Synthesis and Characterization of Soluble Polypyrrole with Improved Electrical Conductivity

G. J. LEE,[1] S. H. LEE,[1] K. S. AHN,[2] K. H. KIM[1]

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

[2] Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse1, 70569 Stuttgart, Germany

ABSTRACT: Polypyrroles doped with two dopants were prepared by chemical polymerization in aqueous solutions of pyrrole monomer. The solutions contained dodecylbenzenesulfonic acid (DBSA) as a dopant, tetraethylammonium tetrafluoroborate (TEABF$_4$) as a codopant, and ammonium persulfate (APS) as an oxidant. The PPy composites [polypyrrole-dodecylbenzenesulfonates (PPy-DBS) codoped with tetrafluoroborate (BF$_4^-$)—PPy-DBS-BF] were soluble in m-cresol, NMP, and conditionally soluble in chloroform. Cyclic voltammetry was measured to know the electrochemical property of PPy-DBS-BF. The maximum electrical conductivity of room temperature for PPy-DBS-BF is 1.18 s/cm, which is greatly higher than that of polypyrrole doped with DBS$^-$ (0.04 s/cm). The composition and structural characterization of PPy-DBS-BF were inferred from elemental analysis, nuclear magnetic resonance, and Fourier transform infrared spectroscopy. Scanning electron microscopy was performed to know the morphology of PPy-DBS-BF. The results of UV-Vis spectra and electron spin resonance measurements showed that polaron and bipolaron existed as charge carrier of soluble PPy-DBS-BF. From the temperature dependence of the electrical conductivity, it was suggested that possible conduction mechanism for soluble PPy-DBS-BF should be hopping conduction. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 2583–2590, 2002

Key words: soluble polypyrrole; chemical polymerization; dodecylbenzenesulfonic acid; tetraethylammonium tetrafluoroborate; codoping; hopping mechanism

INTRODUCTION

Soluble conducting polymers have the advantage of real application in that these polymers overcome the main shortcoming—insolubility—of chemically and electrochemically polymerized conducting polymers. While polypyrrole has high conductivity and good environmental stability, it has been known to have no solubility in organic solvents as well as in water.[1] However, J. Y. Lee et al.[2] synthesized soluble polypyrrole chemically with dodecylbenzenesulfonic acid (DBSA) as the dopant, and this was soluble in m-cresol, chloroform, etc. In the DBSA$^-$ doped system, the protonic acid with a large size reduced inter- and intramolecular interactions of the polymer chain, which improve the solubility of polypyrrole greatly in organic solvents. Y. Shen and M. Wan[3] found that this kind of sulfonic acid influenced the solubility of polypyrrole when soluble polypyrrole was synthesized by the doping method. Also, others reported that soluble 3-substituted soluble polypyrroles were obtained by attaching long flex-

Table I   Results of Elemental Analysis for PPy-DBS-BF

Concentration (M)		Elemental Analysis (%)					
DBS$^-$	BF$_4^-$	N	C	H	S	O	BF$_4$
0.30	0.00	9.30	66.78	4.95	6.15	11.90	0.92
0.30	0.15	8.97	65.00	6.18	3.36	10.70	5.79
0.15	0.15	7.97	61.60	4.53	2.54	11.30	12.06
0.10	0.15	9.21	64.70	6.30	2.85	11.00	5.94
0.05	0.15	9.34	65.30	6.33	1.49	10.80	6.74

ible side chains to the conjugated backbone.[4,5] While these all-soluble conducting polymers are enhanced in their processibility, their electrical conductivity value is lower than that of previous conducting polymers. It is because weak interchain interaction results in more distant hopping of charge carriers.[6]

In our work, new soluble polypyrrole-dodecylbenzenesulfonates (PPy-DBS) codoped with tetrafluoroborate (BF$_4^-$)—PPy-DBS-BF—were synthesized to improve the electrical conductivity. The changes of solubility and conductivity of PPy-DBS-BFs were examined with the change of concentrations of DBSA at constant contents of BF$_4^-$. Also, we characterize the structure and electrical properties of PPy-DBS-BF using EA, ^{1}H nuclear magnetic resonance (NMR), cyclic voltammetry (CV), Fourier transform infrared (FTIR), UV-Vis, scanning electron microscopy (SEM), four-probe DC method, and electron spin resonance (ESR) experiments.

EXPERIMENTAL

Materials

Pyrrole (Acros) was distilled under reduced pressure. An oxidant, ammonium persulfate (APS, Aldrich) and dopants, dodecylbenzenesulfonic acid, sodium salt (DBSA-Na salt, Aldrich), and tetraethylammonium tetrafluoroborate (TEABF$_4$, Aldrich) were used as received.

Chemical Syntheses

The amount of 0.3M pyrrole and x M DBSA, Na salt (x = 0.05, 0.1, 0.15, 0.3) in 100 mL distilled water were well stirred with 0.15M TEABF$_4$ at room temperature. After adding 0.6M APS in 20 mL very slowly, the resulting dark black solutions were vigorously stirred for 24 h. Methanol was

poured into the reaction mixture to terminate the reaction. The resulting polypyrrole powder was filtered and washed several times with distilled water, methanol, and acetone sequentially, and dried in a vacuum oven for 48 h. After the PPy-DBS-BF powder was dissolved in chloroform, the solution was filtered through a Teflon membrane with pore size of 1 μm and spin-cast on a glass plate to obtain film.

Measurements

The solubilities of PPy-DBS-BF in m-cresol were estimated by the weight method.[3] To assure the sample quality by examining the structure of PPy-DBS-BF, FTIR was recorded with Shimadzu spectrometer by the KBr pellet method. CV was performed using a potentiostat/galvanostat (EG&G, 700A). ESR was conducted using a EPR spectrometer (Bruker, ER 200 E-SRC) at 25°C in nitrogen atmosphere. UV-Vis spectroscopy was performed on a UV-3100 spectrometer in chloroform solutions of PPy-DBS-BF. SEM was performed for the morphology analysis with a Hitachi S-2500. Electrical conductivity was measured by the four probe technique using an Keithley 2001 at a temperature range of about 80–300 K. A quartz probe was placed in a chamber packed with liquid nitrogen to measure low temperature conductivity.

RESULTS AND DISCUSSION

Elemental Analysis

The elemental analyses of PPy-DBS-BF, performed with elemental analyzer (Elemental Analyser system Vario EL/Carlo-Erba), indicate that the PPy-DBS-BF were codoped with DBS and TEABF$_4$, as shown in Table I. Also, it is showed to excess oxygen in PPy-DBS-BF like other soluble
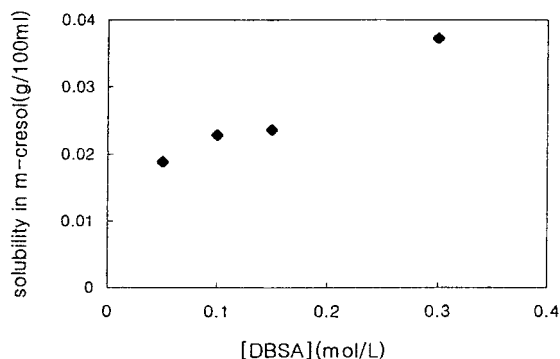
Figure 1 The change of solubility of soluble PPy-DBS-BF with various concentrations of DBS$^-$ in constant [BF$_4^-$] = 0.15M at room temperature.

polypyrrole, which slightly enhanced the polymer solubility in the solvent.[2]

Solubility

PPy-DBS-BF prepared by chemical polymerization can be dissolved in m-cresol and chloroform with an additional portion of DBSA, like PPy-DBS.[2] Figure 1 shows that the solubility relates to the concentration of DBSA. As the concentration of DBS$^-$ increases, the solubility of PPy-DBS-BF also increases. This result is in agreement with the previous assumption that the large dopant reduces inter- and intramolecular interactions by placing itself between the polymer molecules.[2] Also, there is the proposal that a high concentration of large dopant in polymerization media hinders the crosslinking among polymer chains.[3]

Cyclic Voltammetry

Figure 2 shows a cyclic voltammogram of PPy-DBS-BF film casted from solution at [DBS$^-$] = 0.3M and [BF$_4^-$] = 0.15M. The PPy-DBS-BF powder at [DBS$^-$] = 0.3M and [BF$_4^-$] = 0.15M was most dissolved in chloroform. As shown in Figure 2, the values of E_{pa} and E_{pc} are 430 and -100 mV, respectively, at a scan rate of 50 mV/s. Also, Figure 2 shows that the electrochemical reaction of PPy-DBS-BF is irreversible because the peak potential changes with the scan rate.

Infrared Spectroscopy

FTIR measurements were performed with the KBr pellet method in the range of 4000–400 cm^{-1}. In all cases of PPy-DBS-BF, the N—H stretching band at about 3400 cm^{-1} was not de-
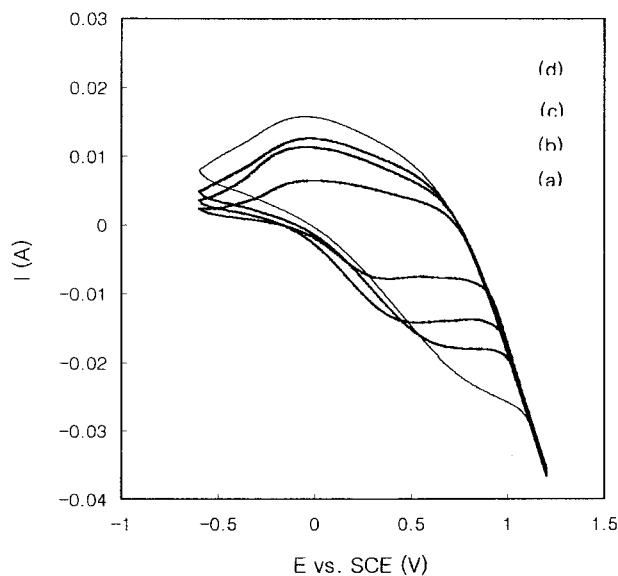

Figure 2 Cyclic voltammogram of PPy-DBS-BF film dissolved in chloroform at [DBS$^-$] = 0.3M and [BF$_4^-$] = 0.15M. (a) Scan rate = 30 mV/s, (b) 50 mV/s, (c) 70 mV/s, and (d) 100 mV/s.

tected. It was reported that its absence was attributed to its masking by the charge carrier absorption band, which was also active in this range from 11,000 to 1600 cm^{-1}.[7] Figure 3 shows the KBr pellet spectra of PPy-DBS-BF in the range of 2000–400 cm^{-1}. The C=C stretching of the benzene ring appears at 1500–1400 cm^{-1} and the peak at about 1300 cm^{-1} is induced by the C—N stretching.[8] Strong asymmetric and symmetric S=O stretching bands appear at 1170 and 1020 cm^{-1}, respectively.[9] All the features in the IR
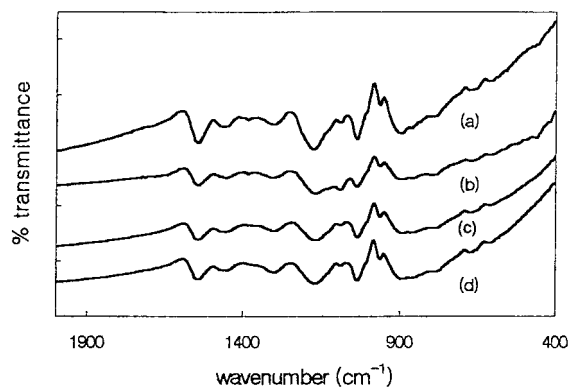
Figure 3 FTIR spectra for PPy-DBS-BF in the KBr pellet: (a) [DBS$^-$] = 0.3M, (b) [DBS$^-$] = 0.15M, (c) [DBS$^-$] = 0.1M, (d) [DBS$^-$] = 0.05M in constant [BF$_4^-$] = 0.15M.
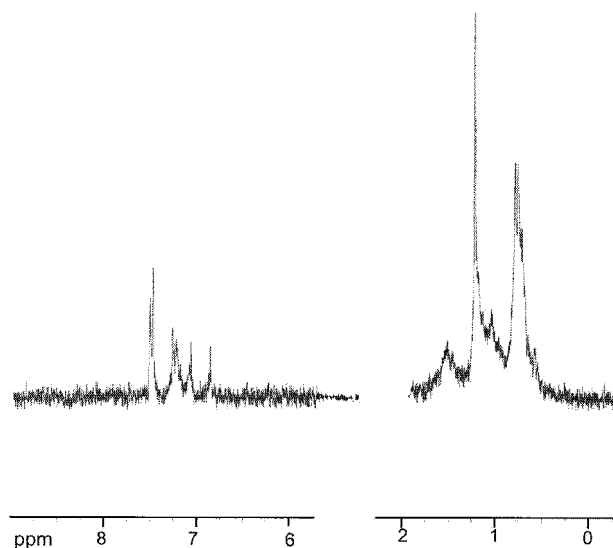
Figure 4 ^{1}H-NMR spectrum in DMSO solution of PPy-BBS-BF prepared with [DBS$^-$] = 0.15M and [BF$_4^-$] = 0.15M.

spectra are consistent with that of other soluble polypyrrole.[2,3] The band at 1123–1080 cm^{-1} due to BF$_4^{-}$[10] cannot assign in spectra because of superposing of SO$_3^-$ absorption band. Ribo et al. showed that FTIR spectra of doped polypyrroles revealed the molecular solid structure but not the individual functional groups.[7] The strong bands of about 900 cm^{-1} have been referred to as "bipolaron bands,"[7] which correspond to "bipolaron peak" in UV-Vis spectra.

NMR Spectroscopy

A further structural characterization could be done by ^{1}H NMR analysis. Figure 4 shows the ^{1}H NMR spectrum in DMSO solution of PPy-DBS-BF prepared with [DBS$^-$] = 0.15M and [BF$_4^-$] = 0.15M. The signal in the 6.6–6.8 ppm region is related to the protons in the α position to the heteroatom in the terminal pyrrole ring. A high peak of protons bonded to Cα atoms indicates a low MW polymer. And, the signal at about 7.0 ppm can be assigned the protons attached to the nitrogen of pyrrole rings. The low signal in the 6.2–6.3 ppm region, where the protons in the β position to the nitrogen of pyrrole rings are located, suggests that the structure of PPy-DBS-BF should have crosslinking partly between polymer chains. Also, two signals in the 7.1–7.2 and in 7.4–7.5 ppm regions may be assigned to the protons in the benzene ring of DBS$^-$. The signals of

significant intensity below 2 ppm are related to aliphatic protons of DBS$^-$.[11,12]

UV-Visible Spectroscopy

Figure 5 is the UV-Vis spectra of chloroform solutions of PPy-DBS-BF in the range of 400–1100 nm. J. L. Bredas et al. demonstrated that the absorption spectra of doped polypyrrole could be explained in terms of initial polaron formation and then bipolaron formation on the PPy chains.[13] In Figure 5, two intense, broad absorption bands are present near 800 and 1000 nm. The absorption around 830 nm is attributed to polaron absorption and the peak at 950 nm indicates to the presence of bipolaron.[7,13] Also, K. Levon et al. reported that absorption appeared at 460 nm, which could be assigned to the oxidation of an aromatic ring in the dopant molecules.[14] In accordance with ESR and IR, this results indicate that polaron and bipolaron are charge carriers in soluble PPy-DBS-BF.
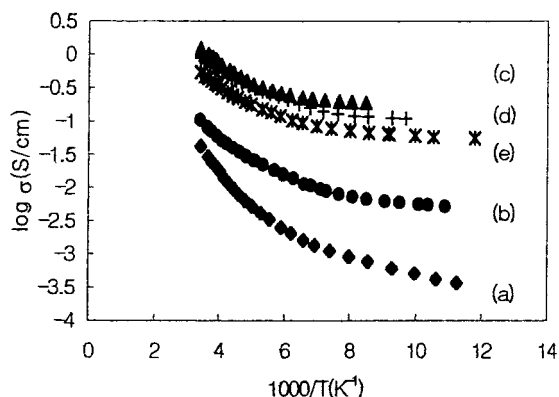
Electrical Conductivity

Electrical conductivity measurements for PPy-DBS-BF were performed with a Valdes' four-probe method[15] in the temperature range of 80–300 K. Figure 6 shows the electrical conductivity as a function of temperature for PPy-DBS-BF based on the Arrhenius equation, as eq. (1):

$$\sigma = \sigma_0 \cdot \exp(-E_a/kT) \tag{1}$$
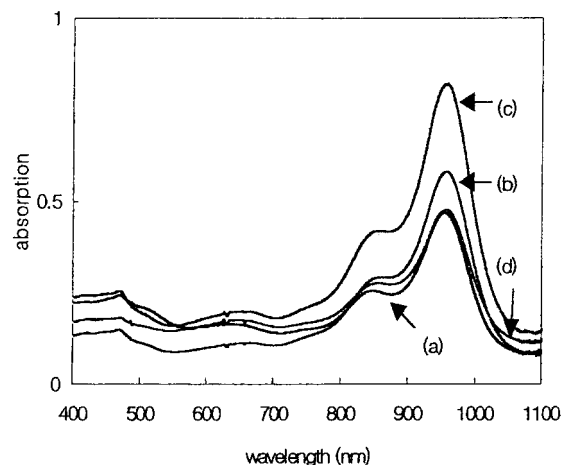
Figure 5 UV-Vis spectra of chloroform solutions of PPy-DBS-BF: (a) [DBS$^-$] = 0.3M, (b) [DBS$^-$] = 0.15M, (c) [DBS$^-$] = 0.1M, (d) [DBS$^-$] = 0.05M in constant [BF$_4^-$] = 0.15M.

Figure 6 Temperature dependence of electrical conductivity of soluble PPy-DBS-BF based on the Arrhenius equation: (a) soluble PPy-DBS, (b) $[DBS^-] = 0.3M$, (c) $[DBS^-] = 0.15M$, (d) $[DBS^-] = 0.1M$, and (e) $[DBS^-] = 0.05M$ in constant $[BF_4^-] = 0.15M$.

where E_a is activation energy and k is the Boltzmann constant.

The values of electrical conductivity at room temperature for all PPy-DBS-BF are presented in Table II. As shown in Table II, the conductivity of PPy-DBS-BF was higher than that of only DBS^- doped polypyrrole, as we expected. We think that small BF_4 anions as co-dopant improve interchain interactions among PPy chains unlike large DBS^- anions.

But in the case of constant $[BF_4^-]$, it was shown that the conductivity of PPy-DBS-BF slightly increased as $[DBS^-]$ increased, until $[DBS^-]$ was $0.15M$. And when $[DBS^-]$ was higher than $0.15M$, it steeply decreased. We suppose that electrical conductivity of our sample is affected by size and concentration of large size dopants. That is, in case of low concentration of DBS^-, it is thought that electrical conductivity of PPy-DBS-BF at constant $[BF_4^-]$ is mainly depended on the concentration of DBS anion. But

Table II   The Electrical Conductivity of Soluble PPy-DBS-BF at Room Temperature

Concentration (M)		Conductivity,
$[DBS^-]$	$[BF_4^-]$	σ (s/cm)
0.30	0.00	0.04
0.30	0.15	0.10
0.15	0.15	1.18
0.10	0.15	0.86
0.05	0.15	0.53
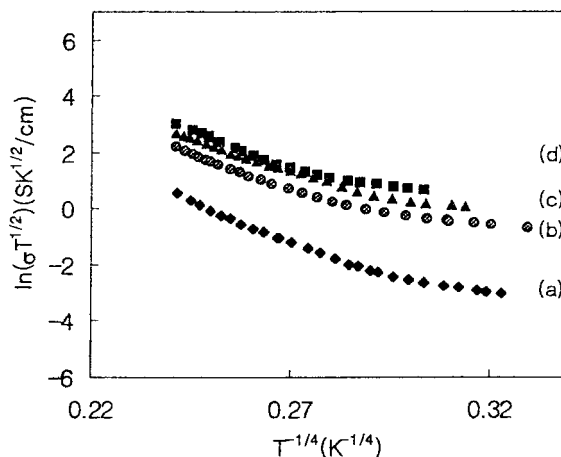
Figure 7 Temperature dependence of electrical conductivity of soluble PPy-DBS-BF based on the Greaves equation: (a) $[DBS^-] = 0.3M$, (b) $[DBS^-] = 0.15M$, (c) $[DBS^-] = 0.1M$, and (d) $[DBS^-] = 0.05M$ in constant $[BF_4^-] = 0.15M$.

when $[DBS^-]$ is higher than $0.15M$, the conductivity of PPy-DBS-BF is greatly influenced by interchain interaction of polymer which is depended on the size of dopant. Therefore, the highest conductivity of PPy-DBS-BF at room temperature was 1.18 s/cm at $[DBS^-] = 0.15M$ and $[BF_4^-] = 0.15M$.

The conduction mechanisms for conducting polymers have been investigated from various models related to temperature dependence of electrical conductivity. According to Zeller,[16] for inhomogeneous samples where partial dedoping or strong morphological disorder dominates the sample properties, transport could be expressed as eq. (2):

$$\text{Log } \sigma = \sigma_0 \cdot \exp(-AT^{-1/2}) \qquad (2)$$

J. K. Lee et al.[6] studied the charge transport properties of chemically synthesized soluble polypyrroles. As a result, it was found that the temperature dependence of electrical conductivity of soluble polypyrroles followed the 3D variable range hopping model,[17] as expressed in eq. (3):

$$\sigma = A \cdot \exp(-BT^{-1/4}) \qquad (3)$$

Greaves[18] suggested the phonon-assisted hopping mechanism applied for amorphous materials in general temperature ranges as in eq. (4):

$$\sigma \cdot T^{1/2} = \exp(-BT^{-1/4}) \qquad (4)$$
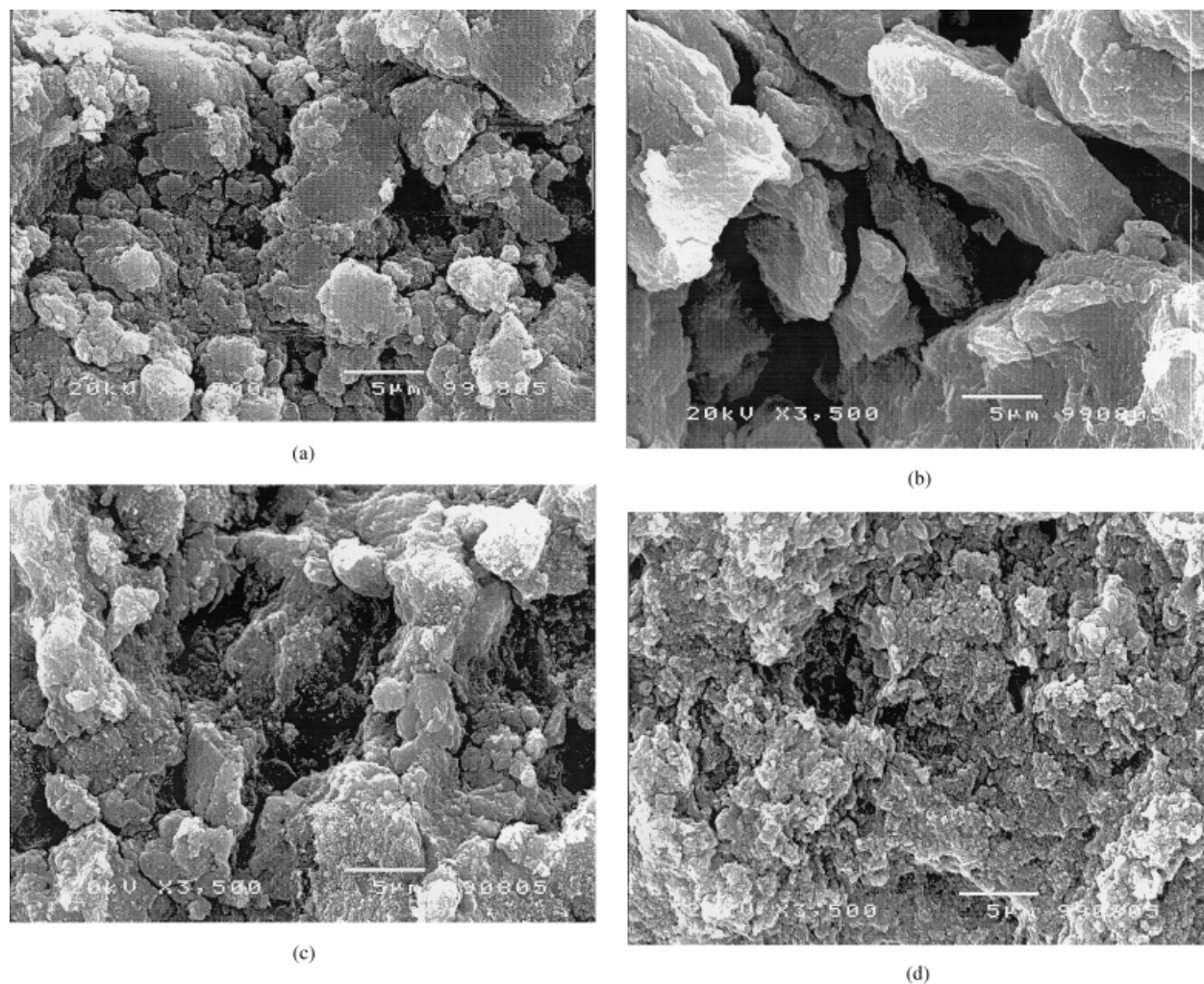
Figure 8   SEM micrographs of PPy-DBS-BF: (a) [DBS$^-$] = 0.3M and [BF$_4^-$] = 0.15M, (b) [DBS$^-$] = 0.15M and [BF$_4^-$] = 0.15M (c) [DBS$^-$] = 0.1M and [BF$_4^-$] = 0.15M, and (d) [DBS$^-$] = 0.05M and [BF$_4^-$] = 0.15M.

To investigate the conduction mechanism, we plot the temperature dependence of electrical conductivity for PPy-DBS-BF. The results showed that the plot of Greaves' model had most linear behavior over the entire measured temperature range, as shown in Figure 7. So, it was suggested that the transport properties of PPy-DBS-BF should be dominantly characterized by hopping, which was due to microscopic scale disorder.

SEM

Scanning electron microscopy was performed to know the morphology of PPy-DBS-BF in various concentrations of dopant. The SEM results of PPy-DBS-BF are shown in Figure 8. As shown in Figure 8, the morphology of pressed pellets showed granular form in similar to that of PPy-DBS. And sample in [DBS$^-$] = 0.15M and [BF$_4^-$] = 0.15M showed the most crystallinity [Figure 8(b)] in coincide with the result of conductivity. Therefore it is thought that the electrical conductivity of conducting polymer is related to the morphology of polymer.

ESR

ESR measurements were performed to examine a charge carrier in nitrogen atmosphere at room temperature. Figure 9 shows the ESR spectra of PPy-DBS-BF, indicating typical spectra like other conducting polymers of which conduction is dominated by polaron.[15,19] It was confirmed that pol-
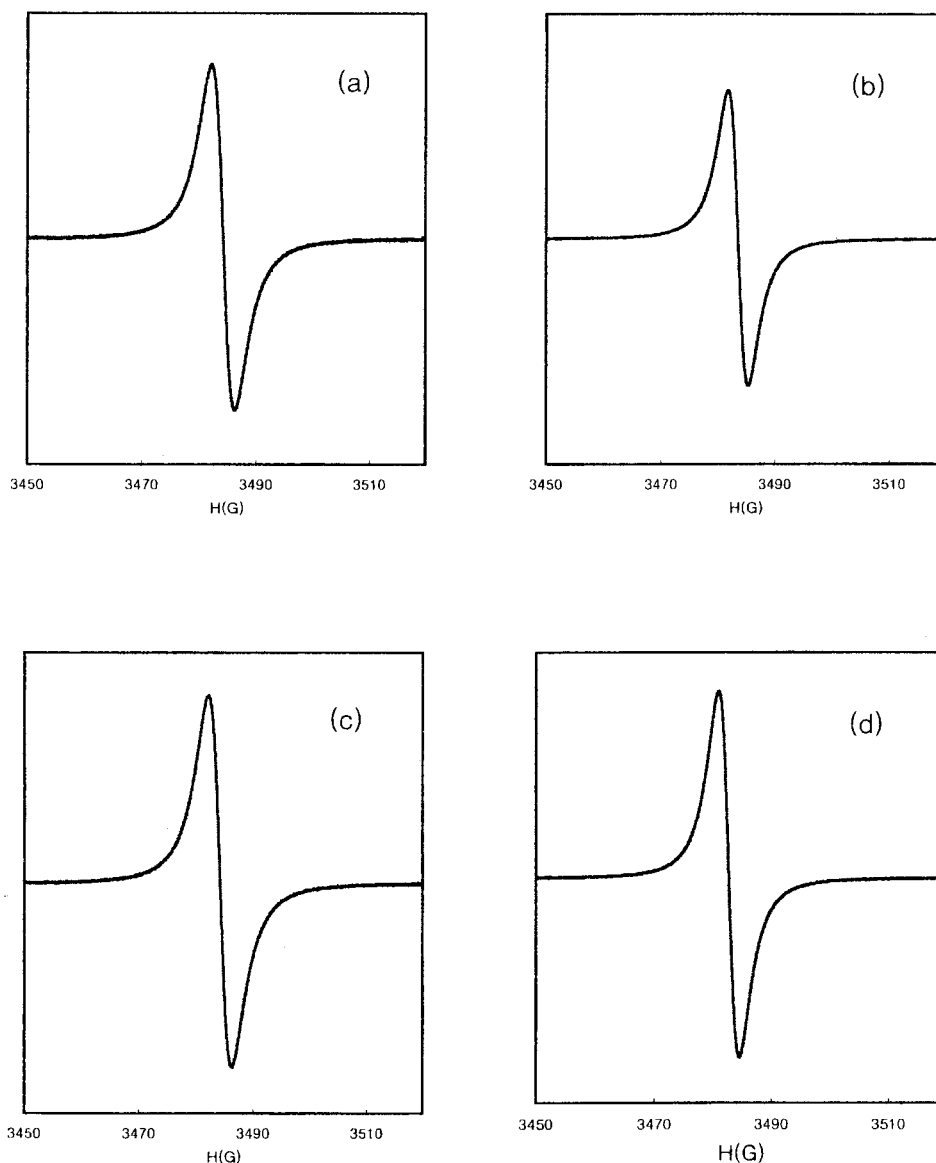
Figure 9 The ESR spectra of PPy-DBS-BF: (a) [DBS$^-$] = 0.05M, (b) [DBS$^-$] = 0.1M, (c) [DBS$^-$] = 0.15M, and [DBS$^-$] = 0.3M.

arons were formed as charge carrier in soluble PPy-DBS-BF.

CONCLUSIONS

The soluble PPy-DBS-BF were prepared by chemical polymerization. It was confirmed using EA and IR that these soluble polypyrroles were codoped with DBS $^-$ and BF$_4^-$. The conductivity of all PPy-DBS-BF is much higher than that of PPy-DBS, because BF$_4^-$ improved the reduced interchain interactions among PPy chains that were due to large DBS$^-$ anions. The maximum electrical conductivity of room temperature for codoped polypyrroles is 1.18 s/cm. The conductivity of PPy-DBS-BF strongly depends on the concentrations of dopants and the morphology. From the temperature dependence of electrical conductivity, ESR spectra, and UV-Vis absorption spectra, it was suggested that the electrical conduction mechanism of soluble PPy-DBS-BF should be polaron and bipolaron hopping.

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