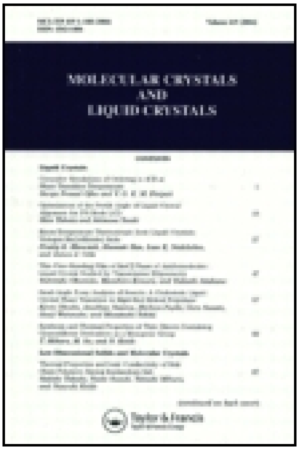


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Chemical and Physical Properties of Electrochemically Prepared Polyindole Hexafluorophosphate (PIPF$_6$)

K. M. Choi [a], J. H. Jang [a] & K. H. Kim [a]

[a] Department of Chemistry, Yonsei University, Seoul, 120, Korea

Version of record first published: 24 Sep 2006.

To cite this article: K. M. Choi, J. H. Jang & K. H. Kim (1992): The Chemical and Physical Properties of Electrochemically Prepared Polyindole Hexafluorophosphate (PIPF$_6$), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 220:1, 201-215

To link to this article: http://dx.doi.org/10.1080/10587259208033441

Mol. Cryst. Liq. Cryst., 1992, Vol. 220, pp. 201–215
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

The Chemical and Physical Properties of Electrochemically Prepared Polyindole Hexafluorophosphate ($PIPF_6$)

K. M. CHOI, J. H. JANG and K. H. KIM
Department of Chemistry, Yonsei University, Seoul 120, Korea

(Received July 24, 1991; in final form October 28, 1991)

Polyindole hexafluorophosphate ($PIPF_6$) was prepared by electrooxidation supplying a potential of 0.7 V. The cyclic voltammetry suggested that the electrode reaction was irreversible, and the electropolymerization of indole formed radical cations. Thermogravimetric analyses of the polyindole-based systems were performed at a temperature range of 25 ~ 800°C under a nitrogen atmosphere. From the TGA results, we concluded that most polyindole systems mainly decomposed at higher temperatures than the polyaniline-based ones. The maximum thermal decomposition rate (R_{max}) for polyindole systems was unaffected by the kind of electron acceptors, but the values of the polyaniline-based materials were affected by dopants. The electrical conductivity of the $PIPF_6$ was measured in a temperature range from -150 to 25°C. The values of log σ at 25°C and of E_a as calculated from an Arrhenius plot were -4.15 S/cm and 0.64 eV, respectively. Our conductivity measurements suggest that a possible conduction mechanism for the $PIPF_6$ pellet is the hopping conduction, and that the charge carriers are polarons. The ESR analysis of the $PIPF_6$ powder was performed at 25°C, and, thus, parameters of ΔH_{pp}, g-value and spectra ratio were obtained.

INTRODUCTION

Recently, our daily life has created demands for new materials that are more convenient, yet smaller, lighter weight, more specialized and complex. The demands for new materials have prompted studies of conducting polymers because of their applications for lighter weight materials in our daily life.

In the late of 1970's, the materials called "polymeric composite systems" were the main focus of research[1,2] resulting in applications of antistatic materials for electronic goods. But, polymeric composite systems had limits due to injection of filler and subsequent applications. At that time, Heeger et al.[3] reported that polyacetylene-based conducting polymers doped with various dopants exhibited a conductivity of 1000 S/cm at room temperature. Since this report, many researchers studied polyparaphenylene-,[4] polyparaphenylene sulfide-[5] and polythiophene-[6] based conducting polymers doped with various dopants, such as electron donors or acceptors. However, these conducting polymers when doped with anions or cations have shown some problems for stability in air.

Dall'Olio et al.[7] reported that the pyrrole was electrochemically polymerized by electrooxidation at anode. When we compare electrochemically and chemically polymerized systems, the electrochemically prepared conducting polymers are relatively stable in air, and the physical properties of these systems are not easily changed by an external stimulus. These electrochemically prepared polymers possibly result from a reversible electrochemical reaction, and, consequently have applications as electrode materials in rechargeable batteries. Owing to this application in electrochemical field of the polypyrrole-based systems, many researchers have shown interest in studies of organic compounds polymerized by electrooxidation. From this approach, it has been reported that the polyaniline-,[8] polyparaphenylene-,[9] polyazulene-,[10] polycarbazole-[11] and polypyrene-[12] based conducting polymers can result from electrooxidations.

Diaz and Hall[8] reported that polypyrrole p-toluenesulfonate (PPTS) as a freestanding film was prepared by electrooxidation from an acetonitrile solution containing 0.2M pyrrole and 0.1M tetraethylammonium p-toluenesulfonate supplying a potential about 0.8 V. Conductivity measurements of the PPTS obtained under various solvent conditions stimulated further study of the relationship between solvent condition and conductivity of the sample. Kitani et al.[9] reported on polyaniline-based systems obtained from electrochemical reaction where the active material of secondary batteries was in a cell of the type Zn/1M $ZnSO_4$/polyaniline. In this work, the polyaniline-based battery had a maximum capacity and the energy density of 108 Ah/Kg and 111 Wh/Kg, respectively. Also, the cell of polyaniline/4M H_2SO_4/PbO_2 showed excellent recyclability.

In order to obtain information of the structural model to predict the formation of polarons or bipolarons, Scott et al.[10] and Kaya et al.[11] performed ESR measurements for polypyrrole-based polymers. Scott et al.[10] reported that the peak intensity of neutral polypyrrole at room temperature is strongly affected by the amount of oxygen absorbed by the polymer. They also concluded that the source of the EPR signal was not related to the species responsible for the electronic conduction. In a study[12] of insulator-metal transition of conducting polymers, Yoshino and Kaneto reported that researches for conducting polymers were very attracted in point of scientific view as well as their applications in the solar batteries,[13] rechargeable batteries,[14] electronic switching elements, electro-optic devices, sensors and radiation detectors.[15]

In a study of numerous polymers prepared from aromatic compounds which have anodic potential below 2 V, polyazulene, polythiophene, polycarbazole, polypyrene and polytriphenylene were obtained through electrooxidation.[16] By controlling solvent effects and electrochemical conditions, attempts were made to produce intermediate around anode that can be formed as anodic precipitates.

We anticipated that indole and its derivatives were polymerized by electrooxidation. As shown in Table I,[16] the indole monomer has a proper anodic peak potential value for electropolymerization, and, so, polyindole-based conducting polymers doped with various anions seem to result from electrooxidation. For this work, the cyclic voltammetry and conductivity measurements suggested the polymerization and conduction mechanisms, respectively, and structural analysis resulted from IR, UV and ESCA measurements. Through thermal analysis of TGA measurements, the thermal characteristics of polyindole-based conducting polymers were studied, and morphology analysis of $PIPF_6$ film was also carried out.

TABLE I

Anodic peak potentials of various aromatic monomers which can be polymerized by electrooxidation[16]

Compounds	Anodic Peak Potentials (V)
Aniline	0.73
Azulene	0.91
Carbazole	1.30
Indole	0.90
Pyrene	1.23
Pyrrole	1.20

EXPERIMENTAL

Materials

Indole used as monomer in this electropolymerization was obtained from the Kanto Chemical Company. Acetonitrile (AN) and benzonitrile (BN) as solvents were purchased from the Merck Chemical Company. Tetraethylammonium hexafluorophosphate ($TEAPF_6$) was also purchased from the Aldrich Chemical Company. The $TEAPF_6$ was fully dried in a vacuum oven at 25°C because of its hygroscopic property, and then taken directly out from the vacuum oven at every experiment.

Acetonitrile was retried for purification, that is, we passed the solvent through a column packed with alumina and trifluoroacetic anhydride to remove the water.

Sample Preparations

Polyindole hexafluorophosphate ($PIPF_6$) was obtained by electrooxidation reaction. Supplying a potential of 0.7 V, the $PIPF_6$ was produced from 0.2M indole in a [AN/BN/water (volume %: 4/1/0.1)] solution containing 0.1M $TEAPF_6$ as a supporting electrolyte. For an electropolymerization reaction, we prepared a specially produced quartz cell. The reaction cell was made as a duplicated vessel, and, thus, the temperature of the solution in cell was maintained at 25°C by a circulator (Lauda Co.) connected with the reaction vessel using rubber pipes.

As shown in other reports,[8] most electropolymerization has been performed in a three-electrode system. In this work, a three-electrode cell system was adopted by using a Pt electrode as the working and counter electrodes, and a Ag/AgCl cell as a reference electrode. A top of reaction cell was manufactured having three joint parts fixed for the three electrodes.

The $PIPF_6$ sample was obtained as insoluble precipitates at the anode supplying a potential of 0.7 V, and was removed from anode, and washed with solvent and dried in a vacuum oven until constant weight was achieved, and finally was obtained as a powder sample.

Elemental Analysis

Elemental analysis of the $PIPF_6$ powder was performed using an elemental analyzer (Perkin Elmer: 240-C). The results are listed in Table II.

Electrochemical Measurements

Electrochemical equipment was available to produce anodic precipitates and to acquire electrochemical information. We performed the electrochemical works with a potentiostat (Hokuto Denko Co.: HA-301) and a function generator (Hokuto Denko Co.: HB-104). The cyclic voltammogram for the solution reaction in the cell was plotted from a plotter (Omega: DAP-780).

Conductivity Measurements

In this paper, the electrical conductivity measurement for the $PIPF_6$ pellet was performed by the four-probe method at temperature ranges from −150 to 25°C. The $PIPF_6$ powder was fully dried in a vacuum oven, and was milled as uniform particles, and then made into a pellet under a pressure of 98.06 MPa. Thus, the pellet had a disc-shape form with a 12 mm diameter and a thickness of 2 mm.

For the conductivity measurements, a sample basket was placed in the middle of a probe equipped with four Pt-lines and a thermocouple. Then, the thermocouple in the probe was connected with a digital thermometer (Seoul Control Co.: SR-6200, G-116), and a low temperature was obtained by using liquid nitrogen. The current and potential were measured with a digital electrometer (Keithley: 616) and a digital multimeter (Keithley: 642), respectively, and the conductivity was measured under a heating rate of 1°C/min.

Thermal Analysis

The thermogravimetric analysis (TGA) of the $PIPF_6$ powder was carried out using a thermal analyzer (Rigaku-8150). The temperature range in the TGA measurements was 25 ~ 800°C. Then, the experiment continued under a nitrogen gas with a heating rate of 10°C/min.

TABLE II

Elemental analysis for polyindole hexafluorophosphate

	Polymer Chains (%)			Dopant
	C	H	N	(%)
$PIPF_6$	60.1	5.0	8.5	26.4

Scanning Electron Microscopy (SEM)

Generally, the growing rate of conducting polymers in this electrochemical system is related to the current density, applied potential, concentration and resistance of the solution. For the SEM measurements, the $PIPF_6$ film was obtained on the anode under a proper potential of 0.7 V, and then was washed with solvent. The morphology analysis of the $PIPF_6$ film was performed using a scanning electron microscope (Hitachi: S-510) and an ion coater (Eiko: IB-3).

ESR Measurements

Since most of conducting polymers have been obtained as insoluble and opaque products, the spectrochemical analyses of these polymers often encounter some difficulty. At this point, electron spin resonance (ESR) measurements for conducting polymers seem to be an appropriate method for analysis. In this work, for the $PIPF_6$ sample that was obtained as a solid powder, the ESR measurement was performed by the solid sample method at 25°C. The $PIPF_6$ powder was filled in an ESR tube, and an ESR spectrum for the $PIPF_6$ powder was obtained using an ESR spectrometer (Bruker, ER 200, E-SRC) under the following conditions: scan range, 100 G; microwave frequency, 9.43 GHz; microwave power, 20dB, 2mW; modulation frequency, 100 KHz; modulation time constant, 1 sec; modulation amplitude, 4 G_{pp}; receiver gain, 1×10^3.

ESCA Analysis

For the ESCA analysis of the $PIPF_6$, the sample was prepared as a disc-shaped pellet. In this work, the ESCA measurement of this pellet was performed by using a X-ray photoelectron spectrometer (Shimadzu: ESCA-750). The XPS used in this work possessed the X-ray source of the Mg-Kα line.

IR Measurements

The $PIPF_6$ powder obtained was an insoluble and opaque material. Thus, the KBr-pellet method was adopted for the FT-IR analysis of the $PIPF_6$ sample. The IR result for the $PIPF_6$ was obtained by using an IR spectrometer (Biorad, FTS-80). In order to protect an air-mixing phenomenon, the $PIPF_6$ pellet was made in a vacuum chamber.

UV Measurements

As the supplying of potential in reaction cell, the anodic intermediates were produced around anode. Then the color of the solution around anode got darker. But, if these anodic intermediates were rapidly diffused to a bulk solution, the products as anodic precipitates could not have been obtained on anode. For this reason, we thought that a spectrochemical analysis of these solutions was needed around anode and at the bulk regions was valuable in this system.

As the electrochemical reaction progressed, the color of solution around anode directly turned to a dark green and diffused to a bulk solution. We then extracted the bulk solution carefully using a microsyringe, and labelled the solution as "PF-

1." We also extracted the dark green solution around anode, and labelled the solution as "PF-2." Finally, when the reaction was fully progressed, the color of solution changed to almost black. We then extracted this final solution using a microsyringe, and labelled the solution as "PF-3." UV measurements for the "PF-1, 2 and 3" solutions were performed using an UV spectrometer (Shimadzu: UV-240).

RESULTS AND DISCUSSION

Cyclic Voltammetry

Obtaining high quality conducting polymers requires consideration of various electrochemical conditions related to electrochemical parameters and other useful information. In the fields dealing with electrode reactions, reversibility is occasionally important. If an electropolymerization reaction responds rapidly to a supply of external potential, then the products show a relatively good quality in comparison to these showing a slower response. Also, the physical properties of products prepared by a three-electrode system are better than those of polymers produced from the two-electrode cell. In an electrochemical system to obtain a conducting polymer, the selection of the proper electrode system and solvents and the control of the external potential and the electrochemical conditions are considerably important.

The cyclic voltammetry of a [AN/BN/water] solution containing 0.2 M indole and 0.1 M TEAPF$_6$ at 25°C was performed. The cyclic voltammogram had been obtained from a consideration of the scan rate (v) and the charging current (i_c) to obtain an exact peak potential in the cyclic voltammogram. In case of a reversible system, the peak potentials (E_p) do not depend on the scan rate, and the peak width (ΔE_p) of the anodic and cathodic peak potentials (E_{pa}, E_{pc}) is usually 58/n mV at 25°C. On the other hand, in the case of the irreversible system, the peak potentials changed with the scan rate.

Figure 1 shows the results of the cyclic voltammetry for an indole solution at a scan rate of 90 mV/sec. As shown in Figure 1, the anodic and cathodic peak potentials were 335 and 260 mV, respectively, and the peak width (ΔE_p) of E_{pc} and E_{pa} is 75 mV. The results indicate that the electrode reaction is irreversible.

SEM Analysis

The conductivity of conducting polymers is related to various factors, such as the structure of the polymer chains, the kind of dopants, density, shape and morphology. Thus, from the morphology analyses of polymer films, we are likely to obtain useful information on the relationship between polymer structure and conductivity. For the SEM analysis of the PIPF$_6$ film, the PIPF$_6$ film coated on the anode was prepared from a [AN/BN/water] solution containing 0.2M indole and 0.1M TEAPF$_6$. The results are shown in Figure 2. Figure 2 shows that the morphology results of the PIPF$_6$ film as sparse granules on the surface. Also, since it did not show an oriented pattern in any special direction, the conducted direction of electrons is not likely to be in any order.

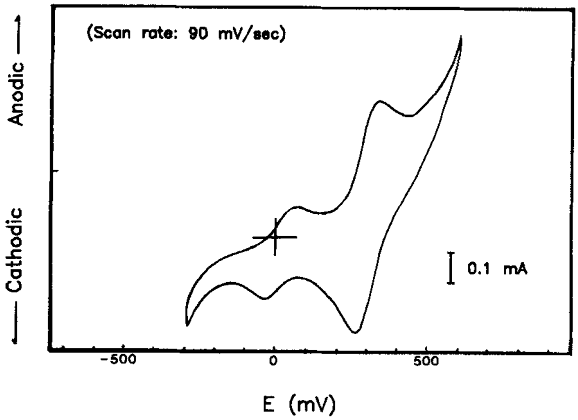


FIGURE 1 Cyclic voltammogram of a polyindole hexafluorophosphate film on a Pt electrode in AN/BN solution at 25°C.

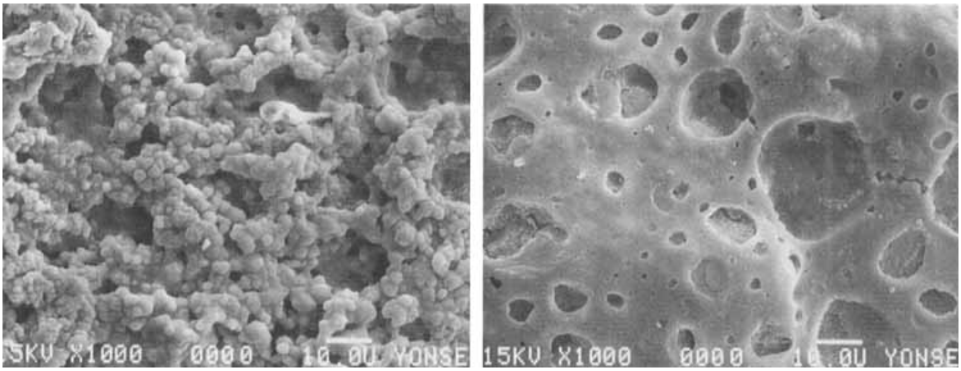


FIGURE 2 Scanning electron micrograph of a polyindole hexafluorophosphate film.

UV Measurements

During the electrooxidation in the indole solution containing $TEAPF_6$ as a supporting electrolyte, the products around anode diffused to a bulk solution, and their colors darkened. As mentioned in the Experimental Section of this paper, the solutions labelled "PF-1, 2 and 3" were prepared, and their UV measurements were performed. Figure 3 shows the results.

In the "PF-2" solution, triple peaks at 350, 374 and 390 nm were observed. This seems to result from the various species produced around anode during the electrooxidation. In the "PF-1" solution, a peak at 375 nm was obtained. In the final solution labelled "PF-3," a main peak at 393 nm and a shoulder peak at 426 nm were obtained. The appearance of a shoulder peak can be explained as a result of red shift owing to electropolymerization.

FT-IR Measurements

As considered in Table I, it appears that the indole monomer can be polymerized by electrooxidation at anode. The anodic precipitates obtained from the anode

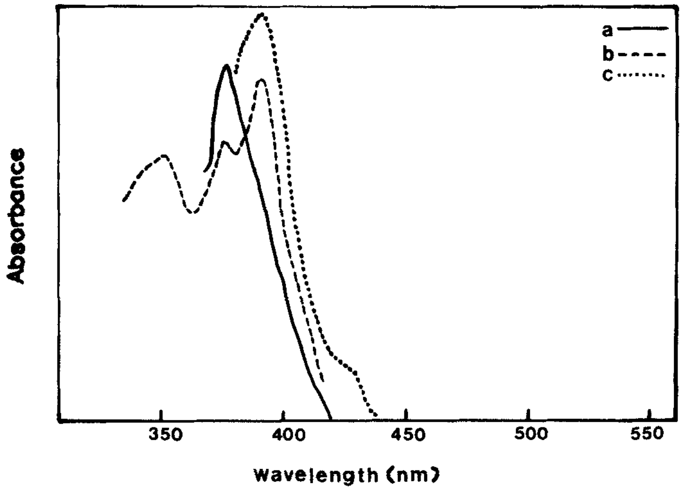


FIGURE 3 UV spectra of a) PF-1, b) PF-2 and c) PF-3 solutions.

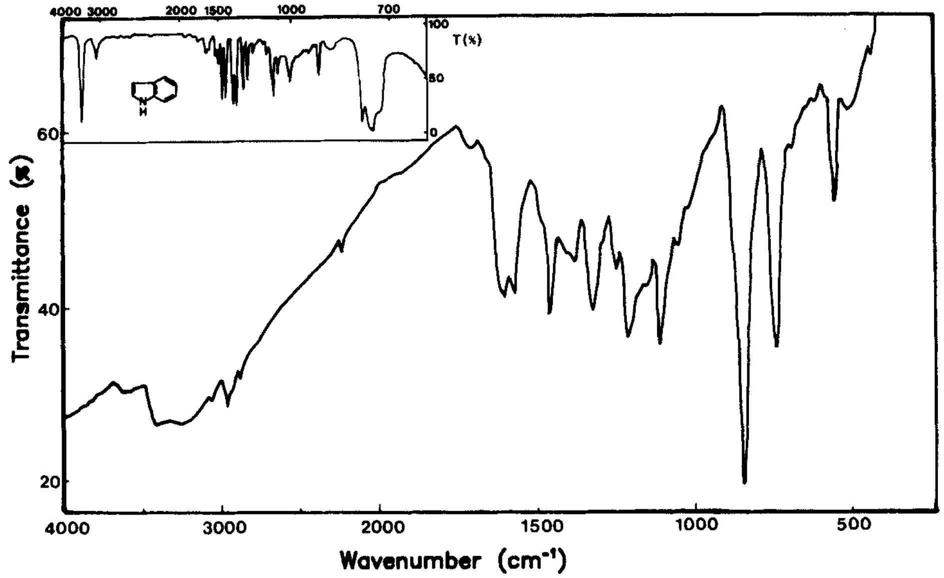
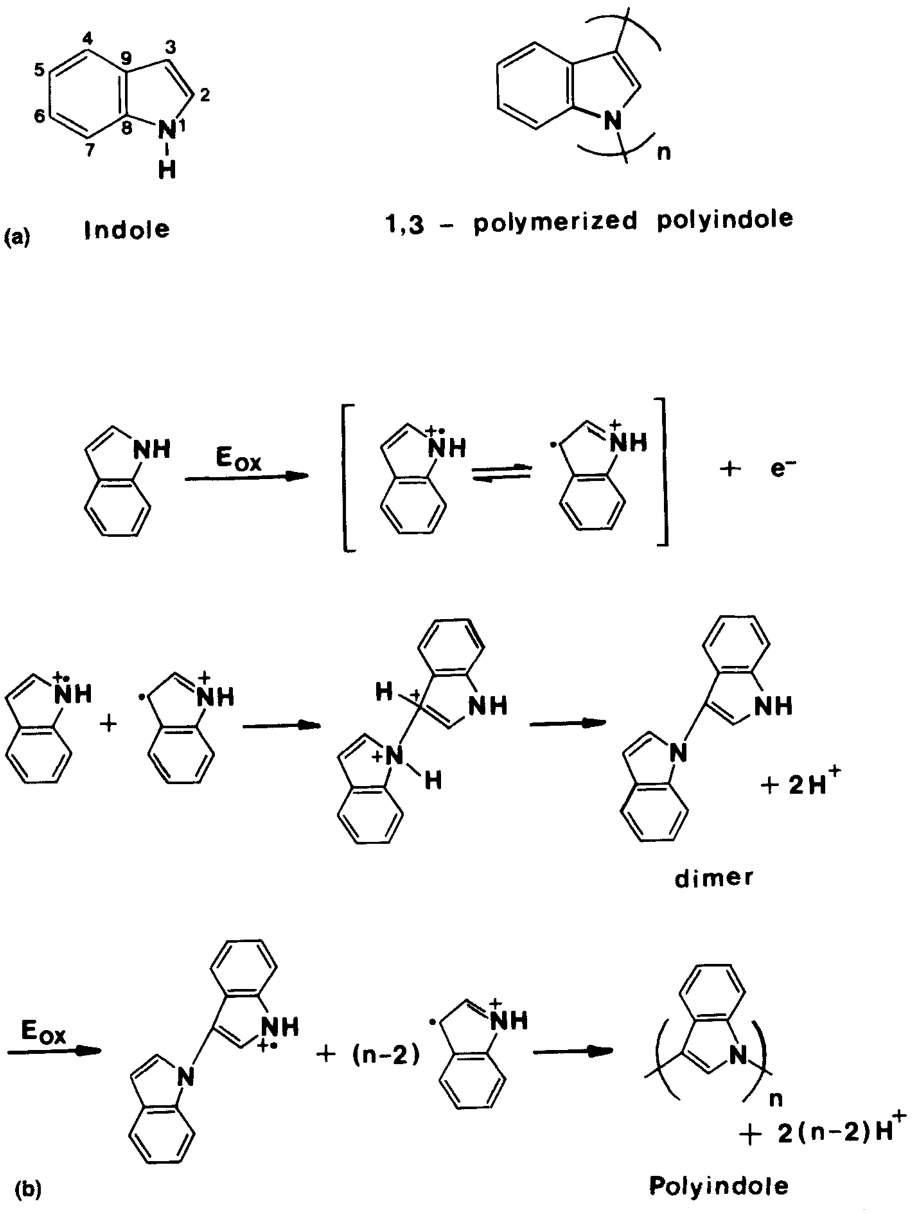


FIGURE 4 The FT-IR spectra of polyindole hexafluorophosphate in KBr pellet.

were thought to be polyindole doped with hexafluorophosphate anions. So, the structure analysis of the anodic product was performed with FT-IR measurements in the KBr pellet method. Spectroscopic analysis for the sample that was obtained as opaque materials was performed with some difficulties.

The FT-IR measurements of the $PIPF_6$ powder were carried out. Figure 4 shows the results. To interpret the IR results, a possible structure of polyindole was considered. In the study of polyindole perchlorate, Waltman et al.[17] suggested that polyindole had a 1,3-polymerized structure, as shown in *a*) of Scheme I. As the



SCHEME I Polymerization mechanism of polyindole

IR result of the $PIPF_6$ was interpreted in this work, their suggestion was referenced.

In Figure 4, the peaks induced by the stretching mode of the secondary amine did not appear. This means that a nitrogen atom in indole monomer participated in the polymerization, that is, the secondary amine in the indole changed to a tertiary amine after electropolymerization. These results proved the 1,3-polymerized structure of indole. Also, the peaks at 1454, 1570 and 1600 cm^{-1}, all obtained from the aromatic alkene, the peak at 1320 cm^{-1} due to amine, and the peaks at 742 and 839 cm^{-1} induced by aromatic alkene were observed.

ESCA Analysis

By numerous works regarding conducting polymers obtained from electropolymerization, the possible electropolymerization mechanism was generally suggested to be the radical cation mechanism. Our work suggests that polyindole was obtained by electrooxidation at anode, producing a radical cation intermediate. Thus, to acquire a neutral charge, the anions produced by the supporting electrolytes were doped into polymer chains positively charged.

To perform the ESCA analysis of the $PIPF_6$ powder, the sample was made into a disc-shape pellet, and N_{1s}– and C_{1s}-spectra for the $PIPF_6$ pellet were obtained. a) and b) of Figure 5 show the N_{1s}- and C_{1s}-spectra of the $PIPF_6$, respectively. In a), the N_{1s}-main peak of 400 eV is observed, and a peak obtained at higher binding-energy is also observed. The appearance of a peak at high binding-energy region can be explained as the nitrogen atoms in polyindole with a positive charge. It is likely that the PF_6^- anions can be doped in the polyindole chains.

In b) of Figure 5, a C_{1s}-main peak at 284.7 eV and a shoulder peak about 285.8 eV were observed. The shoulder peak can be explained as carbon atoms in the polymer chain that have a little cationic character owing to the doping of dopants.

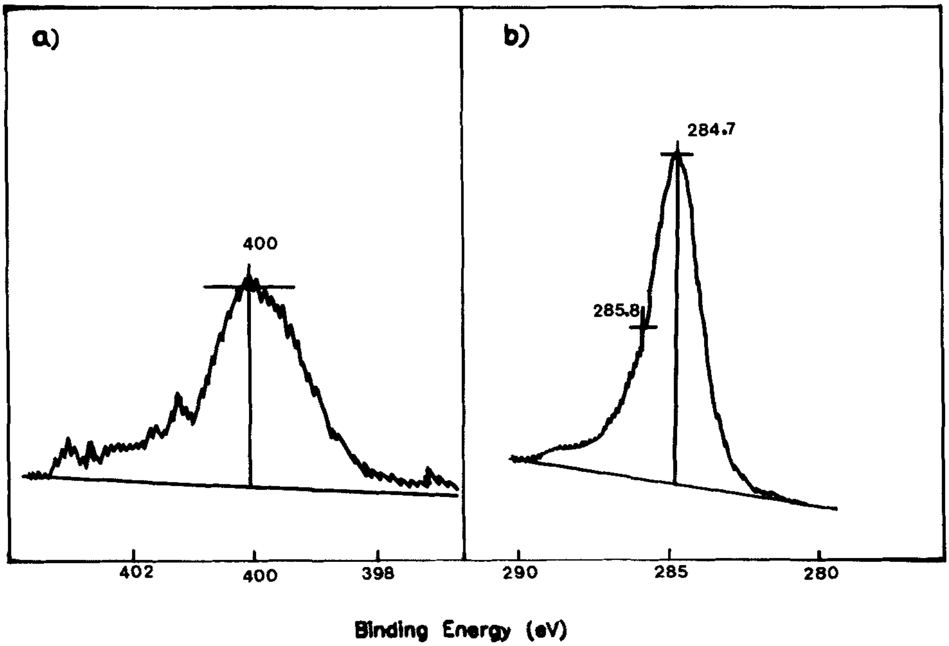


FIGURE 5 ESCA spectra of a polyindole hexafluorophosphate pellet (a: N_{1s} and b: C_{1s}).

Polymerization Mechanism

Many researchers have studied solvent effects and the relationship between the solvent condition and conductivity for conducting polymers obtained from electrooxidation. Most suggest that the possible mechanism of electropolymerization for most aromatic compound-based conducting polymers under acetonitrile solution is the radical cation mechanism.[16]

In this work, the polymerization mechanism of the $PIPF_6$ obtained under a [AN/BN/water] solution suggest the radical cation formation mechanism, as b) of Scheme I explains. Two oxidized indole monomers produced around anode formed a dimer, and the dimer was also oxidized at anode, and it coupled with another oxidized dimer or monomer, and so the electropolymerization was continuously progressed around anode. This suggestion agreed with the results of spectrochemical measurements performed in this work.

TGA Measurements

From thermal analysis of conducting polymers obtained from various methods, we can derive useful information regarding the physical properties of polymers. Thermogravimetric analysis (TGA) for the $PIPF_6$ powder was performed to obtain its thermal characteristics in the temperature range of 25 ~ 800°C under nitrogen stream. To compare the thermal characteristics with the $PIPF_6$ and other polyindole-based polymers, the polyindole perchlorate (PIP) and polyindole tetrafluoroborate ($PIBF_4$) were also prepared by electrooxidation under proper solvent conditions. The reaction rates of thermal decomposition (R: dW/dt) for the PIP, $PIPF_6$ and $PIBF_4$ powders were calculated under a scan rate of 10°C/min. As shown in Figure 6, the R-values plotted increased with the temperature, and this result was compared with that of the polyaniline system.[18]

Figure 6 depicts the distinguishable thermal characteristics for the polyindole- and polyaniline-based systems. The polyindole-based systems mainly decomposed at higher temperature regions than polyaniline-based ones. Therefore, if we advance the conductivities of polyindole-based systems through the studies for their electronic properties, they can be applicated in industrial fields requiring heat resistance at high temperature.

Figure 6 also clarifies that the R_{max}-values of polyaniline systems are mainly affected by the kind of dopants. But, the values of polyindole-based ones have nothing to do with the kind of dopants. That is, the polyindole systems have a merit for various selection of dopants.

Conductivity

Most conducting polymers have the electron donor or acceptor level in the polymers, and the conductivities of these polymers increase with increases in the dopants. Relating conductivity with temperature, conducting polymers show a semiconductor characteristic in which the conductivity increases with temperature. Also, it seems that the trends of conductivity with changing temperature may indicate the conduction mechanism of conducting polymers. Various equations have emerged from the many studies for these amorphous materials.

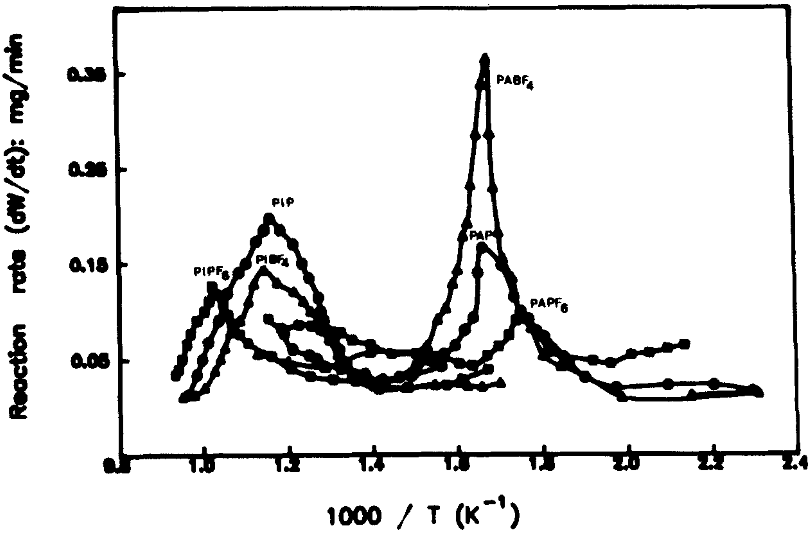


FIGURE 6 The temperature dependences of the reaction rates for various polyaniline- and polyindole-based conducting polymers.

Mott[19] suggested that an equation based on hopping conduction in amorphous semiconductors at the temperature range of 60 ~ 300 K was written as a form of $\exp(-T^{-1/4})$. Greaves[20] also reported variable range hopping conduction expressed in the equation $\sigma \cdot T^{1/2} = \exp(-T^{-1/4})$. Mataré[21] reported the electronic conduction, which includes the grain boundary potential (E_a), expressed in the equation $\sigma = AT^{1/2} \cdot \exp(-E_a/\mathrm{kT})$, where A is constant and dependent on the electric field strength. Zeller[22] suggested tunneling conduction. According to his report, an equation based on tunneling conduction of amorphous materials was expressed as $\sigma = \sigma_0 \cdot \exp(-T^{-1/2})$.

Electrical conductivity for the PIPF$_6$ pellet was performed in the temperature range from −150 to 25°C under low applied fields to ensure Ohmic behavior. Figure 7 shows the result. The conductivity of the PIPF$_6$ pellet increases linearly with the temperature, satisfying the Arrhenius equation, $\sigma = \sigma_0 \cdot \exp(-E_a/\mathrm{kT})$. From the result, the values of log σ at 25°C and E_a were calculated to be −4.15 S/cm and 0.64 eV, respectively.

Many factors and conditions affect the conductivity of amorphous materials. Consequently, general equations based on any conduction mechanism will present some difficulties. We merely attempt to determine the conduction mechanism with the best linearity for the PIPF$_6$ pellet. We obtained various plots applied to equations mentioned above. Among these, we confirmed that a plot based on hopping conduction suggested by Greaves showed the best linearity, and the plot is shown in Figure 8. We conclude that the possible conduction mechanism for the PIPF$_6$ is hopping conduction. Therefore, as for the PIPF$_6$ system, we suggested a model that the doping levels with polaron states along the polymer chains were formed with increasing of doping, and the polarons hopped from one to another state.

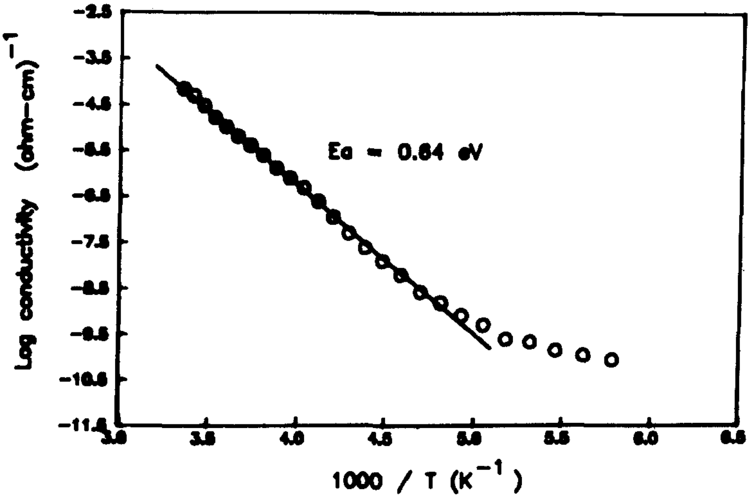


FIGURE 7 The electrical conductivity as a function of temperature for polyindole hexafluorophosphate.

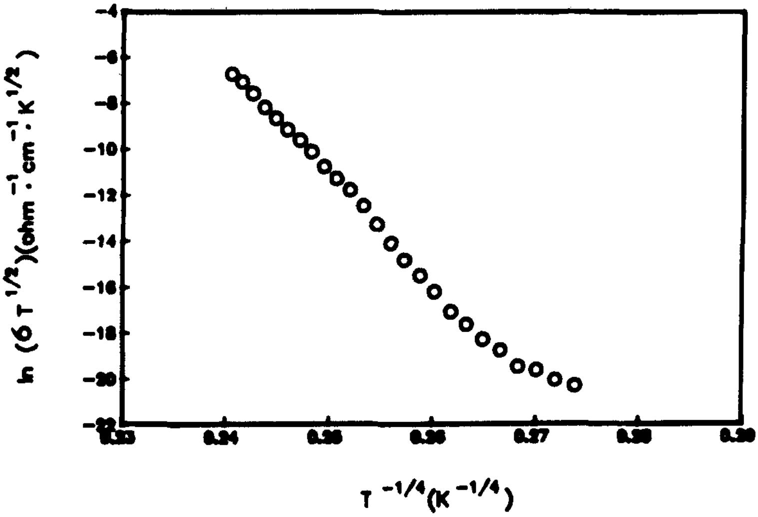


FIGURE 8 The temperature dependence of electrical conductivity for a polyindole hexafluorophosphate based on the hopping conduction.

ESR Measurements

The ESR measurements of conducting polymers offered us valuable information for the structures of polymers. For this reason, some groups have performed the ESR studies[23,24] of the polypyrrole-based systems. Genies and Pernaut[24] reported that the number of spins in polypyrrole had a maximum at a certain electrode potential followed by decreases at higher potentials. Also, in previous works, it has been mentioned that the ESR parameters (ΔH_{pp}, g-value and peak ratio) are related to their conductivity values. According to this suggestion, some researchers

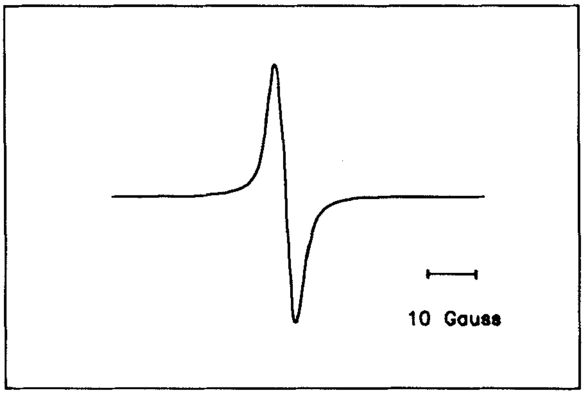


FIGURE 9 ESR spectrum of polyindole hexafluorophosphate at 25°C (microwave frequency: 9.44 GHz).

TABLE III

Comparison of ESR parameters and log conductivity at 25°C for polyindole-based polymers

Polymers	ΔH_{pp} (G)	g-value	Log σ at 25 °C (S/cm)
PIP	2.6	2.00415	- 1.63
$PIBF_4$	2.8	2.00486	- 2.43
$PIPF_6$	3.3	2.00574	- 4.15

were interested in whether ESR parameters were related to the conductivity of polymers.

In this work, the ESR measurements of the $PIPF_6$ powder at 25°C were performed. The results are in Figure 9. The ESR spectrum of the $PIPF_6$ obtained was a single peak like those of most conducting polymers. The ESR parameters obtained from this spectrum are listed in Table III, which lists a comparison of ESR parameters and log σ for polyindole-based systems. The results show that ΔH_{pp} and g-value decrease with increases in conductivity. Thus, we conclude that the ESR parameters in polyindole systems are related to their conductivity.

CONCLUSIONS

The $PIPF_6$ powder was obtained from a [AN/BN/water] solution containing 0.2M indole and 0.1M $TEAPF_6$. The cyclic voltammetry confirmed that the electrooxidation of indole was an irreversible reaction. Spectroscopic analysis of the anodic precipitate indicated the structure of $PIPF_6$ and the radical cation mechanism of the polymerization was confirmed.

The TGA measurements of the $PIPF_6$ powder were performed to obtain information on the thermal and physical properties of polymers. Thermal analysis confirmed that the polyindole-based systems thermally decomposed at higher temperatures than those of the polyaniline-based ones. Also, the maximum reaction rates (R_{max}) of the polyindole systems were not affected by the kind of dopants, but the R_{max}-values of the polyaniline ones were mainly affected by electron acceptors.

The electrical conductivity of the $PIPF_6$ pellet was measured in the temperature ranges from -150 to 25°C, and the values of $\log \sigma$ at 25°C and E_a obtained were -4.15 S/cm and 0.64 eV, respectively. Conductivity measurements conclude that hopping conduction is a possible conduction mechanism for the $PIPF_6$ pellet, and that the charge carriers are polarons. The ESR measurements of the $PIPF_6$ powder at 25°C were performed, and the values of ΔH_{pp} and g-value were obtained.

Acknowledgment

The authors are grateful to Doctors H. W. Rhee and C. Y. Kim, Korea Institute of Science and Technology, for electrochemical measurements.

References

1. E. K. Sichel, M. F. Rubner and S. K. Tripathy, *Phys. Rev. B*, **26(12),** 6719 (1982).
2. J. P. Reboul and G. Moussalli, *J. Poly. Mat.*, **5,** 133 (1976).
3. C. K. Chiang, C. R. Fincher, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau and A. G. MacDiarmid, *Phys. Rev. Lett.*, **39,** 1098 (1977).
4. S. Aeiyach, J. E. Dubois and P. C. Lacaze, *J. Chem. Soc. Chem. Commun.*, 1668 (1986).
5. L. W. Shacklette, R. L. Elsenbaumer, R. R. Chance, H. Eckhardt, J. E. Frommer and R. H. Baughman, *J. Chem. Phys.* **75(4),** 1919 (1981).
6. J. Roncali and F. Garnier, *J. Phys. Chem.*, **92,** 833 (1988).
7. A. Dall'Olio, Y. Dascola, V. Varacca and V. Bocchi, *Comptes Rendus C*, **267,** 433 (1968).
8. A. F. Diaz and B. Hall, *IBM J. Res. Develop.*, **27(4),** 342 (1983).
9. A. Kitani, M. Kaya and K. Sasaki, *J. Electrochem. Soc.*, **133(6),** 1073 (1986).
10. J. L. Brédas, J. C. Scott, K. Yakushi and G. B. Street, *Phys. Rev. B*, **30(2),** 1023 (1984).
11. M. Kaya, A. Kitani and K. Sasaki, *Chem. Lett.*, 147 (1986).
12. K. Yoshino and K. Kaneto, *Mol. Cryst. Liq. Cryst.*, **121,** 247 (1985).
13. S. C. Chen, A. J. Heeger, Z. Kiss and A. G. MacDiarmid, *Appl. Phys. Lett.*, **36,** 1 (1980).
14. P. J. Nigrey, D. MacInnes, D. P. Nairns, A. G. MacDiarmid and A. J. Heeger, *J. Electrochem. Soc.*, **128,** 1651 (1981).
15. K. Yoshino, S. Hayashi, Y. Kohno, K. Kaneto, J. Okube and T. Moriya, *Jpn. J. Appl. Phys.*, **23,** L189 (1984).
16. T. A. Skotheim, "Handbook of Conducting Polymers," Marcel Dekker, Inc., New York (1986).
17. R. J. Waltman, A. F. Diaz and J. Bargon, *J. Phys. Chem.*, **88,** 4343 (1984).
18. K. M. Choi, E. J. Lee, J. W. Park and K. H. Kim, *J. Appl. Poly. Sci.*, **42,** 2129 (1991).
19. N. F. Mott, *Phil Mag.*, **19,** 835 (1969).
20. G. N. Graves, *J. Non-Cryst. Solids*, **11,** 427 (1973).
21. M. F. Mataré, *J. Appl. Phys.*, **56,** 2605 (1984).
22. H. R. Zeller, *Phys. Rev. Lett.*, **28,** 1452 (1972).
23. J. C. Scott, P. Pfluger, M. T. Krounbi and G. B. Streets, *Phys. Rev. B*, **28,** 2140 (1983).
24. E. M. Genies and J. M. Pernaut, *J. Electroanal. Chem.*, **191,** 111 (1985).