

Physicochemical Properties of Electrochemically Prepared Poly(pyrrole hexafluorophosphate)

GI JA LEE,¹ RAN A JEONG,¹ SEUNG HWON LEE,¹ HONG SEOK KIM,¹ DONG HOON LEE,¹ KEU HONG KIM,¹ KYUNGSOO AHN²

¹Department of Chemistry, Yonsei University, Seoul 120-749, South Korea

²Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, 70569 Stuttgart, Germany

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ABSTRACT: Poly(pyrrole hexafluorophosphate) (PPPF₆) was prepared with the potentiostatic method to supply a constant potential of 1.21 V for 5 h in water/acetonitrile (1/99 vol %) solution of 0.2M pyrrole containing 0.1M tetraethylammonium hexafluorophosphate as a supporting electrolyte. The result of elemental analysis and Fourier transform infrared spectrum showed that it was a PPPF₆ that was doped with ~28 wt % PF₆⁻. From the cyclic voltammogram, it was found that the redox reaction of PPPF₆ was irreversible. Scanning electron microscopy was performed to know the morphology of PPPF₆. The result of the differential scanning calorimetry did not show any special peak in temperature range of 25–800°C. From the temperature dependence of the electrical conductivity and electron spin resonance measurement, it was suggested that a possible conduction mechanism for the PPPF₆ polymer should be a small polaron hopping conduction. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 605–612, 1998

Key words: poly(pyrrole hexafluorophosphate) (PPPF₆); potentiostatic method; irreversible; polaron; hopping mechanism

INTRODUCTION

The electrochemical preparation of conducting polymer film has many advantages. The properties of the film can be easily modified by varying the electrolysis conditions: potential, current density, solvent, electrolyte, etc.^{1,2} Besides comparing chemically prepared ones, these films are relatively stable in air, and the properties are not easily changed by an external stimulus.^{3,4} In particular, polypyrrole—which had been first electrochemically prepared—is regarded as the most promising material for batteries and other electrochemical devices recently.^{5,6} Diaz and Kanazawa¹ suggested that the electropolymerization of pyr-

role in acetonitrile (AN) solution should occur *via* the oxidation of pyrrole at Pt electrode to produce an unstable π -radical cation. Coupling of a pyrrole radical cation with a neutral monomer forms a radical cation dimer, and further reaction continues the chain forming sequence.⁷ The coupling reaction occurs primarily in the α position of the pyrrole ring to produce a linear polymer. This reaction has electrochemical stoichiometry, wherein 2.2–2.4 electrons/pyrrole ring are involved in the formation of the polymer.¹ But, in fact, the structure of electrochemically prepared polypyrrole is amorphous and has not exactly been found.⁸

In our previous papers,⁴ poly(pyrrole *p*-toluenesulfonate) was prepared by electrooxidation from 0.2M pyrrole and 0.1M tetraethylammonium *p*-toluenesulfonate, supplying a potential of 1.3–1.7 V under various solvent conditions. From this, we investigated the relationship between solvent condition and conductivity of sample. Ac-

Correspondence to: K. H. Kim.

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ording to Zinger and coworkers,² although the use of organic solvent was costly and hazardous, free-standing films obtained in organic media showed prominent characteristics in their conductivity and mechanical properties. But, when the solution contained 1 vol % H₂O or other hydroxylic solvents, the growing surface became much smoother, and the chemical nature of the surface was probably more homogeneous.^{1,3}

Hagiwara and coworkers⁹ reported that the electrical conductivity of polypyrrole was dependent on the applied potential. Those of stretched films were especially dependent. It assumed that application of a higher potential induced an unfavorable side reaction that causes the film properties to deteriorate. Sato and colleagues¹⁰ investigated the electrical conduction mechanism of polypyrrole films containing various counter ions.

In this work, we prepare a new poly(pyrrole hexafluorophosphate) (PPPF₆), which modified the polymerization potential, time, and solvent—supply a potential at 1.21 V for 5 h in 1/99 vol % water/AN solvent and examine the physicochemical properties—morphology, dopant contents, thermal stability, and electrical properties. Also, we investigate the electrical conduction mechanism of PPPF₆ based on the temperature dependence of electrical conductivity.

EXPERIMENTAL

Materials

Pyrrole (purity: 99%, Acros Organics) was used without purification. AN as a solvent was always passed through a column packed with alumina powder previously dried at 400°C to eliminate water and acrylonitrile. Tetraethylammonium hexafluorophosphate (TEAPF₆) (purity: 99.99%, Fluka Co.) as a supporting electrolyte was dried under vacuum at 25°C for 48 h and 110°C for the removal of water.

Electrochemical Preparations

PPPF₆ was prepared with anodic oxidation of pyrrole in the electrolytic cell containing 0.2M pyrrole and 0.1M TEAPF₆ in AN containing 1 vol % water. This solution was bubbled with argon gas for 30 min before every experiment to remove oxygen. The three-electrode cell consisted of a Pt working electrode (2 × 3 × 0.01 cm), a Pt counter electrode

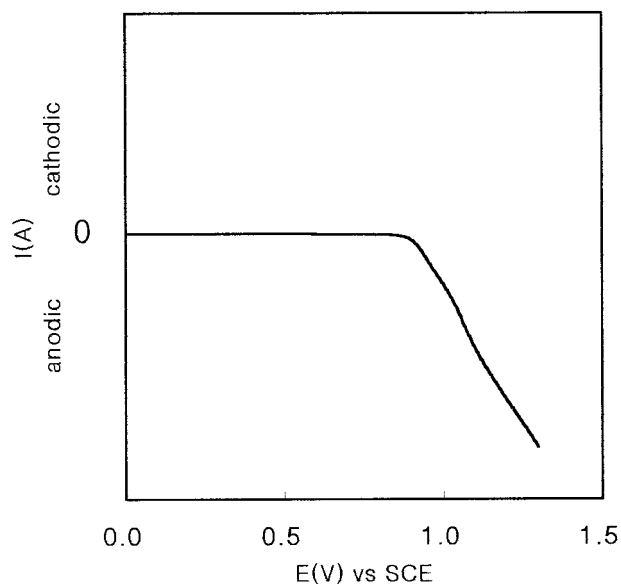


Figure 1 A linear sweep voltammogram of 0.2M pyrrole in the potential range of 0–1.3 V (scan rate: 20 mV/s).

(2 × 3 × 0.01 cm), and a saturated calomel electrode as a reference electrode. Before sample preparation, various electrolysis conditions were applied to obtain the optimum condition for a better electrical conductivity. First, linear sweep voltammetry was performed to observe the anodic behavior of pyrrole. Figure 1 shows a linear sweep voltammogram of 0.2M pyrrole in the potential range of 0–1.3 V at a scan rate of 20 mV/s. As a result of linear sweep voltammetry, we knew that pyrrole could be oxidized only more than 0.8 V. The results of changing electrode potential (0.85, 0.995, 1.110, and 1.21 V) in constant periods (7 h), and polymerization time (1, 3, 5, and 7 h) at a fixed potential (1.21 V) showed that PPPF₆ prepared at 1.21 V for 5 h had the highest electrical conductivity. From these results, we confirmed the following: the higher the potential, the more dopant contents in polymer, thus a higher electrical conductivity. Too many long periods caused a rapid increase in the number of defects in the conjugated backbone and reduced the mobility of the charge carriers.² An EG&G PAR model 270 A potentiostat/galvanostat was used for potentiostatic preparation. The PPPF₆ film was obtained through the following process: precipitation on the anode surface, rinsing with 1/99 vol % water/AN solvent, and drying in a vacuum oven for 3 days.

Measurements

Cyclic voltammetry was conducted for the information about reversibility using a potentiostat/galva-

nostat (EG&G PARC 273A). Elemental analysis was performed with a Carlo-Erba elemental analyzer to determine how much dopant anion was doped in the polymer chain. Fourier transform infrared (FTIR) analysis was recorded with Shimadzu spectrometer by the KBr pellet method to analyze a structure of PPPF₆. Differential scanning calorimetry (DSC) was conducted using a thermal analyzer (DSC-1500) at temperatures in the range of 25–800°C, with a heating rate of 10°C/min in an argon atmosphere. Scanning electron microscopy (SEM) was performed for the morphology analysis with a Hitachi S-2500. Electron spin resonance (ESR) was conducted using a EPR spectrometer (Bruker, ER 200 E-SRC) at 25°C. Electrical conductivity was measured by the four-probe technique using an Keithley 2001 at a temperature range of 80–300 K. A quartz probe was placed in a chamber packed with liquid nitrogen to measure low temperature conductivity.

RESULTS AND DISCUSSION

Cyclic Voltammetry (CV)

CV is a very popular technique for initial electrochemical studies of new systems. CV is a reversal method that records the changes of current on the potential varied linearly with time. It is important for the reversibility that is essential for battery or other electrochemical devices to deal with electrode reaction of conducting polymer, and it can be predicted from the cyclic voltammogram. That is, in the reversible system, the peak potential E_p is independent on potential scan rate v as eq. (1). On the contrary, the peak potential E_p is proportional to the potential scan rate v in the irreversible system, as eq. (2).¹¹

$$E_p = E_{1/2} - 1.109 \left(\frac{RT}{nF} \right) \quad (1)$$

$$E_p = E^0 = \frac{RT}{\alpha n_a F} \left[0.780 + \ln \left(\frac{D_0^{1/2}}{k^0} \right) + \ln \left(\frac{\alpha n_a F v}{RT} \right)^{1/2} \right] \quad (2)$$

Before the preparation of PPPF₆ film, CV was performed in H₂O/AN (1/99 vol %) solution of 0.2M pyrrole containing 0.1M TEAPF₆ in the potential

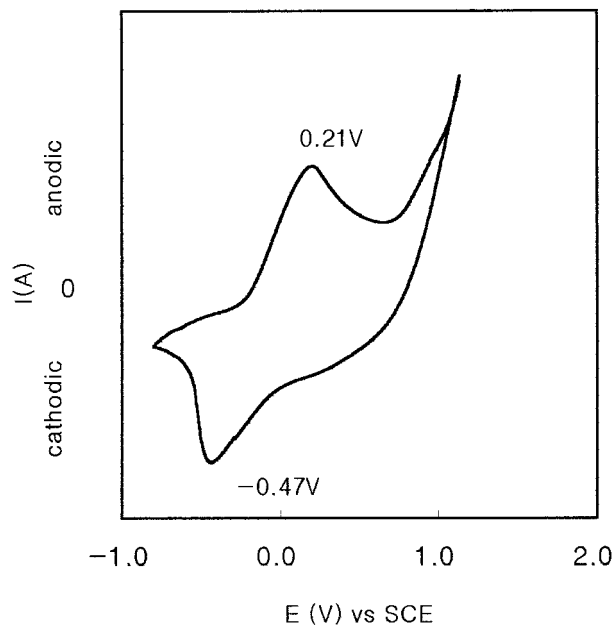


Figure 2 The cyclic voltammogram in 1/99 vol % H₂O/AN solution of 0.2M pyrrole and 0.1M TEAPF₆ at -0.5–1.1 V (scan rate: 10 mV/s).

range of -0.5–1.1 V at a scan rate of 10 mV/s. Results are shown in Figure 2. In Figure 2, the values of E_{pa} and E_{pc} were each 0.21 and -0.47 V, respectively. It was thought that, because a larger anion that had low mobility caused structural changes in polymer chains, the difference of anodic and cathodic peak potential, ΔE_p , had a more than $58/n$ (mV) value. To determine the reversibility of this electrode reaction, CV was conducted in various scan rates (5, 8, and 10 mV/s). Figure 3 shows the changes in anodic and cathodic peak potentials (E_{pa} , E_{pc}) on various scan rates. That is, the peak potential was a function of scan rate, shifting in the negative directions for E_{pc} and in the positive directions for E_{pa} with increasing scan rate. From this result, it is obvious that these anodic and cathodic reactions are irreversible.

Elemental Analysis

Elemental analysis was performed to know how much dopant anion was doped in PPPF₆ film prepared electrochemically at 1.21 V for 5 h. This analytical result is presented in Table I. From this, it is confirmed that this PPPF₆ film was doped ~28 wt % with the PF₆⁻ anion.

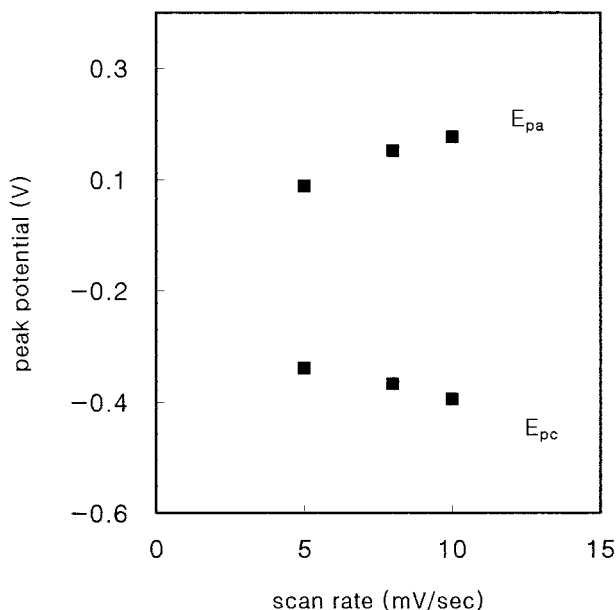


Figure 3 The changes in anodic and cathodic peak potentials on various scan rates (5, 8, and 10 mV/s).

Infrared Spectroscopy

The PPPF₆ film as an anodic precipitate was insoluble in most organic solvent or aqueous solutions and not transparent.¹² So, it was difficult to obtain spectroscopic analysis. FTIR measurements were performed with the KBr pellet method in the range of 4000–400 cm⁻¹. Figure 4 shows the FTIR spectrum of PPPF₆ film. The peak at 3500–3200 cm⁻¹ was induced by the stretching vibration of the secondary amine. The C=C aromatic vibration that consists of conjugated polymer chain occurs at 1610–1500 cm⁻¹. Also, the strongest modes in the range of 1420–1020 cm⁻¹ are attributed to the C—N stretching vibration. Peaks in the range from 900–800 cm⁻¹ indicate the presence of PF₆⁻ anions in the polymer chain.¹³ This result is in agreement with the expected structure of PPPF₆.

Table I Results of Elemental Analysis for PPPF₆ Film

Polymer	Polymer Chain (%)				Dopant Content (wt %)
	C	H	N	O	
PPPF ₆	40.1	4.35	11.7	16.0	27.9

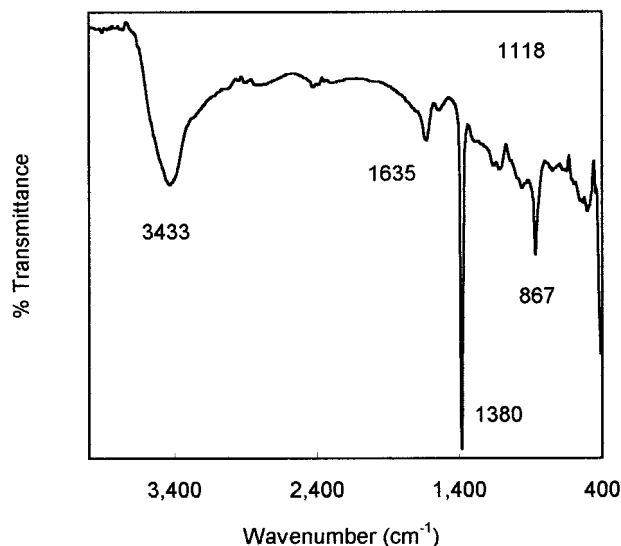


Figure 4 FTIR spectrum for PPPF₆ in the KBr pellet.

SEM Analysis

The morphology of conducting polymers by SEM depends mainly on the structure of the monomer, the nature of the dopant, and thickness of the film.¹⁴ According to Zinger and coworkers,² the structure of polymer films changed into a disordered pattern as its surfaces lost smoothness. The SEM results of the electrode and electrolyte sides of PPPF₆ film are shown in Figure 5. The surface morphology of PPPF₆ in Figure 5(a) is similar to that of the polypyrrole films in ref. 14—irregular granules are compactly crowded on the film, respectively. The surface of the electrode side was more smooth than that of the electrolyte side, as shown in Figure 5(a,b). The porosities showed in Figure 5(b) are thought to be due to the swelling properties of AN as a solvent. Because the SEM results of PPPF₆ film do not show a specially oriented pattern, it is suggested that the conductivity of PPPF₆ is slightly isotropic.

Thermal Analysis

Thermal analysis is a method that measures a change of the property on temperature in the polymer. The DSC records a difference of supplied calorific to maintain the same temperature in reference and sample at constant heating rate. The DSC result showed that PPPF₆ was decomposed in the broad temperature range from 150 to 800°C, without special phase transition. Generally, it has been known that the polypyrrole-based

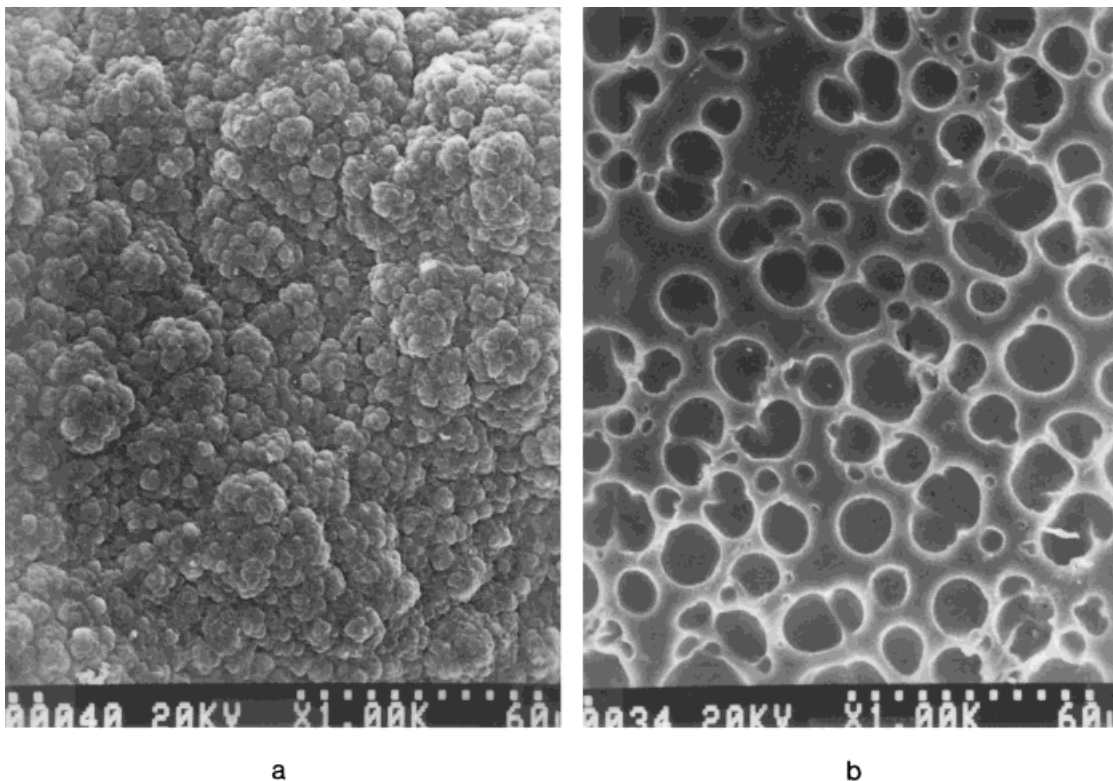


Figure 5 SEM micrographs of PPPF₆: (a) the face of the film in contact with the “solution” and (b) that of the film in contact with the “electrode.”

system mainly decomposed at higher temperature regions than polyaniline-based systems.³ Therefore, it is concluded that PPPF₆ can be used in industrial applications requiring higher thermal stability.

Electrical Conductivity

The conduction mechanisms of conducting polymers have been variously studied until now. In the case of polypyrrole, particularly, it has been known that a polaron or bipolaron moves through the conjugated bonds for charge carriers.^{15,16} But, in the real case, the charge carriers can hop interchain and interparticle gaps, as well as the conjugated double bond system. In this point, we can obtain useful information from the temperature dependence of electrical conductivity for the conducting polymer. Therefore, the conduction mechanisms for conducting polymers have been investigated from various models related to temperature dependence of electrical conductivity. Zeller¹⁷ expressed it as a interrupted strand model. According to his study, a tunneling conduc-

tion of amorphous materials was expressed as eq. (3).

$$\sigma = \sigma_0 \exp(-AT^{-1/2}) \quad (3)$$

In general, the hopping conduction model has been applied for the conducting polymer prepared electrochemically. Watanabe and coworkers¹⁸ reported that the conductivity of polypyrrole followed the Mott's variable range-hopping conduction. That is, Mott¹⁹ showed the conduction mechanism that the charge is transported by the thermally activated hopping electron between localized states near the Fermi level as in eq. (4).

$$\sigma = A \exp(-BT^{-1/4}) \quad (4)$$

But, in conducting polymers, the electron transition is due to movement of the localized state, as well as hopping. Greaves²⁰ showed the hopping mechanism that was applied for amorphous materials in general temperature ranges as in eq. (5).

$$\sigma T^{1/2} = \exp(-BT^{-1/4}) \quad (5)$$

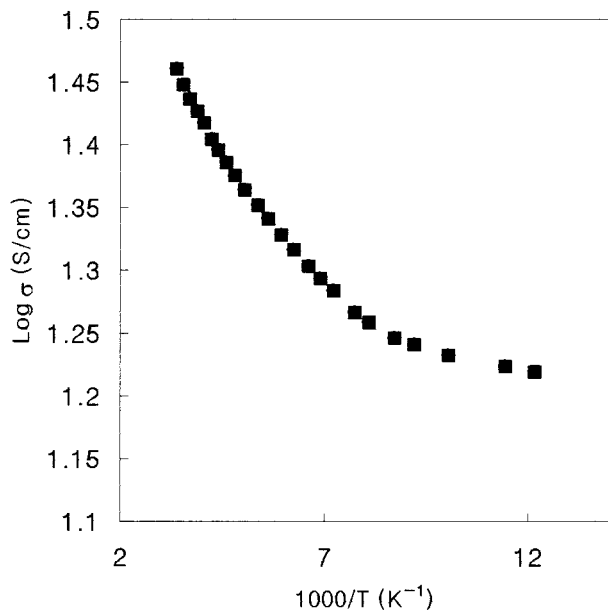


Figure 6 Temperature dependence of electrical conductivity of PPPF₆ based on the Arrhenius equation.

Although it showed many equations for the temperature dependence of electrical conductivity, exact equation was not represented yet because of various factors of electrical conductivity. Therefore, the conduction mechanism is suggested as a model that showed the most linear line.

Electrical conductivity measurements for PPPF₆ were performed with a four-probe direct current method in the temperature range of 80–300 K. Figure 6 shows the electrical conductivity as a function of temperature for PPPF₆ based on Arrhenius equation, as in eq. (6).

$$\sigma = \sigma_0 \exp(-E_a/kT) \quad (6)$$

As shown in Figure 6, the conductivity for PPPF₆ increases with increasing temperature and the values of $\log \sigma$ at 25°C was 1.46 (S/cm). To investigate the conduction mechanism of PPPF₆, the previously reported equations—Zeller, Mott, and Greaves models—were applied, as shown in Figures 7–9. The plots of Greaves's model show good linearity (i.e., it is suggested that the conduction of PPPF₆ is predominantly conducted by hopping).

ESR

ESR measurements were performed to examine a charge carrier. Figure 10 shows the ESR spec-

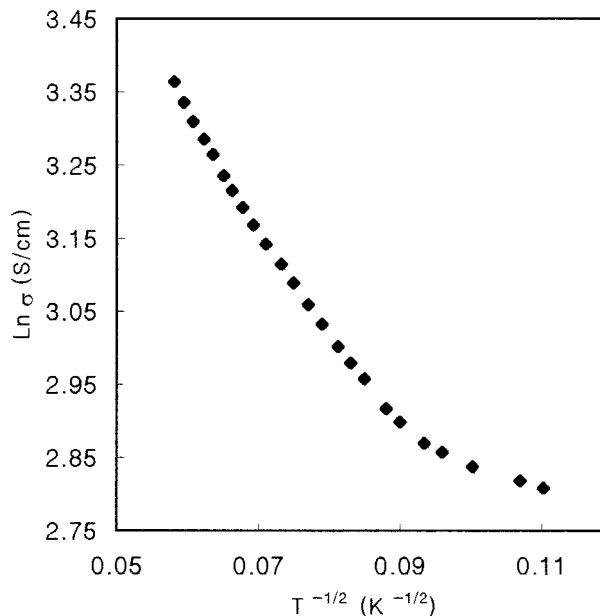


Figure 7 Electrical conductivity as a function of temperature for PPPF₆ based on the Zeller equation.

trum of the PPPF₆ powder at room temperature. It showed a typical spectrum like other conducting polymers.⁹ From Figure 10, the measured peak-to-peak line width ΔH_{pp} and g value are 0.7 G and 2.00257. It was confirmed that in singly charged paramagnetic centers, small polarons were formed by doping of anions as an electron acceptor. The electron in the polaron level caused

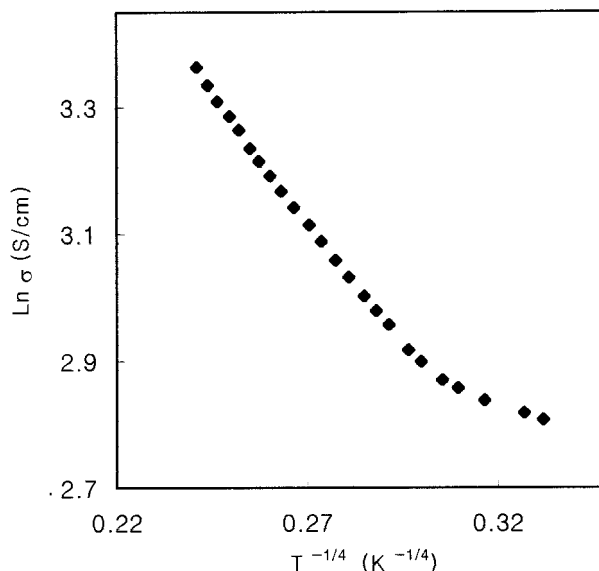


Figure 8 Electrical conductivity as a function of temperature for PPPF₆ based on the Mott equation.

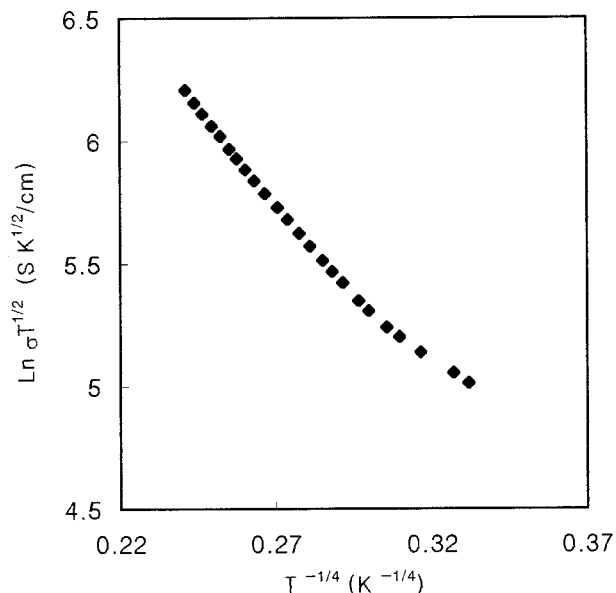


Figure 9 Electrical conductivity as a function of temperature for PPPF₆ based on the Greaves equation.

a local polarization near the positively charged center and, as a result, the electron became a small polaron with a π -cation radical. In general, it has been known that the ESR parameters were related to electrical conductivity.²¹ But, the opposite proposal has been reported later.²² Therefore, the other conducting polymers doped with same anion PF₆ were compared with PPPF₆ in the electrical conductivity and ESR parameters as shown in Table II.^{3,23} From Table II, higher electrical conductivity, lower ΔH_{pp} , and g -value were estimated. Ogasawara and colleagues²⁴ reported that the decrease in ΔH_{pp} was due to the mobile nature of free radicals based on increasing in conjugation length. Also, compared with film and powder of PPPF₆, it was thought of as isotropic and similar to the result of SEM.

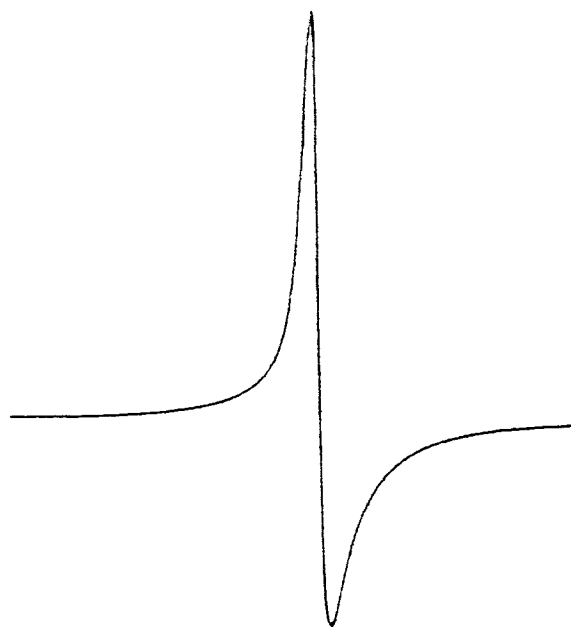


Figure 10 ESR spectrum of PPPF₆ film at 25°C.

CONCLUSIONS

The PPPF₆ film electrochemically prepared at a constant potential of 1.21 V in 5 h was doped as a PF₆ anion ~28 wt %. From the cyclic voltammogram, it was suggested that the electrode reaction for PPPF₆ was irreversible. The DSC result showed that the PPPF₆ was decomposed in the broad temperature range from 150 to 800°C. The morphology of PPPF₆ by SEM showed a compact structure resulting in high electrical conductivity and an isotropic structure that was in agreement with the ESR result compared between film and powder samples. From the temperature dependence of electrical conductivity and ESR spectrum, the observed electrical conductivity was due to polarons as charge carriers that hop from state to state. So, it was suggested that the electrical

Table II Various Parameters of PPPF₆ Compared with Other Conducting Polymers

Polymer	log σ (S/cm) at 25°C	ΔH_{pp}	g value
Poly(aniline hexafluorophosphate)	-1.209	3	2.00578
Poly(indole hexafluorophosphate)	-4.15	3.3	2.00574
PPPF ₆	1.46	0.7	2.00257

conduction mechanism of PPPF₆ is a small polaron hopping conduction.

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REFERENCES

1. A. F. Diaz and K. K. Kanazawa, in *Extended Linear Chain Compounds*, Vol. 3, J. Miller, Ed., Plenum Press, New York, 1992, p. 417.
2. B. Zinger, P. Shaier, and A. Zemel, *Synth. Metal.*, **40**, 283 (1991).
3. K. M. Choi, J. H. Jang, and K. H. Kim, *Mol. Cryst. Liq. Cryst.*, **220**, 201 (1992).
4. G. Heo, D. H. Lee, and K. H. Kim, *J. Appl. Polym. Sci.*, **54**, 849 (1994).
5. T. Momma, S. Kakuda, H. Yarimizu, and T. Osaka, *J. Electrochem. Soc.*, **142**, 1766 (1995).
6. B. F. Y. Yon-Hin, M. Smolander, T. Crompton, and C. R. Lowe, *Anal. Chem.*, **65**, 2067 (1993).
7. W. H. Smyrl and M. Lien, in *Applications of Electroactive Polymers*, B. Scrosati, Ed., Chapman & Hall, London, 1993, p. 36.
8. M. G. Kanatzidis, *C&EN*, **December 3**, 36 (1990).
9. T. Hagiwara, M. Hirasaka, K. Sato, and M. Yamaura, *Synth. Metal.*, **36**, 241 (1990).
10. K. Sato, M. Yamaura, T. Hagiwara, K. Murata, and M. Tokumoto, *Synth. Metal.*, **40**, 35 (1991).
11. A. J. Bard and L. R. Faulkner, in *Electrochemical Methods: Fundamentals and Applications*, John Wiley & Sons, New York, 1980, p. 136.
12. G. Tourillon and F. Garnier, *J. Phys. Chem.*, **87**, 2289 (1983).
13. J. W. Robinson, in *Handbook of Spectroscopy*, Vol. II, CRC Press, Boca Raton, FL, p. 97.
14. K. M. Choi, K. H. Kim, and J. S. Choi, *J. Phys. Chem.*, **93**, 4659 (1989).
15. J. L. Bredas, J. C. Scott, K. Yakushi, and G. B. Street, *Phys. Rev. B*, **30**, 1023 (1984).
16. J. C. Scott, J. L. Bredas, K. Yakushi, P. Pfluger, and G. B. Street, *Synth. Metal.*, **9**, 165 (1984).
17. H. R. Zeller, *Phys. Rev. Lett.*, **28**, 1452 (1972).
18. A. Watanabe, M. Tanaka, and J. Tanaka, *Bull. Chem. Soc. Jpn.*, **54**, 2278 (1981).
19. N. F. Mott, *Philos. Mag.*, **19**, 835 (1969).
20. G. N. Greaves, *J. Non-Cryst. Solids*, **11**, 427 (1973).
21. T. C. Chung, A. Feldblum, A. J. Heeger, and A. G. MacDiarmid, *J. Chem. Phys.*, **74**, 5504 (1981).
22. J. C. Scott, P. Pfluger, M. T. Krounbi, and G. B. Street, *Phys. Rev. B*, **28**, 2140 (1983).
23. K. M. Choi and K. H. Kim, *J. Appl. Polym. Sci.*, **44**, 751 (1992).
24. M. Ogasawara, K. Funahashi, T. Demura, T. Hagiwara, and K. Iwata, *Synth. Metal.*, **14**, 62 (1986).