The Chemical and Physical Properties of Electrochemically Prepared Polyaniline Perchlorate (PAP)

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SYNOPSIS

Polyaniline perchlorate (PAP) was synthesized by electrochemical oxidation from $0.2 M$ aniline in acetonitrile solution containing $0.1 M$ tetraethylammonium perchlorate as supporting electrolyte. From polarographic and cyclic voltammetry results, the values of the half-wave potential ($E_{1/2}$), transfer coefficient (α), and number of electrons related to the electrode reaction (n) were calculated to be 825 mV, 0.894, and 1, respectively. The morphology of the PAP film was observed by using an SEM analyzer. From thermal analysis of the PAP sample, the reaction rate (R) for its thermal decomposition was obtained from the TGA result and a exothermic peak at 330°C was also observed in the DSC curve. The electrical conductivity of the PAP pellet was measured at temperatures from -170 to $25°C$. From a plot of conductivity vs. $1/T$, the activation energy (E_a) was obtained to be 0.14 eV. The conduction mechanism in a pressed pellet of PAP is suggested to be electronic hopping conduction. The values of the ESR parameters were calculated from an ESR curve for PAP at room temperature.

INTRODUCTION

Electroactive organic polymers are worth considering both from the theoretical point of view and for technological applications because of their electronic properties. Recently, studies of various conducting polymers synthesized by the electrochemical oxidation of aromatic compounds have been performed in many laboratories.[1-7] Bargon et al.[1] reported on the electrochemical results of the anodic synthesis of several aromatic compounds, polyazulene, polythiophene, polycarbazole, polypyrene, and polytriphenylene. Their free-standing films peeled off a Pt electrode have electrical conductivities between 10^{-3} and 1 (Ω cm)$^{-1}$. For the practical extensive utilization of these compounds as electronic switching materials,[2] electrooptic devices,[3] electrode materials in rechargeable and storage batteries,[4] solar batteries,[5] radiation detectors[6] and sensors,[7] a number of studies have been vigorously carried out.

In electrooptic devices, the color changes associated with insulator-metal transitions are induced by doping with various dopants, and thus various electronic states, polarons, solitons, and bipolarons can be formed. One of the important merits of conducting polymers is that their specific weight is much lower than that of ordinary inorganic materials. Thus, from the point of demand for lower weights, their practical utility in rechargeable batteries is promising.

The materials which are expected to meet these aims are polypyrrole- and polyaniline-based conducting polymers, so that extensive studies on these polymers have been undertaken. Polyaniline-based conducting materials can be prepared by chemical and electrochemical techniques. These polymers are stable in air and water and have a satisfactory conductivity. Also, as the color changes can be induced by change in the oxidation state, the polyaniline-based conducting polymers can be used as the electrode material in electrochromic displays. In a report on polyaniline as the active material for secondary batteries, the cell type with $Zn/1 M$ $ZnSO_4$/polyaniline had a maximum capacity of 108 Ah/kg, and

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the type with polyaniline/$4M$ H_2SO_4/PbO_2 showed excellent recyclability.[8] Also, various utilizations such as radiation detectors with SF_6-doped polythiophene and electrooptic devices of ClO_4^-, BF_4^-, AsF_6^-, and PF_6^--doped polythiophene systems have been reported.[9]

Perchlorate anion-doped conducting polymers can be synthesized by both chemical and electrochemical methods. That is, perchlorate anion-doped polymers can be prepared chemically by oxidative polymerization of a monomer in the presence of a strong oxidant such as $Fe(ClO_4)_3$, and the perchlorate anion-doped polymers can be obtained electrochemically by the electrooxidation of an optional monomer in acetonitrile (AN) solution containing tetraethylammonium perchlorate (TEAP). Mermilliod et al.[10] synthesized polypyrrole perchlorate by chemical oxidation using a strong oxidant, $Fe(ClO_4)_3$, and use of this sample as electrode material was reported. Also, the characteristics of polypyrrole perchlorate prepared by electropolymerization at the anode electrode in an acetonitrile solution containing $0.1M$ pyrrole and $0.5M$ Bu_4NClO_4 has been studied.[11]

But studies on the perchlorate-doped polyaniline systems are not extensive. Thus, in this work, the electrochemical mechanism for anodic electrode reaction, the morphology of polyaniline perchlorate (PAP) film, the thermal characteristics predicted from the TGA and DSC results, and the conduction mechanism in PAP obtained by electrooxidation are studied or determined.

EXPERIMENTAL

Materials

Acetonitrile (AN) as the solvent and tetraethylammonium perchlorate (TEAP) as a supporting electrolyte were obtained from the Merck and Aldrich chemical companies, respectively. Before each experiment, TEAP was fully dried in a vacuum oven due to its hygroscopic properties. Aniline was passed through a column packed with alumina for removal of water and acrylonitrile, the main impurities. After the treatment with alumina, it was distilled from calcium hydride to obtain the highest-purity state.

Sample Preparation

Polyaniline perchlorate (PAP) was prepared from $0.2M$ aniline in AN solution containing $0.1M$ tetraethylammonium perchlorate (TEAP) as the sup-

porting electrolyte. The three-electrode cell arrangement was employed with 2 cm^2 Pt plates as a working and a counter electrode and a saturated calomel electrode (SCE) as the reference electrode. Before the experiments, the solutions in the reaction cell were fully stirred with a magnetic bar to ensure proper distribution, and a nitrogen stream was bubbled through for 30 min to remove the dissolved oxygen. Also, the temperature of the solution was maintained at 25°C by using a special cell connected to a circulator. An external voltage of 2 V was supplied to obtain precipitates at the anode. The rate of polymerization depends on various factors, the resistance of the electrolytic solution, concentration of aniline, applied voltage, and current density.

The materials synthesized by anodic oxidation were obtained as insoluble and electrically conductive precipitates. The product was removed from the anode electrode, washed with acetonitrile, and dried in a vacuum oven until constant weight was achieved. A black conducting powder, predicted to be perchlorate anion-doped polyaniline, was obtained.

Elemental Analysis

An analysis of the component ratios of C, H, and N atoms in the polymer chains and dopant contents for the anodic precipitates anticipated to be polyaniline perchlorate (PAP) is necessary. Elemental analysis was performed by using an elemental analyzer (Perkin-Elmer, Model No. 240 C), and the results are listed in Table I.

Electrochemical Measurements

Polarography and cyclic voltammetry measurements were performed using a potentiostat (Tacussel, Polaropulse Type PRG-5) and the potential sweeps applied from a function generator (Tacussel, Model No. GSTP 3). The polarogram and cyclic voltammogram were plotted by using a polarographic recorder (Tacussel, Model No. EPL 1) and an X-Y

Table I   Elemental Analysis for an Electrochemically Prepared Polyaniline Perchlorate

Polyaniline-Based Polymer	Polymer Chain (%)			Dopant (%)
	C	H	N	
PAP powder	62.88	5.56	11.19	20.37

recorder (Rikadenki, Model No. RW-11 T), respectively. In every experiment, the temperature of the solution was maintained at 25°C by using a circulator (Lauda Co.) connected to the reaction cell filled with the 0.2 M aniline in AN solution containing 0.1 M TEAP.

The solution was stirred with a magnetic stir bar and was purged with a nitrogen stream to remove the dissolved oxygen. The Pt plates were precleaned and conditioned by potential pulsing between the hydrogen and oxygen evolution regions.

Conductivity Measurements

The conductivity of a pressed pellet of the polyaniline perchlorate (PAP) was measured by using Pt wires as probes for the four-probe method.[12] PAP precipitates were obtained at the anode electrode by supplying an external potential of 2 V vs. SCE, and the amount of precipitate was controlled by monitoring the electrical current. The material was removed from the Pt plate, washed with AN solution, and fully dried in a vacuum at 25°C. The fine PAP powder obtained through this process was made into a pressed pellet under a pressure of 98.06 MPa. The diameter and thickness of this disc-type pellet were 12.5 and 2mm, respectively.

The conductivity of the pressed pellet of PAP was measured over a temperature range from −170 to 25°C, with the required temperature obtained using liquid nitrogen. The specimen was placed in a temperature-controlled chamber and the temperature of the sample basket measured by using a digital thermometer (Seoul Control Co., SR-6200, Model No. G-116). The current and the voltage were measured with a digital electrometer (Keithley, No. 616) and a digital multimeter (Keithley, No. 642), respectively. The conductivities of the specimen were carefully measured with a heating rate of 1°C/min.

ESR Measurements

Electron spin resonance (ESR) measurements were performed with an EPR Spectrometer (Bruker, Model No. ER 200 E-SRC). The PAP sample was placed in the ESR tube as powder at 25°C, and the ESR curve in Figure 11 obtained under the following conditions: scan range, 300 G; microwave frequency, 9.45 GHz; microwave power, 20 dB, 2 mW; modulation frequency, 100 KHz; modulation time constant, 200 ms; modulation amplitude, 4 Gpp; receiver gain, 1.25 × 10³.

Thermal Analysis

The thermogravimetric analysis (TGA) and the differential scanning calorimetry (DSC) measurements for the PAP powder were performed with a thermal analyzer (Rigaku, Model No. 8150). TGA analysis under a nitrogen atmosphere was carried out over the temperature range of 25–800°C with a heating rate of 10°C/min. All data obtained from the thermal analyzer system were fed into computer analysis equipment; thus the results of the weight loss vs. heating rate and the rate of thermal decomposition were directly computed from the TGA and DSC data.

Scanning Electron Microscope (SEM)

A PAP film coated on a Pt plate was obtained using an external potential of 2 V from a DC power supply (Tacussel Co.). By using an ion coater (Eiko; IB-3), the surface of the PAP film was covered with gold. SEM analysis of the sample film was performed using a scanning electron microscope (Hitachi, Model No. S-510).

RESULTS AND DISCUSSION

Polarography

Polarographic measurements of the 0.2 M aniline in AN solution containing 0.1 M TEAP were performed at 25°C. Then a small quantity of triton X-100 was added to the test solutions as maximum suppressor to remove the polarographic maximum peak. In a potential step method applicable in the diffusion-controlled region, the diffusion-limited current (i_d) is given by the Cottrell equation, $i_d = nFA \sqrt{D_0} \, C_0^*/\sqrt{\pi t}$, where D_0 is the diffusion coefficient and C_0^* is the bulk concentration. Thus, by substituting a mercury drop's radius and the drop's surface area into the Cottrell equation, the well-known Ilkovic equation can be employed.

Analysis of polarographic wave involves several related factors, the diffusion-limited current (i_d), bulk concentration (C_0^*), and half-wave potential ($E_{1/2}$). The value of $E_{1/2}$ obtained from the polarogram offers a variety of information to us; thus the absolute value of $E_{1/2}$ for each system must be calculated. The relationship between current and the corresponding potential for a reversible reaction has been presented as

$$E = E_{1/2} + (2.303RT/nF) \log[(i_d - i)/i] \quad (1)$$

where n is the number of electrons transferred in the reversible reaction. The values of $E_{1/2}$ and n can be calculated absolutely from the y-intercept and the slope, respectively, of a plot of E vs. $\log[(i_d - i)/i]$. In the case of an irreversible reaction, it is considered that the wave has less than the theoretical slope for the number of electrons transferred. Thus, a related equation for current and corresponding potential for an irrversible reaction is

$$E = E_{1/2} + (2.303RT/\alpha nF) \log[(i_d - i)/i] \quad (2)$$

where α is the transfer coefficient. Generally, irreversible polarographic waves are more drawn out than reversible ones, and the values of $E_{1/2}$ are much more extreme than the formal potential of an electrode. Thus, in case of an irreversible couple, the thermodynamic factors or free energies are not available, but the kinetic information, the value of the transfer coefficient (α), various rate constants (k), and the number of electrons transferred in the electrode reaction (n) can be determined. The values of αn and $E_{1/2}$ can be directly obtained from a plot of E vs. $\log[(i_d - i)/i]$ in irreversible systems.

A polarogram of the $0.2 M$ aniline in AN solution containing $0.1 M$ TEAP was obtained at 25°C. The reversibility of this polarographic wave was tested by considering the value of $|E_{3/4} - E_{1/4}|$ which should equal $56.4/n$ (mV) at 25°C. Now the values of $E_{1/4}$ and $E_{3/4}$ computed from this wave are 800 and 860 mV, respectively, and the value of $|E_{3/4} - E_{1/4}|$ is 60 mV. We predicted from this quick test

that this couple is irreversible; thus eq. (2) can be employed.

A plot of E vs. $\log[(i_d - i)/i]$ for this case is shown in Figure 1. The value of $E_{1/2}$ obtained from the y-intercept of Figure 1 is 825 mV and the value of αn calculated from the slope is 0.894. Generally, the magnitude of α turns out to lie between 0.3 and 0.7, and it can usually be approximated by 0.5 in the absence of actual measurements. From this polarographic result, the electrochemical information can be obtained. In addition, cyclic voltammetry analysis was also performed to obtain more supporting evidence.

Cyclic Voltammetry

Linear sweep voltammetry (LSV) and the cyclic voltammetry (CV) can be used to obtained a 3-dimensional potential–current–time profile; in particular, the cyclic voltammogram gives information on both anodic and cathodic reactions. In cyclic voltammetry, the reversibility can be checked from the dependence of the peak potential (E_p) on scan rate (v). That is, the peak potentials are independent of scan rate in reversible waves and are a function of scan rate in irreversible waves. From a cyclic voltammogram, the reversibility can be also determined by checks using various equations related to the cathodic and anodic peak potentials (E_{pc}, E_{pa}).

When using continuous changing potentials, the faradaic current must be computed from a base line of the charging current in a cyclic voltammogram.
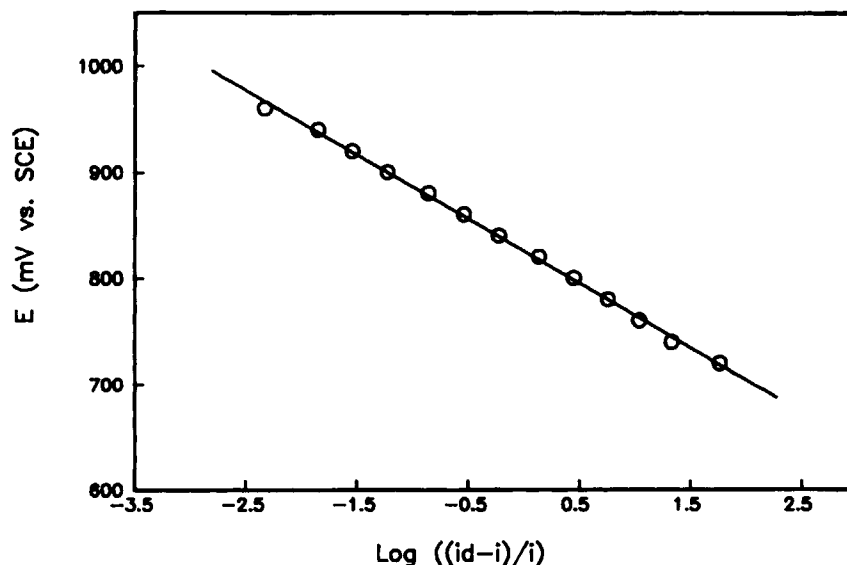

Figure 1   A plot of E vs. $\log((i_d - i)/i)$ for $0.2 M$ aniline in acetonitrile solution containing $0.1 M$ TEAP at 25°C.
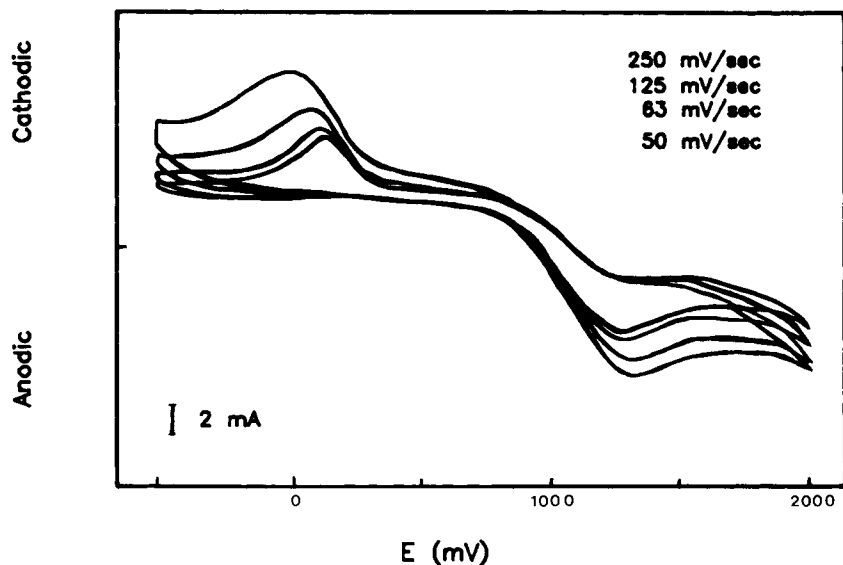
Figure 2 Cyclic voltammogram of a polyaniline perchlorate film on a Pt electrode in acetonitrile solution.

That is, since the charging current (i_c) and the peak current (i_p) are proportional to the values of v and $\sqrt{v}$, respectively, selection of a proper value for $|i_c|/i_p$ is important.

Cyclic voltammograms of the AN solution containing $0.2M$ aniline and $0.1M$ TEAP were obtained in the potential range from -500 to 2000 mV at $25°C$. The results with various scan rates (v) are shown in Figure 2, collectively. Single cathodic and anodic peaks for every scan rate can be found in Figure 2. From comparison with the polarographic

results, it is reasonable to assume that the value of n is 1 and α is 0.894. As shown in the Butler–Volmer relation,[13] the value of $\alpha > 1/2$ gives us kinetic information about this electrode reaction. That is, it can be predicted from this α-value of 0.894 that the oxidation rate constant for this electrode process is large; thus the anodic oxidation reaction can take place easily.

Also, Figure 3 shows the changes in anodic and cathodic peak potentials with various scan rates. In Figure 3, the peak potential is a function of scan
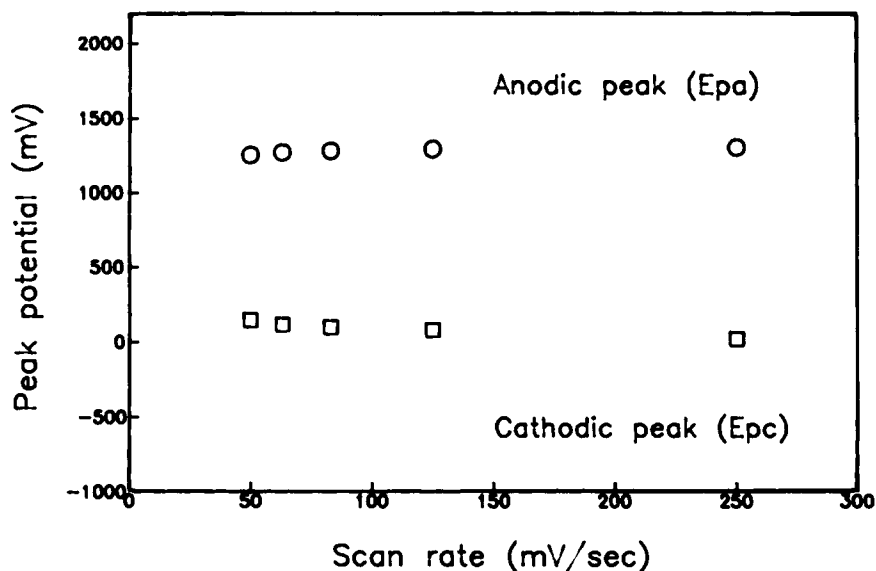

Figure 3 Variations in the anodic and cathodic peak potentials for various scan rates for $0.2M$ aniline in AN solution containing $0.1M$ TEAP at $25°C$.

rate, shifting in the negative (for a reduction, E_{pc}) and the positive (for an oxidation, E_{pa}) directions with increasing scan rate. From this result, it is obvious that these anodic and cathodic reactions are irreversible, and these results from the cyclic voltammetry analysis agree with the predictions from the polarographic results.

Thermal Analysis

TGA and DSC measurements for the PAP powder were performed to obtain information on its thermal characteristics in the temperature range of 25–800°C. The results under a nitrogen atmosphere are shown in Figure 4. In the TGA curve, most of the weight loss for the PAP sample occurs mainly in the temperature range of 260–343°C. Also, in the DSC measurements for the PAP system, along with the corresponding TGA curve, they show an exothermic peak at 330°C, as shown in Figure 4.

The reaction rates ($R:dW/dt$) from the TGA results were computed directly by a thermal analyzer connected to an IBM-PC. For a comparison of thermal characteristics for PAP and other polyaniline-based conducting polymers, TGA measurements for various polyaniline-based systems were made, and their reaction rates were also computed. The results are shown in Figure 5. Also, the values of temperature (T_{max}) and reaction rate (R_{max}) at the maximum peak point in the reaction rate for each poly-

aniline-based sample are listed in Table II. Among the samples of Figure 5, polyaniline p-toluenesulfonate (PATS), polyaniline tetrafluoroborate (PABF₄), and polyaniline perchlorate (PAP: elec.) were synthesized using the electrochemical anion (TS^-, BF_4^-, ClO_4^-) doping method, whereas the polyaniline perchlorate (PAP: chem.) was obtained using the chemical doping method with perchlorate anions using a strong oxidant, $Fe(ClO_4)_3$.

In Figure 5, the beginning and ending temperature points for weight loss for the electrochemically prepared polymers are almost the same, and their thermal decompositions are induced at a higher temperature region than the chemically prepared polymer (PAP: chem.). That is, it is clear that the polyaniline-based polymers show distinguishing thermal characteristics of the anion doping method.

Scanning Electron Microscopy (SEM)

The PAP film coated on a Pt electrode for morphology analysis of the film surface was prepared from the the AN solution containing $0.2M$ aniline and $0.1M$ TEAP, using a potential of 2 V vs. SCE. Depending on the amount of polymer growth on the Pt anodic electrode, bunchy precipitates of grape shape were produced, and the color of the solution changed from achromic to yellow, brown, red-brown, and almost black.
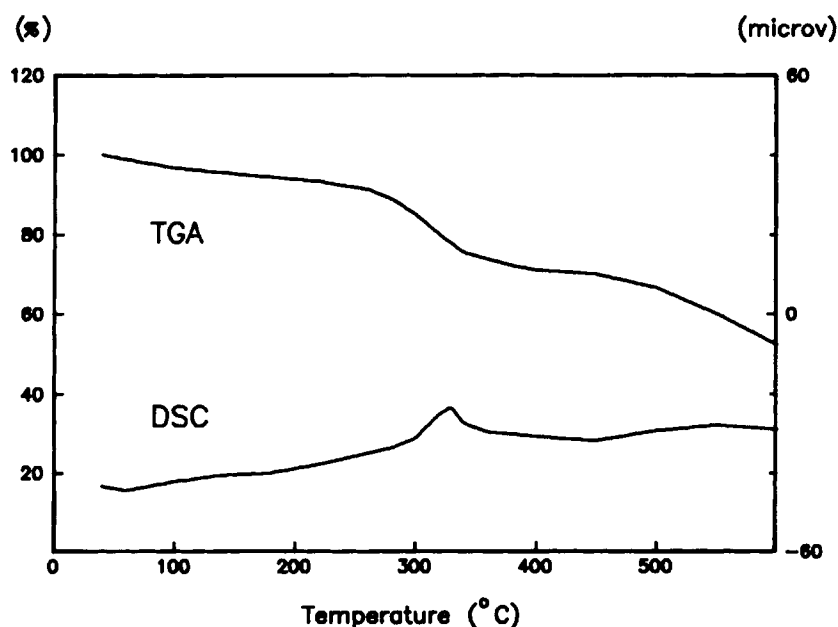

Figure 4 TGA and DSC curves of the electrochemically prepared polyaniline perchlorate in nitrogen.
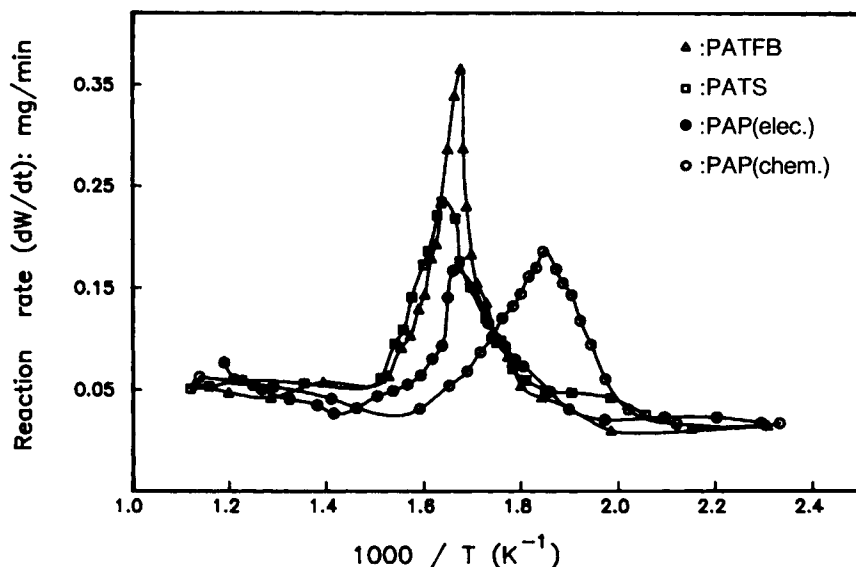
Figure 5 The temperature dependencies of the reaction rate for various polyaniline-based polymers.

The morphology of the PAP film on the Pt electrode is shown in Figure 6. There the PAP sample shows a bark shape pattern, and bunchy materials of white color are scattered over the film surface.

Conductivity

Conducting polymers can be prepared by filling the polymer matrix with conductive materials such as carbon black or metal fibers and by the generation of charge carriers in the polymer chains. The possible conducting mechanisms for these conducting polymers are different. In this case of electron donor- and acceptor-doped conducting polymers, generally the polymers have overlapping sets of molecular orbitals which provide for reasonable carrier mobility along the polymer chains. Thus, various conduction models have been suggested for along the polymer chains, and mechanisms for interchain transport of charge carriers doped by extrinsic means have often been proposed. But, in the actual employment of

Table II   The Values of Maximum Reaction Rate and Related Temperature from TGA Results for Polyaniline-Based Conducting Polymers

Polyaniline Derivatives	R_{max} (mg/min) at T_{max}
PABF$_4$	0.366 (at 324°C)
PATS	0.234 (at 338°C)
PAP (elec.)	0.166 (at 327°C)
PAP (chem.)	0.185 (at 269°C)

various models and related equations in previous reports[14-18] their physical characteristics and complex relation factors must be considered carefully. There are many factors from the structural factors, such as chain planarity, degree of crystallinity, chain kinks, and crosslinks, to electronic coupling between chains, size and shape of the dopants and the structure of polymer arrays.

The conducting mechanism in a pressed pellet of PAP can possibly be expressed in the form of one of the following equations. The electrical conductivity as a function of temperature based on the hopping conduction mechanism has been reported to have the form $\exp(-const/T^{\alpha})$ observed in amorphous semiconductors ($\alpha = 1/4$) by Mott[14] and sputtered granular metal films ($\alpha = 1/2$) by Sheng.[15] These related equations are based on the fundamental assumption that the concentration of charge carriers is independent of temperature. Greaves[16] reported that a variable range hopping conduction can be expressed by the following equation,

$$\sigma \cdot T^{1/2} = \exp[-(B/T^{1/4})] \qquad (3)$$

where B is a constant. Also, the electronic conduction mechanism which includes the grain boundary potential is given by Matare's equation[17]

$$\sigma = AT^{1/2} \cdot \exp(-E_a/kT) \qquad (4)$$

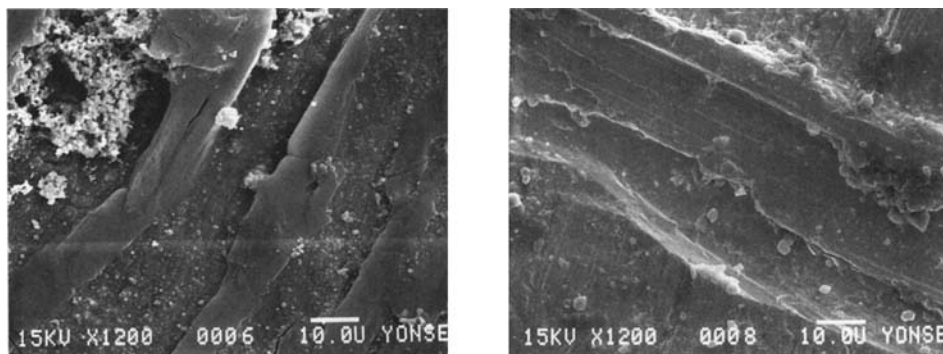where A is a constant related to the electric field strength and effective mass of electrons and E_a is

Figure 6 Scanning electron micrographs of an electrochemically prepared polyaniline perchlorate film.

the height of the potential barrier. Zeller[18] reported that in the case of tunneling conduction the conductivity equation as a function of temperature can be expressed as follows:

$$\sigma = \sigma_0 \cdot \exp(-A'T^{-1/2}) \tag{5}$$

The electrical conductivity for the pressed pellet of PAP was measured by the four-probe technique in the temperature range from -170 to $25°C$ under a low applied field to ensure Ohmic behavior. The result, that is, the temperature dependence of the conductivity, is shown in Figure 7. There the conductivity for the pressed pellet of PAP increases linearly with increasing temperature, satisfying the Arrhenius equation, $\sigma = \sigma_0 \cdot \exp(-E_a/kT)$. Thus, the value of the activation energy (E_a) was obtained

to be 0.14 eV from the slope of the plot, according to the Arrhenius relationship.

Equations (3)-(5) were used for the PAP sample. That is, the temperature dependencies of the electrical conductivity, according to eqs. (3)-(5) for the hopping, electronic (including the grain boundary potential) and tunneling conductions, were calculated and are shown in Figure 8-10, respectively. As shown in these plots, the results of the hopping and electronic conductions including the grain boundary potential show good linearities. But, Figure 10 for the tunneling conduction mechanism shows a few deviations from the linearities of Figures 8 and 9. Thus, it can be suggested that the conduction mechanism in the pressed pellet of PAP is electronic hopping conduction. That is, it is predicted that the observed conductivity is induced from doping with
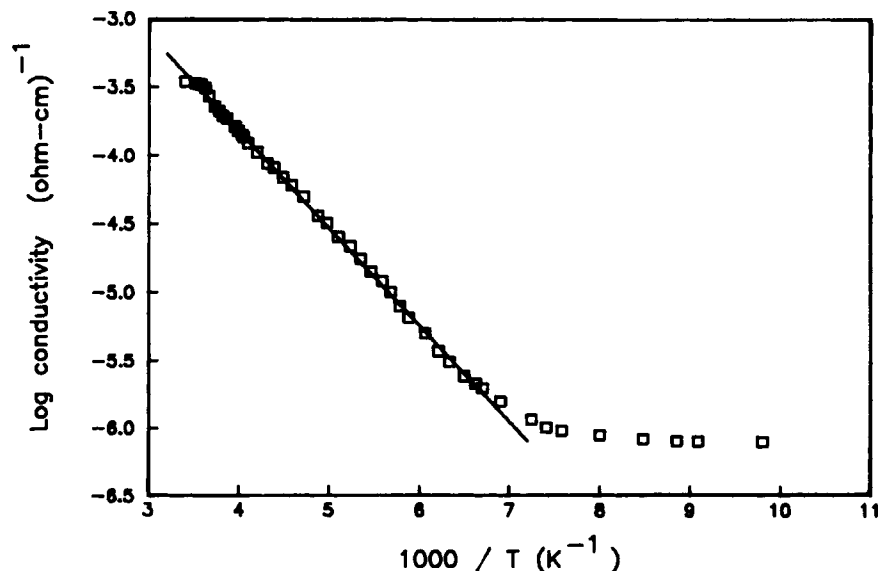

Figure 7 The electrical conductivity as a function of temperature for a polyaniline perchlorate prepared by electrochemical oxidation.
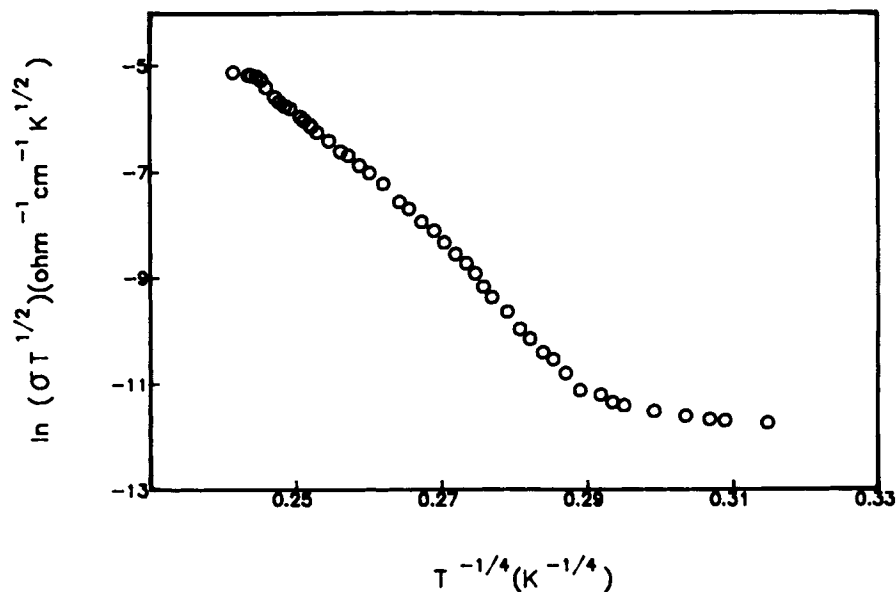
Figure 8 The temperature dependence of the electrical conductivity of the electrochemically prepared PAP based on the hopping conduction mechanism.

ClO_4^- anions which as electron acceptors create a positive character.

ESR Measurements

Previous ESR studies[19-21] of organic conducting polymers have been performed to obtain structural evidence for the polymers and to support the suggested conduction mechanisms. Also, many efforts have been made to consider the relationships be-

tween the ESR parameters and the electronic conduction mechanisms. Namely, the relationships among ESR factors, g-value, peak-to-peak linewidth (ΔH_{pp}) in the first-derivative spectrum and ratios between peak heights and the conductivity values of conducting polymers can be considered. For this, a previous report on polypyrrole-based systems[19] gives us valuable information. But these correlations between the ESR parameters and the transport mechanism or structural information in a polymer
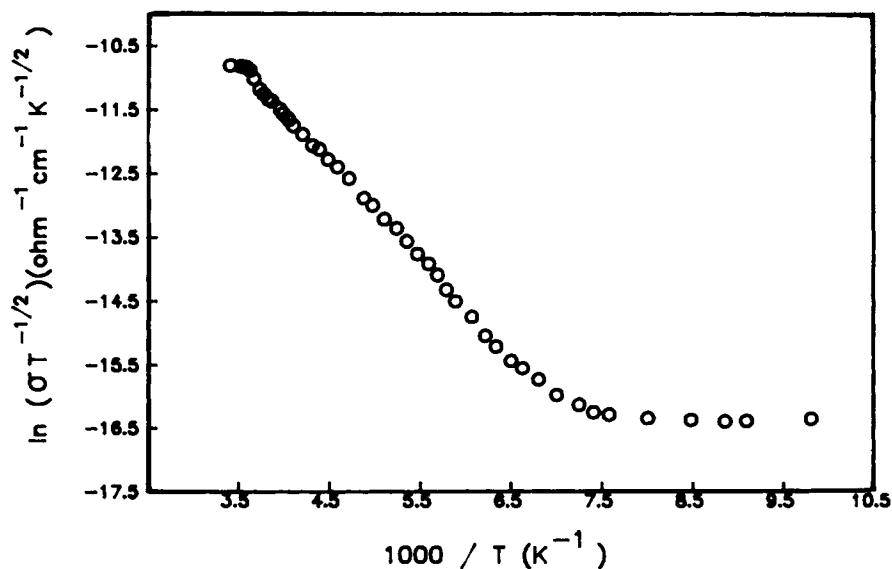

Figure 9 The temperature dependence of the electrical conductivity of the electrochemically prepared PAP based on $\sigma = AT^{1/2} \exp(-E_a/kT)$.
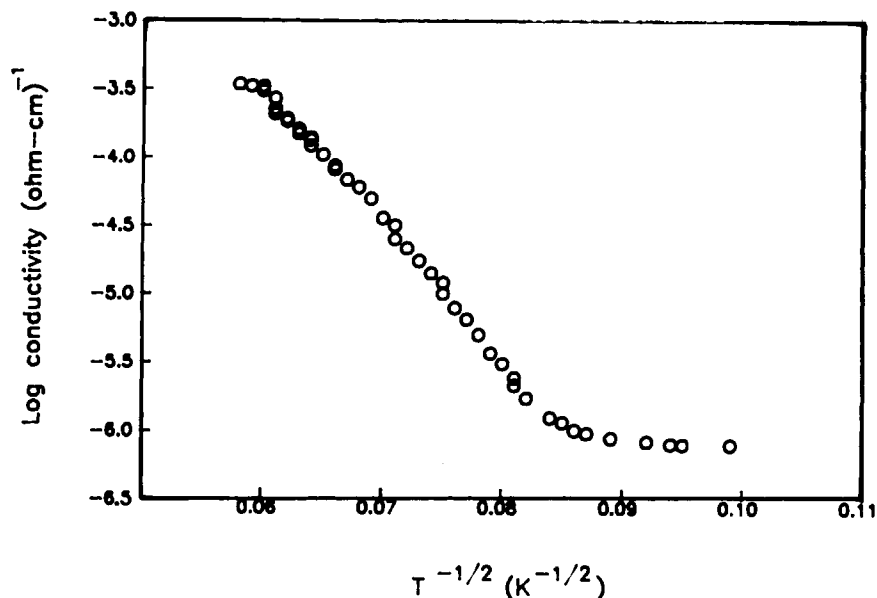
Figure 10 The temperature dependence of the electrical conductivity of the electrochemically prepared PAP based on the tunneling conduction mechanism.

must be explained carefully. Thus more serious research in this area is necessary.

Figure 11 shows a single ESR peak for PAP powder like that of other polyaniline-based conducting polymers. The measured values of ΔH_{pp} and the g-value are 3.3 G and 2.00465, respectively.

CONCLUSIONS

From the results of the polarography and the cyclic voltammetry in AN solution containing the $0.2M$

aniline and $0.1M$ TEAP, it is obvious that the anodic oxidation progressed as an irreversible reaction related to single electrons. Then, the ClO_4^- anions, which play a role in the initiation of polymerization, are electrochemically doped and form the polaron states along the polymer chains as electron acceptors. The values of $E_{1/2}$ and α were also obtained to be 825 mV and 0.894, respectively. In view of the α-value of 0.894, it can be predicted that the anodic oxidation reaction can take place easily.

In the electrical conductivity measurements, the value of E_a was obtained to be 0.14 eV, and the elec-
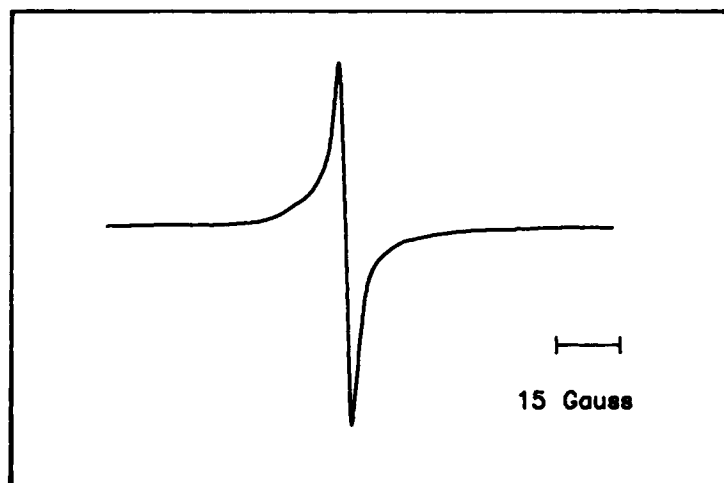

Figure 11 ESR spectrum of the electrochemically prepared PAP at 25°C (microwave frequency = 9.45 GHz).

tronic hopping conduction model is suggested. Also, a single ESR peak caused by the free electrons in the polyaniline chains is obtained. From the conductivity and ESR results, it is suggested that polaron states with a band gap of 0.14 eV are formed near the polyaniline chains, due to the doping injection of ClO_4^- anions as electron acceptors. Thus, the observed conduction is due to this electronic state, with hopping from state to state.

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