Electropolymerization and Physicochemical Properties of Polypyrrole p-Toluenesulfonate

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SYNOPSIS

Polypyrrole p-toluenesulfonate (PPTS) polymers were synthesized by the electrochemical technique from 0.2M pyrrole in 0 : 100, 1 : 99, 5 : 95, and 10 : 90 water/acetonitrile solutions containing 0.1M tetraethylammonium p-toluene sulfonate (TEATS) as a supporting electrolyte. Following the cyclic voltammetry measurements, the number of electrons involved in the reaction was determined to be unity. The results of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) showed that the weight loss was most rapid in the temperature range from 533 K to 768 K, and the maximum value of the reaction rate was 0.27 mg/min at 651 K. From the temperature dependence of the electrical conductivity and electron spin resonance (ESR) measurement, a small polaron hopping conduction was suggested for PPTS polymers. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Recently, electrochemically polymerized conducting polymers have attracted our attention. Conducting polypyrrole film, available via the electrochemical oxidation of pyrrole, has been reported as electrode material.[1,2] Polypyrrole thin films are electroactive and electrochromic[1] and have been useful for ion gate applications and displays.[2] Numerous studies for pyrrole-based conducting polymers have been reported by Pfluger et al.[3] Street et al.[4] obtained free-standing films of insulating neutral polypyrrole through electrochemical reduction of ionized polypyrrole under drybox conditions. They suggested that the oxidation of neutral polypyrrole occurs by homogeneous charge extraction from the π-system of the unaffected polypyrrole.

Comparing our electrochemically and chemically polymerized systems,[5-10] the electrochemically prepared conducting polymers are relatively stable in air, and the physicochemical 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 could have applications as electrode materials in rechargeable batteries. Due to this application, many researchers have shown interest in studies of organic compounds polymerized by electro-oxidation. Diaz and Kanazawa[11] attempted to explain the electropolymerization mechanism of pyrrole in acetonitrile solution containing BF_4^- anions. They suggested that polymerization should take place through a π-radical cation of pyrrole, produced by one electron transfer, which would act as the monomer for polymerization by reaction with neighboring pyrrole molecules. On the other hand, BF_4^- plays a role in the initiation step of polymerization, showing that the oxidation takes place at a higher cathodic potential than is necessary for the oxidation of the monomer and that the oxidation of the polymeric form of the pyrrole gives rise to the conducting state of the polypyrrole layer.[12]

For conducting polymers, research is needed from the scientific point of view as well as their applications in the solar batteries,[13] rechargeable batteries,[14] electro-optics devices,[15] radiation detectors,[16] and base materials in the semiconductor and computer industries.[17] Recently, studies of polypyrrole-,[18] polyaniline-,[19] polythiophene-,[20] polypyrene-,[21] and polyazulene-[21] based conducting polymers synthesized by electro-oxidation have reported their stabilities in air.

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Marcos et al.[22] claimed that the electropolymerization mechanism of pyrrole was based on electro-oxidation. On the other hand, Diaz and Hall[18] studied polypyrrole perchlorate films prepared by electro-oxidation and concluded that the conductivities depended on solvent conditions.

In this work, we will present the results of a mechanistic study of polypyrrole doped with p-toluenesulfonate obtained from an electropolymerization and elucidate thermal stability, morphology, and electrical properties.

EXPERIMENTAL

Materials and Sample Preparations

Pyrrole used as monomer in our electropolymerization was obtained from the Fluka Chemical Company. Acetonitrile (AN) as a solvent and tetraethylammonium p-toluenesulfonate (TEATS) as a supporting electrolyte were purchased from the Merck Chemical Company and the Aldrich Chemical Company, respectively. Owing to the hygroscopicity of TEATS, it was dried under vacuum at 25°C for 48 h and then dried at 110°C. AN was always passed through a column packed with alumina powder previously dried at 400°C.

Polypyrrole p-toluenesulfonates (PPTS) were prepared from 0.2M pyrrole in 0 : 100(1), 1 : 99(2), 5 : 95(3), and 10 : 90(4) water/AN (volume %) solutions containing 0.1M TEATS as a supporting electrolyte. This solution was deoxygenated by stirring it with a nitrogen stream for 50 min before every experiment. The temperature of the reaction system
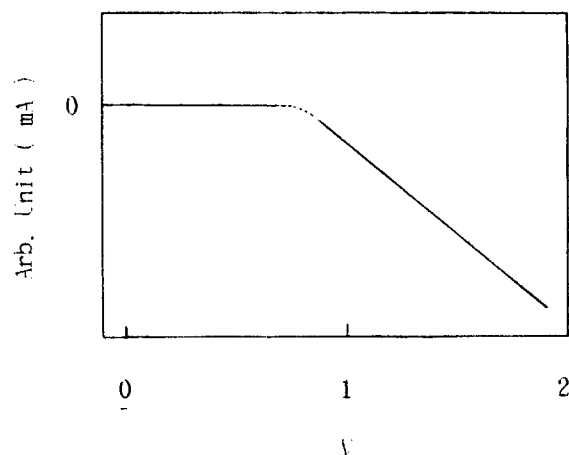
Table I   Results of Elemental Analyses for Polypyrrole p-Toluenesulfonate (PPTS) Prepared from 0.2M Pyrrole in 0 : 100 (1), 1 : 99 (2), 5 : 95 (3), and 10 : 90 (4) Water/Acetonitrile Solutions Containing 0.1M Tetraethylammonium p-Toluenesulfonate as a Supporting Electrolyte

Polymer	Elements			
	C	H	N	O
PPTS 1	6.01	5.62	1.00	1.80
PPTS 2	6.08	5.54	1.00	1.90
PPTS 3	6.11	5.64	1.00	2.01
PPTS 4	6.07	5.90	1.00	2.11

was maintained at 15°C using a Lauda Circulator. The three-electrode cell was equipped with a Pt working electrode (1 × 4 × 0.01 cm), a Pt counter electrode (1 × 2 × 0.01 cm), and a standard saturated calomel electrode. Pyrrole doped with p-toluenesulfonate was electropolymerized in the potential range between 1.3 and 1.7V for 5–6 h. The anodic insoluble precipitates produced by the electropolymerization were removed from the electrode and confirmed to be the electrically conductive polymers. The rate of material growth depended directly on the current density, showing a linear dependence with time. The current density varied with the resistance of the electrolytic solution, the concentration of pyrrole, and the applied potential. Figure 1 shows the current versus applied potential in electropolymerization of pyrrole doped with p-toluenesulfonate. Elemental analysis (Perkin-Elmer 240C) was performed to determine the dopant content in the final product. This analytical result is presented in Table I.

Thermal Analysis

The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements of the PPTS powders were carried out using a thermal analyzer (Rigaku-8150). TGA analysis at temperatures in the range of 25–800°C with a heating rate of 10°C min^{-1}.

Scanning Electron Microscopy (SEM)

For the SEM measurements, the sample film was washed with solvent and SEM was performed by using a Hitachi S-510 and an ion coater, Eiko IB-3.
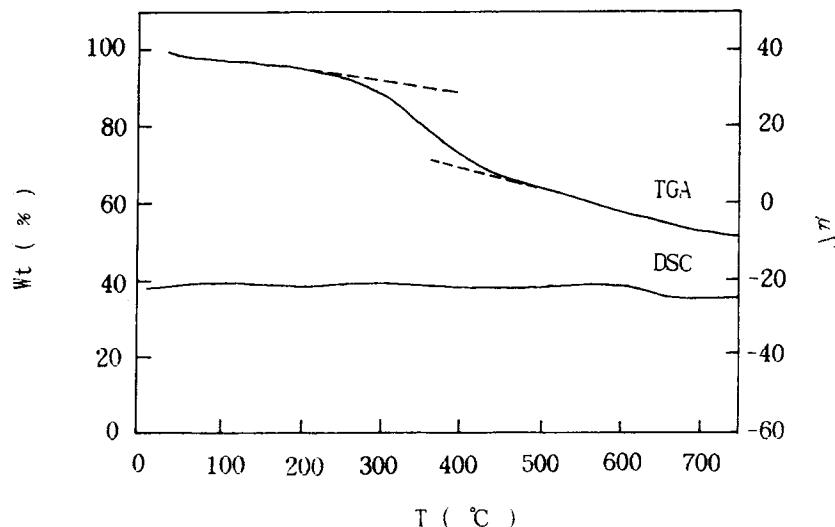

Figure 1   Current vs. applied potential in electropolymerization of pyrrole doped with p-toluenesulfonate.

Figure 2 TGA and DSC curves of a polypyrrole p-toluenesulfonate (PPTS) prepared from 0.2M pyrrole in 0 : 100 (1) water/acetonitrile solution containing 0.1M tetraethyl-ammonium p-toluenesulfonate (TEATS) as a supporting electrolyte.

Electrochemical Measurements

The electrochemical works were performed with a potentiostat/Galvanostat (EG&G PARC 273A). The cyclic voltammograms were plotted with an electrochemical analyzer (EG&G PARC 270).

Electrical Conductivity Measurements

Electrical conductivity was measured by the four-point technique at temperatures from 123 to 363 K. The PPTS 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. The presssed pellet has a disk-shape form with a 10 mm diameter and a thickness of 2 mm. Before the measurements, the sample was heated at a temperature near the melting point to remove residual trapped carriers or dipole effects. The sample in a sample basket was placed in the middle of a probe equipped with four Pt-lines and a thermocouple. The thermocouple was connected with a digital thermometer (Seoul Co. SR-6200, G-116), and a low temperature
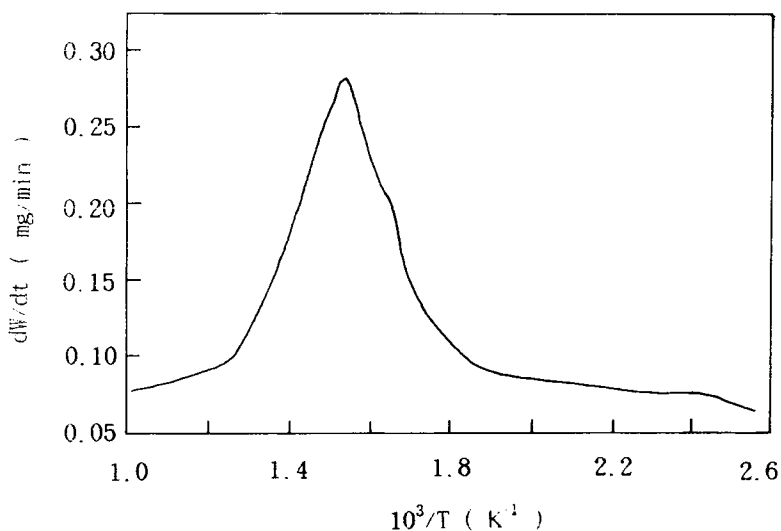

Figure 3 Temperature dependence of the reaction rate for polypyrrole p-toluenesulfonate (PPTS) prepared from 0.2M pyrrole in 0 : 100 (1) water/acetonitrile solution containing 0.1M TEATS as a supporting electrolyte.
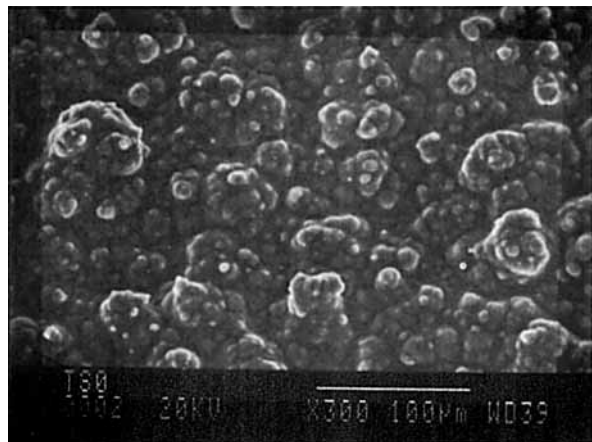
Figure 4 Scanning electron micrograph of polypyrrole
p-toluenesulfonate (PPTS) prepared from 0.2M pyrrole
in 0 : 100 (1) water/acetonitrile solution containing 0.1M
TEATS as a supporting electrolyte.

was obtained by using liquid nitrogen. The conductivity was measured while raising the temperature at a heating rate of 1°C/min. The current and potential were measured by a Keithley 616 digital electrometer and a 642 digital multimeter, respectively.

ESR Measurements

Electron spin resonance (ESR) measurements were carried out with a Bruker ESR spectrometer (ER 200, E-SRC). The PPTS powder was placed in the ESR tube and measurement was performed under the following conditions. Scan range, 50 G; micro-

wave frequency, 9.45 GHz; microwave power, 20 mW; modulation frequency, 100 KHz; modulation time constant, 100 s; modulation amplitude, 0.4 G; receiver gain, 125; temperature, 25°C.

RESULTS AND DISCUSSION

Thermal Analysis

Thermal analysis gives useful information on properties of polymers measured as a function of temperature. TGA is a dynamic method in which the weight loss of a polymer sample is measured continuously as the temperature is changed at a constant rate. TGA and DSC for the PPTS powder were performed to obtain their thermal characteristics in the temperature range of 25–700°C under nitrogen atmosphere. In Figure 2, the TGA curve for PPTS under nitrogen atmosphere shows the weight loss beginning at about 260°C and continuously increasing to 35% at about 495°C. The corresponding DSC curve shows that no phase transition occurs in the measured temperature range.

The reaction rate (dW/dt) is plotted against the reciprocal of absolute temperature. Figure 3 shows that the weight loss is most rapid in the temperature range from 260 to 496°C. The maximum value of the reaction rate (R_{max}) is 0.27 mg/min at 378°C. The R_{max} value of PPTS is less than that of polyaniline tetrafluoroborate (PABF$_4$; 0.366 mg/min at 324°C),[8] but larger than those of polyaniline hexafluorophosphate (PAPF$_6$; 0.092 mg/min at 300°C)[8] and polyaniline perchlorate (PAP; 0.166 mg/min
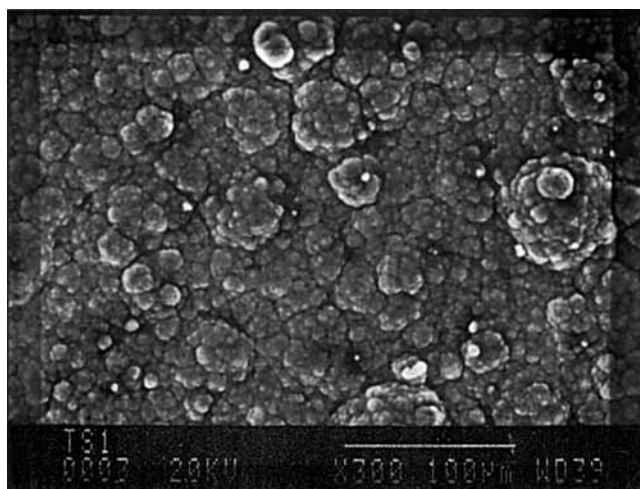

Figure 5 Scanning electron micrograph of polypyrrole p-toluenesulfonate (PPTS) prepared from 0.2M pyrrole in 1 : 99 (2) water/acetonitrile solution containing 0.1M TEATS as a supporting electrolyte.

at 327°C).[6] The polypyrrole-based system mainly decomposed at higher temperature regions than polyaniline-based systems. The thermal stability of PPTS is greater than that of PA-based materials. Therefore, it is concluded that PPTS can be utilized in industrial applications requiring higher thermal stability. The R_{max} values, as shown in Table II, are not seriously affected by the water/AN volume% containing 0.1M TEATS as a supporting electrolyte. This implies that the maximum reaction rates are independent of solvent effect.

SEM Analysis

The morphology of the polymer depends mainly on the structure of the monomer, the nature of the dopant, and the thickness of the polymer film grown on the electrode. The PPTS thin films were grown on an anodic Pt electrode from 0.2M pyrrole in 0 : 100, 1 : 99, 5 : 95, and 10 : 90 water/AN solutions containing 0.1M TEATS for SEM analysis, respectively. The surfaces of the PPTS films resemble a growth of aggregate shaped as blossoms and also, irregular granules are densely crowded on the films. The scattered granules shaped as blossoms are regarded as toluenesulfonate dopants, and good conductivity is originated from this compact structure which is independent of water/AN ratio. From SEM analysis it is concluded that the direction of electron conductivity is not likely to be in any order, since the morphology of film surface does not show an oriented pattern in any special direction (Figs. 4–7).
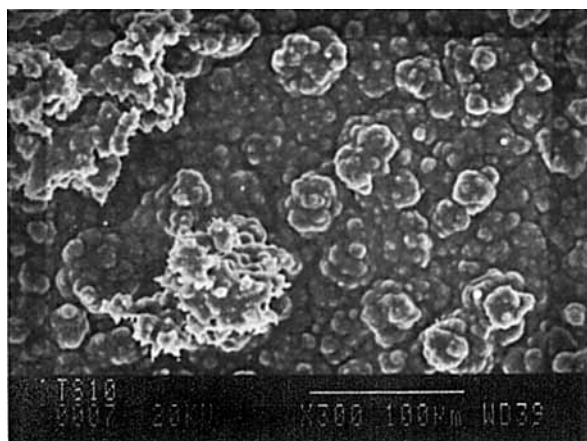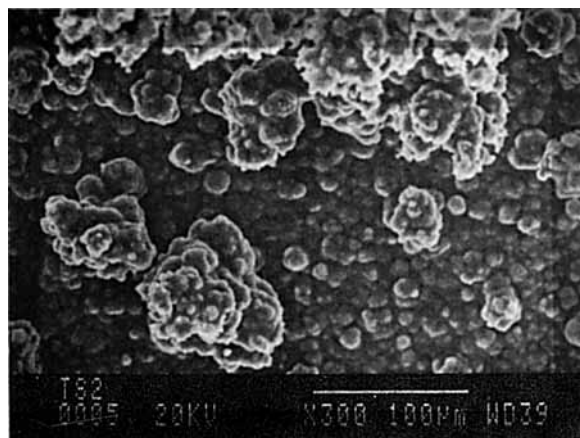

Figure 7   Scanning electron micrograph of polypyrrole p-toluenesulfonate (PPTS) prepared from 0.2M pyrrole in 10 : 90 (4) water/acetonitrile solution containing 0.1M TEATS as a supporting electrolyte.

Cyclic Voltammetry

The cyclic voltammograms in Figure 8 were obtained from 0.2M pyrrole in 5 : 95 water/AN solution containing 0.1M TEATS at 25°C. After deoxygenation of this solution by a stream of nitrogen, the potential was scanned in the range of 0 ~ 1600 mV with several scan rates. As shown in Figure 8, the number of electrons transferred in this electrode reaction is one. The current has a shorter time to decrease for fast scans, and the curves decay less in the faster scans. The peak height changes in proportion to the square root of the scan rate as well as to the concentration of the active species. Figure 9 shows the variations of the anodic and cathodic peak potentials with scan rate, while the cathodic peak potential decreases with it. From this it is concluded that the anodic and cathodic reactions for PPTS polymers are irreversible processes.

Figure 6   Scanning electron micrograph of polypyrrole p-toluenesulfonate (PPTS) prepared from 0.2M pyrrole in 5 : 95 (3) water/acetonitrile solution containing 0.1M TEATS as a supporting electrolyte.

Table II   Maximum Reaction Rates (R_{max}) Obtained from TGA Results in Polypyrrole p-Toluenesulfonate (PPTS) Prepared from 0.2M Pyrrole in 0 : 100 (1), 1 : 99 (2), 5 : 95 (3), and 10 : 90 (4) Water/Acetonitrile Solutions Containing 0.1M Tetraethylammonium p-Toluenesulfonate as a Supporting Electrolyte

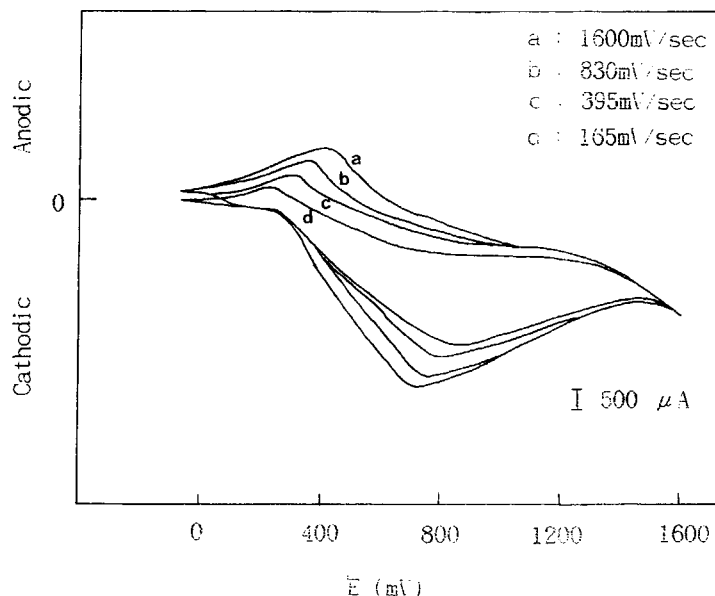| Polymers	R_{max} (mg/min) at T_{max}
PPTS 1	0.270 at 378°C
PPTS 2	0.275 at 376°C
PPTS 3	0.281 at 372°C
PPTS 4	0.287 at 369°C

Figure 8   Cyclic voltammogram of PPTS film on a platinum electrode in 5 : 95 water/
AN solution at 25°C.

Electrical Conductivity

Most conducting polymers have conjugated double bonds, and the conduction bands formed by the overlapping of the π-orbital exist along the polymer chains. The conductivity of these polymers increases with the doping of various dopants and with increase in temperature. In this point of view, the conducting polymers are often prepared by filling the polymer matrix with conductive anions and by the generation of charge carriers in the polymer chains. The possible conducting mechanisms for these conducting polymers are different. In the case of electron donor- and acceptor-doped conducting polymers, generally the polymers have overlapping sets of molecular orbitals which provide for carrier mobility along the polymer chains. Due to this, various conduction models have been suggested. As for the hopping
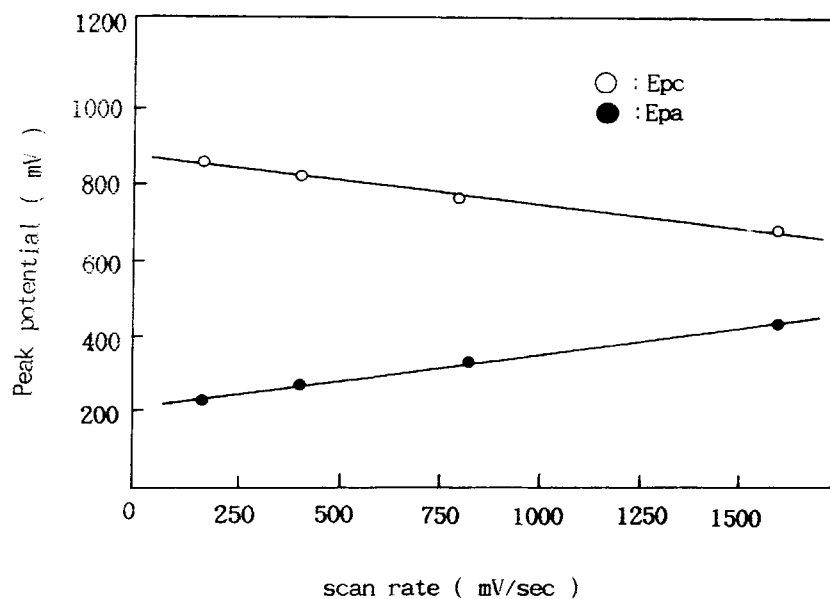

Figure 9   Anodic and cathodic peak potential vs. scan rate for PPTS film in 5 : 95 water/
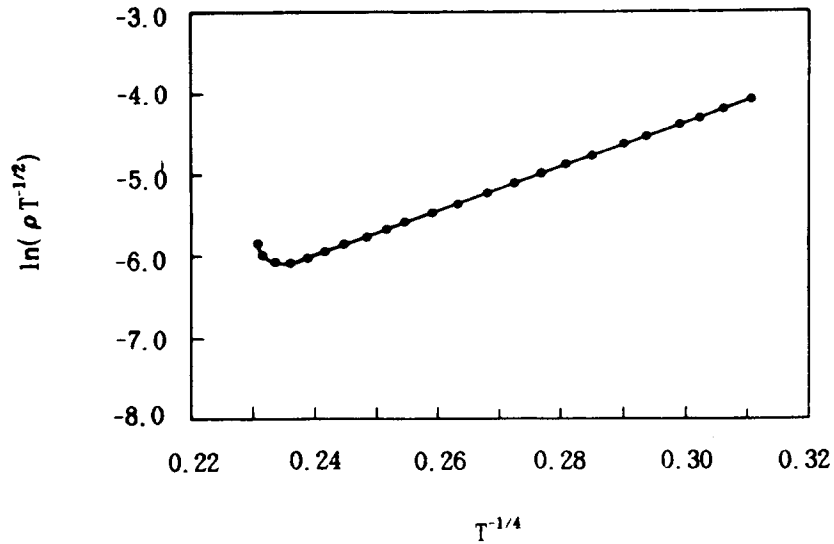AN solution at 25°C.

Figure 10 Temperature dependence of the electrical resistivity for PPTS1 based on $\rho T^{-1/2} = \exp(B/T^{-1/4})$.

conduction mechanism of polymeric materials, Mott's[23] and Greaves's[24] equations are based on a model in which charge is transported by the thermally assisted hopping of electrons between localized states near the randomly distributed traps and their equations are based on the assumption that the concentration of charge carriers is independent on temperature. On the other hand, Matare's equation[25] for a system including grain boundary barriers, Zeller's[26] and Orton and Powell's[27] equations for tunneling and thermoionic emission conductions have been known for the conducting polymers. Using

a constant potential supply, we obtained enough anodic precipitate to make a pellet and this precipitate was removed from the electrode, rinsed with AN, dried under vacuum, and made into a pellet. The temperature dependence of the resistivity of the pressed pellet was plotted according to the previously reported equations.[23–27] The temperature dependences of the electrical conductivity of PPTS, as shown in Figures 10–13, show good linearity, satisfying the Mott's and Greaves's model. That is, the conduction of PPTS is predominately carried out by hopping. Therefore, it is suggested that the elec-
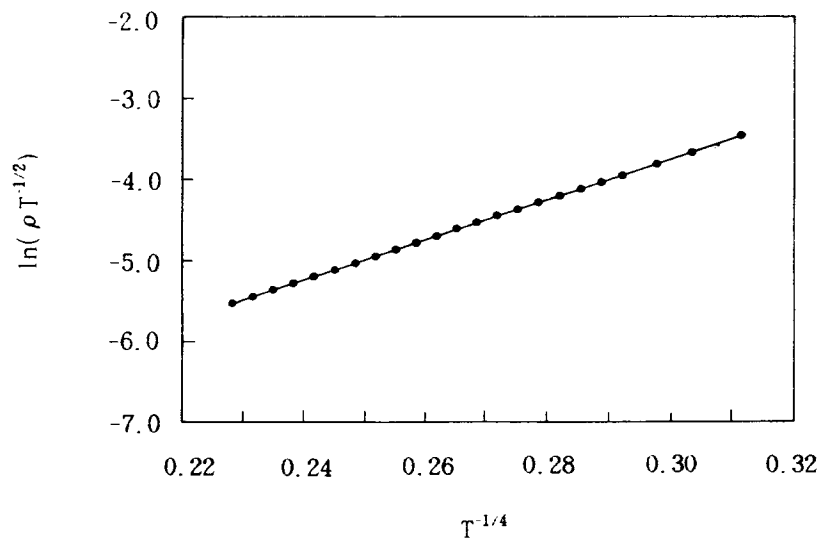

Figure 11 Temperature dependence of the electrical resistivity for PPTS2 based on $\rho T^{-1/2} = \exp(B/T^{-1/4})$.
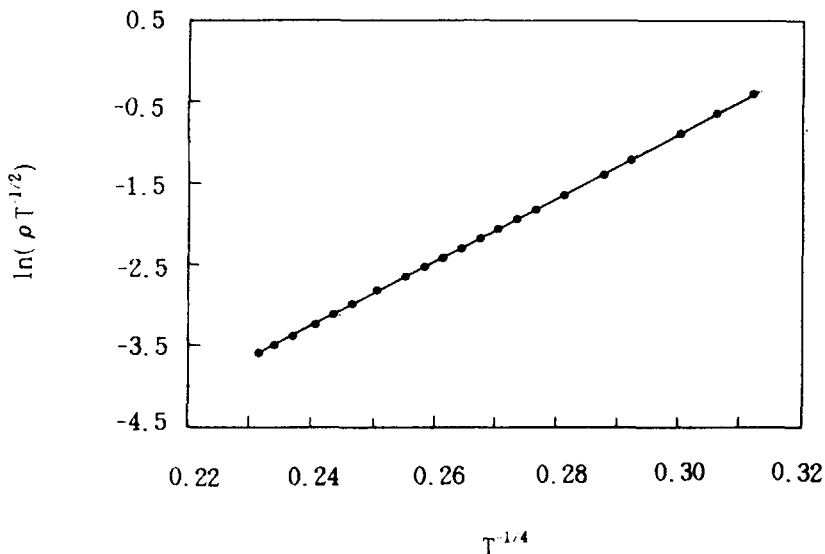
Figure 12   Temperature dependence of the electrical resistivity for PPTS3 based on $\rho T^{-1/2} = \exp(B/T^{-1/4})$.

trical conduction mechanism of PPTS is a small polaron hopping.

ESR

Electron spin resonance measurement was attempted and obtained for evidence of the formation of singly charged paramagnetic centers, solitons. A number of ESR measurements[5-10,28] of conducting polymers have been performed to verify the suggested conducting mechanisms and obtain evidence of the soliton. In previous ESR studies,[29] it was proved that the conductivity is related to the ESR

peak-to-peak line width and the A/B ratio for ESR spectrum of conducting polymer. The ESR spectrum of the PPTS sample at room temperature shows a single peak in Figure 14. The measured peak-to-peak line width, A/B ratio, and g value are 0.73G, 1.73, and 0.00473, respectively.

In conclusion, from the ESR spectrum, it is confirmed that singly charged paramagnetic centers are formed by the following doping of anions as an electron acceptor, a small polaron with 0.034 eV gap near the conduction band. The electron in this level causes a local polarization near the positively charged center, and as a result, the electron becomes
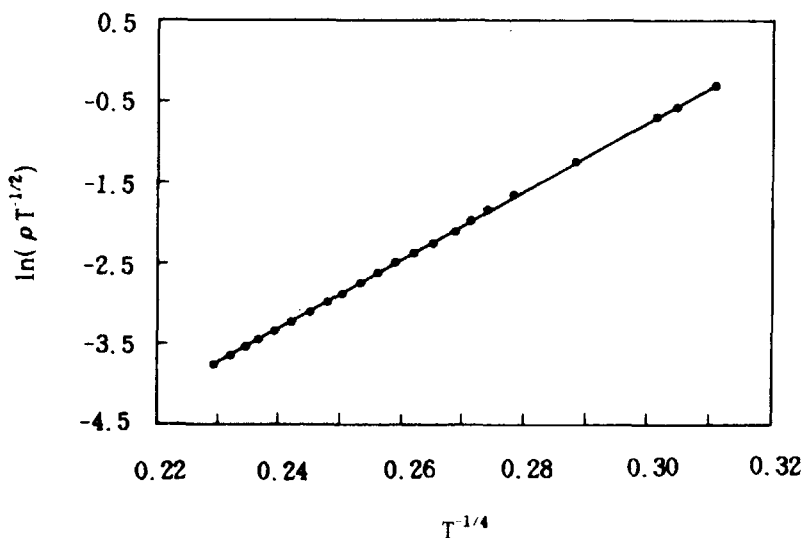

Figure 13   Temperature dependence of the electrical resistivity for PPTS4 based on $\rho T^{-1/2} = \exp(B/T^{-1/4})$.
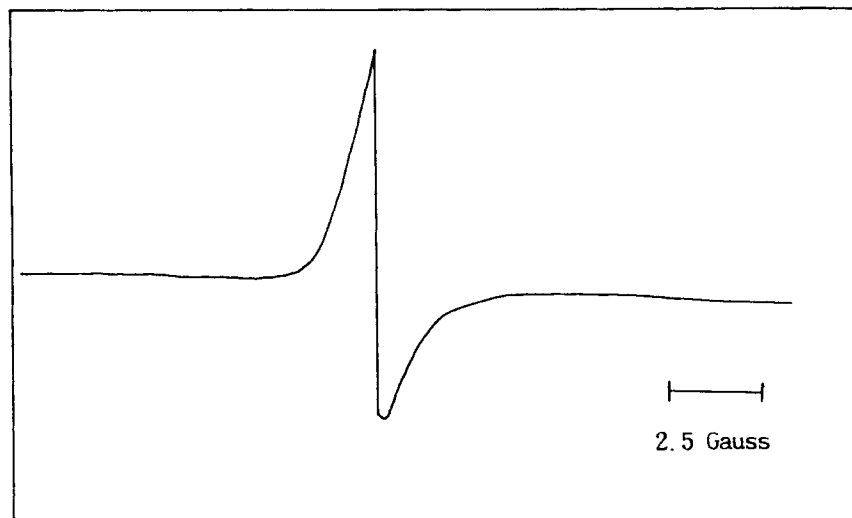
Figure 14   ESR spectrum of a polypyrrole p-toluenesulfonate at 25°C on microwave frequency 9.45GHz.

a small polaron with π-cation radical. The observed conduction of PPTS is due to these small polarons as charge carriers that hop from state to state in the PPTS polymer.

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