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Modification of Conductive Properties and Processability of Polyparaphenylene, Polypyrrole and Polyaniline

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Declaration: Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for any degree or examination.

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ABSTRACT

In the last 25 years, studies of the properties of electrically conductive polymers (CP) have made a significant progress. As a result, it can be concluded that the problems intrinsic for the single conductive polymers can be solved by means of the composites and blends. The formation of the blends and composites from CP essentially extends the possibilities for the development of different electronic devices based on electrically conductive polymers.

This study focuses on the modification of conductive properties and processability of polyparaphenylene (PPP), polypyrrole (PPy) and polyaniline (PANI) selected from a large amount of known CP. Polyparaphenylene has attracted attention for its high thermal stability, ability to obtain high electrical conductivity both n- and p-types upon doping as well as for its promising electron structure. In addition, electrical conductivity and electronic structure can be controlled in a relatively wide range, using different doping as well as preparation technologies. On the other hand, the processing ability of PPP in the thin film mode is quite complicated. Thin film processability is a well-known advantage of polypyrrole and polyaniline. However, the stability of structural and conductive properties of these two polymers is much lower than that of PPP. The combining of various CP in the multilayer structures allows one to avoid the limitations typical of the individual use of these materials.

PPP was prepared according to the procedure of Kovacic by the oxidative cationic polymerization of benzene. This method makes a polymer particularly suitable for producing highly conductive materials by doping.

The syntheses of PPy and PANI by the *in-situ* doping method resulted in a maximizing yield of fine powdered products. The sulfonic acids and their sodium salt used as dopants during in-situ polymerization provide PPy and PANI with sufficiently high conductivity. Additionally, dodecylbenzene sulfonic ion imparts essential solubility in organic solvents to synthesized polymers. In pressed form, the synthesized polymers were applied to prepare the PPy-PANI bilayers using electrochemical processing. All the investigated bilayer structures showed strong linear current-voltage characteristics and ohmic contact formation between the pellets and films. In addition, electrical resistance between the layers was relatively low, allowing for PANI and PPy to be used as flexible conductive intermediate layers for hybrid organic-inorganic devices.

For polyparaphenylene, a high temperature doping method was developed to enable the preparation of the conductive polymer with controlled electrical conductivity and high stability. From the kinetics investigations of halogen doping of PPP, it can be concluded that the high temperature doping of PPP is primarily initiated by the thermally activated incorporation process. The different energies of conductive defect formation were explained by the bipolaron (dications with formation energy 0.8-0.9 eV) and polaron (radical cations with formation energy 1.5-1.9 eV) dominating defects formation. Based on the experimental investigations, an optimal technology for halogen doped PPP structures preparation was developed, combining preliminary thermal treatment of samples at 520^{0}C with a two-step doping at the same temperature.

The PPP structures obtained by the proposed technology have high conductivity and stable mechanical properties, which allow for the obtained structures to be used as electrodes for the electrochemical deposition of PPy films from an aqueous solution. The conductivity investigations confirm the high adhesion of PPy films to the PPP substrate.

PPP inclusions were used to prepare thin composite films of electrochemically polymerized PPy onto light transparent indium/tin oxide (ITO) and tin oxide (SnO_2) coated glass substrates from aqueous-acetonitrile media, containing suspension of high temperature doped PPP. Based on the comparison of galvanostatic characterization of the electrodeposition process of composite films and electrodeposition characteristics of individual PPy films onto the same substrates in comparable conditions, it can be concluded that PPP inclusions contribute to the electrodeposition process.

A light transparent substrate enables one to obtain the light absorption spectra of the prepared thin films. The optical investigations, providing the temperature-dependent conductivity investigations with subsequent Mott’s parameters calculations, additionally confirmed the nature of conductive defects formation in the obtained structures.

By the SEM image analysis of the obtained films, the influence of PPP inclusions on the morphology of composite films was shown. As a result of the film/ITO cross-sections studies, an improved adherence of composite films to the substrate layer was proved.

Finally, this study demonstrates that the combined method for the formation of multilayers and composite coatings, consisting of PPy as a film forming agent and PPP with high thermal and conductivity stability, enables one to avoid the low ability of PPP to processing and to extend the possibilities for the development of new electronic devices with stable electrical parameters.

KOKKUVÕTE

“Polüparafenüleeni, polüpürrooli ja polüaniliini elektriliste omaduste ja töödeldavuse uurimine kasutamiseks mitmekihilistes struktuurides ja komposiitidena.”

Viimasel aastakümnel teostatud elektrit juhtivate polümeermaterjalide uurimistulemuste alusel võib järeldada, et elektrit juhtivad polümeermaterjalid (EJP) on hõivamas olulist kohta traditsiooniliste elektronmaterjalide kõrval. Vaatamata küllaltki põhjalikele EJP füüsikaliste ja keemiliste omaduste uuringutele on siiski paljud probleemid, mis on omased eriti individuaalsetele materjalide, veel lahendamata. Tänaseks võib aga järeldada, et EJP kombineeritud kasutamine mitmekihilistes struktuurides annab võimaluse leida lahendusi mitmetele probleemidele ning laiendada oluliselt EJP kasutamisvõimalusi elektronseadiste komponentidena. Käesolev uurimistöö on pühendatud polüparafenüleeni, polüpürrooli ja polüaniliini elektriliste omaduste ja töödeldavuse uurimisele, eesmärgiga kasutada neid materjale mitmekihilistes struktuurides ja komposiitidena.

Polüparafenüleen on hõivamas olulist kohta teiste samalaadsete materjalide seas tänu märkimisväärsele füüsikaliste ja keemiliste omaduste stabiilsusele eriti kõrgendatud temperatuuridel. Samuti on elektrit juhtiva polüparafenüleeni valmistamise ja legeerimise tehnoloogia suhteliselt lihtne, mis võimaldab saada nii n- kui ka p-tüüpi elektrijuhtivusega materjali piisavalt kõrge elektrijuhtivusega. Käesolevas uurimistöös kasutati benseeni oksüdeeriva katioonse polümerisatsiooni teel valmistatud pulbrilist polüparafenüleeni. Selliselt sünteesitud polüparafenüleeni kasutamine mitmekihilistes struktuurides õhukeste kiledena on aga äärmiselt keeruline. Teisalt on aga suhteliselt lihtne valmistada õhukesi kilesid elektrokeemilise sünteesi abil polüpürroolist ja polüaniliinist. Nimetatud EJP elektriliste omaduste stabiilsus, eriti kõrgematel temperatuuridel, jääb aga kaugele maha polüparafenüleeni stabiilisusest. Polüpürrooli ja polüaniliini sünteesiti elektrokeemiliselt *in-situ* legeerides erinevaid sulfoonhappe soolasid kasutades. Saadud kiled olid hea elektrijuhtivusega, dodetsüülbenseensulfoonhappe soola kasutamine muutis saadud produktid ka lahustuvateks orgaanilistes lahustites. Polüpürrooli ja polüaniliini pulbrist pressitud tablettidele sadestati vastavalt elektrokeemiliselt polüaniliini ja polüpürrooli kiled. Saadud kahekihilistel struktuuridel olid lineaarsed volt-amper sõltuvused suhteliselt madala kihtidevahelise takistusega. Selliselt valmistatud struktuurid on perspektiivsed vahekihtidena kasutamiseks hübriidsetes struktuurides koos anorgaaniliste pooljuhtühenditega.

Käesoleva uurimistöö tulemusena on esmakordselt välja pakutud võimalus kõrgtemperatuurse termilise käsitluse tulemusena valmistada kõrge elektrijuhtivusega ja stabiilsete elektriliste omadustega materjal. Selliselt töödeldud polüparafenüleeni kasutamise teeb eriti huvipakkuvaks võimalus kombineerida polüparafenüleeni teiste elektrit juhtivate polümeermaterjalidega nagu eeskätt on seda polüpürrool. Polüparafenüleenist ja polüpürroolist valmistatud mitmekihilised struktuurid ja komposiitmaterjalid on tänu

polüparafenüleeni lisamisele oluliselt parema elektriliste omaduste stabiilsusega, parem on kihtide vaheline adhesioon.

Kõrgtemperatuurne legeerimine osutus efektiivseks meetodiks kõrgendatud elektrijuhtivuse ja stabiilsusega materjali valmistamiseks. Joodi ja broomiga legeeritud polüparafenüleeni legeerimise kineetika uuringutest järeldus, et elektrijuhtivuse tõus kõrgtemperatuurse legeerimise protsessil on põhjustatud peamiselt termiliselt aktiveeritud lisandi sissedifusioonist polümeeri struktuuri. Elektriliselt aktiivsete defektide tekkeenergiate analüüs lubab järeldada, et elektrijuhtivuse mehhanism halogeenidega legeeritud polüparafenüleenis on selgitav polaroonide ja bipolaroonide tekkega. Polüparafenüleeni legeerimise protsessi uuringutest järeldub, et kõrge elektrijuhtivuse ja hea stabiilsusega halogeenidega legeeritud polüparafenüleeni valmistamiseks on optimaalne temperatuur 520 ^{0}C järgneva kaheastmelise legeerimisega samal temperatuuril.

Kõrge elektrijuhtivusega ja stabiilsusega halogeenidega legeeritud polüparafenüleen osutus huvipakkuvaks elektroodimaterjaliks, millele sadestati järgnevalt elektrokeemiliselt polüpürrooli. Huvipakkuvaks osutus ka polüparafenüleeni elektrokeemilise sadestamise protsessil lahusesse kõrgtemperatuurselt modifitseeritud polüparafenüleeni osakeste lisamine. Sel teel valmistati ITO ja SnO_2 läbipaistvatele aluspindadele õhukesi polüparafenüleen/polüpürrool-komposiitkilesid ja -struktuure.

Võrreldes polüpürrooli elektrokeemilise sadestamise protsesse ilma kõrgtemperatuurselt modifitseeritud polüparafenüleeni osakesteta ja viimaste osalusel, võis järeldada polüparafenüleeni soodustavat rolli polüpürrooli sadestamisel.

Läbipaistvatele aluspindadele sadestatud struktuuride spektroskoopilised uuringud kinnitasid samuti eelnevalt elektrijuhtivuse temperatuurisõltuvuse analüüsi alusel välja pakutud domineerivate defektide esinemist.

Skaneeriva elektronmikroskoopia uuringud võimaldasid järeldada polüparafenüleeni soodsat mõju polüpürrool-polüparafenüleen-morfoloogiale, samuti paranes kihtidevaheline adhesioon.

Kokku võttes võib järeldada, et kõrgtemperatuurselt modifitseeritud polüparafenüleeni kasutamine koos polüpürrooliga annab võimaluse laiendada polüparafenüleeni tehnoloogilise kasutamise võimalusi samal ajal parandades struktuuride elektriliste omaduste stabiilsust, mis on väga oluline hübriidsete anorgaaniliste-polümeersete struktuuride valmistamiseks ja kasutamiseks fotoelektrilistes seadistes nagu päikesepatareid.

LIST OF PUBLICATIONS

This thesis is based on the following papers, which will be referred to in the text by their Roman numerals I-VII.

I A. Öpik, **I. Golovtsov**, A. Lobanov and K. Kerm, The conductivity mechanism of polyparaphenylene, doped with halogens and alkali metals, Synthetic Metals, 55-57 (1993) p. 4924-1429.

II **I. Golovtsov**, A. Öpik, Conducting polyparaphenylene prepared by high temperature doping, Proc. Estonian Acad. Sci. Engin., 2/1 (1996) p.107-123.

III **I. Golovtsov,** A. Öpik, High temperature diffusion of halogens and alkali metals into polyparaphenylene, Synthetic Metals, 101 1999 p. 463-464.

IV S. Bereznev, **I. Golovtsov** and A. Öpik, Electrical properties of polyaniline and polypyrrole bilayer structures, Synthetic Metals, 121 (1-3) (2001) p. 1415-1416.

V **I. Golovtsov** and A. Öpik, Temperature-dependent conductivity of polyparaphenylene/polypyrrole multilayer structures, Synthetic Metals, 121 (1-3) (2001) p. 1363-1364.

VI **I. Golovtsov** and A. Öpik, Thermodynamic modeling for investigation of the polyparaphenylene, Proceedings of Baltic Polymer Symposium**,** Tallinn, October 11-12, 2001 p. 67 – 73.

VII **I. Golovtsov**, A. Öpik, Multilayer structures based on polyparaphenylene-polypyrrole blend semiconductive films deposited on light transparent substrates, Proceedings of Baltic Polymer Symposium, Nida, September 18-20, 2002 p. 156-161.

ABBREVIATIONS

APS	ammonium persulfate
CP	conductive polymers
DBSA	dodecylbenzene sulfonic acid
DBSNa	dodecylbenzene sulfonic acid sodium salt
IR	infrared irradiation
ITO	indium–tin oxide
NS	naphthalene sulfonate
PANI	polyaniline
PANI-DBSA	polyaniline doped with dodecylbenzene sulfonic acid
PANI-TOSA	polyaniline doped with p-toluene sulfonic acid
PPP	polyparaphenylene
PPPBr	polyparaphenylene doped with bromine
PPPCl	polyparaphenylene doped with chorine
PPPI	polyparaphenylene doped with iodine
PPPK	polyparaphenylene doped with potassium
PPPNa	polyparaphenylene doped with sodium
PPy	polypyrrole
PPyDBS	polypyrrole doped with dodecylbenzene sulfonate
PPyBr	polypyrrole doped with bromide
PPyI	polypyrrole doped with iodide
PPyNS	polypyrrole doped with naphthalene sulfonate
$PPyNO_3$	polypyrrole doped with nitrate
SCE	saturated calomel electrode
SEM	scanning electron microscopy
TGA	thermo-gravimetric analysis
TOSA	p-toluene sulfonic acid
TOSNa	p-toluene sulfonic acid sodium salt
UV	ultraviolet irradiation
VIS	visible light
VRH	variable-range hopping

CONTENTS

1. INTRODUCTION

1.1 Electrical conductivity of polymers

Polymers have been traditionally considered as insulating materials. Indeed, a conventional application of polymers is a safe isolation of metallic conductors. The serendipitous discovery of highly conducting polyacetylene, however, marked the birth of a new field [1-3]. The potential advantages of polymers are low-cost manufacturing and their ability to be processed as films using melt- or solution-processing.

To exhibit electrical conductivity, the polymers must have ordered conjugation with extended π electrons and sufficiently large carrier charge concentration. In typical inorganic semiconductors, the electrical conductivity and semiconductive properties are determined by the crystalline and defect structure. Charge carrier concentration is controlled by injected impurity atoms, and the mobility of charges is determined by the nature of the material and the crystallinity of inorganic materials. A key property of conductive polymers is the presence of conjugated double bonds along the backbone of the polymer. In conjugation, the bonds between the carbon atoms are alternately single and double.

Modern studies of defect-structure and charge transport in polymers are directed to obtain the nature of charges in polymers. A distinguishing feature of polymeric and, more generally, organic materials that exhibit semiconducting electrical behaviour is their molecular nature. In the solid state, organic molecules retain their identity and interact weakly as molecular entities through van der Waals or electrostatic forces. For example, in a linear polymer electron interactions within a given macromolecular chain are much stronger than between chains. In most polymers, the macromolecules are not packed into perfect single crystals. Thus, the two central structural distinctions between polymers and familiar covalent crystalline semiconductors are the molecular character and the lack of periodic long-range order of polymeric materials.

The combined influence of molecularity and disorder can lead to profound differences between the fundamental physical phenomena that occur in traditional covalent network semiconductors and those that are characteristic of semiconducting organic materials. The molecular character of polymers makes electronic motion along the individual macromolecules one-dimensional.

In polyacetylene-type polymers, which possess a degenerate ground state with the two limiting resonance structures having equal energy, the theoretically considered charge carriers are solitons. They result from charge injection in the chain, and represent a topological kink in the system, a domain wall connecting the two possible bond alternation phases. The kink has an equal possibility of being anywhere in the chain, and being associated with a small mass, it is mobile. This mobile soliton extends over several C-C bonds. One conductivity mechanism proposed for conductive polymers is charge-hopping between different polymer chains, i.e. ”intersoliton hopping”. An electron is jumping between localized states on adjacent polymer chains; the role of the soliton is to move around and to exchange an electron with a closely located charged soliton, which is localized [4]. The mechanism at work in intersoliton hopping is very similar to that operating in most conducting polymers somewhere in between the metallic state at high doping and the semiconducting state at very low doping. All conjugated polymers do not carry solitons, but polarons can be found in most of them. Charge transport in polaron-doped polymers occurs via electron transfer between localized states being formed by charge injection on the chain [5].

In polymers having a nondegenerate ground state, such as benzoic rings or polyheterocycles, both theoretical calculations and experimental results indicate that the charge carriers are polarons and bipolarons [6], although some experimental results suggest that a truly metallic state with free carriers may be reached at very high carrier concentration. Polarons have either a positive or a negative single charge and possess an unpaired electron, whereas bipolarons are spinless doubly charged carriers. These species do not coincide with domain separators in the chain, but bipolarons can be defined as mobile charges coupled to geometrical chain distortions. The banding scheme is remaining identical on both sides of the distortion. They modify the electronic structure of the conjugated system by introducing two new energy states within the forbidden gap in the commonly used band model. This gives rise to new spectral transitions, two in the case of bipolarons and three with polarons.

A conjugation is not enough to make a polymer material conductive. In addition, by analogy with the inorganic semiconductors, charge carriers in the form of extra electrons or ”holes” have to be injected into the material. The conductive defects formation can be affected either chemically, thermochemically or electrochemically. This process is usually called doping by analogy with the processing of inorganic semiconductors. The conductivity of best-reported polyacetylene samples ca. 10^5 S/cm that is quite near to metallic conductivity is one of the reasons why conductive polymers are usually called synthetic metals. However, normally the conductivities of different polymers are in the range 1-1000 S/cm. The conductivity can be also increased by careful synthesis, which decreases defects density, by processing polymer films or by the modification of doping technologies. This fact has opened up new vistas for organic and polymer chemists, for physicists and materials scientists, including chemical engineers [7].

1.2 Functional materials based on conductive polymers

To show how plastic can be made to conduct electric current, The Royal Swedish Academy of Sciences had decided to award the Nobel Prize in Chemistry in 2000 to the leading scientists Shirakawa, MacDiarmid and Heeger who have revolutionized the development of electrically conductive polymers [7-10].

Twenty five years of very intensive studies gave many results, both forthcoming and unexpected. In addition, the innovative development of the field changed the tendency in the basic approaches. Early studies focused on improving the conductivity of organic polymers upon doping, but it has been generally accepted that most real devices are likely to exploit the intrinsic semiconductive properties of these materials [11]. The study of semiconductive properties of organic polymers is often termed "molecular electronics" and the area has proven to be highly interdisciplinary in nature. Chemists, physicists and theorists alike are continually exploring new materials and devising novel technologies.

The intensive investigations of the chemical, electrochemical, structural, optical, electrical, and magnetic properties have formed the theoretical basis for the preparation of functional materials based on conductive polymers for several applications. The most well-known of these new materials already have found applications in industrial products.

Polyacetylene, the most widely investigated conductive polymer, has been used for the fabrication of diodes and transistors [12]. Polyaniline, commercially manufactured as a corrosion inhibitor, is used also as a conductor for electromagnetic shielding of electronic circuits [13-18].

Polyethylenedioxythiophene doped with polystyrenesulfonic acid is manufactured as an antistatic coating material to prevent electrical discharge exposure on photographic emulsions [19, 20] and also serves as a hole injecting electrode material in polymer light-emitting devices; polydialkylfluorene derivatives are used as the emissive layer in full-colour video matrix displays [21-24]. Several conductive polymers are major candidates for pilot productions - polyphenylene vinylidene derivatives as an active layer for electroluminescent displays (mobile telephone displays) [25], polythiophene derivatives for field-effect transistors [26]. Some technologies and devices are comparatively near to industrial production, for example, those based on electrochromic properties of polyaniline “smart windows” that can vary the amount of light they allow to pass [10, 18]. The numerous conductive polymers are prospective for industrial use and environmental control. These also include polypyrrole, a thin layer for various sensing devices, biosensors and prosthesis technologies (artificial muscles), attractive for molecular medicine [27]. It should also be mentioned that novel science developments do not always have a secure future. Polypyrrole, for example, has been tested as a microwave-absorbing “Stealth” (radar-invisible) screen coating [28-29]. Possible electronic devices based on conductive polymers need untraditional detecting methods, which may be based on detailed studies. The unrelenting intensity of investigations in the field must respond to the possible negative tendencies before the facilities of conductive polymers in aggregate with plastic explosives be made use of.

There is often a big step between the first chemical synthesis of a molecular substance and the development of processing methods for practical applications. To promote the field of application, a better control of the CP preparation technology is required. At the moment, unknown parameters in the CP preparation technology are still numerous and thus the number of the practical applications of CP is limited. Chemistry, physics and engineering of semiconducting polymers have recently attracted attention of many researchers from diverse disciplines. However, knowledge of the basic phenomena is still insufficient.

1.3 Conductive complexes based on PPP

This study focuses on the modification of conductive properties of and processability of PPP, PPy and PANI selected from a large amount of known CP. It should be pointed out that PPP is the basic material in this research, therefore the properties of PPP, mostly concerning its doping ability, need to be introduced.

The experimental investigation of physical and chemical properties and the methods for doping of conductive polymers are usually complicated. One of the main ideas of synthesis proposed in literature is to obtain the polymer with a molecular weight as high as possible. However, polyparaphenylenes consisting of more than seven monomer units have been found to be insoluble and non-melt-processable [30]. From literature it can be concluded that the physical, chemical and conductive properties of polyphenylene depend upon the method used to prepare it.

The polymerization of benzene with the $AlCl_3$ -$CuCl_2$ system is one of the most successful methods of polyparaphenylene preparation reported in literature. The mild polymerization conditions (37 ^{0}C, 30 min) give a product with less than 0.2-1% extractables, which contains only minor amounts (<1%) of chlorine and polynuclear structures [30-31]. Virgin PPP prepared via the Kovacic method reported a polymer with a bulk room-temperature conductivity of 10^{-15}-10^{-10} S/cm [32-34]. The temperature dependence of the conductivity fitted by an Arrhenious expression has an activation energy of 0.7 eV [33]. The ionization potential of undoped polyparaphenylene was found to be some 0.8 eV greater than that of trans-polyacetylene (4.7 eV) [35-38]. Ionization potential gives a measure of which dopants will be of sufficient oxidative strength to ionize the polymer. In general, the Kovacic method gives a polymer particularly suited to a give highly conducting material upon doping. For example, Acceptor doping with AsF_5 increases the conductivity to values as high as 500 S/cm (obtained on highly compressed, nearly space-filled pellets), comparable to that obtained with (highly porous) polyacetylene. Elemental analysis of doped pellets indicated an average composition containing 0.26 ± 0.08 mol of AsF_5 per monomer (C_6H_4) unit, and an average C/H ratio near 1.5 [34]. Profile analysis through the pellet revealed the inhomogeneity of dopant penetration. Dopant concentration near the surface of the pellet gave an average composition of $[C_6H_4(AsF_5)_{0.42}]_x$, while in the interior the average composition corresponded to $[C_6H_4(AsF_5)_{0.24}]_x$. Acceptor doping of PPP was usually performed by exposing either powders or pellets to AsF_5 gas at pressures of up to 450 Torr at room temperature or below using vacuum line techniques [34]. Similar techniques were used with other doping agents, which possess reasonable vapor pressures at room temperature (Br_2, SbF_5, $MoCl_5$, etc.) [33, 39-41]. The doping kinetics arises from a combination of dopant penetration into the bulk of the pellet as well as into the polymer matrix itself. The increase in conductivity as a function of time for a PPP pellet exposed to 450 Torr AsF_5 shows that the doping process proceeds in steps [33, 34].

With doping agents having no appreciable vapour pressure, such as NO^+ salts, I_2 or strong Lewis acids, the polymer was placed in contact with a solution of the doping agent in a suitable solvent system and then washed free of by-products. Results interesting in terms of PPP film processing were obtained using simultaneous polymerization and doping of benzene (*in-situ* doping) to highly conducting polyphenylene complexes using a catalyst-oxidant strong enough to be dopant for the polymer [42-44].

Donor doping with alkali metals was reported to be usually accomplished by help of an appropriate electron transfer agent, such as naphthalene (as the alkali metal naphthalide) in an appropriate solvent, such as tetrahydrofuran. Neutral naphthalene was then removed from the doped polymer of by washing with solvent. In addition, pellets were doped by contact with an eutectic alloy of sodium and potassium. This method tends to wet the surface with unreacted alloy. In each case, the alkali metal doped polymer was reported extremely air and water sensitive and must be handled using the vacuum line and dry box (argon) techniques [45].

It was concluded that not all agents capable of doping polyacetylene to the conductive state would be capable of the same for polyparaphenylene. For example, while iodine and bromine are good dopants for polyacetylene, they were reported to have very little effect upon the conductivity of polyparaphenylene. Even when a particular dopant is capable of oxidizing or reducing either polymer to a high conductivity level, there are some distinct differences in the magnitudes of conductivity levels. Some dopants, such as AsF_5 and K (at room temperature), were reported to be equally effective, other dopants, such as $FeCl_3$, Li, and K (annealed samples), were found to give widely different conductivities for PPP and polyacetylene [33, 36, 40]. In the latter case, structural factors may be playing a decisive role in influencing the degree of charge localization (at dopant sites), degree of disorder, or degree of three-dimensional coupling, all of which can affect conductivity. Another problem following from the use of appropriate solvents, electron transfer agents and complex catalyst-oxidizing systems is reduced conductivity stability, mechanical properties and structural inhomogeneity of the resulting materials. One possible solution of the designated problems could be based on the application of the high temperature modification method for temperature annealing and doping processes of PPP at the controlled sample temperature and the dopant activity. These main conditions provide an attractive method for electron materials technology control.

One of the main aims of the presented experimental work was to obtain methods providing conductive complexes based on PPP doped with iodine, bromine and alkali metals without using any appropriate solvent, but giving a material with a wide range of electrical conductivity (up to 100 S/cm) and with high thermal stability. As it follows from literature, in practice these problems have not been investigated.

2 AIMS OF THE PRESENT STUDY

2.1 Aims and definition of objectives

The parameters of electronic devices important in terms of technology depend strongly on the properties, mainly on the defect structure of the initial material used. This main idea formulates the aims and defines the objectives of the present work. On the other hand, most importantly, any experimental investigation is aimed at possible practical applications of the materials as well as the development and optimization of technologies of their preparation processes.

Today, different photoelectrical devices, such as solar sells and LEDs, are promising for a CP having nondegenerate ground states. In the light emitting cells, the semi-conductive polymer could be surrounded asymmetrically with a hole-injecting (usually ITO) on the one side, and a low work function, electron injecting metal (e.g., aluminum, magnesium or calcium) on the other side. The emission of light is then the result of radiative charge carrier, electrons from one side and holes from the other, recombination. The luminescence depends on the energy gap between the LUMO and HOMO levels. The photoemission properties are determined by the electronic structure of the material not in the same way but with assignable similarities as conductive and light adsorption properties.

On the other hand, generally simple construction of CP based devices becomes extremely complicated for a theoretical description because of multilayer type structures. There are many parameters that need special technological control for CP basis as well as for other constructive elements in order to form a device successfully.

There are many reasons why polyparaphenylene, polypyrrole and polyaniline were selected from the large number of known CP. The first one is basically a simple synthesis by oxidizing polymerization from monomers directly to polymers. However, the conductive properties of synthesized materials crucially depend on the conditions of synthesis - reagents purity, relative concentrations, temperature, time etc. On the other hand, it gives a possibility to modify the different properties of materials in the step of chemical synthesis**.** This statement is certainly realistic for all the three named polymers, to a great extent, being more typical for PPy and PANI, which can be easily obtained by this method in the conductive form, adding dopants into the reacting mixture. The polymerization of benzene has a higher degree of self-stabilization and the conductivity of the resulting polymer is not so sensitive to impurities injected to the polymer during the synthesis at low (near room) temperatures. The syntheses of the three named polymers have much in common but the abovementioned differences have a defined dissimilarity in approaches.

The PPP was used as one of the most thermoresistant materials among conductive polymers in order to obtain structures with properties, including heightened temperature stability. The stability of physico-chemical and conductive properties was also the key idea for the application of polyparaphenylene as a model for detailed investigations. Polyparaphenylene has attracted attention not only by its high thermal stability and by its ability to obtain high electrical conductivity both n- and p-types upon doping [33], but also by its promising electron structure [36-38]. In addition, the electrical conductivity, and, that is important, the electronic structure can be controlled in a relatively wide range, using different doping and preparation technologies.

One question mark hanging over polymer-based electronics is how long they last and how the devices and materials may degrade or wear out. Therefore, particular attention is attracted to the conductivity stability of the investigated polymer structures.

The structures made using high temperature annealing, doping or modification usually obtain heightened stability of their functional properties. A long lifetime is assumed for the devices based on PPP. In these terms, the possibility of evaluating the conductivity stability of PPP is of interest.

Additional inspiration was derived the long-term experience of investigations concerning A_2B_6 type semiconductive materials conducted at the Chair of Physical Chemistry of Tallinn University of Technology [46]. The results of the investigation and preparation of the electronic materials with predicted physical and chemical properties are considered to be appropriate also for conductive polymers. For a successful procedure, it was necessary to describe the materials preparation process as the model where the characteristic physical or chemical parameters of the materials are presented as the functions of temperature, pressure or composition, and to control this model by experiments (so-called thermodynamic modeling method) [47]. Thermodynamic modeling of electronic materials also assumes the description and investigation of materials defect structure [48-50].

Concerning A_2B_6 type electronic materials preparation, the high-temperature conductivity investigations are used as a description model of the electronic materials defect structure - the dependence of the structural defect concentrations on the temperature or component vapour pressure. Using the investigations of temperature-dependent conductivity of CP, also covering the conductivity mechanism of a polymer in relation to the parameters of the preparation process of the conductive structure, the CP structural, conductive and electronic properties can be described and the ways of how to control and improve the process can be pointed out. The spectrum of the characteristic parameters of the final materials and devices is wide and may include electrical conductivity, magnetic properties, optical properties, microstructure and morphology of thin films, and the thermal stability of materials. Therefore, it is necessary to show the correlation between the parameters describing the process and the parameters describing the final material in terms of developing effective technologies for obtaining electronic materials.

With reference to PPP, in the present study, the high-temperature technique is used for the electrical conductivity and kinetic investigations. The results are described by the help of the conductivity and diffusion models and used to determine the dominating defects.

The thin film processing is a very complicated problem for PPP, but polypyrrole is one of the most famous CP because of its high and simple processability to thin high quality flexible films, using simple electropolymerization technologies. The problems intrinsic for a single conductive polymer can be solved by means of progress of the composites and blends in order to avoid different limitations in advancement of CP applications.

To achieve easily controllable film processing by electropolymerization or spin casting was the other reason why PPy and PANI were selected for the investigations. However, the stability of structural and conductive properties of PPy and PANI is much lower than the stability of PPP. Therefore, the substantial influence of preparation and handling conditions was an additional argument to carry out major experimental work using the instruments and facilities of our own laboratory, starting from the stage of polymers synthesis. In order to avoid undesirable manipulations on the investigated structures, the systems for doping and thermochemical modification of electronic materials, high and low temperature electrical conductivity measurements, electrochemical and spectral investigations were located in an immediate proximity.

2.2 Object and goals

The object of the study was derived from similarities in the main properties and methods of receiving of PPP, PPy and PANI as well as from the possibilities of their joint use in practical applications. Thus, according to the aims of this work, research was conducted in the following directions:

- chemical synthesis of selected CP by oxidative polymerization in mild and comparable conditions in order to obtain maximized yield of synthesized products taking into account the following:
  - using *in-situ* doping polymerization to obtain PPy and PANI with electrical conductivity suitable for applying synthesized products as electrode materials for use in electrochemical processing;
  - to obtain PPP in the form suitable for reaching an increased level of electrical conductivity by the high temperature doping with different dopants;
- development of a high temperature doping and modification method for PPP by means of
  - investigation of doping kinetics and determination of high temperature diffusion parameters in order to obtain PPP structures with high stability of predicted conductive properties, determination of optimal technologies for these preparations;
  - investigation of the possibility of modification of the properties of PPP, including electronic parameters with the help of high temperature doping method;
- formation of films, composites and multilayer structures using PPy and PPP, increasing the processability of each other, also including structures onto light transparent (glass-ITO, glass-SnO_2) substrates for their potential applications as electronic devices.

3. EXPERIMENTAL METHODS AND CALCULATION MODELS

3.1 Preparation of polyparaphenylene, polypyrrole and polyaniline

3.1.1 Chemical synthesis of PPP

PPP was prepared according to the procedure of Kovacic by the oxidative cationic polymerization of benzene [30-31]. Benzene was polymerized directly to PPP through the use of a Lewis acid catalyst - $AlCl_3$ and an oxidizing agent - $CuCl_2$. Benzene was used for synthesis after special purification by distillation with metallic sodium. Cupric chloride was dried at 125 ^{0}C in vacuum for at least 24 h prior to use. The temperature of polymerization was 23-36 ^{0}C, the time of the synthesis – 3.5...4.5 h. The mixture was covered with an atmosphere of dry helium.

Subsequent to washing by hot concentrated HCl and distilled water, the synthesized product (brown powder) was annealed in vacuum at temperature 120 ^{0}C for 24 h. This method makes a polymer particularly suited to give a highly conductive material by doping.

Because of PPP insolubility, a direct determination of the molecular weight of PPP is not possible, additional information on the molecular weight of PPP was obtained by infrared spectroscopy.

The quantitative analysis of the absorption values for “para-“ and “mono-” bands of quaterphenyl, quinquephenyl and sexiphenyl yields a linear relationship between the ratio of Σ mono /Σ para and the number of benzoic rings [32]. The synthesized PPP consists of 14-16 benzoic rings.

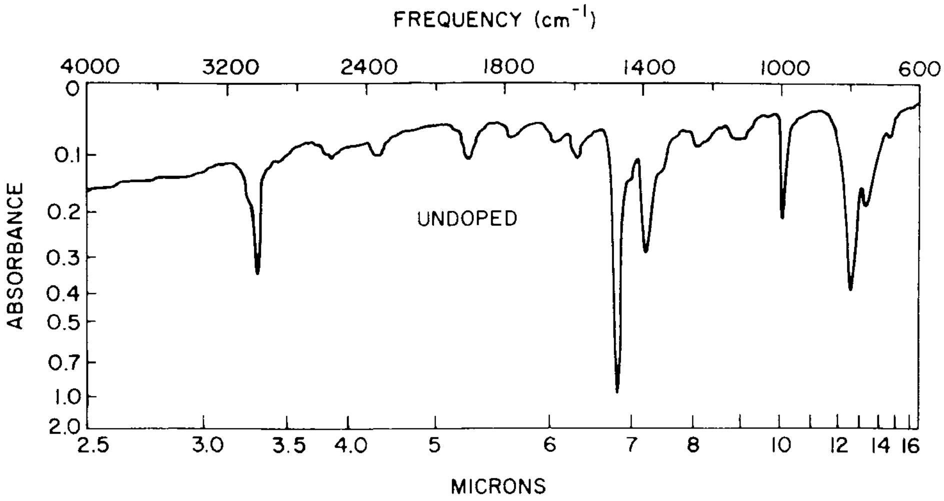

Figure 3.1. IR spectrum of the synthesized PPP

Since PPP is an insoluble non-melt-processible polymer, it is generally handled as a free - flowing powder or as pellets pressed. The PPP pressed pellets were used for the following processing – high temperature doping and modification described below in section 3.2.4.

3.1.2 In-situ doping oxidative polymerization of PPy and PANI

Pyrrole and aniline were distilled under vacuum prior to use. Dodecylbenzene sulfonic acid (DBSA) and sodium salt (DBSNa), p-toluene sulfonic acid (TOSA) and sodium salt (TOSNa) as dopants and ammonium persulfate (APS) as oxidant were used as received. Conductive PPy and PANI were chemically synthesized by the *in-situ* doping oxidative polymerization of aniline and pyrrole at 0-2 °C: 0.5 M APS aqueous solution was added dropwise to the 0.5 M aniline (or pyrrole) aqueous solution. The time of synthesis was 6 h and 48 h for PANI and PPy, respectively. The molar ratio of aniline/oxidant/dopant=1/1/0.5; pyrrole /oxidant/dopant=1/0.5/0.33. In the next investigations, the synthesized PPy and PANI fine powders were pressed into pellets with a diameter of 25 mm under a pressure of 500 MPa, using evacuable die.

3.1.3 High temperature modification and doping of PPP

For the thermochemical modification and doping as well as for the investigations to follow, pellets with a diameter of 20 mm under a pressure of 800 Mpa, using evacuable die, were pressed from the PPP powder. In order to increase crystallinity, the polymer pellets were then annealed in vacuum at 180 ^{0}C for 24 h. Apparently, this process opens up in the pellet some voids (via loss of volatiles, such as chlorine and low molecular weight oligomers), which facilitates dopant penetration. To investigate the thermal stability of PPP above the room temperature, the PPP pellets were thermally treated in vacuum at a variety of temperatures, ranging from 300 to 650 ^{0}C for 24 h. In thermally treated undoped PPP samples, the dependence of the C/H molar ratio and the loss of mass on the annealing temperature were investigated. For the thermal treatment of the undoped PPP in vacuum and for the preparation of the PPP samples doped with iodine (PPPI), bromine (PPPBr), alkali metals, such as sodium (PPPNa) and potassium (PPPK), the high temperature modification method was used. According to the aims of the present investigations, the thermochemical modification and doping processes were performed to different doping degrees, determined mainly by the doping temperature, doping time and resulting conductivity level.

The halogen doping of PPP was made by exposing the polymer to halogen vapour at temperatures from 300 to 650^{0}C. The PPP pellets were loaded into one end of the quartz tube, the halogen - to the other end of the tube. Next, the tube was evacuated, sealed and loaded into the double-zone furnace. The temperatures of the PPP and the halogen were controlled separately by the temperatures of zones [II in Appendix A]. Upon doping, pellets changed their colour from brown to dark, also with a metallic hue. Since the gaseous-phase doping was performed in a closed system, the process was accompanied by the generation of by-products that are also gases at doping temperatures. In order to investigate the influence of these by-products to the doping process, a step-by-step doping was performed. It means that after every hour of doping, the by-products were removed from the system, then the ampoule was sealed again, and the process of doping was continued.

In the case of doping with potassium and sodium, the PPP pellets and the alkali metal were loaded into the one-zone tube. The doping was performed at 250^0C. To investigate the conductivity stability of donor doped PPP, the pressed pellets were doped with eutectic alloy of sodium (77.6 %) and potassium (22.4%) at 250^0C. The alkali metal-doped polymer is extremely air and water sensitive and was handled using the dry box (helium) techniques.

The halogen content in the doped samples was determined by the Leipert-Münster method and the content of the potassium - by the flame emission technique. The dopant content values are specified as the number of dopant atoms per 100 PPP monomer units.

3.2 Technologies for multilayers and composites preparation

The prepared materials were used for different multilayers and composites preparation:

- for bilayer structures consisting of electrochemically deposited PPy and PANI films on PPy and PANI substrates made by chemical oxidative polymerization, using different sulfonic acids and their salts as dopants;
- for polyparaphenylene/polypyrrole multilayer structures consisting of electrochemically deposited PPy from aqueous solution onto electrodes prepared from the high-temperature modified and doped PPP;
- for multilayer structures consisting of semiconductive polyparaphenylene (PPP)-polypyrrole (PPy) composite thin films deposited onto indium/tin oxide (ITO) glass and (SnO_2) glass substrates by the electropolymerization of pyrrole from aqueous-acetonitrile media containing particles of the high temperature doped PPP.

In the last two cases, the high-temperature modified and doped PPP was used as a substrate for electrochemical polymerization and as one of the components of composite films, respectively.

3.2.1 Electrodeposition of PPy and PANI films

The electrochemical syntheses of doped PANI and PPy films with an average thickness of 25 µm onto chemically prepared PANI and PPy electrodes were performed galvanostatically between 0.7 V and 0.9 V vs. SCE in a standard three-electrode cell with a platinum wire counter electrode using VoltaLab™ 32 potentiostat/galvanostat. The doped PANI films syntheses were performed in a 0.1 M aniline + 0.2 M DBSA or 0.1 M TOSA de-aerated solutions; doped PPy films – in a 0.3 M pyrrole + 0.1 M DBSA, TOSA, DBSNa and TOSNa de-aerated solutions [IV in Appendix A].

3.2.2 Electrodeposition of PPy from aqueous solution onto high-temperature doped and modified PPP

The electrochemical deposition of PPy onto the prepared PPP electrodes was provided using a standard three-electrode electrochemical cell and potentiostat/galvanostat VoltaLab™ 32. Pyrrole (Fluka) was freshly distilled under vacuum prior to polymerization. P-toluene sulfonic acid sodium salt (TOSNa), dodecylbenzene sulfonic acid sodium salt (DBSNa), nitric acid potassium salt (KNO_3) were used as the dopants. A platinum slab and a SCE were used as a counter and a reference electrode. Current density of electrochemical polymerization was defined by voltammetry for every used electrode. Black, homogeneous films were obtained readily at the electropolymerization time within 10-35 min. In order to avoid any contact with oxygen contained in the air, the samples were dried, held and transferred to a conductivity investigation system in a drying vessel [III in Appendix A].

3.2.3 Electrodeposition of polyparaphenylene (PPP)-polypyrrole (PPy) composite thin films onto ITO and SnO_2 substrates

The electrochemical deposition of PPy and PPP-PPy composite films onto ITO and SnO_2 glass electrodes pretreated in warm sulfuric acid was made using a standard three-electrode electrochemical cell and potentiostat/galvanostat VoltaLabTM 32.

Pyrrole (Fluka or Sigma) was freshly distilled under vacuum prior to polymerization. A platinum slab and a SCE were used as a counter and a reference electrode. Current density of electrochemical polymerization was defined by voltammetry. In order to avoid any contact with oxygen contained in the air, the samples were dried, held and transferred in a drying vessel to a conductivity investigation system.

The polyparaphenylene-polypyrrole (PPP-PPy) composite films were deposited onto ITO and SnO_2 glass substrates from pyrrole aqueous-acetonitrile solutions containing suspension of high temperature doped and modified PPP. As the dopants for electrochemical synthesis of PPy, the iodide (I), bromide (Br), nitrate (NO_3), p-toluene sulfonate (TOS), naphthalene sulfonate (NS), and dodecylbenzene sulfonate (DBS) ions were used. The sodium and potassium salts used as the dopants have low solubility in acetonitrile. For electrochemical synthesis, the solutions of pyrrole (0.08 M) – dopant (0.08/3 M)- acetonitrile (CH_3CN 98%) – water (not exceeding 2%) were made homogeneous by addition of water.

The optimal concentrations of the reagents and current densities were selected in order to obtain the high quality film growth. The electropolymerization yield was calculated by the charge transmitted through the electrochemical cell using the modified Faraday's law [51].

3.3 Conductivity measurements and temperature-dependent conductivity investigation

The electrical conductivity of doped samples was measured also at room temperature. The four-in-line probe was used to measure the conductivity of doped samples. The special probe head, containing four equally spaced spring-loaded electrodes, was lowered onto the sample until the four probes were in close contact with the sample. A constant current source was used to pass a steady current through the outermost probes and the voltage drop across the inner two contacts was measured. The conductivity measurements often involve the formation of stable electrical contacts with the investigated sample, for thin or air sensitive films or films with weak mechanical properties it might be complicated. The electrodag (high adhesive carbon-aqueous solution) was used in order to achieve a better electrical contact with thin films deposited onto ITO and SnO_2.

The doping and modification process of PPP was controlled with the help of conductivity measurements. The doping was provided in the four-probe and two-zone quartz ampoule at controlled semiconductive material temperature, vapor-phase activity and doping time. The two-zone furnace, quartz ampoule for doping and conductivity measurements, in addition to cryostat, permitted to provide conductivity investigations using liquid nitrogen cryogenic technology, were integrated into the system, whereas each sample passed all the stages of investigation (Fig. 3. 2).

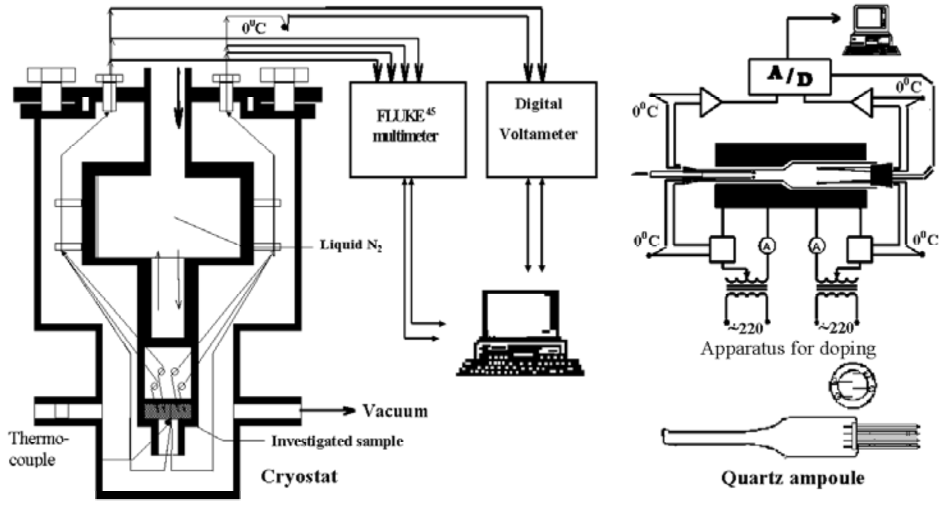

Figure 3.2. Schematic drawing of the system for high temperature modification, doping and conductivity measurements

The doping and modification process was performed at temperatures up to 650^0C and the temperature-dependent conductivity measurements at temperatures from –190 to 650^0C. For thin PPy films, doped PPP-PPy composite films and for doped PPP/PPy film systems, the temperature-dependent conductivity was investigated at temperatures from -190^{0}C to 100^{0}C. The same apparatus and equipment (Fig. 3. 2) have been used also to investigate the conductivity stability of doped PPP samples and PPP/PPy film multilayer structures. The conductivity measurements were performed under dynamic vacuum treatment at residual pressure 10^{-2} Torr.

3.4 Light adsorption and morphological investigations

One of the simplest and at the same time informative methods for materials structure studies is UV-VIS-IR spectroscopy. As shown above, IR spectrum was used for the pure PPP identification and molecularity determination. Conductive forms of polymers contain a fair quantity of impurities. Therefore, interpretation of IR spectra for doped forms of CP becomes problematic. UV-VIS spectroscopy investigation is also complicated because reliable data can be obtained studying the solutions of the investigated materials. However, the light transparent substrate and thin films formation technology allowed for optical spectra for thin PPy and PPP-PPy composite films to be obtained (using Shimadzu UV-2401 PC - UV-VIS Recording Spectrophotometer). In addition, the analysis of optical transmittance spectra and temperature-dependent conductivity investigation results of PPP-PPy composite films can be discussed in terms of band structure and conductivity mechanism of PPy and high temperature modified PPP.

According to the aims of the presented work, PPy and PPP-PPy composite films electrochemically deposited onto light transparent substrates (glass/ITO and glass/SnO_2) were characterized by scanning electron microscopy. SEM data of thin composite films, easily characterizing the film morphology, can also describe the layer-to-layer interface and the adhesion by the investigations of the cross sections. In addition, it can be informative for further device construction, development and optimization of the materials preparation technologies.

3.5 Calculation models

Results of the investigation and preparation of the electronic materials with the predicted physical and chemical properties can be considered appropriate also for conductive polymers. To accomplish the aims set forth, it was necessary to describe the materials preparation process, as the model where the characteristic physical or chemical parameters of the materials are presented as the functions of temperature, pressure or composition, and to control this model by experiments (so-called thermodynamic modeling method). Thermodynamic modeling of electronic materials also assumes the describing and investigation of materials defect structure.

Numerous experimental investigations were aimed at the modification of conductive properties of PPP by doping or thermochemical modification, as well as the majority of the multilayer and composite structures obtained and investigated, include the doped PPP as one of the layer or component. Therefore, this study includes a detailed analysis of the reasons and mechanisms of the conductivity increase in PPP, prepared by the high temperature doping with halogens and alkali metals. These reasons are directly connected with dopant incorporation into polymer as a result of the diffusion processes. To achieve a better understanding of the diffusion processes during the gaseous-phase doping of PPP, some important mathematical approximations are used.

In this thesis, additionally, a number of mathematical models were applied to discuss the conductive mechanism and electronic properties of the investigated materials, multilayers and composites. Therefore, the main mathematical and calculation models will be presented.

3.5.1 Diffusion equations

The method of high temperature doping for the preparation of the conducting PPP was determined as a diffusion process**.** The kinetics of high temperature doping of PPP with iodine and bromine as well as with potassium, as a rule, has some characteristics similar to the doping kinetics of polyacetylene with iodine [52, 53], investigated by Fick's diffusion [54]. Therefore, the same method for describing the doping mechanism was used.

It was assumed that the Fick's diffusion takes place and the polymer sample is a homogeneous solid slab (with a thickness h) bounded by two parallel planes normal to the x-axis, of abscissae $x = 0$ and $x = h$. The sample is in contact with the gaseous dopant. After the infinite time of doping t, the PPP will have reached the dopant concentration Cs.

The initial conditions:

$t = 0$; $C = 0$; for $0 < x < h$.

The boundary conditions:

$t > 0$; $x = h$, $x = 0$; $C = Cs$.

Considering the diffusion coefficient independent of the concentration C, according to Jost [54], the diffusion profile is described by Eq. (3.1)

$$C = Cs\left(1 - \frac{4}{\pi}\sum_{\nu=0}^{\infty}\frac{1}{(2\nu+1)}\,sin\,\frac{(2\nu+1)\pi x}{h}\,exp\left(-\left(\frac{(2\nu+1)}{h}\right)^2 Dt\right)\right) \qquad (3.1)$$

Equation (3.1) gives the local concentration of the dopant C as a function of time. It was difficult to measure the diffusion profile of the dopant along the samples, therefore only the total amount of the dopant M picked up by the PPP sample could be obtained

$$M = \int_0^h C \cdot dx = 2\int_0^t - D\left(\frac{\partial C}{\partial x}\right)_{x=0} dt \qquad (3.2)$$

The mean dopant concentration $\bar{C}$ presents the average concentration of the dopant along the sample:

$$\bar{C} = \frac{M}{h} \tag{3.3}$$

It can be derived at once from the measurements of the dopant content in samples. The general solution for the diffusion process is described by Eq. (3.4)

$$\bar{C} = Cs\left(1 - \frac{8}{\pi^2}\sum_{\nu=0}^{\infty}\frac{1}{(2\nu+1)^2}exp\left(-\left(\frac{(2\nu+1)\pi}{h}\right)^2 Dt\right)\right) \tag{3.4}$$

For a sufficiently large diffusion time *t*, the first term in the series (Eq. (3.4)) gives a good approximation

$$\bar{C} = Cs\left(1 - \frac{8}{\pi^2}exp\left(-\frac{\pi^2 Dt}{h^2}\right)\right) \tag{3.5}$$

On the other hand, the solution of the Fick’s law for concentration as a function of time and depth variables under the condition of constant surface concentration *Cs* is the complementary error function

$$C(x,t) = Cs \cdot erfc\left(\frac{x}{2\sqrt{D \cdot t}}\right) \tag{3.6}$$

The integration of this equation with certain approximation gives the amount of infused species per unit area

$$Q(t) = \int_0^{\infty} C(x,t) = 2Cs\sqrt{D\frac{t}{\pi}} \tag{3.7}$$

For the small diffusion time *t*, Eq. (3.7) gives a good approximation for mean concentration

$$\bar{C} \approx \frac{4Cs}{h}\sqrt{\left(\frac{Dt}{\pi}\right)} \tag{3.8}$$

The data obtained always show that the halogens, especially bromine, can chemically substitute for the H atoms in the PPP structure [II in Appendix A].

The model, which simultaneously takes into account the diffusion and a chemical fixation of the dopant molecules along the polymer fibrils, was satisfactorily used for the interpretation of the results of polyacetylene doping with iodine through gaseous phase and from pentane solution [52, 53]. It can also be supposed that the fixation of iodine or bromine in the fibrils is due to a quasichemical reaction between halogen and polyparaphenylene. Such a fixation reaction was expected to follow the first order kinetics. From the modified Fick's second law, for a supposed first order reaction with a constant diffusion coefficient *D* according to Crank [55] and Danckwerts [56], the kinetics of the dopant fixation in the polymer can be obtained as

$$\ln(C) = \ln(Cs) - x\sqrt{\frac{k}{D}}\ , \tag{3.9}$$

where *k* is the rate constant of the dopant fixation in the polymer fixation in the polymer. *Cs* is the saturated concentration of dopant on the PPP sample surface. *C* is the concentration of dopant on the depth *x* for the thin slice. It is possible to suppose $C \approx C(\Delta h_n/2)$ (h_0 is a thickness of the sample before the first grinding; h_1 is a thickness of the sample after the first grinding; Δh_1 is a thickness of the thin slice sample after grinding). Thus, the ratio of the rate constant over the diffusion coefficient from several thin slice concentrations $C(\Delta h_n/2)$ obtained as the result of doping at certain temperature can be measured and the intercept at $(\Delta h_n/2)=0$ gives the saturated concentration value *Cs*. At the same time, according to Eq. (3.5) or (3.8), the diffusion coefficient value *D* can be obtained, and then according to Eqs. (3.9), the rate constant *k* can be calculated.

Based on the assumption that the resulting conductivity in doped CP, in general, is in agreement with the dependence of the dopant content on the doping time, the conductivity measurements can be also used to characterize the doping kinetics and dopant diffusion. The density of the conductive paths is determined by the attachment of the dopant atoms, so that the conductivity can be expressed:

$$\sigma(t) = \sigma_0 + K\sqrt{D \cdot t} \tag{3.10}$$

where *K* is a constant dependent on the geometrical form and parameters of the sample.

$$\sigma = \sigma_0 \cdot \exp - \left(\frac{Ea''}{kT}\right) \tag{3.11}$$

This approximation is essential once the surface saturation concentration has been achieved, a plot of conductivity against $t^{1/2}$ must be linear and by substituting the value of the diffusion coefficient *D*, expressed in the Arrhenious law mode, in Eq. (3.10), a value of activation energy *Ea"* of the conductive defect formation (Eq. (3.11)) should yield.

3.5.2 Conductivity mechanism

Conductivity depends on the number density of charge carriers (number of electrons *n*) and how fast they can move in the material (mobility μ):

$$\sigma = n \cdot \mu \cdot e \tag{3.12}$$

where *e* is the electron charge. In semiconductors, one must also add an extra term due to positive charge carriers (holes) in Eq. (3.12). Conductivity depends on the temperature: it generally increases with the temperature decreasing for "metallic" materials (some of which become superconductive below a certain critical temperature *Tc*), while it generally decreases with lowered temperature for semiconductors and insulators. Charge transport in conductive polymers is usually explained by the variable-range hopping (VRH) model originally proposed for amorphous semiconductors [57]. On the assumption of photon-assisted hopping between the localized states, the VRH model relates the conductivity σ to temperature *T* as:

$$\sigma = \sigma_0 \cdot \exp\left(-\frac{T_0}{T}\right)^{1/n} \tag{3.13}$$

The exponential factor *n* in Eq. (3.13) is connected with the dimensionality of the charge transport in solids. According to the Mott's electrical conductivity model, the value of *n* is 4 for three-dimensional, 3 for two-dimensional, 2 for charge transport in quasi one-dimensional systems and 1 for strictly one-dimensional systems. In the last case, Eq. (3.13) is transformed to an Arrhenious law expression and the activation energy *Ea* of the temperature-dependent conductivity can be calculated from the simplest ($n = 1$, $T_0 = Ea/k$, *k* – Boltzmann's constant) assumption.

At lower conductivity levels, the physics of a quasi one-dimensional system is used more often than the charge transport model proposed by Epstein [58]. According to this model, CP are considered as inhomogeneous systems consisting of partially crystalline and amorphous regions. Epstein *et al.* suggested that the charge carriers are subjected to one-dimensional localizations when they pass through the amorphous regions in between the crystalline regions. Hence, the one-dimensional transport dominates over the three-dimensional, but the last one must be taken into account (Eq. (3.14)).

Because of similarity of these functions (Eqs. (3.13) and (3.14)), the exact determination of the temperature-dependent conductivity model on the investigated temperature range is complicated. The only possibility is to examine the statistical distribution of temperature-dependent conductivity data.

$$\sigma = \frac{\sigma_0}{T^{1/2}} \cdot \exp\left(- \frac{T_0}{T} \right)^{1/4} \tag{3.14}$$

The constants T_0 and σ_0 read

$$T_0 = \frac{\lambda \cdot \alpha^3}{k_B \cdot N(E_F)} \tag{3.15}$$

and

$$\sigma_0 = e^2 \cdot R^2(T) \cdot \nu_0 \cdot N(E_F)\,, \tag{3.16}$$

where

$$R(T) = \frac{9}{8 \cdot \pi \cdot \alpha \cdot k_B \cdot T \cdot N(E_F)} \tag{3.17}$$

λ is a dimensionless constant having a value ~ 18.1.

Simultaneous solution of Eqs. (3.15) and (3.16) gives for the density of states on the Fermi level

$$N(E_F) = \frac{1.996 \times 10^{48}}{\nu_0} \cdot (\sigma \ \cdot \sqrt{T}) \cdot (T_0)^{1/2} \tag{3.18}$$

and for an average hopping energy

$$W = \frac{3}{4 \cdot \pi \cdot R^3 \cdot N(E_F)} \tag{3.19}$$

The only unknown parameter in Eq. (3.18), the jump-rate prefactor ν_0, can be estimated from an optical photon frequency $\nu_{ph} \sim 10^{13}$ s^{-1}. Colson and Nagels in [59] have suggested that

$$\nu_0 = \nu_{ph} \cdot \exp(2 \cdot \alpha \cdot R) \tag{3.20}$$

Kuivalainen and Stubb *et al.* found in that in heavily $FeCl_3$ doped PPP $\nu_0 = 10^{16}$ s^{-1} [60]. The simultaneous solution of the presented equations (3.15–3.20), using experimental temperature-dependent conductivity data, usually provides unreasonable values. Therefore, approaches to calculations of an electronic structure need to be more flexible. The electronic-structure calculations are based on the density-functional theory and its quantum-mechanical implementations, such as the average hopping energy W, the hopping distance $R(T)$, the density of states on the Fermi level $N(E_F)$ and the inverse rate of falloff of wave function α. Those parameters should have a physical reason related to the electronic structure of the investigated materials, which determinates not only conductive but also optical properties. One of the aims of the present work was an attempt to define some correlation between the values of band gap and the Mott's parameters calculated using the temperature-dependent conductivity measurements.

3.5.3 Optical analysis

The light absorption of any material caused by its electronic structure, which is exposed to the light radiation with energy expressed as $h\nu$, where ν is the radiance frequency.

The absorption coefficient α can be calculated using the relation

$$\alpha = \frac{4\pi k_f}{\lambda} \tag{3.21}$$

and the extinction coefficient k_f can be calculated from the relation

$$k_f = \frac{2.303\lambda \log(1/T_0)}{4\pi d} \tag{3.22}$$

where λ is the wavelength of the incident radiation, T_0 is transmittance and d is the thickness of the film [61].

The relation between α and photon energy $h\nu$ can be expressed as

$$\alpha = \frac{A(h\nu - E_G)^{m/2}}{h\nu} \tag{3.23}$$

where $m = 1$ for a direct transition and $m = 4$ for an indirect transition, E_G is the band gap and A is a constant [62]. According to the presented relations, the straight-line portion of $\alpha^{m/2}$ versus $h\nu$ plots extrapolated to cut the x-axis can give the values of band gap for electrochemically synthesized PPy and for high temperature doped PPP on the basis of optical investigation of films deposited on light transparent substrates. However, a detailed analysis of the light adsorption spectra compared with the direct determination of refractive indexes of all matters influenced on the experimental data.

4 RESULTS AND DISCUSSION

4.1 High temperature doped and modified PPP

One of the main ideas of this experimental work was to obtain the methods that can give conductive complexes based on PPP doped with iodine, bromine and alkali metals with a wide range of electrical conductivity (up to 100 S/cm) and high thermal stability without using any appropriate solvent. As it follows from literature, these problems have practically not been investigated before.

The conductivity of PPP could be modified by the simple temperature (beginning from about 500 ^{0}C) annealing in vacuum. However, with the use of high temperature doping with active dopants like halogens, the resulting level of conductivity can be obtained on six orders of magnitude higher. Thus, the incorporation and distribution of the dopants like in classical semiconductive materials can be considered as the main reason for the conductivity increase in PPP.

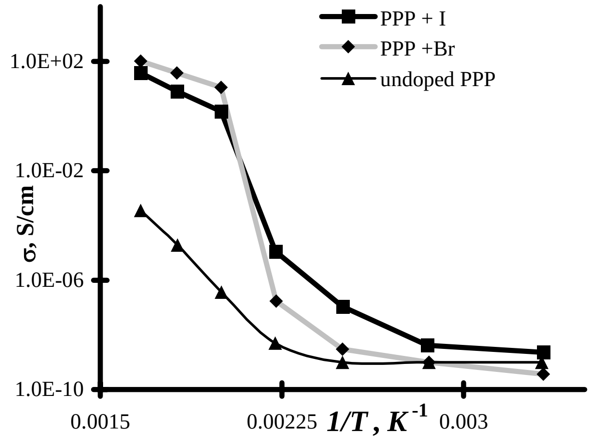

Figure 4.1. Temperature dependence of conductivity of thermally treated in vacuum undoped PPP pellets and doped with halogens (Br, I) at a variety of temperatures ranging from 300 to 650 ^{0}C for 24 h [II in Appendix A]

Figure 4.1 illustrates a general influence of thermal and thermochemical modification on the conductivity of PPP. From the point of view of conductive properties, the undoped PPP is practically thermo-resistant up to 400 ^{0}C. At the temperatures 500 ^{0}C and higher, the conductivity increases up to a level of 10^{-4} S/cm.

Investigations of the C/H molar ratio and the weight loss dependence on the temperature for undoped PPP samples (Fig. 4.2) show that the C/H molar ratio and the increase of weight loss with an increase in the annealing temperature are similar to the conductivity modification. The increase of the C/H molar ratio has a number of explanations: the loss of low molecular fractions of PPP, the carbonization of the material or the combination of the named processes.

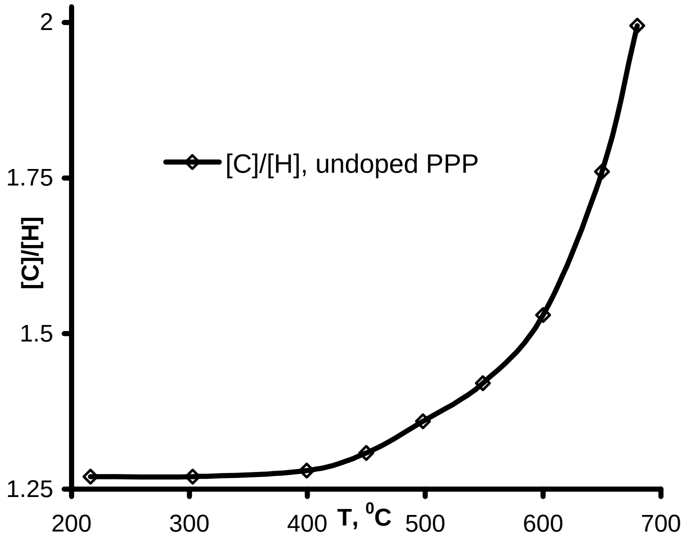

Figure 4.2. C/H molar ratio for the undoped PPP samples thermally treated in vacuum

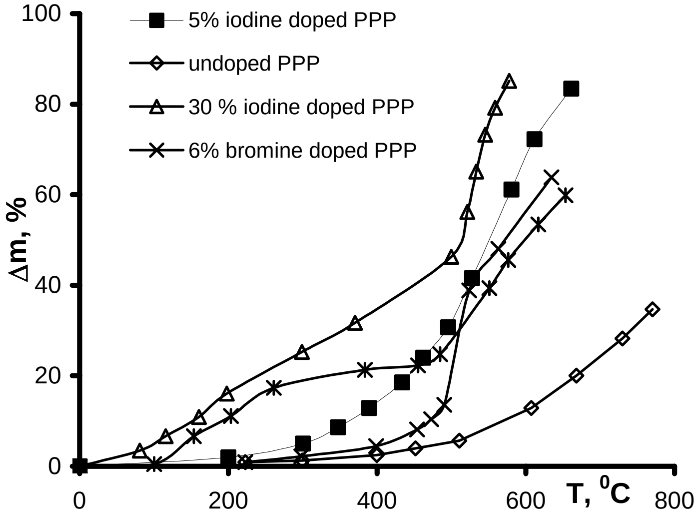

Figure 4.3. TGA analysis of undoped, iodine and bromine doped PPP [63]

The most significant increase in the conductivity of PPP, as a result of halogen doping, takes place between 400-500 ^{0}C. The TGA results show that at the same temperature range, most of the incorporated dopant desorbs from the conductive PPP structures (Fig. 4.3).

4.1.1 Kinetics of the high temperature doping of polyparaphenylene

Detailed characteristics of the process of dopant incorporation into PPP were obtained by the investigations of doping kinetics [II, III in Appendix A].

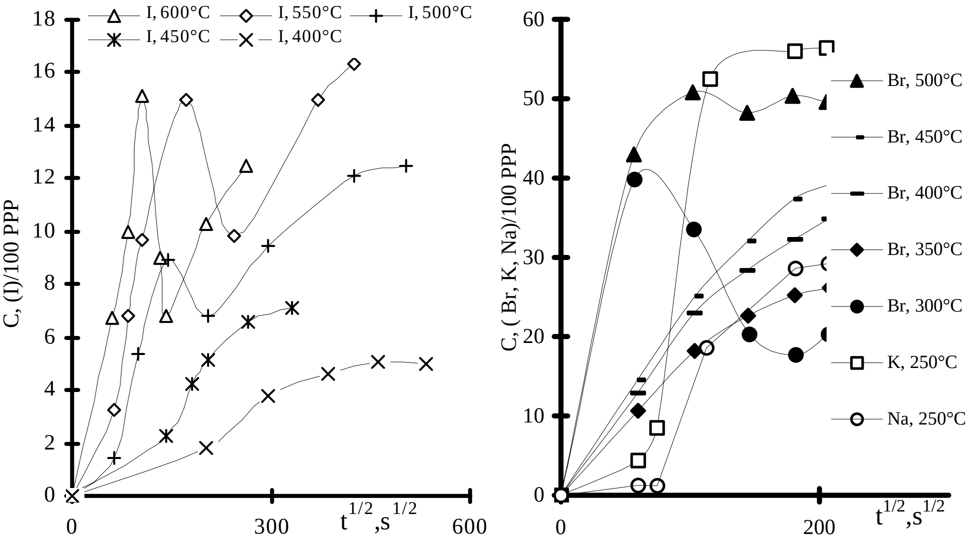

Figure 4.4. Mean concentration (C expressed as the number of dopant atoms per 100 of PPP monomer units) of halogens and alkali metals in PPP plotted vs. the square root of doping time [III in Appendix A]

In Fig. 4.4 the kinetics of high temperature doping of PPP with iodine, bromine and also with potassium and sodium is presented in a typical form, as the dependence of the dopant mean content obtained by the polymer during the doping process on the doping time. Figure 4.4 shows that the character of the doping kinetics depends on the temperature of doping. In general, with increasing temperature, the rate of the doping process increases. For most of the doping temperatures, after a rapid increase of the dopant content in the PPP structure, a decelerated increase follows.

An interesting result was obtained for the process of PPP doping with iodine for doping temperatures > 450^0C - after the first fast period of doping, a period follows when the halogen content in PPP samples decreases.

A similar feature was observed for the bromine doping of PPP but at lower temperatures of doping. The possible explanation of this phenomenon is the existence of thermal and chemical destruction in PPP upon the high temperature doping conditions.

At doping temperatures beginning from 500^0C, a similar decrease for the conductivity of PPP can be observed in Fig. 4.5. These results confirm additionally the assumption that the thermo-chemical destruction influences the electrical conductivity of doped PPP and the doping process.

In general, the kinetics of conductivity modification of PPP with halogen doping (Fig. 4.5) confirms the incorporation and distribution of dopants as the main reason for the conductivity increase in PPP. However, with regard to the conductivity of PPP obtained as the result of halogen doping, an additional discussion is required.

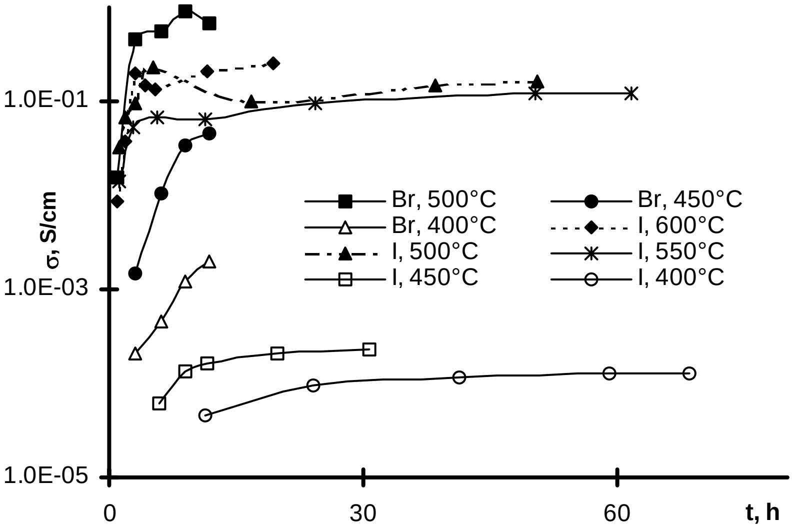

Figure 4.5. Dependence of room temperature conductivity on doping time for iodine and bromine doped PPP at different doping temperatures

Figure 4.6 presents the conductivity of iodine and bromine doped PPP as a function of dopant content obtained as the result of doping at different temperatures. Figure 4.6 shows that samples with a high content of the dopant, but doped at temperatures <450^{0}C, have the conductivity values similar to those of undoped PPP, and the samples doped at higher temperatures have a higher conductivity at the same halogen content in PPP structure. From these results can be concluded that the dopant exists in the PPP structure also in an electrically inactive form and with the temperature increasing it transforms into an electrically active form.

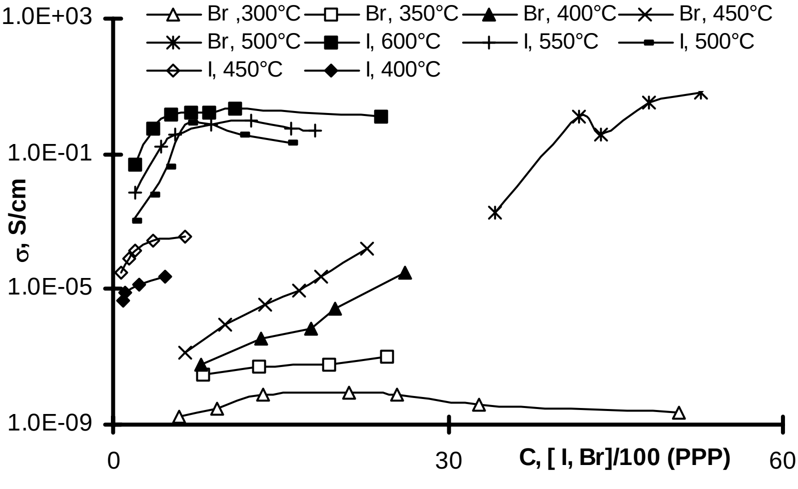

Figure 4.6. Conductivity of iodine and bromine doped PPP as a function of dopant content

The gas-phase high temperature doping was performed in the closed system. As it was also shown by the TGA analysis, the doping at temperatures 300-600^{0}C was probably accompanied by the generation of gaseous by-products. The total vapour pressure in the ampoule consisted of the partial pressures of the halogen and by-products and increased during the doping process.

To avoid the negative influence of by-products on the doping process and also to increase the process efficiency, the step-by-step doping was proposed [II, III in Appendix A].

Figure 4.7 shows the results of the experiment, in which after every hour of doping, the by-products were removed from the system (step-by-step doping).

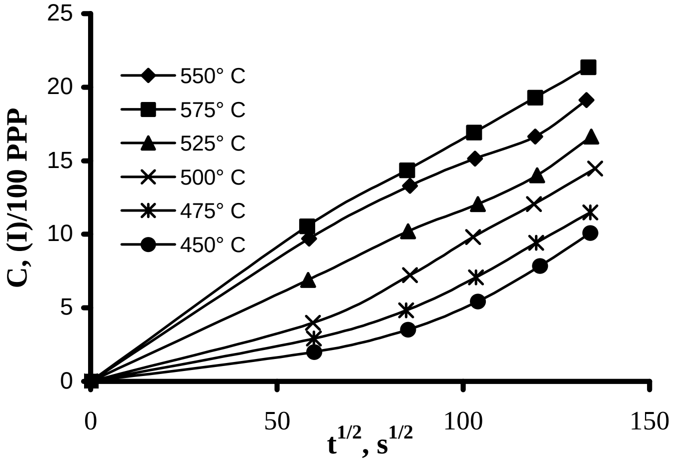

Figure 4.7. Mean concentration of iodine in PPP plotted vs. square root of doping time of step-by-step doping

In this case, the doping process was faster and the doping process control was easier that was additionally verified by the conductivity measurements (Fig. 4.8.).

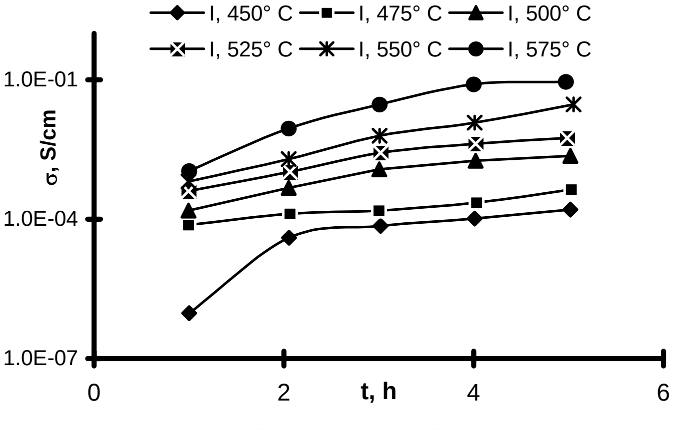

Figure 4.8. Electrical conductivity of PPP on time of step-by-step doping

In contrast to continuous doping, the step-by-step method eliminates the drastic influence of thermochemical destruction on conductivity kinetics.

Combining the experience of step-by-step doping with the influence of thermal treatment on the undoped PPP structures studied by the TGA and C/H molar ratio investigations, an important suggestion for the improvement of doping technology was made. Generally, the C/H molar ratio and the weight loss increase with an increase in the annealing temperature. However, the increase of the C/H molar ratio at temperatures near 500^0C is much lower than it could be assumed from weight loss investigations. It confirms that the residual part of impurities ($AlCl_3$, $CuCl_2$) can be desorbed from PPP without sufficient pyrolysis of the polymer structure. Therefore, the preliminary thermal treatment of samples at 520^0C for the high conductive PPP preparation can be used for a better control of the conductive polymer preparation.

The step-by-step doping at temperatures close to 525^0C gives a practically linear increase of the dopant mean content and the resulting conductivity. According to the desired values of conductivity, the duration of doping and the number of doping steps can be defined. Taking into account that the problems connected with the additional heating-cooling and evacuation have a negative influence on the structural properties of the material and also, to avoid the additional complicated operations like the quartz sealing, two-step doping was accepted as optimal.

On the basis of the experimental results, the optimal technology for PPP structures preparation by the high temperature doping method was achieved by means of combining the preliminary thermal treatment of samples at 520^0C with the following high temperature two-step doping at the same temperature. This method gives a material with electrical conductivity and stability in certain terms optimal to proceed the following procedures.

The doped PPP structures with high stability and mechanical properties were used as electrode material for the electrochemical deposition of PPy films from aqueous solution. Also, high temperature doped PPP was used for the preparation of polyparaphenylene-polypyrrole (PPP-PPy) composite films with high conductivity and stability of electrical properties by electrochemical deposition onto the different light transparent substrates - indium/tin oxide (ITO) and tin oxide (SnO_2) coated glass from aqueous-acetonitrile media containing suspension of high temperature doped PPP. These results are discussed below in section 4.2.

4.1.2 High temperature diffusion of halogens and alkali metals in PPP

4.1.2.1 Diffusion coefficients of halogens and alkali metals in PPP

Based on the investigations of the kinetics of high temperature doping of PPP with iodine, bromine and also with potassium and sodium, the reasons and mechanism of conductivity increase in PPP prepared by high temperature doping with halogens and alkali metals were analyzed in detail.

These reasons were related directly to dopant incorporation into a polymer as a result of diffusion processes. It allows for the use of mathematical models of

Fick's diffusion into a homogeneous solid slab, which is in contact with the gaseous or liquid dopant. Using different mathematical approximations of the general diffusion model (Eq. (3.5) and (3.8)), the diffusion coefficients were evaluated.

The doping process of PPP with alkali metals at 250^0C was found in a good agreement with the proposed diffusion model. It means that the kinetics of PPP doping with alkali metals complies with approximations of the general diffusion model.

Slightly lower values of potassium and sodium diffusion coefficients (4.2×10^{-8} and 3.5×10^{-8} cm^2/sec, respectively) than expected from the high activity of these dopants in liquid form were determined by the time required to establish contact between the sample and the liquid dopant [II, III in Appendix A]. It was confirmed also by the doping kinetics results (by the distinct existence of slow increase of alkali metals content in PPP during the first hour of doping). This effect refers to the existence of a preliminary period during the doping process.

Interestingly, the influence of different characteristics for the initial stage of doping was also important for halogen gas phase doping of PPP. The more efficient control of the results of the doping process gives the doping through the gaseous phase especially at low dopant (including alkali metals) pressures [II in Appendix A].

Using different mathematical approximations of the general diffusion model (Eq. (3.5)) for a long time diffusion and Eq. (3.8) for a small time diffusion), the diffusion coefficients of halogens in PPP were calculated from the mean concentration kinetics (Figs. 4.4, 4.7).

In the model event, the values of diffusion coefficients calculated by approximations for small and long time diffusion must be quite close to each other (not congruent because of Eq. (3.5) and (3.8) mathematically have approximate features) like diffusion coefficients calculated from doping kinetics of polyacetylene with iodine from pentane solution at room temperatures [52, 53].

However, the high temperature doping process appeared to be more complicated. The difference between the values of diffusion coefficients calculated using different mathematical approximations of the general diffusion model could be explained by the influence of thermochemical destruction of a polymer and by the existence of a preliminary period on the doping process characteristics [II, III in Appendix A].

The doping kinetics was also studied from the point of view of the conductivity change. Furthermore, these data, as a rule, agreed with the kinetic characteristics obtained from the analysis of the mean concentration dependence (Fig.4.1.).

Figure 4.9 illustrates the increase the electrical conductivity as the function of $t^{1/2}$ measured directly during the high temperature doping process in the specially constructed double zone quartz ampoule with four tungsten electrodes. For low doping temperatures 230-350^0C, the PPP samples were predoped before investigations.

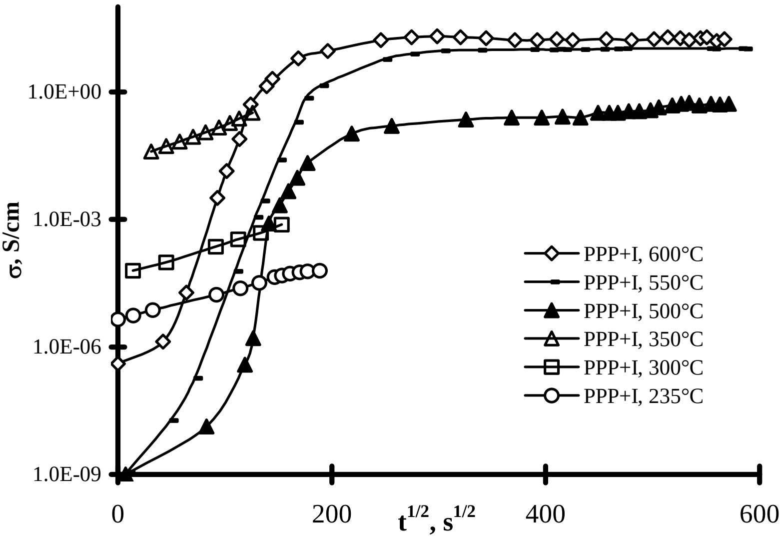

Figure 4.9. Conductivity increase in PPP samples measured during the high temperature doping with iodine [III in Appendix A]

The linear plot of conductivity against $t^{1/2}$ yielded a straight line. Therefore, the diffusion coefficients could be calculated on the basis of the values of initial and final concentrations (*Ci* and *Cf*), respectively. *Ci* and *Cf* were obtained by the chemical analysis before and after the conductivity measurements. For the conductivity investigations above 500 ^{0}C, the measurements were started from the undoped form of PPP (*Ci* = 0), and *Cf* was obtained by the chemical analysis. The diffusion time values were obtained from the linear regions of the curves in Fig. 4.9.

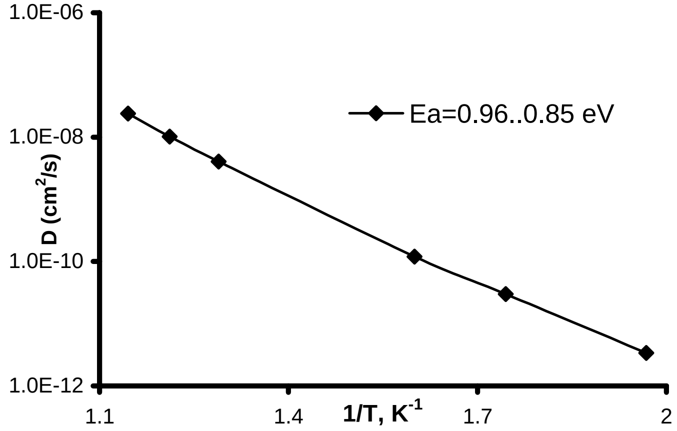

Figure 4.10. Diffusion coefficients of the iodine diffusion in PPP calculated from the conductivity investigation data vs. doping temperature T^{-1}

The calculated coefficients (Fig. 4.10) were in agreement with the direct calculations of the diffusion coefficients, using the data of doping kinetics characterized by the modification of the dopant mean content in PPP [II in Appendix A]. Thus, the important connections between the incorporation of the dopant and conductivity modification were obtained.

4.1.2.2 Activation energies of halogens diffusion, conductivity increase and conductive defect formation in PPP

From the kinetics investigations of halogen doping of PPP, it was concluded that the high temperature doping of PPP is primarily initiated by the thermally activated incorporation process [II, III in Appendix A]. This means that the values characterizing the process of dopant injection in a form of numerical evaluations, such as diffusion coefficients, depend on the temperature, obeying the Arrhenious law. It allows for the evaluation of the activation energies of the halogens diffusion (*Ea* obtained using data of doping kinetics characterized by the modification of dopant mean content in PPP, Fig. 4.4).

The results of kinetics investigations, using different doping techniques and mathematical approximations of the general diffusion model, give the values of the activation energies (*Ea*) of iodine diffusion in PPP about 0.81-1.05 eV and of bromine diffusion in PPP *Ea* = 0.24-0.44 eV [II, III in Appendix A].

On the other hand, the doping kinetics can be characterized by conductivity measurements and these data, as a rule, agreed with kinetics investigation obtained by the analysis of the dependence of dopant mean concentration on the doping time. The activation energies of the conductivity increase (as the result of formation of the conductive defects) in PPP were obtained from the conductivity kinetics investigations. The conductivity kinetics studies included data for predoped samples, showing the strong linear conductivity kinetics and therefore the conductive defect formation during the doping proved to be mostly reasoned by the dopant incorporation.

Interestingly, for iodine doping of PPP, the values of the activation energies obtained from the dopant content data (Fig. 4.4 and 4.7) were similar to those obtained using the conductivity measurements (Fig. 4.9). For temperatures 230-350^{0}C and 500-600^{0}C, the value of activation energy of conductivity increase was found about 0.85 and 0.96 eV (Fig. 4.10)

However, the modification of conductivity of PPP during the doping process is not related only to the incorporation of the dopant but also to the thermochemical modification of the PPP structure. The summarized influence of all these factors can be also determined as the conductive defect formation process, which can be characterized by the energy of the conductive defect formation. From this point of view, the linear regions of the curves presented in Fig 4.1 of the conductivity modification, as the result of thermal treatment of PPP and as the result of high temperature doping of PPP with halogens, can be used for the analysis of the possibility of conductive defect formation on the basis of activation energies calculation. The obtained values for the bromine doping of

PPP at temperatures 500-600^{0}C was 1.54 eV and the activation energy of conductive defect formation during the high temperature annealing in vacuum of virgin PPP was 3.6 eV. In the latter values, all the reasons of conductivity increase in PPP, both – the high temperature annealing and incorporation of the dopant were summarized.

With an approximation that every incorporated dopant atom gives the one charge-transfer defect, the values of activation energy of conductive defects formation during the high temperature doping of PPP with iodine were also calculated, using the conductivity measurements (Fig. 4.9). The activation energy of conductive defect formation as the result of iodine doping of PPP at temperatures 500-600^{0}C calculated from the data presented in Figs. 4.1 and 4.9 is quite close (1.98 eV).

For conductive defects formation in PPP, the following definition can be proposed. There is an energy barrier, which is needed to be raised to create a conductive complex between the dopant and PPP. In the preliminary doped samples (after high temperature doping connected with thermochemical modification), the creation of conductive complexes and additional injection of the dopant proved to be easier at essentially lower temperatures. Energetically, the subsequent process is limited mostly by the diffusion of the dopant into the PPP structure ($Ea \approx 0.8$-0.85 eV).

Based on the experimental results, it was supposed that at different temperatures the doping and thermochemical modification provides two types of conductive defects in the PPP structure. According to the charge transport theory proposed for CP, the different energies of conductive defect formation were related to the possibility of the bipolaron (dications with the formation energy of about 0.8-0.9 eV) and polaron (radical cations with the formation energy of about 1.5-1.9 eV), dominating defects formation [III in Appendix].

The obtained energies of dominative defect formation, also as activation energies of conductive defect formation in thermally treated and doped PPP, are in good correlation with the electron transition energy calculations presented by Khanna, as dependent on the PPP chain length and doping level [62].

On the basis of experimental results it was also concluded that with the increase of the doping temperature and dopant concentration, the defect state in the doped PPP is changing. The parallels between dopant incorporation and conductive defect formation allowed for a conclusion that the process of high temperature doping referred to a diffusion process was determined by the conductive structure creation [III, in Appendix A].

4.1.3 Kinetics of bromine doping in the polymer

The presented results [II, in Appendix A] show that the bromine-doping proceeds much easier than the diffusion of iodine. The doping kinetics investigations (Fig. 4.4.) showed that the characteristic of the initial stage of bromine doping, especially at 300^{0}C, differed from iodine and alkali metal doping. For bromine diffusion, the diffusion coefficient and activation energy values calculated by different approximations (*Ea* = 0.24-0.44 eV) also varied significantly. In addition, the bromine-doped samples showed the close level of conductivity at two or more times higher the incorporated dopant content than in iodine-doped samples (Fig. 4.6.).

It was supposed that some sort of quasichemical reaction between bromine and PPP takes place and this reaction does not result an increase in conductivity. Assuming that it is necessary to include a chemical reaction in addition to diffusion for describing the bromine doping of polyparaphenylene, the dopant distribution along the samples was taken into account. The rate constants and activation energy for the quasichemical reaction of bromine with polyparaphenylene were calculated using Eq. (3.9).

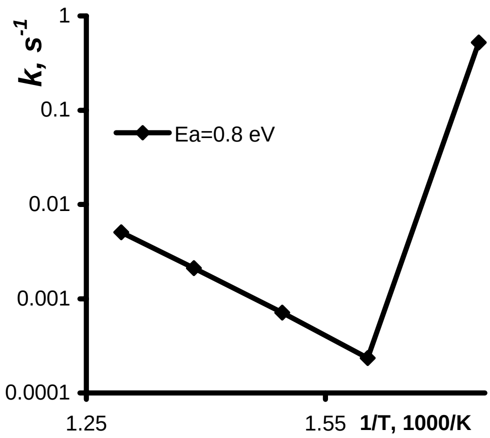

Figure 4.11. Dependence of the rate constant *k* for the quasichemical reaction of bromine with polyparaphenylene on the doping temperature (1/T), *Ea*=0.8 eV

The activation energy of the quasichemical reaction of bromine with PPP (Fig. 4.11) was summarized from a number of interconnected processes - incorporation of dopant in an electrically active form, electrically inactive and chemically combined forms - typical for the PPP doping with iodine and bromine. Perhaps some of these processes were appeared strongly in the case of bromine doping.

For doping at 300 ^{0}C, a very high level of the rate constant was obtained, which then drastically decreased for more than three orders of magnitude with the temperature increasing from 300 to 350 ^{0}C. With a further temperature increase, the value of the rate constant grew with a sufficiently high activation energy value. Thus, the experimental results confirm that for the interpretation of the bromine doping of polyparaphenylene it is necessary to include a chemical reaction in addition to diffusion.

One conclusion important for the PPP preparation technology control is that for bromine doping, lower bromine pressures are recommended, for instance, bromine doping of PPP at the dopant pressure 0.15 atm gives more controllable conductivity results.

The value of activation energy 0.8 eV is similar to the typical values of activation energy of iodine diffusion in PPP and to the activation energy of conductive defect (bipolaron) formation. High temperature doping of PPP with bromine as a method of thermochemical modification allows bipolarons to be more easily induced dominative conductive defects in the PPP structure.

4.1.4. Processing and application ability of high temperature doped PPP

The aim of any research is to define or at least to designate possible practical application of the investigated phenomena. As stated above, the possibility of practical application of conductive polymers is a complex problem, including theoretical, structural and technological aspects, both positive and negative. Very low processability of PPP is the main, however, not a single problem.

4.1.4.1 Alkali metal doped PPP

PPP has attracted major interest, in particular because its ability to donor doping, which gives an n-type semiconductive material with essentially high conductivity, but the conductive properties of alkali metal doped PPP are quite sensitive to moisture and oxygen present in the environmental air (Fig. 4.12).

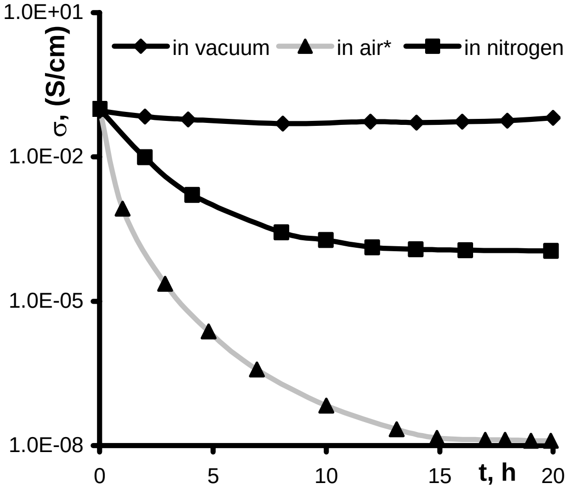

Figure 4.12. Dependence of room temperature conductivity of PPP samples doped with eutectic alloy of sodium (77.6 %) and potassium (22.4%) on time handled in different environments: in vacuum, in nitrogen, in air* (relative humidity 30 % at temperature - 20 ^{0}C). Parameters of the doping process - temperature 100 ^{0}C and doping time 12 h

The conductivity decrease of samples in the atmosphere of nitrogen could be explained by the chemical reaction of the alkali doped PPP structure with ~5% of oxygen in the nitrogen present. The results show that alkali metals doped PPP structures have quite unstable electrical characteristics when kept in air. The decrease of conductivity during the first hour was more than 3 orders of magnitude and after 12 h of keeping in air the conductivity of samples became close to the conductivity level of undoped PPP. On the basis of experimental results it was concluded that in the case of alkali metals doped PPP, the instability of the conductivity was determined by the influence of oxygen and moisture present in the environmental air. The positive direction of the results presented in Fig. 4.12 is that the conductivity of the PPP doped with alkali metals is quite stable in vacuum. Another positive moment is that conductivity decrease connected mainly with dopant activity in the PPP structure, may be reduced by the following doping with the alkali metal naphthalide in an appropriate solvent such as tetrahydrofuran. At the same time, the properties obtained by the PPP structure as a result of high temperature doping have to be retained. The application of alkali metals doped PPP for multilayers and composites preparation needs a higher level of dry technologies and special equipment. Thus, it was proposed as the aim for future studies.

4.1.4.2 Halogen doped PPP

For high temperature acceptor doping of the investigated PPP, fewer limitations to handling technologies exit. However, the existence of halogens in the doped PPP structure can be a factor for complicating the electric contact deposition because of high reacting ability of halogens to most of the contact metals. One of the simplest ways of the formation of metal contact to PPP follows from an ability of PPP powder to pressing. In the case of the noble metals or tungsten application, the high temperature doping method gives a possibility to obtain the doped PPP – metal contact partly surrounded by the doped polymer structure. However, this is not the most cost-effective method but the use of copper and corrosion-resistant alloys for similar aims can lead approximately to the same result. Using the high temperature doping technology, the halogen doped PPP structures were prepared containing the wire netting of sufficiently active metals, preliminary pressed into the PPP sample.

Figure 4.13 shows the influence of the atmospheric air on the stability of room temperature conductivity of halogen doped PPP. Particular attention was given to the conductivity stability of PPP samples that were in close contact with sufficiently active metals. The conductivity stability of doped PPP samples was constantly monitored using the four-in-line probe method.

For the halogen doped PPP, the conductivity decrease was explained mostly by the desorption of halogens from the PPP structure. The conductivity stability was observed to be dependent on the conductivity level obtained as the result of doping. In general, the decrease of the conductivity is lower for highly doped samples.

The wire netting inside the doped samples decreases the electrical conductivity of the doped material probably because of some type of corrosion behaviour between the active dopant and the metallic material. The influence of moisture on the conductivity stability was significant for the halogens doped PPP samples, especially when the doped material was in close contact with a sufficiently active metal or contained a sufficient amount of hydrophilic salts. On the basis of the stability investigation, it was assumed that metallic (noble metals and possibly copper) net wire can be used for creating electrical contact with the halogen doped PPP.

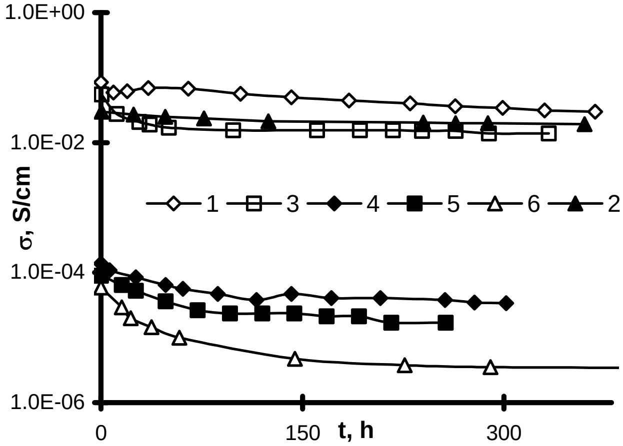

Figure 4.13. Air and water excited conductivity decay in doped PPP samples: 1-PPP(Br), water; 2 - PPP(I), water; 3 - Cu-net-wired PPP(I),air; 4 - Cu-net-wired PPP(I), water; 5 - FeNiCr-net-wired PPP(I), air; 6 - FeNiCr-net-wired PPP(I), water

Another useful result was the assumption that high temperature doped or modified PPP is stable enough, suitable as an electrode material to realize the electrochemical deposition of PPy films from aqueous solution. Polymeric systems, combining specific functional properties, like different electrical conductivity, with thermal stability and a possibility of film coatings deposition, have attracted great interest that could lead to different applications of these systems.

4.2 Processing and investigation of conductive structures including films, multilayers and composites

4.2.1 Multilayers obtained by use of electrodeposition technologies

A typical method for PPy film preparation is the electrochemical polymerization onto different metallic (Au, Pt, stainless steel) substrates. Special technologies (chemical, mechanical polishing and etching) are needed for the substrate treatment before the electrochemical deposition to achieve better adhesive properties. The preparation of the polymeric multilayer structures with different types of electrical conductivity is of major significance. The use of polymeric materials as a substrate for the electrochemical synthesis can give improved adhesive properties of the deposited PPy layer to the polymeric PPP substrate.

The doped PPP structures were used as electrode material for the electrochemical synthesis of PPy films from pyrrole aqueous solution, using typical inorganic and sulfonic ions as the dopants. The PPy films were galvanostatically electrodeposited onto the halogen doped PPP. This method was supposed to give homogeneous PPy coatings with good adhesion to the PPP electrodes.

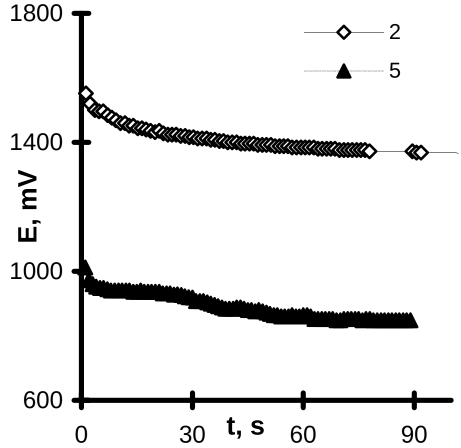

Figure 4.14. Variation of electrochemical potential vs. SCE during the galvanostatic polymerization of PPy at the PPP electrodes in 0.1 M pyrrole/0.1 M TOSNa aqueous solution

Galvanostatic tests presented in Fig. 4.14 show some characteristics of electrodeposition, which exert a noticeable effect on the quality and properties of resulting structures. The decrease of electrochemical potential is caused mainly by the mass transport problem. The decrease or instability of electrochemical potential during the electrochemical polymerization is connected with electrochemical properties of electrode surface, including anode polarization, increasing reactivity of anode, gas (hydrogen) evolution and charge transfer resistance. A film with high homogeneity can be obtained in the conditions of time independent elecrtropolymerization potential and current density.

Table 4.1. Results of electrochemical deposition of PPy onto high temperature doped PPP electrodes

Sample number	Electrode material	Dopant	Electrical conductivity of doped electrode, S/cm	Current density, mA/cm^2	Electropolymerization potential vs SCE, V	Quality of PPy films
1	PPP	I_2	0.9000	2.300	1.799-1.510	medium
2	PPP	I_2	0.0200	2.000	1.595-1.240	high
3	PPP	I_2	0.0095	3.800	0.930-1.072-1.008	low
4	PPP	Br_2	0.9000	2.100	1.024-0.832	low
5	PPP	I_2	15	2.066	0.900-0.840	low

This thesis is not concentrated on the detailed analysis of electrochemical problems. The electropolymerization processing of conductive polymer materials (PPy and PANI) was selected because it allows for easily controllable processing of film coatings. However, some conclusions related to a polymer's ability to be a substrate for successful elecropolymerization have been made.

Table 4.1 presents some experimental results associated with the properties of doped PPP electrode, current density and electropolymerization potential of the PPy film deposition process and the quality of PPy films. It was found that the quality of PPy film higher for deposition onto PPP substrates with a conductivity of 0.01-10 S/cm and the iodine doped PPP is found preferable.

Table 4.2 Electrochemical deposition parameters and conductivity of PPP/PPy structures

	Current density	Electrodeposition potential	Conductivity σ (S/cm)	
	I (mA/cm^2)	E vs. SCE (V)	Substrate	Film
PPPI / PPy-DBS	0.5	0.73	0.010	4.20
PPPI / PPy-NO_3	0.2	0.72	0.049	1.92
PPPI / PPy-TOS	2.0	1.05	0.188	7.80

Table 4.2 illustrates electrodeposition parameters found experimentally for the high quality PPy films deposition onto iodine doped PPP electrodes using different doping anions. The resulting conductivity of films deposited by use of optimal parameters was found dependent mostly on the type of the doping anion. The possibility of using the iodine doped PPP structures with a widely varying conductivity as electrodes for the electrochemical deposition of the high quality PPy films from aqueous solution is an important step for the enhancing of the PPP processability.

Similar problems were also investigated for a number of bilayer structures prepared by the electrochemical deposition of PPy and PANI films in aqueous media onto electrodes based on chemically synthesized conductive PPy and PANI [IV in Appendix A].

Table 4.3 Conductivity and solubility of doped PPy and PANI obtained by *in-situ* doping oxidative polymerization of aniline and pyrrole

	Conductivity (S/cm)	Solubility	
		Chloroform	Metacresol
PPy-TOSNa	7.9	-	+-
PPy-DBSNa	5.3	+	++
PPy-TOSA	15.1	-	+
PPy-DBSA	3.6	+	++
PANI-DBSA	0.4	+++	+++
PANI-TOSA	0.04	+	+

The synthesized by *in-situ* doping oxidative polymerization PPy and PANI were obtained as fine powders. The sulfonic acids and sodium salts used as the dopants during *in-situ* polymerization make PPy and PANI with high conductivity. Dodecylbenzene sulfonic ion additionally imparts to synthesized polymers essential solubility in organic solvents (Table 4.3).

The properties of chemically synthesized PPy and PANI were found widely dependent on the method and conditions of synthesis. From this point of view, one of the main ideas was to provide syntheses with a maximizing yield of highly conductive product in preferably comparable conditions. Another idea was to obtain PPy/PANI and PANI/PPy bilayer structures using chemically synthesized PPy and PANI in the pressed form as a substrate for the deposition of PPy and PANI films by electrochemical technologies. The soluble conductive form of PPy and PANI is suitable for spin casting thin film formation. In the pressed form, the synthesized PPy and PANI were used for PPy PANI bilayers preparation using electrochemical processing. The PPy PANI bilayers can be determined as hybrid structures, consisting of a pressed electrode of one CP covered with a conductive film of another CP.

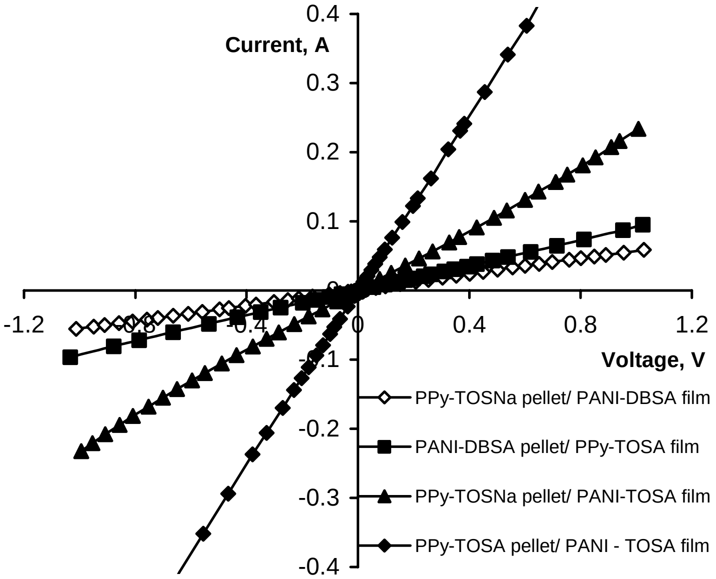

Figure 4.15. Typical current-voltage characteristics of the obtained bilayer structures

As it follows from the results presented in [IV in Appendix A], the bilayer structures with a better quality of pellets and with a high adhesion of films to pellet substrates were prepared by the deposition of the PPy films doped with DBSA, DBSNa, TOSA and TOSNa onto the pellets of PANI doped with DBSA. The deposition rate and the properties of the doped PPy and PANI films were found to depend significantly on the nature of the substrate surface. In general, the conductive properties of electrochemically synthesized PPy and PANI were found to depend on the method and conditions of electrodeposition process.

All the investigated bilayer structures show strong linear current-voltage characteristics (Fig. 4. 15) and therefore ohmic contact exists between pellets and films. In addition, the electrical resistance between the layers was relatively low [IV in Appendix A] that opens for PANI and PPy a number of application possibilities, such as flexible conductive intermediate layers for different devices, including hybrid organic-inorganic ones [65, 66].

The hybrid organic inorganic multilayer structures could be classified as the structures consisting of semiconductive polyparaphenylene (PPP)-polypyrrole (PPy) composite thin films deposited onto indium/tin oxide (ITO) glass and (SnO_2) glass substrates by electropolymerization of pyrrole from aqueous-acetonitrile media containing particles of high temperature doped PPP. Galvanostatic characterization of the electrodeposition process of the composite films, in contrast to the electrodeposition characteristics of individual PPy films obtained in comparable conditions onto the same substrates, proves the contributing role of PPP inclusions in the electrodeposition process. The conductive PPP particles take part in the electrochemical deposition process, facilitating formation of organic covering to inorganic indium/tin oxide (ITO) and tin oxide (SnO_2) coated glass substrate.

4.2.2 Temperature-dependent conductivity and Mott's parameters evaluation

4.2.2.1 Temperature-dependent conductivity of multilayer structures consisting of high-conductive polypyrrole films synthesized onto high temperature doped PPP substrates

Variation of electrical conductivity is the main property of CP and most of the results discussed in this thesis are based on electrical investigations. One of the main methods of the work was the adaptation of conductivity measurements for both structural investigations and for the development of preparation technologies of structures based on the conductive polymers. The conductivity as a function of temperature was measured for multilayer structures, consisting of high-conductive polypyrrole films synthesized onto high temperature doped PPP substrates. Temperature-dependent conductivity was also investigated for films of high-conductive polypyrrole synthesized electrochemically and removed from the PPP substrate after electrochemical deposition.

Figure 4.16 shows the dependence of conductivity on the temperature for PPy and PPPI/PPy multilayer structures. The temperature dependence of conductivity tends to be greater for PPy films with lower conductivity. Some visible anomalies in the conductivity of PPy concerned mainly with instability of PPy electrical properties under vacuum treatment. In general, the temperature-dependent conductivities are remarkably similar, indicating mainly to one type of thermally activated conductivity for the PPy films, still showing different regions for multilayer structures.

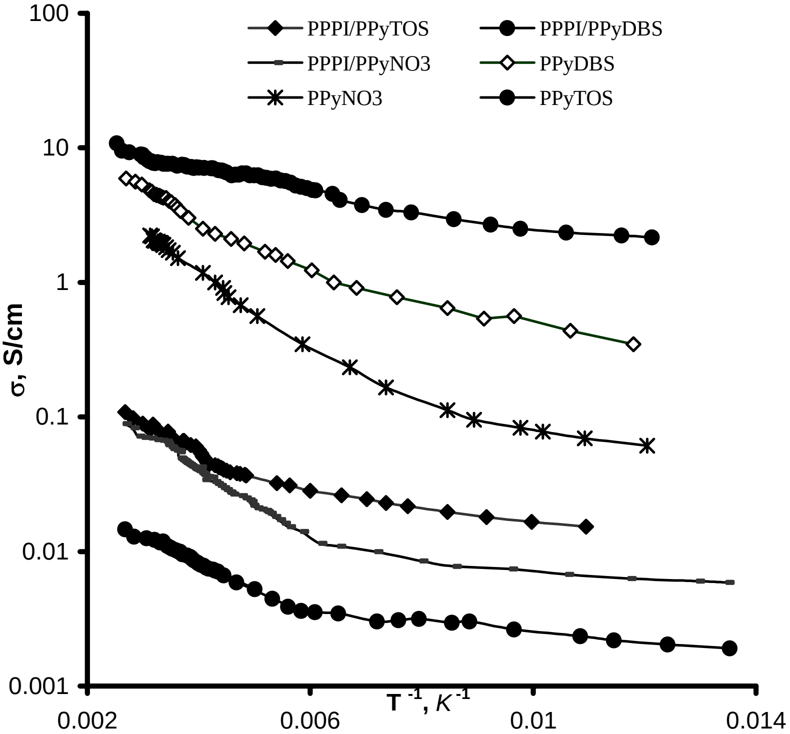

Figure 4.16. Plot of conductivity vs. T^{-1} for PPP/PPy structures and PPy films

In contrast to high conductive PPy, the more precise crossover to the greater increase of the temperature-dependent conductivity at higher temperatures was observed in multilayer structures [V in Appendix A]. Based on the temperature-dependent conductivity investigations, it was concluded that the conductivity mechanism in PPPI/PPy multilayer structures at relatively high temperatures becomes more similar to the Epstein model [58] and it indicates some similarity with the results obtained for slightly $FeCl_3$ doped PPP [60] and for thin PPP films prepared by the precursor rout [67]. In addition, the conductivity investigations of PPP/PPy structures indirectly enable one to confirm the quality of PPy films and to estimate the adhesion of electrochemically deposited PPy to iodine doped PPP substrates.

4.2.2.2 Temperature-dependent conductivity of thin polyparaphenylene (PPP)-polypyrrole (PPy) composite films

The temperature-activated conductivity of thin semiconductive polyparaphenylene (PPP)-polypyrrole (PPy) composite films deposited onto indium/tin oxide (ITO) glass and (SnO_2) glass substrates by the electropolymerization of pyrrole from aqueous-acetonitrile media containing particles of high temperature doped PPP was also investigated. The comparative studies of PPP-PPy composite films and PPy films obtained under the similar conditions, excluding existence of PPP particles, were made.

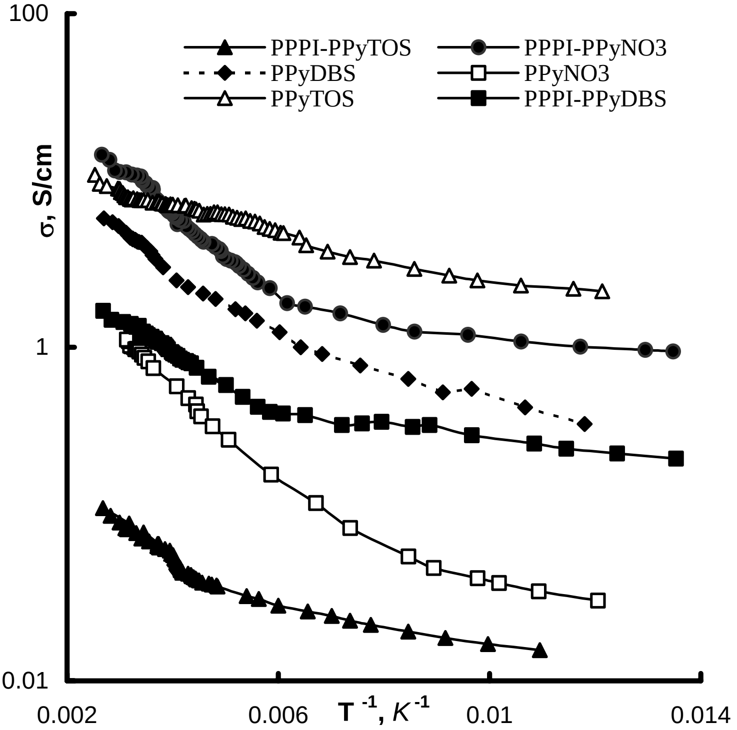

Figure 4.17. Plot of conductivity of PPP-PPy composite films vs. temperature

In the thin PPP-PPy composite films, the temperature-activated conductivity was also observed (Fig. 4.17). In contrast to plots for PPy thin films, for PPP-PPy composite films, the curve slope depends on the temperature range of temperature-dependent conductivity measurements significantly.

As a result of comparing the electrical properties of the PPP-PPy composite films (Fig. 4.17) and PPP/PPy multilayer structures (Fig. 4.16), it was concluded that the conductive properties of PPPI-PPy composite films become similar to the conductive properties of PPP/PPy multilayer structures, because of the influence of PPP particles included in the thin film structure. The changes in the curve slope of temperature-dependent conductivity (Fig. 4.17) for PPPI-PPy composite films and for PPP/PPy multilayers (Fig. 4.16) take place at close temperatures.

4.2.2.3 Temperature dependent conductivity for PPP doped with halogens and alkali metals

The temperature dependent conductivity was also investigated for PPP doped with halogens and alkali metals to different doping degrees determined mainly by doping temperature, doping time and resulting conductivity level [I, VII in Appendix A].

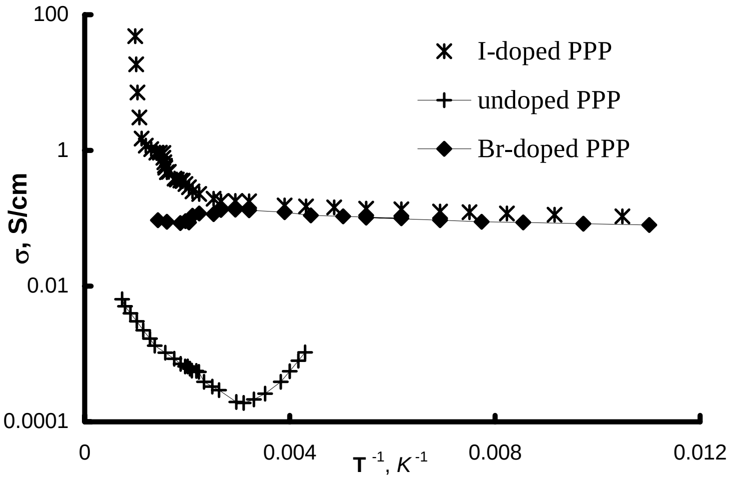

Figure 4.18. Conductivity vs. temperature for undoped PPP, I-doped and Br-doped samples

Figure 4.18 illustrates the typical dependence of the conductivity on the temperature of undoped PPP, I-doped and Br-doped samples. The conductivity of virgin PPP synthesized by the Kovacic method is 10^{-12}-10^{-13} S/cm. Therefore it was complicated to measure temperature dependent conductivity at insulating level using our experimental equipment. The conductivity of undoped PPP was increased up to 10^{-4} S/cm by the thermal treatment for 64 h at 500^0C in vacuum. The rapid increase in conductivity at temperatures exceeding 600^0C was caused by polymer pyrolysis (some type of graphitization behaviour). In the case of doped samples, a more complicated thermochemical destruction was supposed, confirmed by the investigations of doping kinetics.

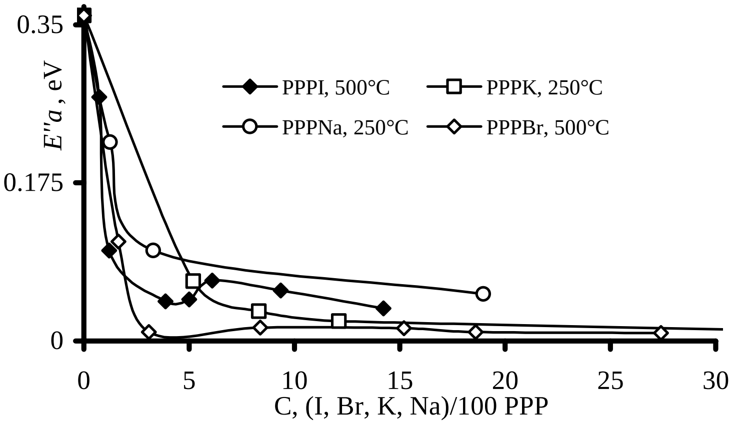

Figure 4.19. Activation energy Ea of the conductivity for PPP doped with iodine, bromine, sodium and potassium from the dopant content in PPP (number of dopant atoms per 100 of PPP monomer units)

The electrical properties of PPP, including temperature-dependent conductivity, are determined by the parameters of doping, such as temperature, dopant vapour-phase activity and doping time. Figure 4.19 illustrates how the activation energy of temperature dependent conductivity can be controlled for halogen and alkali metal doped PPP [VI in Appendix A].

The plot in Fig. 4.15, showing drastically different curve-slopes, indicates a sharp difference between the activation energy of temperature dependent conductivity for highly and lightly doped samples, being in agreement with the studies of other conductive polymers [11, 57].

4.2.2.4 Mott's parameters evaluated from the temperature-dependent conductivity data

The activation energy of conductivity is a very informative parameter for semiconductors. However, using a more detailed approach by means of taking into account the conductivity mechanism, the parameters characterizing electronic structure can be calculated.

The role of an intrinsic excitation in a charge transport mechanism of CP is not very well understood yet. Therefore, temperature-dependent conductivity studies would provide important information about the semiconductive properties of CP, including PPP, PPy, PPP/PPy multilayer structures and composite PPP-PPy films.

Based on temperature-dependent conductivity investigations, it was concluded that the variable-range hopping expressions account for nearly all the obtained conductivity data, except some visible anomalies in the conductivity of PPy caused by the instability of PPy electrical properties under vacuum treatment. Taking into account the statistical distribution coefficients of temperature-dependent conductivity data, the Epstein model (Eq. (3.14)) for the high temperature doped PPP [VI, I in Appendix A] and the Mott ($1/T^{1/4}$) three-dimensional model for electrochemically deposited PPy [V, VII in Appendix A] were assumed preferable.

Based on temperature-dependent conductivity investigations in PPy films, in high temperature treated and doped PPP, in electrosynthesized PPy films, in PPPI/PPy multilayers and in PPPI-PPy composite films, the Mott's parameters were calculated using mathematical models for the determined mechanisms [V, VI, VII in Appendix A]. The parameters of doping or/and preparation processes of PPP determine the electrical and diffusion properties of the conductive defects**.** In this thesis, defect complexes in PPP could be characterized by band structure calculations based on the zone theory of amorphous solids implemented for conductive polymers.

In general, the Mott's parameters calculation gave drastically different results for highly and lightly doped PPP samples [VI, in Appendix A]. This phenomenon is explained by the influence of the main reasons of conductivity increase in PPP. In the first stage of high temperature doping, the electronic structure is strongly modified by each incorporated dopant atom and the high rate of thermo-chemical destruction additionally increases the conductive defects concentration in PPP. As a result, the activation energy of conductivity in PPP decreases rapidly.

Then the rate of thermo-chemical destruction in the solid structure drops off to a value of close to equilibrium with the activity of by-products, the main part of the PPP structure is doped or thermally modified and the decrease of activation energy of conductivity becomes slower. The essential part of the dopant is composed of an electrically inactive form and the following conductivity increase is mostly determined by the residual destruction processes. As a result, the electronic structure of PPP is weakly modified.

The most important conclusion following from the Mott’s parameters calculations is that, using the high temperature doping and the modification method, a wide range control of the electrical and electronic properties of PPP was obtained. This result opens up new possibilities for the development and control of CP preparation technology. In addition, the results of the modification of the electrical properties according to the conditions of doping, thermochemical modification and other preparation methods contribute substantially to the basis of thermodynamic modeling, thereby extending its potential applications [VI in Appendix A].

The method of electrochemical formation of PPy films imposes some limitations to the possibility of modification of the PPy electronic properties. The properties of electrochemically synthesized PPy depend on deposition conditions, to a great extent including substrate material [V in Appendix A].

The investigations of PPy electrochemical depositions onto high temperature modified and doped PPP substrate demonstrated not only a possibility of such kind deposition. Using temperature dependent conductivity measurements of synthesized PPy films and subsequent Mott’s parameters calculations in [V in Appendix A] were shown that the Mott three-dimensional conductivity model is preferable for PPy films deposited onto high temperature modified and doped PPP substrate.

The temperature-depend conductivity investigation of multilayers structures, consisting of temperature modified and doped PPP as substrate and deposited PPy films, showed the interference of both PPP and PPy on electrical properties of PPP/PPy multilayer structures. The increasing influence of PPP properties on the electrical characteristics of multilayer structure as a whole with an increase in temperature of measurements was demonstrated by the experimental data presented in Fig. 4.16 and subsequent calculations in [V, VII in Appendix A].

The Mott’s parameters for PPy and the PPPI-PPy composite films were also evaluated in [VII in Appendix A].

On the basis of experimental (temperature-dependent conductivity investigations) and calculation (Mott’s parameters evaluation) results it was concluded that the PPPI-PPy composite films have acquired the electronic properties of PPP/PPy multilayers. This effect was found to be dependent on the properties of PPP injected in a film and possibly related to the formation of some self-assembled structure.

4.2.3 Optical investigation of thin PPy and PPP-PPy composite films

The Mott’s parameters calculation, based on the temperature-dependent conductivity measurements, was also theoretically based on the zone theory of amorphous solids. Therefore, it is not impossible to find some correlation between the conductivity mechanism and the band gap value obtained by optical investigations. The charge carriers in the polyconjugated systems can be generated by both photoexcitation and chemical/electrochemical doping. The similarities in physical properties of carriers created by these methods play a significant role in developing of a comprehensive understanding of the nature of charge carriers in CP.

The light transparent substrate and thin films formation technology allowed for obtaining optical spectra data for thin PPy and PPP-PPy composite films (Fig. 4.20).

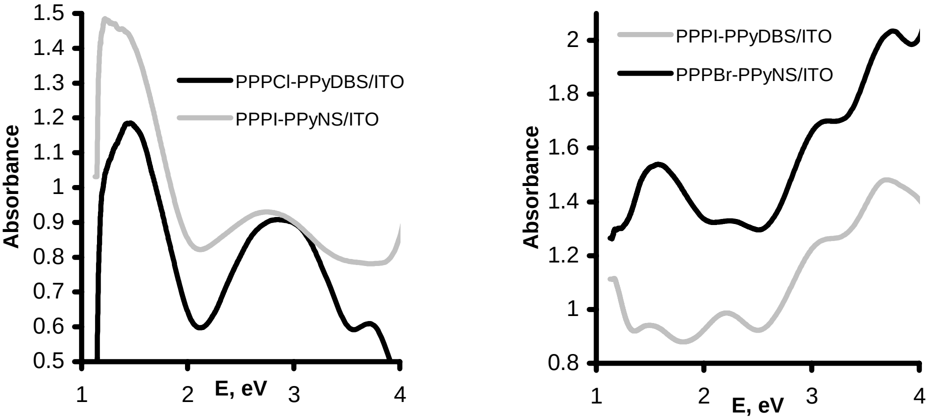

Figure 4.20. Optical spectra of PPP-PPy composite films

The existence in the optical spectra of several absorption bands with high intensity was possibly related to as π-π* transition for both of composite film components. In the analysis of the results according to the model presented in section 3.5.3, one of the intensive absorptions corresponding to band gap energy about 3.7 – 3.6 eV was found more typical for PPP. Another high intensity absorption corresponds to band the gap energy 2.6 – 2.5 eV more typical for π-π* transition in PPy. In general, optical spectra show high doping level of the obtained film structures. The composite films show better light absorption in a long-wave area that is typical for PPy. Because the investigated samples have a multilayer (including thick layer of glass) and composite structure, a strict determination of polarons in composite films was complicated and determination of the bipolarons practically impossible.

One conclusion important for the technology control of semiconductive structures based on the conductive polymers is that using different dopants and varying with the PPP/PPy ratio the optical properties could be modified in an essentially wide range. It opens up the possibility to form semiconductor materials with a primary absorbance in attractive spectral areas.

In addition, according to the experimental data, the band gap sufficiently depends on the dopant nature that gives a further promise for the fabrication of a CP structure with predicted electronic properties.

Figure 4.21 illustrates the influence of high temperature doped PPP on optical properties of PPP-PPy composite films. The presented spectra were obtained by means of possibly perfect compensation of PPy light adsorption using PPy film deposited on the same type substrate from the same solution at the same current densities and during the same polymerization time as investigated PPP-PPy composite film, however, excluding PPP particles. In this case, the data reflect the existence of absorption bands in some approximation detecting, the influence of high temperature doped PPP on the optical properties of composite films. Analyzing the presented spectra, the different direct transitions were obtained from α^2 versus $h\nu$ plots. A comparative look of these values is given in Table 4.4.

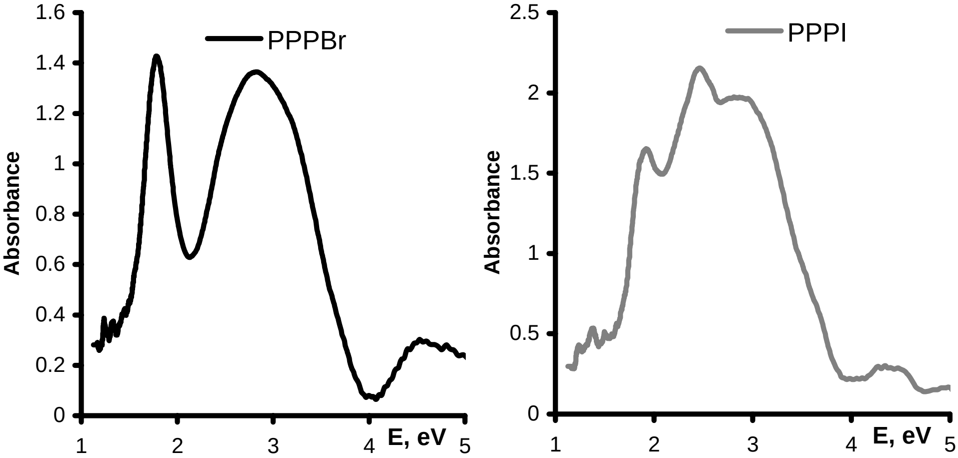

Figure 4.21. Influence of high temperature doped PPP on UV-VIS spectra of PPP-PPy composite films

Table 4.4. Optical parameters obtained for halogen doped PPP

material	Band gap (eV)			
	E_{G1}	E_{G2}	E_{G3}	E_{G4}
PPPI	1.77	2.05	2.34	3.58
PPPBr	1.67	1.95	2.45	3.70

The results strongly indicate the band gap E_{G4} typical for the π-π* transition in PPP. There is a slight indication of the band gap E_{G3} that possibly could be related to π-π* transition in PPy, the light absorption which was imperfectly compensated.

An interesting conclusion can be drawn from the comparison of optical investigations with the methods used to study the physical and chemical characteristics of PPP structure at different conditions of doping by typical dopants, which include halogens and alkali metals. In the halogen-doped PPP, containing different amounts of doping impurity, the defect structures were analyzed and the estimation of dopant diffusion parameters into PPP and conductive defects formation in PPP was given as compared to those of activation energies (section 4.1.2.2). The obtained values of conductive defect formation energies during the bromine doping of PPP at temperatures 500-600^{0}C was found 1.54 eV, of iodine doping of PPP at temperatures 500-600^{0}C - 1.98 eV and the activation energy of conductive defect formation during the high temperature annealing in vacuum of virgin PPP - 3.6 eV.

It was also found to be in good correlation with electron transition energy calculations, dependent on the PPP chain length and doping level [64]. In addition, these different energies of conductive defect formation were related to a possibility of the bipolaron and polaron states formation. From this point of view, a number of optical data (Fig. 4.21), indicating band gaps E_{G1} and E_{G2} with energies 1.67-2.05 eV, can be mentioned as verification of the conductive defect formation nature in PPP obtained during the high temperature doping. The activation energy of conductive defect formation during the high temperature annealing in the vacuum of virgin PPP - 3.6 eV was found close to the band gap value for π-π* transition in the PPP obtained from optical investigations.

4.2.4 SEM characterization of thin PPy and PPP-PPy composite films onto ITO and SnO_2 substrates

The obtained film structures were also characterized by scanning electron microscopy (Fig. 4.18). SEM images indicate that the prepared films have a smooth surface but different morphology, depending on formation conditions. Additionally, by the investigation of cross sections (d, e, f in Fig. 4.22), to a certain degree, the adherence of film structures to inorganic substrate was characterized. Composite films have a higher level of adhesion to the substrate layer and better mechanical properties than films that contain only PPy and the corresponding dopant.

The composite films containing PPPI particles had a better structure than the composite films including PPPBr or PPPCl particles. It may be connected with the improved properties of iodine doped PPP including conductivity, dopant distribution, structure and thermal stability [VII in Appendix A].

The thickness of films for organic dopants (TOS, NS and DBS) was in agreement with the electropolymerization yield calculated by the charge transmitted through the electrochemical cell, using the modified Faraday’s law

[51]. For inorganic dopants, some quantity of electricity was expended to the dopant incorporation process or/and PPy electrooxidizing. Therefore, the calculated and measured thickness differed.

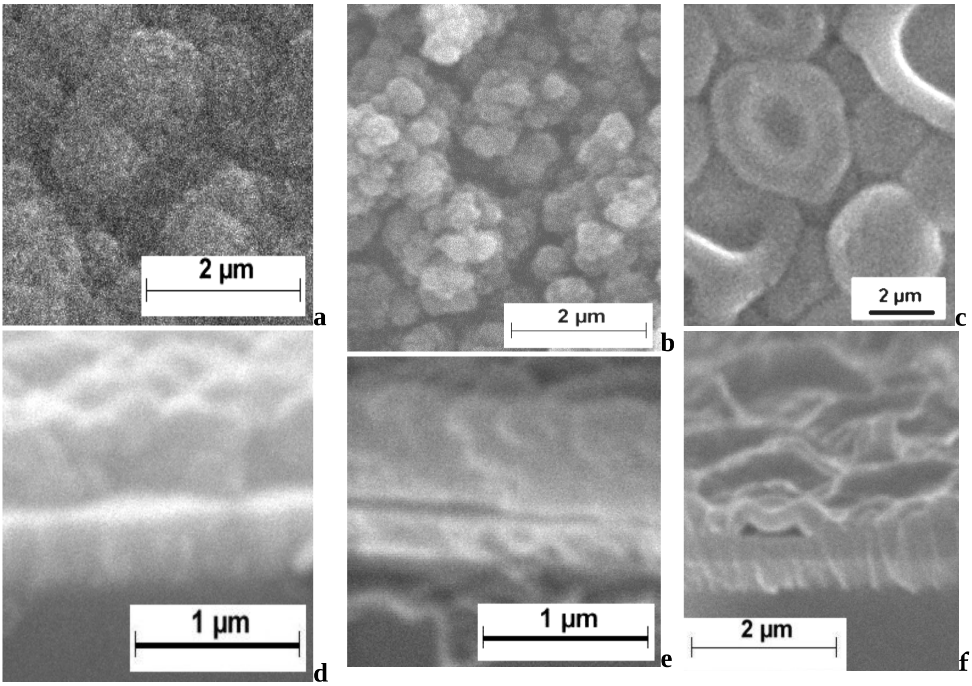

Figure 4.22. SEM of PPy and PPP-PPy composite films deposited on transparent substrates: (a) PPyDBS, (b) PPPI-PPyBr, (c) PPPI-PPyTOS; cross section: (d) PPPI-PPyDBS (e) PPyDBS, (f) PPPI-PPyTOS

In general, the SEM images show smoothness and confirm a high conductivity of the film both for organic and inorganic dopants. The composite films (c, d, f in Fig. 4.22) mainly indicate improved morphology, better mechanical properties and adhesion to the substrate layer. Improved adhesion of composite films possibly confirmed that the conductive PPP particles take part in the electrochemical deposition process, facilitating formation of organic covering to inorganic substrate. One additional conclusion, which follows from comparative SEM and electrochemical investigations, is that by means of modifying the preparation condition of composite coatings, the films with different morphologies and degrees of developed surface can be obtained.

4.2.5 Stability of structures under vacuum treatment

The PPP structures prepared by high temperature doping show high temperature stability in oxygen non-containing environments. However, investigating the temperature-dependent conductivity of the film, composite and multilayer structures were composed of PPy as one of the elements, some visible anomalies in the conductivity of structures were observed (section 4.2.2.2). It was supposed to be connected mainly with the instability of PPy electrical properties under vacuum treatment. The conductivity of electrochemically synthesized PPy was found sensitive to ionic impurities and moisture enclosed in the film that gives a possibility of proposing an application for PPy as active material in environmental sensors [68-70].

In order to obtain some estimation of the vacuum annealing influence on the electrical properties of the investigated structures, the dependence of samples conductivity on the vacuum annealing time plotted as $(\sigma_t-\sigma_{t0})/\sigma_{t0}$ versus $t^{1/2}$, where σ_t is the conductivity at time t and σ_{t0} is the initial conductivity is presented (Figure 4.23).

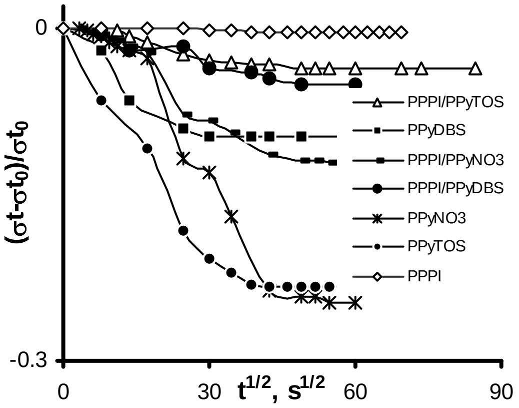

Figure 4.23. Conductivity decay of investigated structures at room temperature under the vacuum treatment

An extremely weak influence of vacuum treatment on the conductivity of high temperature doped PPP is caused by the high temperature doping technology. In addition to high thermal stability, it assumes heightened ability and the long lifetime of the possible devices based on PPP.

The conductivity decrease in PPP/PPy structures shows that the PPy film coatings have a strong influence on the stability of the electrical properties of multilayer structures. The possible explanation of the conductivity decrease in PPP/PPy is the presence of oxygen or/and moisture in PPy films.

The results of the studies of conductivity stability showed different curve slopes for PPy films containing different doping ions. After a certain time of conductivity decrease under vacuum treatment, the conductive parameters of films stabilized near the conductivity level, specific for each film. This level was found dependent on film thickness, doping anion nature and, possibly, on electrodeposition parameters. From this point of view, the investigations of the conductivity stability structures based on conductive polymers can be used for CP preparation control and also fulfill the basis for the application of the thermodynamic modeling method for structures with predicted properties preparation.

The application areas of the novel materials were connected firstly with their attractive properties but are also limited by negative features. From this point of view, the combined method for the formation of multilayers and composite coatings, consisting of PPy as film forming agent and PPP with high thermal and conductivity stability, allows for avoiding the low ability of the PPP to processing. In addition, it will extend the possibilities for the development of different electronic devices with stable electrical parameters, including hybrid organic-inorganic structures.

5. CONCLUSIONS

PPP was prepared according to the procedure of Kovacic by the oxidative cationic polymerization of benzene. The mild polymerization conditions (temperature of polymerization was 23-36 ^{0}C, the time of the synthesis - 3,5...4,5 h) gave a product with less than 0.2-1% extractables, which contained only minor amounts (<1%) of chlorine and polynuclear structures. The synthesized product found was an insoluble, non-melt-processible brown powder. The molecular weight determined by the infrared spectroscopy was that the synthesized PPP consisted of 14-16 benzoic rings. This method makes a polymer particularly suitable for producing highly conductive materials by doping [II in Appendix A].

The syntheses of PPy and PANI by the *in-situ* doping method resulted in a maximizing yield of fine powdered products. The sulfonic acids and their sodium salt used as dopants during in-situ polymerization make PPy and PANI with sufficiently high conductivity. Additionally, dodecylbenzene sulfonic ion imparts essential solubility in organic solvents to synthesized polymers. In pressed form, the synthesized polymers were applied for the PPy-PANI bilayers preparation using electrochemical processing. All the investigated bilayer structures show strong linear current-voltage characteristics and therefore ohmic contact between pellets and films. In addition, the electrical resistance between the layers was relatively low, that opening a number of possibilities for PANI and PPy to be applied as flexible conductive intermediate layers for different devices, including hybrid organic-inorganic ones [IV in Appendix A].

The high temperature doping method was developed as the possibility to prepare the conductive polymer - polyparaphenylene - with controlled electrical conductivity and high stability. The incorporation and distribution of the dopants like in classical semiconductive materials, was considered as the main reason for the conductivity increase in PPP. The high temperature doping was found being accompanied by the thermal destruction of the polymer, which affects the dopant incorporation process. For the thermochemical destruction control throughout iodine doping, the step-by-step doping method was suggested, and for bromine doping, the lower bromine pressures were recommended. By the step-by-step doping method, a higher level of control on the resulting conductivity in PPP than by the continuous doping at the related doping temperatures was obtained [II in Appendix A].

Based on the investigations of the kinetics of high temperature doping of PPP with iodine, bromine, potassium and sodium, the reasons and mechanism of the conductivity increase in PPP prepared by the high temperature doping were analyzed in detail. These reasons were considered connected directly with dopant incorporation into the polymer as the result of diffusion processes. The alkali metals doping process was found in a good agreement with the proposed diffusion model. The low values of potassium and sodium diffusion coefficients (4.2×10^{-8} and 3.5×10^{-8} cm^2/sec) at 250^0C were determined by the time required to establish contact between the sample and liquid dopant. The main problem for the PPP doped with alkali metals was found to be connected with the instability of conductive properties in air. The technology of high temperature doping determines the weak influence of vacuum treatment on the conductivity of high temperature doped PPP [III, II in Appendix A].

From the kinetics investigations of halogen doping of PPP, it was concluded that the high temperature doping of PPP is primarily initiated by the thermally activated incorporation process. The results of kinetics investigations give the values of the activation energies (*Ea*) of iodine diffusion in PPP about 0.81-1.05 eV and of bromine diffusion in PPP *Ea* = 0.24-0.44 eV. With an approximation that every incorporated dopant atom gives one charge-transfer defect, the values of the activation energy of conductive defects formation with high temperature doping were also calculated using the conductivity measurements. The obtained values of conductive defect formation energies during bromine doping of PPP at temperatures $500\text{-}600^0C$ were found at 1.54 eV, during iodine doping of PPP - 1.98 eV and the activation energy of conductive defect formation during high temperature annealing in vacuum of virgin PPP - 3.6 eV. The difference in the energies of conductive defect formation was explained by the bipolaron (dications with formation energy about 0.8-0.9 eV) and polaron (radical cations with formation energy about 1.5-1.9 eV) dominating defects formation. The parallels between dopant incorporation and conductive defect formation permitted one to conclude that the process of high temperature doping referred for as a diffusion process was determined by the conductive structure creation [III, II in Appendix A].

The temperature dependent conductivity was investigated for PPP doped with halogens and alkali metals to different doping degrees determined mainly by the doping temperature, doping time and the resulting conductivity level. Based on temperature-dependent conductivity studies, it was found that using the high temperature doping and the modification method, a wide range control of the electrical and to a significant extent, on electronic properties of PPP can be obtained [VI, I in Appendix A].

Based on the analysis of the experimental results, the optimal technology for halogen doped PPP structures preparation by the high temperature doping method was developed, combining the preliminary thermal treatment of samples at 520^0C with the following high temperature two-step doping at the same temperature. The PPP structures obtained using the proposed optimal technology have high stability and mechanical properties that confirmed the possibility of using the obtained structures as electrodes for the electrochemical deposition of

PPy films from aqueous solution. The conductivity investigations confirm the high adhesion of PPy films to PPP substrate. Based on temperature-dependent conductivity investigations, the preferable conductivity mechanisms in PPy films, in the high temperature doped PPP substrate electrode and in PPP/PPy multilayer structures were determined. The Mott's parameters were calculated using mathematical models for the determined mechanisms [V in Appendix A].

In addition, the high temperature doped PPP with halogens was used to prepare polyparaphenylene-polypyrrole (PPP-PPy) composite films with high conductivity and controlled stability of electrical properties by electrochemical deposition onto the different light transparent substrates - indium/tin oxide (ITO) and tin oxide (SnO_2) coated glass from aqueous-acetonitrile media containing suspension of high temperature doped PPP. Based on temperature-dependent conductivity investigations, it was found that conductive properties of PPPI-PPy composite films are similar to the conductive properties of PPy films deposited onto the high temperature doped PPP substrate. On the basis of experimental and calculation results, it was concluded that the PPPI-PPy composite films have acquired the electronic properties of PPP/PPy multilayer structures [VII in Appendix A].

The light transparent substrate and thin film formation technology allowed for obtaining optical spectra data, which indicates π- π^* transition for both of the composite film components. A number of optical data indicating band gaps 1.67-2.05 eV verifies the conductive defect formation nature in PPP obtained during the high temperature doping. The activation energy of conductive defect formation during the high temperature annealing in vacuum of virgin PPP - 3.6 eV was found close to the band gap value for π- π^* transition in PPP obtained from optical investigations. One conclusion important for the technology control of semiconductive structures based on conductive polymers is that, using various dopants and modifying PPP/PPy ratio, the optical properties could be modified in a wide range [VII in Appendix A].

SEM images indicate that the prepared films were obtained with a smooth surface but different morphology, depending on the formation conditions. Composite films have a higher level of adhesion to ITO or SnO_2 substrate layer and better mechanical properties than films that contain only PPy and the corresponding dopant. Improved adhesion of composite films possibly confirmed that the conductive PPP particles take part in the electrochemical deposition process, facilitating formation of organic covering to the inorganic substrate. By means of modifying the preparation condition of composite coatings, films with different morphologies and degrees of developed surface can be obtained.

The combined method for the formation of multilayers and composite coatings, consisting of PPy as a film forming agent and PPP with high thermal and conductivity stability, enables one to avoid the low ability of the PPP to processing and to extend the possibilities for the development of different electronic devices with stable electrical parameters, including hybrid organic-inorganic structures.

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APPENDIX A

ARTICLE I

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ARTICLE II

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ARTICLE III

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ARTICLE IV

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ARTICLE VII

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APPENDIX B

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APPENDIX B

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