pyrrolymethyl 4-methyl-1-benzenesulfonate and Ce(IV) in DMF.

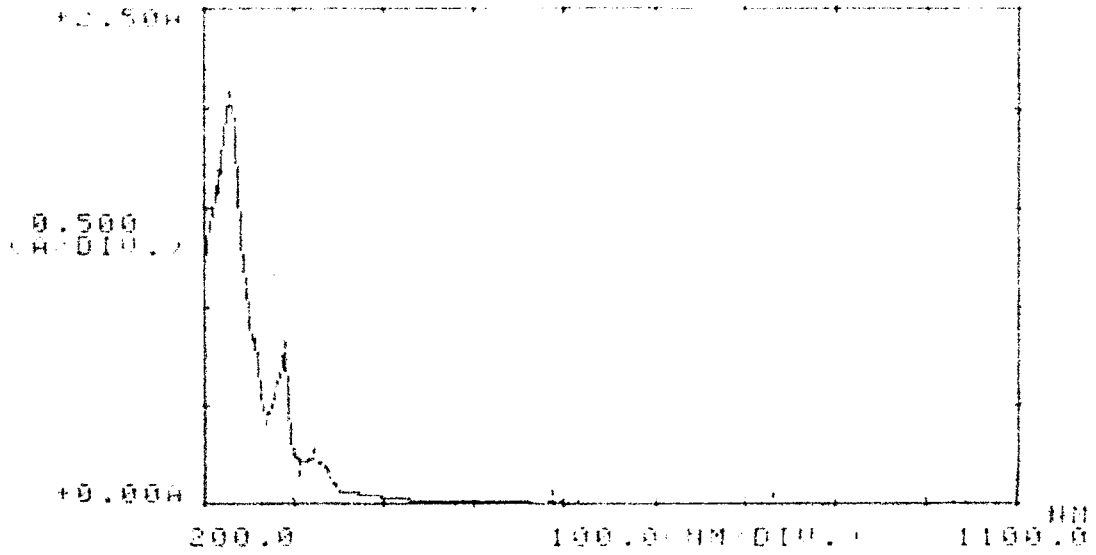


Figure 4.22: Ce(IV) in DMF

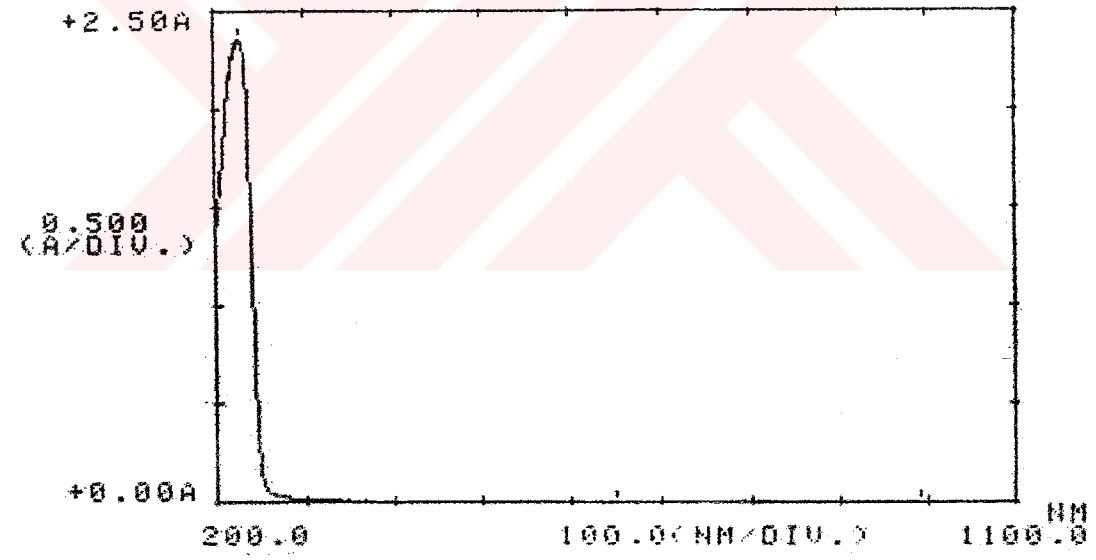


Figure 4.23: Pyrrole in DMF.

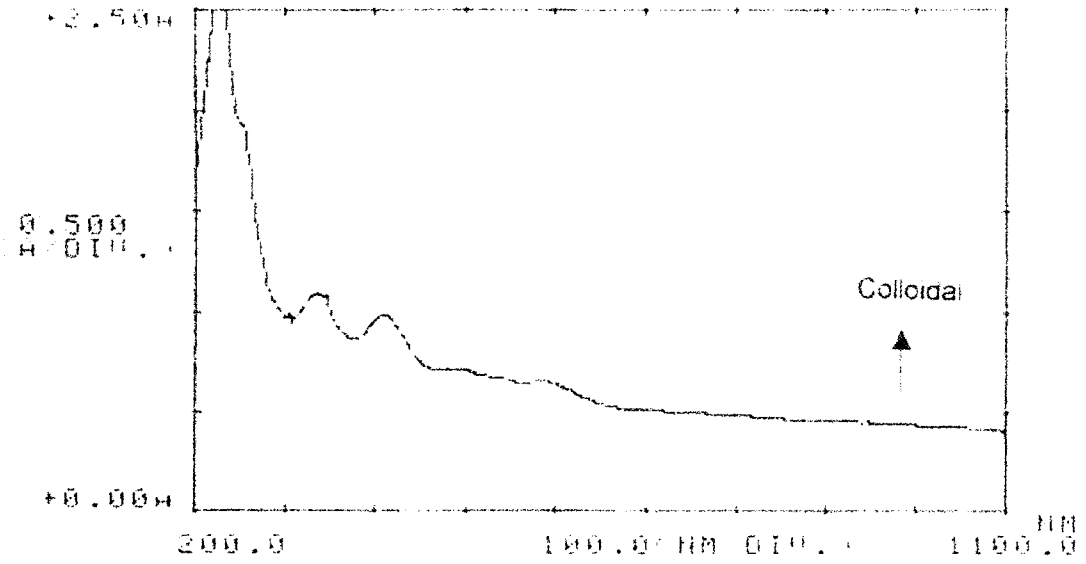


Figure 4.24: 1-pyrrolymethyl 4-methyl-1-benzenesulfonate, pyrrole and Ce(IV) mixture in DMF.

4.8.3 ^{1}H-NMR Spectrum of 1-pyrrolylmethyl 4-methyl-1-benzene sulfonate and pyrrole copolymer

Proton NMR of sample was able to obtain, the spectrum is shown below. Where it has got peaks 7.28, 7.08, 6.8 ppm indicates the benzene structure and β,β protons of pyrrole. The peak at 5.76 ppm indicates the CH_2 group which attached to N of the pyrrole ring and O of the sulfo ester.

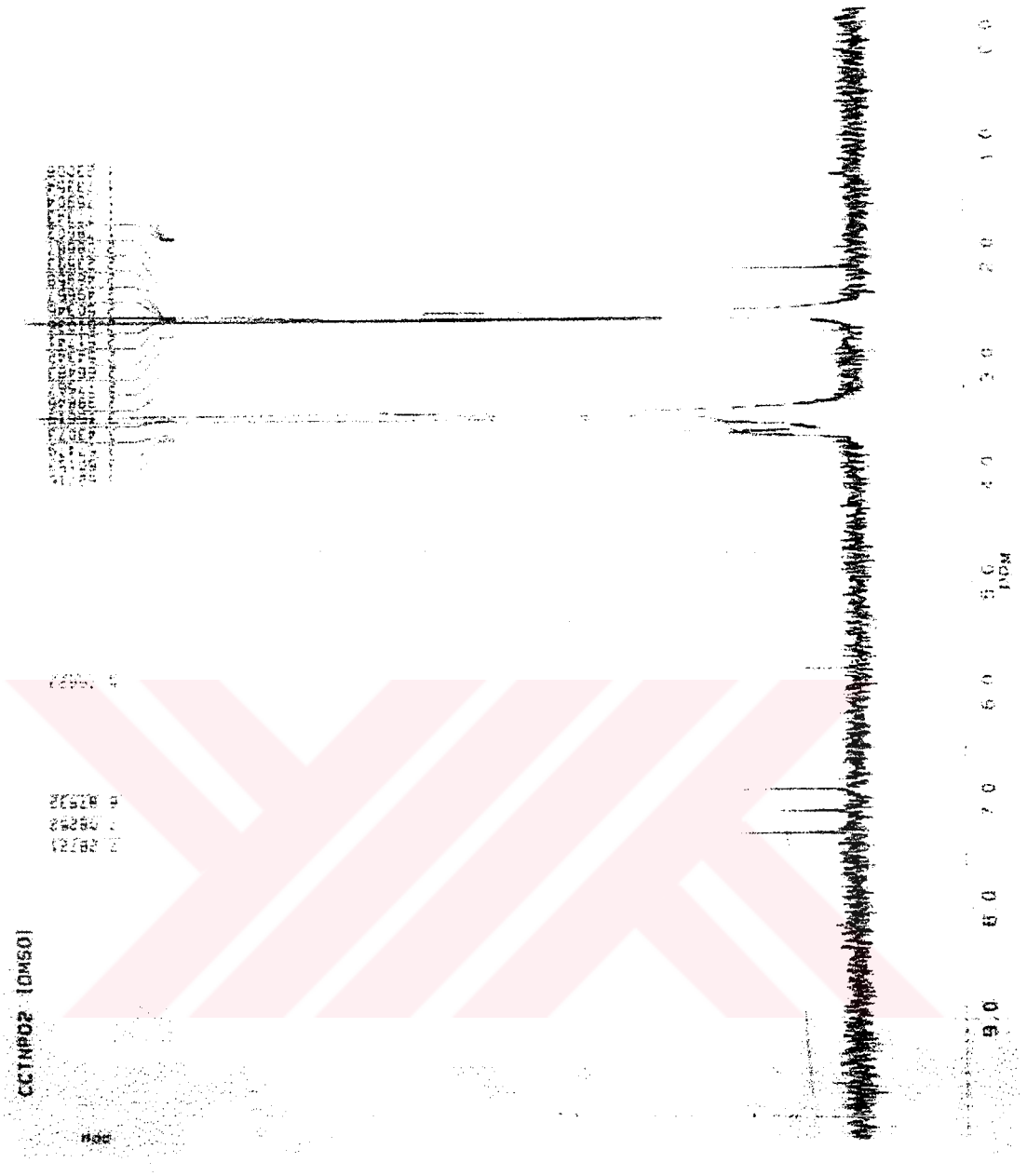


Figure 4.25: Proton NMR spectrum of the soluble copolymer.

4.8.4 Mechanism

The mechanism is the as same as the mechaism shown in section 4.1, except monomer difference.

5. CONCLUSION

N-substituted pyrroles and pyrrole copolymers prepared chemically by Fe(III) or Ce(IV) in acetonitrile due to the monomer structures, which are N-methylolpyrrole and pyrrole copolymer, 1-(3-hydroxypropyl)pyrrole-pyrrole copolymer, 1-H-pyrrolylmethyl octanoate and pyrrole, and 1*H*-1-pyrrolylmethyl 4-methyl-1-benzenesulfonate, pyrrole. These copolymers exhibit differences in their conductivity and solubility properties.

The results presented in this study show that the solubilities and conductivities of the products depend on the pyrrole derivated monomers concentration/ oxidant concentration /pyrrole concentration ratio.

Consequently, if the 1*H*-1-pyrrolylmethyl 4-methyl-1-benzenesulfonate / CAN / Pyrrole ratio is suitably selected, fairly conductive and soluble 1*H*-1-pyrrolylmethyl 4-methyl-1-benzenesulfonate and pyrrole copolymers could be synthesized. This means that one can overcome the solubility problem of PPy and use conventional methods for characterization. By the advantage of obtaining soluble polypyrrole- 1*H*-1-pyrrolylmethyl 4-methyl-1-benzenesulfonate copolymers, methods such as UV-visible spectroscopy, ^{1}H_NMR spectroscopy gives the possibility of investigation the formation and the structure of copolymers in detail. Besides, producing soluble PPy copolymers will overcome the application difficulties resulting from the insolubility of PPy and open new applicaiton areas such as surface coatings.

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I was born in 1977 in Bolu. I had graduated from İstanbul Suadiye Lisesi in 1995. İn 1996 I have begun university education in Chemistry departmen in Science and Literarure Faculty of Uludağ University. I have graduated from there in the year 2000. At the same year, ı have started Masters of Science education in İstanbul Technical University in Chemistry department. İn the 2001 I became an assistant at the same department.