

# A Study of Polyindole Perchlorate (PIP) Prepared by Electropolymerization

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## SYNOPSIS

Polyindole perchlorate (PIP) was obtained by electrochemical oxidation using a potential of 0.7 V as anodic precipitates. A cyclic voltammetry was performed in acetonitrile solution containing 0.2 M indole and 0.1 M tetraethylammonium perchlorate. The result suggested that this electrode reaction was reversible, and the peak width ( $\Delta E_p$ ) of the anodic and cathodic peaks obtained was 58 mV. The result of IR measurements clarified that the polyindole was obtained by a 1,3-polymerized mechanism. As for the ESCA analysis of the PIP pellet, besides a main N<sub>1s</sub> peak at 399.6 eV, a high binding energy peak at 402.3 eV was observed. Also, in the case of the C<sub>1s</sub> peak, besides a main peak at 284.6 eV, a shoulder peak at high binding energy was measured. These results suggested that an electropolymerization of indole was performed by the formation of radical cations. A thermogravimetric analysis was performed in a temperature range from 25 to 800°C. The rate of thermal decomposition ( $R$ ) for the polyindole- and polyaniline-based polymers was calculated by a computer connected with a thermal analyzer. From the thermal analysis, it was concluded that the polyindole-based polymers decomposed at higher temperatures than did the polyaniline-based samples. The  $R_{max}$  values of the polyindole systems were not related to the kind of dopants, but in the case of the polyaniline systems, they were seriously affected by the kind of electron acceptors. The electrical conductivity of the PIP pellet was performed in a temperature range from 150 to 25°C. The values of  $\log \sigma$  at 25°C and  $E_a$  obtained were  $-1.63$  s/cm and 0.508 eV, respectively. From the results, we suggested that a possible conduction mechanism and charge carriers for the PIP pellet were hopping conduction and polarons, respectively. The ESR measurements for the PIP powder were performed at room temperature, and the values of various ESR parameters were calculated. © 1992 John Wiley & Sons, Inc.

## INTRODUCTION

According to the demands in daily life and industry, various conducting polymers that have numerous functions have been studied as new polymeric materials.<sup>1-13</sup> The initial studies for these materials have been performed mainly in the systems of polyacetylene<sup>1</sup> polyparaphenylene,<sup>2</sup> polyparaphenylene sulfide,<sup>3</sup> and polyparaphenylene vinylene and polythiophene.<sup>4</sup> Among the conducting polymers that have conjugated double bonds, the bands along the polymer chains are formed by the overlapping

of  $\pi$ -orbitals, and, thus, conductivities of these polymers increase by the doping of various dopants. Then, the anions or cations doping in polymers act as an electron acceptor or donor, respectively. Based on the results of spectrochemical analysis using a Raman and a Mössbauer for iodine-doped polyacetylene, Lefrant<sup>5</sup> reported that iodines doping in polyacetylene substituted as anions of  $I_3^-$  and  $I_5^-$ . In the polyacetylene-based conducting polymers, the forms of various electron donors and acceptors in polymers and their conductivities at 25°C are summarized in Table I.<sup>6</sup>

Recently, many researchers have studied electropolymerization for aromatic compound-based conducting polymers. In this approach, polypyrrole-,<sup>7,8</sup> polyaniline-,<sup>9</sup> polycarbazole-,<sup>10</sup> polyazulene-,<sup>11</sup> and

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**Table I** Existent Forms of Various Dopants in Polyacetylene and Values of Conductivity at 25°C (Ref. 6)

Reactants	Dopant Forms in Polymer	Reaction Condition	Conductivity at 25°C (s/cm)
I <sub>2</sub>	I <sub>3</sub> <sup>-</sup> , I <sub>5</sub> <sup>-</sup>	Vapor	360–1000
AsF <sub>5</sub>	AsF <sub>5</sub> <sup>-</sup>	Vapor	560
FeCl <sub>3</sub>	FeCl <sub>4</sub> <sup>-</sup>	CH <sub>3</sub> NO <sub>2</sub>	897
NaC <sub>10</sub> H <sub>8</sub>	Na <sup>+</sup>	THF	80
Na <sub>2</sub> Ph <sub>2</sub> CO	Na <sup>+</sup>	THF	100
LiPh(CH <sub>2</sub> ) <sub>6</sub> Ph	Li <sup>+</sup>	Pentane	20
Fe(ClO <sub>4</sub> ) <sub>3</sub>	ClO <sub>4</sub> <sup>-</sup>	Toluene	500

polypyrrole-<sup>12</sup>based materials have been mainly investigated. Among these polymers, the polypyrrole-based conducting polymers have been usually studied, and the results of polyaniline-based systems have often been reported. Diaz and Hall<sup>13</sup> reported that polypyrrole *p*-toluenesulfonate film was obtained by electrochemical oxidation, supplying a potential of 0.8 V in acetonitrile solution containing 0.2M pyrrole and 0.1M tetraethylammonium *p*-toluenesulfonate (PPTS). From a study of solvent effects using solvents of acetonitrile, ethylene glycol, glycol, and water, the PPTS film obtained from a solvent condition of acetonitrile/water (99/1) was shown to be the highest conductivity among materials prepared from these solvent conditions, i.e., the PPTS with a maximum conductivity was obtained under a solvent condition of acetonitrile containing a little water. The result may be applicable to other aromatic compound-based systems.

In a study of polypyrrole perchlorate as an electrode material, and from cyclic voltammetry and ac impedance measurements, Mermilliod et al.<sup>7</sup> reported a capacitance of 100 Ah/kg for a capacitor equipped with an electrode of polypyrrole perchlorate. They also noted that the redox potential decreased with increasing massic capacity. In a report on the applications of polyaniline as cathode active materials in rechargeable batteries, Somasiri and MacDiarmid<sup>12</sup> measured the capacity and energy density based on the weight of polymer employed in constructing the cell as 151 Ah/kg and 159 Wh/kg, respectively. From studies of these polymers as electrode materials, the commercialization of polyaniline-Zn and polyacetylene-Li batteries has been already realized.

Additionally, from a scientific point of view, the study of polymers prepared by electrochemical methods is also valuable, namely, we need electrochemical information to obtain the advanced poly-

meric materials. For this approach, Bargon et al.<sup>11</sup> performed electrochemical studies of aromatic compound-based conducting polymers. In case of conducting polymers obtained by electrochemical oxidation, various relational factors must be considered. When an oxidation possibility of solvents or electrolytes increases the potential above 2 V, the anodic precipitates are obtained mainly from aromatic monomers that have anodic peak potentials below 2 V. We also ought to consider the stability of radical cations formed as intermediates, i.e., radical cations are not diffused to the bulk solution until they are electropolymerized around the anode. The stability of radical cations is also related to the solvent effects. To obtain anodic products as precipitates, the selection of proper solvents is very important. Also, we should seriously consider the selection of proper electrodes and electrode compositions. In most previous works, a three-electrode cell system was adopted to obtain the conducting polymers prepared by the electrooxidation.

As mentioned above, we predict that polyindole-based systems can be obtained by electropolymerization of indole or its derivatives. In research reported in this paper, we obtained polyindole perchlorate (PIP) from indole in an acetonitrile/water (vol %; 99/1) solution containing tetraethylammonium perchlorate (TEAP) as a supporting electrolyte. In our research, we also determined the conduction and polymerization mechanisms for the PIP and elucidated the results of morphology, thermal stability, and spectroscopic analysis.

## EXPERIMENTAL

### Materials

Acetonitrile (AN) as a solvent and TEAP as a supporting electrolyte were obtained from Merck and

Aldrich Chemical Co., respectively. Indole was obtained from Kanto Chemical Co. and fully dried in a vacuum oven at 25°C. AN was purified by vacuum distillation and the solvent was passed through a column packed with alumina and trifluoroacetic anhydride to remove the water.

### Sample Preparations

PIP was electrochemically obtained from 0.2 M indole in an AN/water (vol %: 99/1) solution containing 0.1 M TEAP as a supporting electrolyte. For electropolymerization, the three-electrode cell system was adopted, i.e., Pt electrodes shaped with a 2 cm<sup>2</sup> plate were equipped as the working and the counter electrodes, and a Ag/AgCl cell was also equipped as a reference electrode. Three electrodes were fixed using joints placed on top of a quartz reaction cell. To maintain the temperature of the solution in the reaction cell, a double-soled reaction cell was prepared. With a circulator (Lauda Co.) linked to the outside part of this double-soled cell, the temperature of the solution in every experiment was controlled. To remove dissolved oxygen, a nitrogen stream was passed through the solution using a glass equipper.

The PIP sample was obtained by using a potential of 0.7 V on anode as insoluble precipitates. With an external potential of 0.7 V supplied, the color of the solution around the anode changed from yellowish green to dark brown and finally to maroon. For UV measurements, the solution in contact with the anode was extracted during electropolymerization. Anodic precipitates were removed from the anode and rinsed with AN and dried in a vacuum oven for 2 days until constant weight was achieved.

### Elemental Analysis

Regarding the conductivity of conducting polymers as affected by the contents of the dopants, an analysis of dopants has been performed in most previous works. Elemental analysis for the PIP sample was performed by using an elemental analyzer (Perkin-Elmer, 240-C). The results are listed in Table II.

### Electrochemical Measurements

Electropolymerization of indole and electrochemical measurements were performed by using a potentiostat (Hokuto Denko Co., HA-301), with potential sweeps applied from a function generator (Hokuto Denko Co., HB-104). The cyclic voltammograms were also plotted using a plotter (Omega, DAP-780).

**Table II** Elemental Analysis of Polyindole Perchlorate

Polymer	Polymer Chains (%)			Dopant (%)
	C	H	N	
PIP	64.0	3.5	9.5	23.0

### Conductivity Measurements

In the electrical conductivity of the PIP pellet, we performed the conductivity measurements by the four-probe method at a temperature range of -150–25°C. The PIP powder was made into a pellet using a pressure of 98.06 MPa. Thus, we prepared the sample powder as a disc-shaped pellet with 12 mm diameter and 2.1 mm thickness.

For conductivity measurements, a probe covered with a thermos bottle through liquid nitrogen was used. The temperature of the sample basket in the probe was measured using a digital thermometer (Seoul Control Co., SR-6200, G-116) connected to a ceramic thermocouple, and the low temperature was obtained using liquid nitrogen. The current and potential were measured with a digital electrometer (Keithley, 616) and a digital multimeter (Keithley, 642), respectively. The conductivities were calculated from measurements of current and potential at each temperature with a heating rate of 1°C/min.

### Thermal Analysis

The thermogravimetric analysis (TGA) for the PIP sample was performed with a thermal analyzer (Rigaku-8150). The TGA analysis under a nitrogen stream was performed in the temperature range of 25–800°C with a heating rate of 10°C/min. The TGA analyzer was connected to an IBM computer, from which we directly obtained the rate of thermal decomposition.

### Scanning Electron Microscope (SEM)

A PIP film coat on the anode was obtained from indole in an AN/water solution containing TEAP as a supporting electrolyte. The polymer film on the anode was rinsed in AN and dried in a vacuum oven at 25°C. For the SEM analysis, the surface of the PIP film was covered with gold using an ion coater (Eiko; IB-3), and the SEM measurements were performed using a scanning electron microscope (Hitachi, S-510).

### ESR Measurements

Electron spin resonance (ESR) measurements for the PIP solid powder were performed using an ESR spectrometer (Bruker, ER 200, E-SRC). The PIP powder was placed in an ESR tube, and an ESR spectrum was obtained at room temperature under the following conditions: scan range, 100 G; microwave frequency, 9.45 GHz; microwave power, 20 dB, 2 mW; modulation frequency, 100 kHz; modulation time constant, 1 s; modulation amplitude, 4 G<sub>pp</sub>; receiver gain,  $1.25 \times 10^2$ .

### ESCA Analysis

ESCA analysis for the PIP pellet was performed using an X-ray photoelectron spectroscopy (Shimadzu, ESCA-750), and the X-ray source adopted was the MgK $\alpha$  line.

### IR Measurements

Generally, electrochemically prepared conducting polymers were insoluble in organic solvents and were not transparent. For these reasons, a spectroscopic analysis of these polymers is not easy. FTIR measurements for the PIP sample was performed by the KBr pellet method using IR spectroscopy (Biorad, FTS-80). For protecting the air-mixing phenomenon, a sample pellet was made in a vacuum chamber.

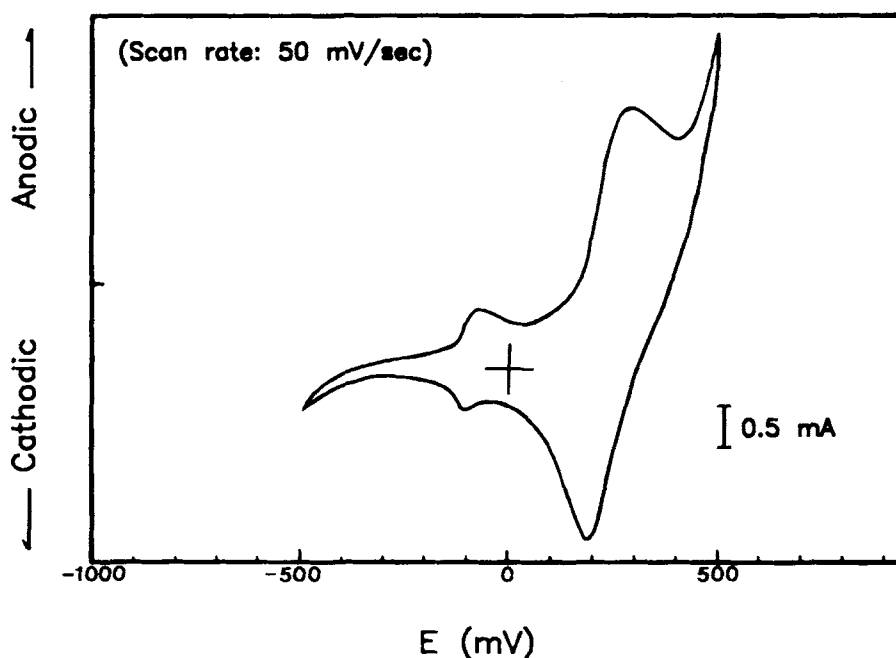
### UV Measurements

During the polymerization at the anode, the color of the solution around the anode initially changed to a yellowish green, and the products were diffused to a bulk solution. Supplying the external potential produced dark green materials around the anode, and the color of the solution around the anode darkened. We then extracted the yellowish green bulk solution using a microsyringe and labeled the solution "PIP-1." We also extracted the solution around the anode and labeled this dark brown solution "PIP-2." As the reaction progressed, the color of the solution around the anode changed to maroon. We extracted the maroon-colored solution and labeled it "PIP-3." The UV measurements for these "PIP-1, 2, and 3" solutions were performed with a UV spectroscopy (Shimadzu, UV-240).

## RESULTS AND DISCUSSION

### Electrical Measurements

In a field treated with the electrode process, the relationship between the potential and corresponding current in reversible and irreversible systems is very important. In a real electrochemical reaction under normal experimental conditions, the electrode reaction always indicated an irreversible system. This means that the systems have a potential difference



**Figure 1** Cyclic voltammogram of a PIP film on a Pt electrode in AN solution at 25°C.

between equilibrium and nonequilibrium, a difference called overvoltage. In trying to obtain anodic precipitates of a superior quality, we ought to consider the explanation mentioned above. If the kinetics of the electron transfer are rapid, it is a reversible system, and the relationship between potential and current can be expressed by the following Nernst equation:

$$E = E_{1/2} + (RT/nF)\ln[(i_1 - i)/i]. \quad (1)$$

Here,  $E_{1/2}$  is the half-wave potential;  $n$ , the number of electrons transferred to the electrode reaction; and  $i_1$ , the diffusion-limited current. By using eq. (1), we can calculate the values of  $E_{1/2}$  and  $n$  from a plot of potential vs.  $\ln[(i_1 - i)/i]$ .

As for cyclic voltammetry, the peak position and the difference between anodic and cathodic peak potentials ( $E_{pa}$ ,  $E_{pc}$ ) furnished us with kinetic information and reversibility. In the cyclic voltammogram, we must consider the exception of charging current owing to the continuous potential change. Consequently, the faradaic current should be calculated from a base line of the charging current. Because the faradaic current is proportional to the square of the scan rate, and the charging current is proportional to the scan rate, proper scan rate selection is important.

The reversibility of the electrode reaction can be directly calculated from the peak position in the cyclic voltammogram. If an electrode system is reversible, the values of the anodic and cathodic peak potentials are independent of the changing scan rate. On the other hand, in the case of irreversible systems, the anodic and cathodic peak potentials change with changes in the scan rate. Therefore, changes in peak potentials and scan rates are important in determining of reversibility for an electrode system. Also, in a reversible electrode system, the peak width ( $\Delta E_p$ ) of anodic and cathodic peak potentials has a value of  $58/n$  (mV) at 25°C.

Cyclic voltammetry was performed in an AN/water (99/1) solution containing 0.2M indole and 0.1M TEAP, in a potential range from -0.5 to 0.5 V at 25°C. The results are shown in Figure 1, which also shows a couple of anodic and cathodic peak potentials. In this electrode system, the values of the anodic and cathodic peak potentials were independent of the scan rate. Thus, this suggests that the electrode reaction was reversible. From the peak couple in Figure 1, the values of  $E_{pa}$  and  $E_{pc}$  were calculated to be 0.263 and 0.205 V, respectively, at a scan rate of 50 mV/s and the peak width ( $\Delta E_p$ ) was 58 mV.

## SEM Analysis

As the anodic electropolymerization progressed with a potential supply of 0.7 V, the dark green precipitates formed on the anode. The color of the solution

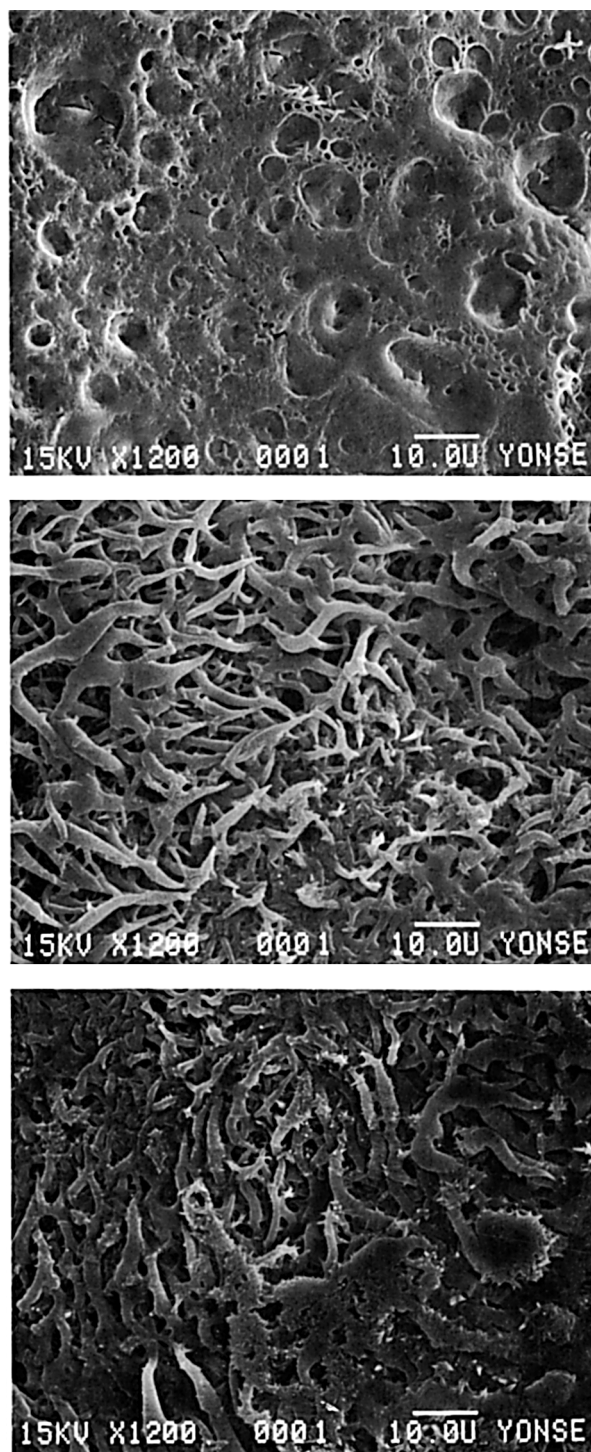


Figure 2 Scanning electron micrograph of a PIP film.

around the anode darkened and finally changed to maroon. For morphology analysis of the PIP film coating on the anode, the SEM measurements for this film were carried out, and the result is shown in Figure 2. As shown in the morphology analysis of the PIP film coating on the electrode, many fibrous trunks nearly and compactly covered the film surface. The fiber appeared to be polyindole chains. Also, scattered, star-shaped materials like dopants appeared to hold the fiber.

### UV Measurements

The color of an indole solution containing the TEAP darkened with the supplying of the potential. For the UV measurements, the solutions around the anode and bulk solution were extracted using a microsyringe. As the electropolymerization progressed, the final solution was also extracted. The UV measurements of these solutions as classified by the reaction course were performed, and the results are shown in Figure 3.

The UV results of the solution around anode showed triple peaks at 345, 373, and 388 nm. The peaks were attributed to various species produced around the anode. For the solution labeled "PIP-1," a peak at 373 nm was observed. In the solution labeled "PIP-3," a main peak at 338 nm and a shoulder peak at 390 nm were also obtained. The appearance of the shoulder peak can be attributed to the red shift associated with electropolymerization.

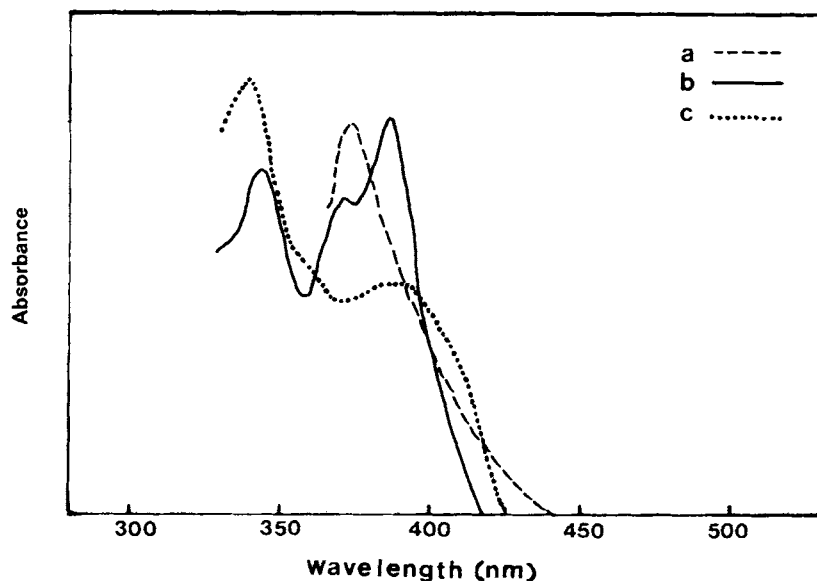
### FTIR Measurements

Previous works<sup>14,15</sup> have shown that most conducting polymers are insoluble in general organic solvents, and, therefore, spectroscopic analyses such as IR measurements are not easy. In this work, the PIP sample obtained was a powder from the anodic polymerization. The IR measurements were carried out using the KBr pellet method. Figure 4 shows the FTIR measurements for the PIP sample.

The IR spectra results for the PIP sample do not show absorption bands at a range of 3100–3500  $\text{cm}^{-1}$  induced by the stretching mode of the secondary amine. This means that each nitrogen atom in polyindole chains changed from a secondary to a tertiary amine. An explanation for this is that a nitrogen atom in each indole monomer participated in the polymerization. Figure 4 depicts peaks in a range of 1440–1600  $\text{cm}^{-1}$  that were induced by the stretching mode of aromatic alkene, a peak at 1310  $\text{cm}^{-1}$  induced by the stretching (C—N) amine, and a peak at 734  $\text{cm}^{-1}$  induced by the bending mode of aromatic alkene. This result suggests a polymerization mechanism in the indole.

### ESCA Analysis

Many researchers have performed various spectroscopic analyses to determine the polymerization mechanisms for electrochemically prepared conducting polymers. ESCA measurements can check the charged states of nitrogen or carbon atoms.



**Figure 3** UV spectra of (a) PIP-1, (b) PIP-2, and (c) PIP-3 solutions.

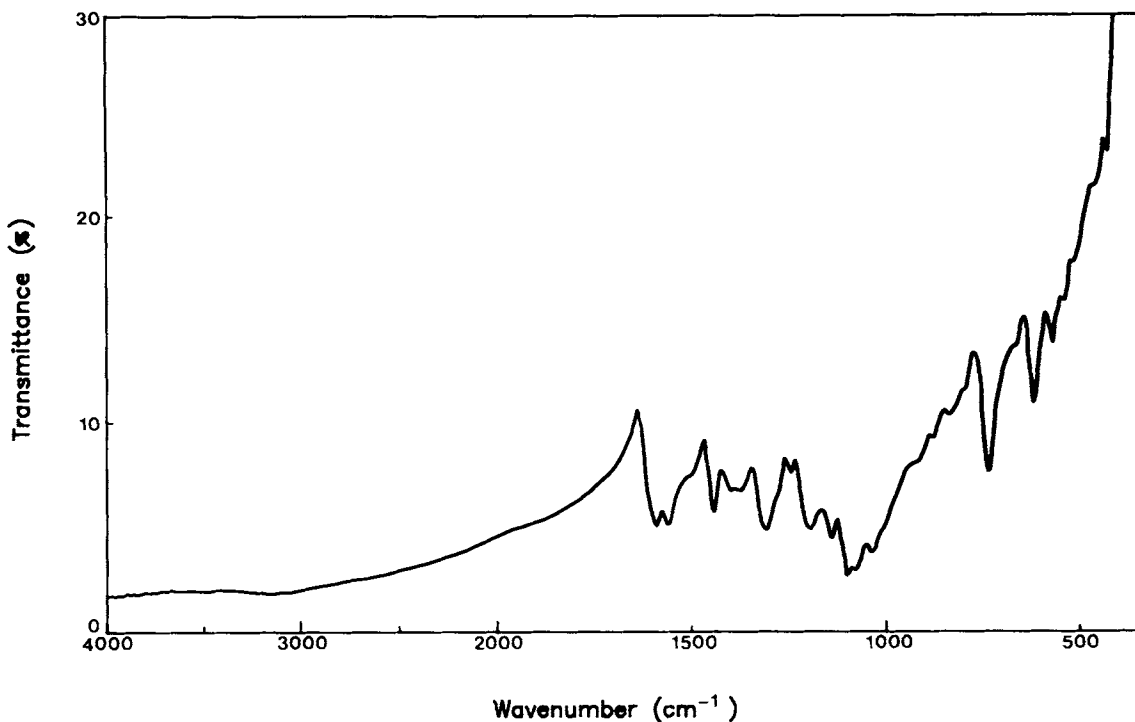


Figure 4 The FTIR spectra of PIP in a KBr pellet.

Pfluger et al.<sup>16</sup> reported their results of XPS analysis for polypyrrole perchlorate. The XPS results showed that for polypyrrole perchlorate prepared by electrooxidative polymerization the main and shoulder peaks of  $N_{1s}$  were observed at 400 and 405 eV, respectively. The appearance of a high binding energy peak at 405 eV can be explained by the nitrogen atoms in the polymer being positively charged.

In this work, ESCA analysis of the PIP pellet was carried out. Figure 5 shows the  $N_{1s}$  and  $C_{1s}$  spectra of the PIP sample. Figure 5 (a) depicts a small peak at 402.3 eV, as well as a main  $N_{1s}$  peak at 399.6 eV. This ESCA analysis suggests that the nitrogen atoms in the polyindole chain have a cationic character from electrooxidation, and, thus, the perchlorate anions are easily doped in the polymer, satisfying the charge neutrality. Figure 5 (b) shows a  $C_{1s}$  peak of the PIP pellet, with a main  $C_{1s}$  peak at 284.6 eV and a shoulder peak around 286 eV. This result can be explained in that the carbon atoms in the polymer chains have some positive characters owing to the doping of the anionic dopants: the perchlorate anions.

### Polymerization Mechanism

Electropolymerization mechanisms of conducting polymers have been studied in various analyses. Bargon et al.<sup>17</sup> reported that polyazulene, polythio-

phene, polycarbazole, polypyrene, and polytriphenylene were polymerized by electrooxidation. Many researchers performed electrochemical and spectroscopic analyses for these aromatic compound-based conducting polymers. The results suggest possible electropolymerization mechanisms for these systems. Generally, in case of the electropolymerization performed under an AN solvent, research<sup>6,17</sup> indicates that polymerization occurred with the formation of radical cations. These results mentioned above were confirmed mainly by solvent effects<sup>13,17</sup> in polypyrrole-based systems.

From these results, we surmised that the polymerization mechanism of indole by electrooxidation was a radical cation mechanism. The possible 1,3-polymerization mechanism of indole is shown in Scheme I. As shown in the scheme, an indole monomer existing around the anode was oxidized by supply of a potential. Then, the monomer changed to a radical cation. The radical cation coupled with another radical cation and then formed a dimer. The dimer was also electrooxidized, and in that way, the polymerization continued.

### Thermal Analysis

Thermogravimetric analysis (TGA) of the PIP powder was performed in the temperature range of 25–800°C under nitrogen atmosphere. As a point of

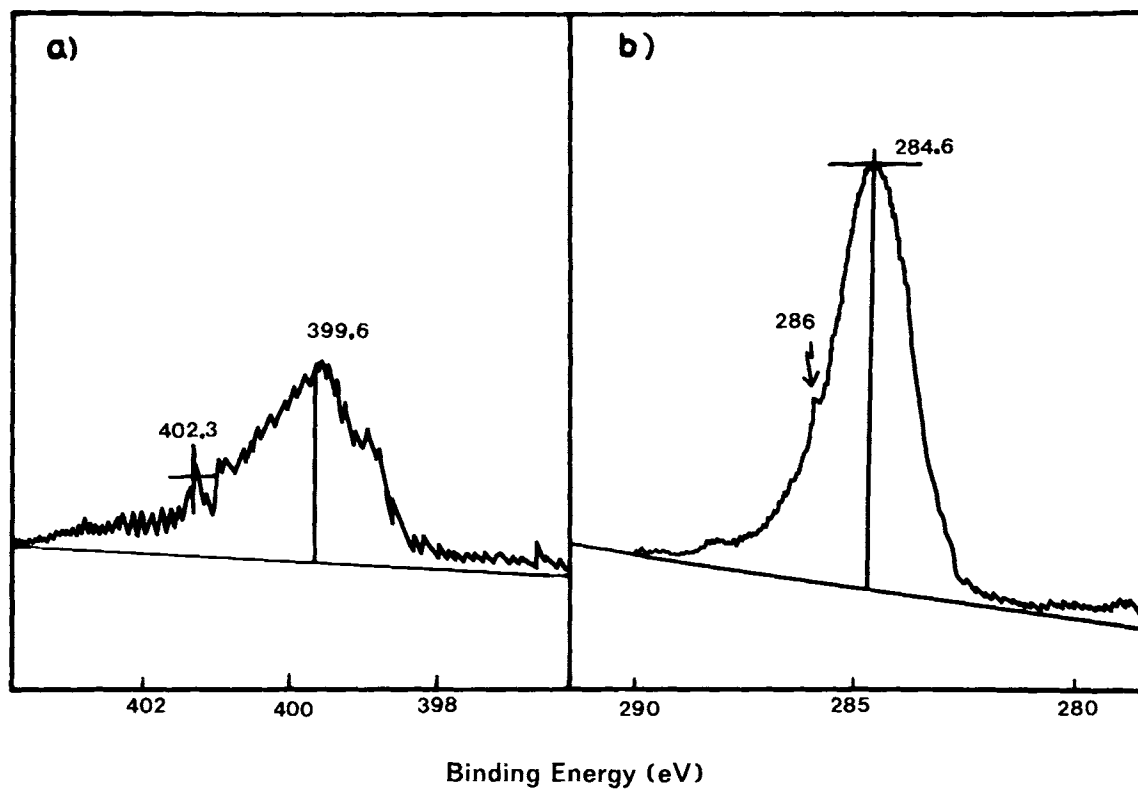
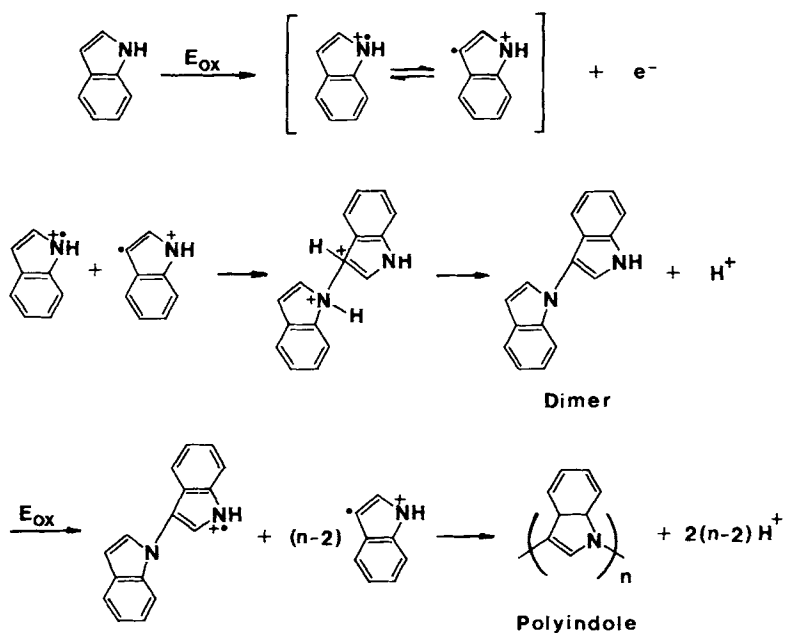


Figure 5 ESCA spectra of a PIP pellet: (a)  $N_{1s}$ ; (b)  $C_{1s}$ .

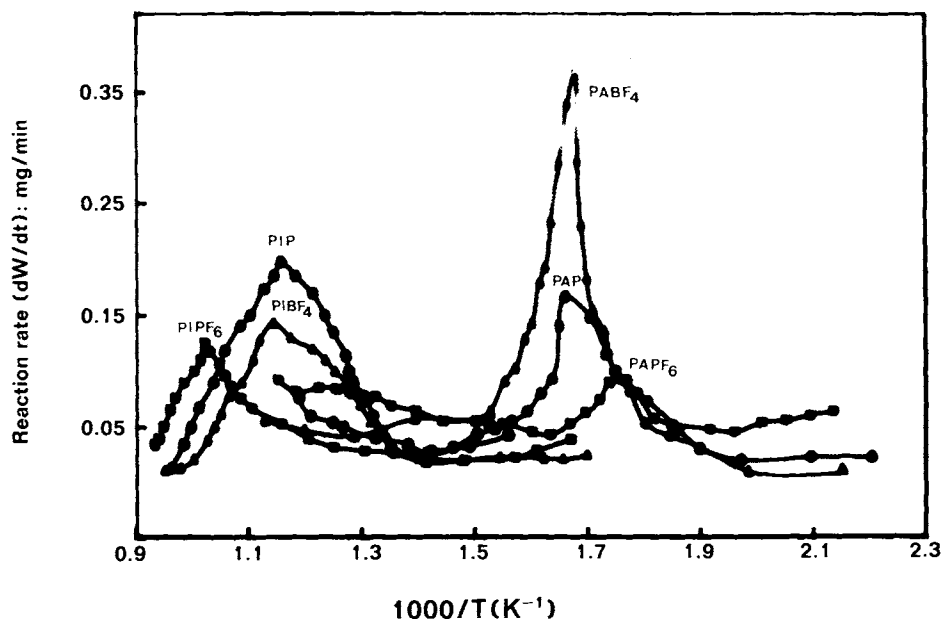
application in industry, the study of thermal properties for polyindole-based systems is expected to provide useful information on the industrial appli-

cations of these systems. Generally, conducting polymers are lightweight and have a high conductivity among other polymeric systems. On the other



Scheme I Polymerization mechanism of polyindole.





**Figure 6** The temperature dependencies of the reaction rates for various polyaniline- and polyindole-based conducting polymers.

hand, they easily decompose under heat, and their thermal properties changed under various thermal conditions. Thus, thermal analysis is important in determining the industrial applications of conducting polymers.

To compare the thermal properties of the polyindole- and polyaniline-based systems, the indole- and aniline-based polymers doped with various anions, such as perchlorate, tetrafluoroborate, and hexafluorophosphate, were prepared by electrooxidation. Thus, the TGA measurements of polyindole perchlorate (PIP), polyindole tetrafluoroborate (PIBF<sub>4</sub>), polyindole hexafluorophosphate (PIPF<sub>6</sub>), polyaniline perchlorate (PAP), polyaniline tetrafluoroborate (PABF<sub>4</sub>), and polyaniline hexafluorophosphate (PAPF<sub>6</sub>) were performed, and the rates of thermal decomposition ( $R$ ) were calculated by a computer connected with a thermal analyzer.

Figure 6 shows the maximum reaction rate ( $R_{max}$ ) for the polyindole- and polyaniline-based polymers, with the results also listed in Table III. As shown in Figure 6, the results confirm that these conducting polymers show distinguishable thermal characteristics, i.e., the polyindole-based systems decomposed mainly at higher temperature ranges than did the polyaniline-based ones. This means that the thermal stability of polyindole-based polymers is greater than that of the polyaniline systems. Therefore, the polyindole-based systems have industrial applications requiring higher temperature stabilities. It is also

observed that the  $R_{max}$  values for the polyindole system are not seriously affected by the kind of dopants. But, in the case of polyaniline-based systems, these values are affected by the kind of dopant anions. Thus, when these conducting polymers are applied in various fields, this characteristic should be considered.

### Conductivity

Most conducting polymers have conjugated double bonds, and the conduction bands formed by the overlapping of the  $\pi$ -orbital exist along the polymer chains. The conductivity of these polymers increases with the doping of various dopants and with in-

**Table III** Maximum Reaction Rates Obtained from TGA Results in Polyindole- and Polyaniline-based Systems

	$R_{max}$ (mg/min) (at $T_{max}$ )
PIP	0.198 (at 591°C)
PIPF <sub>4</sub>	0.143 (at 601°C)
PIPF <sub>6</sub>	0.126 (at 702°C)
PAP	0.166 (at 327°C)
PABF <sub>4</sub>	0.366 (at 324°C)
PAPF <sub>6</sub>	0.092 (at 300°C)

creases in temperature. In most amorphous materials, the application of the band structure and the determination of the possible conduction mechanism must be carefully considered.

In previous works,<sup>18-22</sup> many researchers have indicated the conduction mechanisms for these amorphous systems. As for the hopping conduction mechanism of polymeric materials, Mott's<sup>18</sup> equation was generally known for the temperature range of 60–300 K. He expressed the equation based on the hopping conduction in amorphous semiconductors as a form of  $\exp(-T^{-1/4})$ . Sheng et al.<sup>19</sup> reported that the hopping conduction of sputtered granular metal films was experimentally expressed as a form of  $\exp(-T^{-1/2})$ .

In this work, the results of conductivity measurements were applied to the following equations for various conduction mechanisms. Greaves<sup>20</sup> reported that a variable range hopping conduction is expressed by the following equation:

$$\sigma T^{1/2} = \exp(-T^{-1/4}) \quad (2)$$

Mataré<sup>21</sup> also reported that the electronic conduction, which included the grain boundary potential ( $E_a$ ), could be written by the following equation:

$$\sigma = AT^{1/2} \cdot \exp(-E_a/kT), \quad (3)$$

where  $A$  is a constant dependent on the electric field strength, and  $E_a$  is the height of the potential barrier.

Also, Zeller<sup>22</sup> reported that the tunneling conduction mechanism was suggested by the following expression:

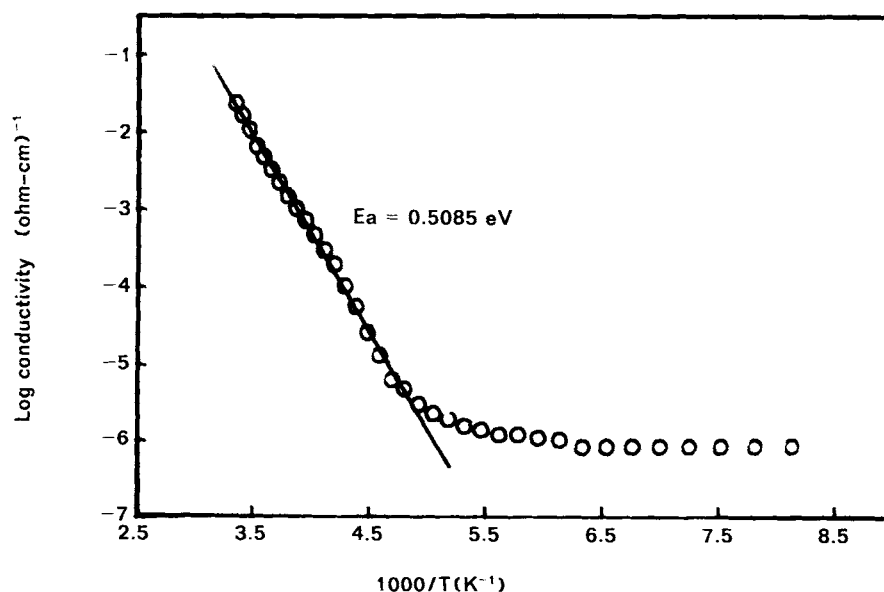
$$\sigma = \sigma_0 \cdot \exp(-T^{-1/2}). \quad (4)$$

The electrical conductivity for the PIP pellet was performed by the four-probe method in the temperature range from  $-150$  to  $25^\circ\text{C}$  under a low applied field to ensure ohmic behavior. The results are shown in Figure 7. Generally, the temperature dependence of conductivity for conducting polymers is shown to be like that for semiconductors. In Figure 7, the conductivity of the PIP pellet increases linearly with increases in temperature, satisfying the Arrhenius equation,  $\sigma = \sigma_0 \cdot \exp(-E_a/kT)$ . The results show the values of  $\log \sigma$  at  $25^\circ\text{C}$  and  $E_a$  to be  $-1.63$  s/cm and  $0.508$  eV, respectively.

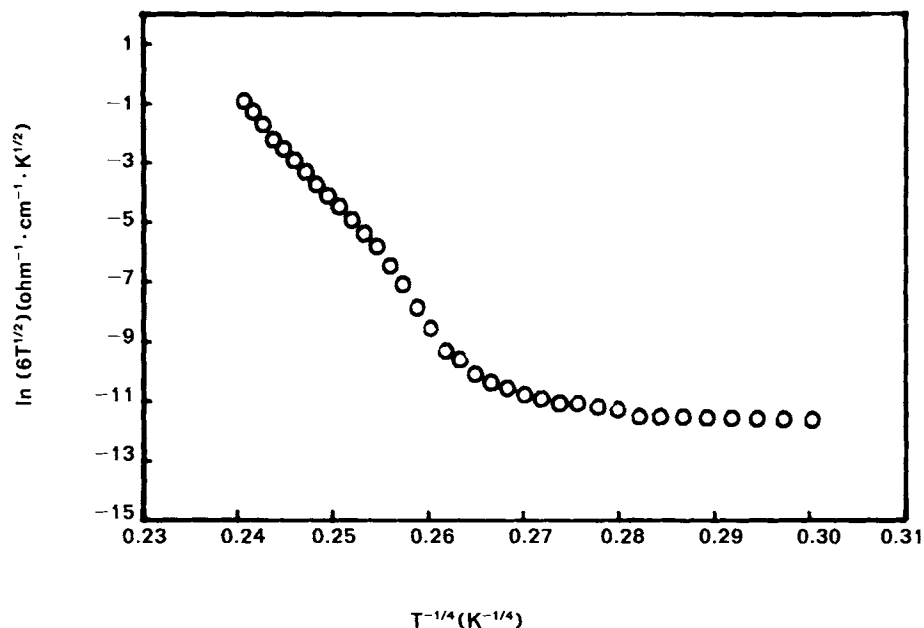
The plots for temperature dependence of electrical conductivity based on eqs. (2)–(4) in the PIP pellet were obtained. For the results shown in Figure 8, we confirmed that a plot based on eq. (2) for the hopping conduction had the best linearity compared with other plots. We submit that the possible conduction mechanism for PIP and charge carriers are hopping conduction and polarons, respectively.

### ESR Measurements

To analyze the structure of electrochemically prepared conducting polymers, many researchers have

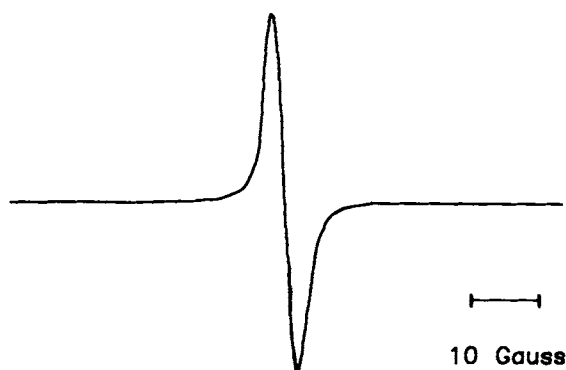


**Figure 7** The electrical conductivity as a function of temperature for a PIP.



**Figure 8** The temperature dependence of electrical conductivity for a PIP based on the hopping conduction mechanism.

attempted various spectroscopic analyses for these polymers. Scott et al.<sup>23</sup> reported ESR measurements for polypyrrole perchlorate for various ESR parameters. The PIP sample obtained was in the form of a powder. The sample powder was placed in an ESR tube, and the ESR measurements for the PIP powder were performed using the solid-sampling method at room temperature. As shown in the results of Figure 9, the PIP contained a single ESR peak, like most other conducting polymers. The various ESR parameters calculated from these results include the values of  $\Delta H_{pp}$  and  $g$  value to be 2.6 Gauss and 2.00415, respectively.



**Figure 9** ESR spectrum of PIP at 25°C (microwave frequency: 9.43 GHz).

## CONCLUSIONS

The PIP sample was obtained from 0.2M indole in AN solution containing 0.1M TEAP as a supporting electrolyte, supplying a potential of 0.7 V. The cyclic voltammetry suggested that the electrooxidation of indole is reversibly progressed and the peak width ( $\Delta E_p$ ) of the anodic and cathodic peaks was 58 mV. The spectroscopic measurements suggest that the possible polymerization mechanism of polyindole is a radical cation mechanism.

From the TGA results for the polyindole- and polyaniline-based systems in a temperature range of 25–800°C, the maximum values of reaction rates ( $R_{max}$ ) were plotted against the temperature. The results show that the polyindole-based polymers decomposed at higher temperatures than did the polyaniline-based ones. As for the  $R_{max}$  values of these polymers, the values of the polyindole systems were not related mainly to the kind of dopants. On the other hand, the polyaniline-based ones depended on the kind of dopants.

The electrical conductivity for the PIP pellet was measured in a temperature range from –150 to 25°C. The values of  $\log \sigma$  at 25°C and  $E_a$  were –1.63 s/cm and 0.508 eV, respectively. The conductivity results suggested that a possible conduction mechanism for the PIP and charge carriers were the hopping conduction and polarons, respectively.

An ESR analysis for the PIP powder was per-

formed at 25°C by the solid-sampling method. From the ESR result, various ESR parameters were calculated, and the values were compared with that of other systems.

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