

Synthesis and Properties of Soluble Polypyrrole Doped with Dodecylbenzenesulfonate and Combined with Polymeric Additive Poly(ethylene glycol)

H. K. Lim, S. O. Lee, K. J. Song, S. G. Kim, K. H. Kim

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

Received 2 August 2004; accepted 23 November 2004

DOI 10.1002/app.21824

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Soluble polypyrrole (PPy) samples advanced in electrical conductivity σ were chemically synthesized with dodecylbenzenesulfonate (DBS) sodium salt as a dopant, with poly(ethylene glycol) (PEG) as an additive, and with ammonium persulfate as an oxidant. The PPy-DBS-PEG samples were soluble in organic solvents (*N*-methylpyrrolinone and *m*-cresol). The greater the molar percentage ratio was of DBS, the greater the solubility was of synthesized PPy composites (PPy-DBS-PEG). The maximum electrical conductivity at room temperature for PPy-DBS-PEG was 1.02 S/cm, which was in fact the true conductivity of 100/10 (mol %) PPy/DBS. The chemical composition and doping level of PPy-DBS-PEG were determined by elemental analysis. The results of Fourier transform infrared spectroscopy were used for the structural

characterization of PPy-DBS-PEG. The scanning electron microscopy results showed that the electrical conductivity was related to the morphology of PPy-DBS-PEG. According to thermogravimetric analysis, PPy-DBS-PEG was more thermostable than PPy-DBS. Electron spin resonance measurements showed that the polaron and bipolaron acted as charge carriers of PPy-DBS-PEG. According to the temperature dependence of the electrical conductivity, PPy-DBS-PEG was a semiconductor and followed the three-dimensional variable-range hopping model. The improved electrical conductivity apparently resulted from the reduction of the crosslinking and structural defects of the PPy chains. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1170–1175, 2005

Key words: polypyrroles; surfactants

INTRODUCTION

Polypyrrole (PPy) is one of the most widely studied conducting polymers because of its high conductivity, good environmental stability, innocuous characteristics, and easy synthesis. Therefore, PPy has the advantage of real applications in microelectronics, the information industry, and biomedicine. However, PPy is not soluble in organic solvents and water because of the strong intermolecular and intramolecular interactions and crosslinkings of PPy chains.¹ Therefore, to overcome the insolubility problem of PPy, many researchers have studied soluble PPy. Recently, soluble PPy has been synthesized with large dopants such as dodecylbenzenesulfonate (DBS) and naphthalenesulfonate. A large dopant reduces the intermolecular and intramolecular interactions of PPy chains and improves the solubility of PPy in an organic solvent.^{2,3} However, PPy doped with a bulky dopant is reduced in its electrical conductivity because of the longer hopping distance of the charge carriers resulting from weak interchain interactions.^{4,5} The addition of poly-

mers influences the sterical stabilization of PPy chains.⁶ In this study, a new soluble and conducting PPy doped with DBS and combined with polymeric additive poly(ethylene glycol) (PEG) was synthesized. Its physicochemical properties, obtained from solubility measurements, electrical conductivity measurements, elemental analysis, Fourier transform infrared (FTIR), scanning electron microscopy (SEM), and electron spin resonance (ESR) experiments, were investigated.

EXPERIMENTAL

Synthesis

Pyrrole (Acros, Tokyo, Japan), ammonium persulfate (APS; Aldrich, Milwaukee, WI) as an oxidant, dodecylbenzenesulfonic acid (DBSA) sodium salt (Aldrich) as a dopant, and PEG (PEG 1000, Kanto) as an additive were used as received. Pyrrole (0.15M), DBSA, and PEG in 300 mL of distilled water were well stirred at 0°C. The molar ratio of the dopant DBSA and the additive PEG (DBSA/PEG) was changed from 10/40 to 25/25, 40/10, or 50/0, and the total amount of DBSA/PEG was 50 mol % of the pyrrole monomer. APS (0.075 mol) was dissolved in 100 mL of distilled water and added slowly to the aforementioned solu-

Correspondence to: K. H. Kim.

Contract grant sponsor: Yonsei University.

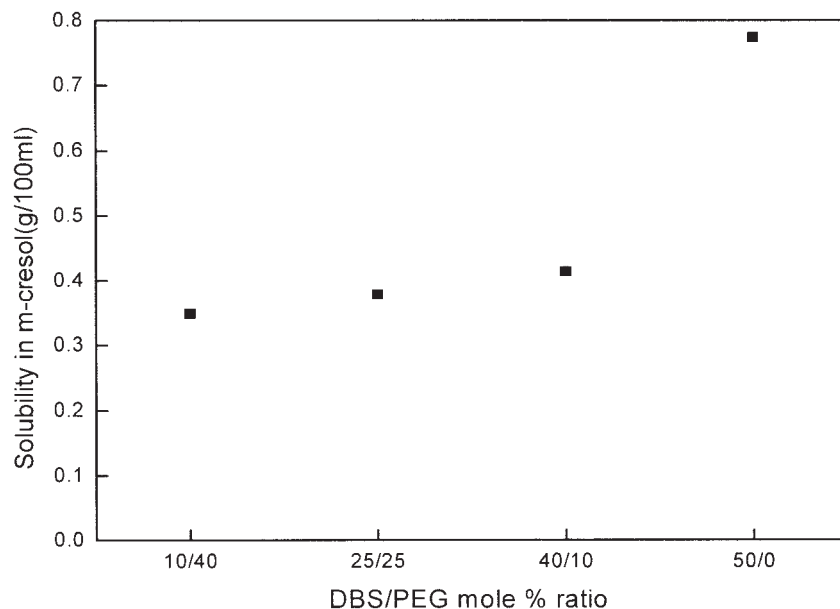


Figure 1 Solubility of soluble PPy-DBS-PEG samples with various molar percentage ratios and a constant pyrrole concentration of 100 mol %.

tion by a microsyringe. The reaction mixture was vigorously stirred at 0°C. After 24 h, the reaction mixture was poured into a large amount of methanol to terminate the reaction. The precipitate was filtered and washed with distilled water, methanol, and acetone several times and was finally dried in a vacuum oven for 24 h. To determine the solubility of the synthesized PPy-DBS-PEG, a weight method⁷ was employed, and the solubility was estimated. Thus, PPy-DBS-PEG was dissolved in 25 mL of *m*-cresol by ultrasonication and filtered through 1- μ filter paper. The solvent of the filtered solution was dried, and the sample powder was weighed.

Measurements

The FTIR measurements (Impact 400, Nicolet, Waltham, MA) were carried out with the KBr pellet method. The chemical composition and doping level of PPy-DBS-PEG were determined with an elemental analyzer (Flash EA 1112 series, CE Instruments, Wigan, UK). Thermogravimetric results were obtained

with a TA Instrument 2050 thermogravimetric analyzer at a heating rate of 10°C/min from 25 to 500°C under a nitrogen atmosphere. SEM was performed to examine the section morphology of PPy-DBS-PEG samples with a Hitachi S-2700 (Tokyo, Japan). ESR experiments were conducted with an electron paramagnetic resonance spectrometer (ESP-300S, Bruker, Buchs, Switzerland) at 25°C. PPy-DBS-PEG powders were molded into disks via pressing, and the electrical conductivity of the disks was measured by the standard four-probe technique with a Keithley 2001 multimeter (Cleveland, OH) and 224 calibrator source from -180 to 25°C.

RESULTS AND DISCUSSION

Solubility

The synthesized PPy-DBS-PEG samples had good solubility in *m*-cresol and *N*-methylpyrrolidinone. Figure 1 shows the relationship of the solubility and the composition of a DBS-PEG mixture. The solubility of the PPy-DBS-PEG samples increased when the molar percentage ratio of DBS was higher. The large molecular size of DBS surrounded by PPy chains effectively reduced the intermolecular and intramolecular interactions and crosslinking among the PPy chains.⁸

Elemental analysis

The elemental analyses of the PPy-DBS-PEG samples indicated the chemical compositions of the resulting polymers. Table I shows the analytical results and indicates that the more increased the molar percentage ratio

TABLE I
Elemental Analysis Results for Soluble PPy-DBS-PEG Samples

PPy/DBS/PEG molar ratio (%)	Elemental analysis (%)				
	N	C	H	S	O
100/10/40	12.83	56.86	4.84	4.60	17.97
100/25/25	10.79	58.82	5.85	3.96	16.67
100/40/10	9.12	60.95	6.58	3.35	14.84
100/50/0	11.49	58.19	5.55	4.12	15.81

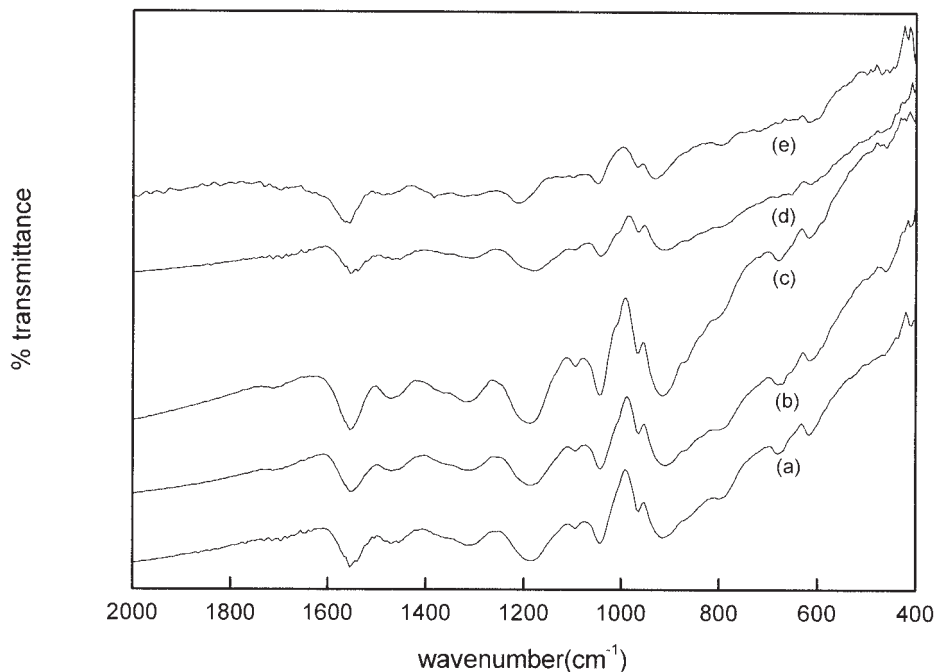


Figure 2 FTIR spectra of soluble PPy-DBS-PEG samples: (a) 10:40 (mol %) DBS/PEG, (b) 25:25 (mol %) DBS/PEG, (c) 40:10 (mol %) DBS/PEG, (d) 50:0 (mol %) DBS/PEG, and (e) pure PPy with a constant pyrrole concentration of 100 mol %.

was of DBS, the more doped the samples were with the DBS dopant. Thus, the solubility depended on the molar percentage ratio of DBS. According to the data in Table I, PEG was not integrated into the resulting PPy polymer. This was supported by the IR data obtained for

these PPy-DBS-PEG samples and other PPy-PEG samples.⁶ One molecule of DBS incorporated three molecules of pyrrole. The compositions of PPy, DBS, and PEG were 100/10/0, 100/25/0, 100/40/0, and 100/50/0 for four samples with different PPy/DBS/PEG ratios.

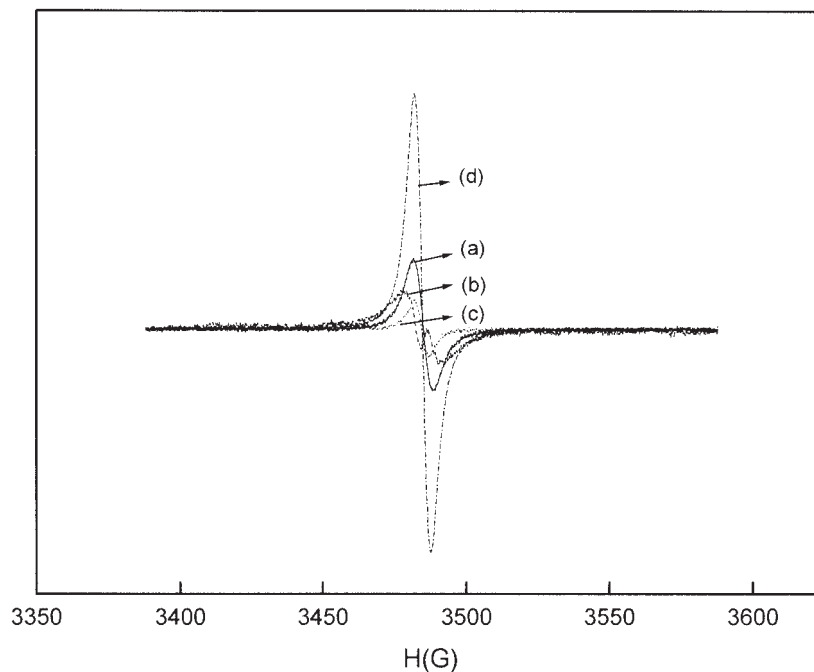


Figure 3 ESR spectra of soluble PPy-DBS-PEG samples: (a) 10:40, (b) 25:25, (c) 40:10, and (d) 50:0 (mol %) DBS/PEG with a constant pyrrole concentration of 100 mol %.

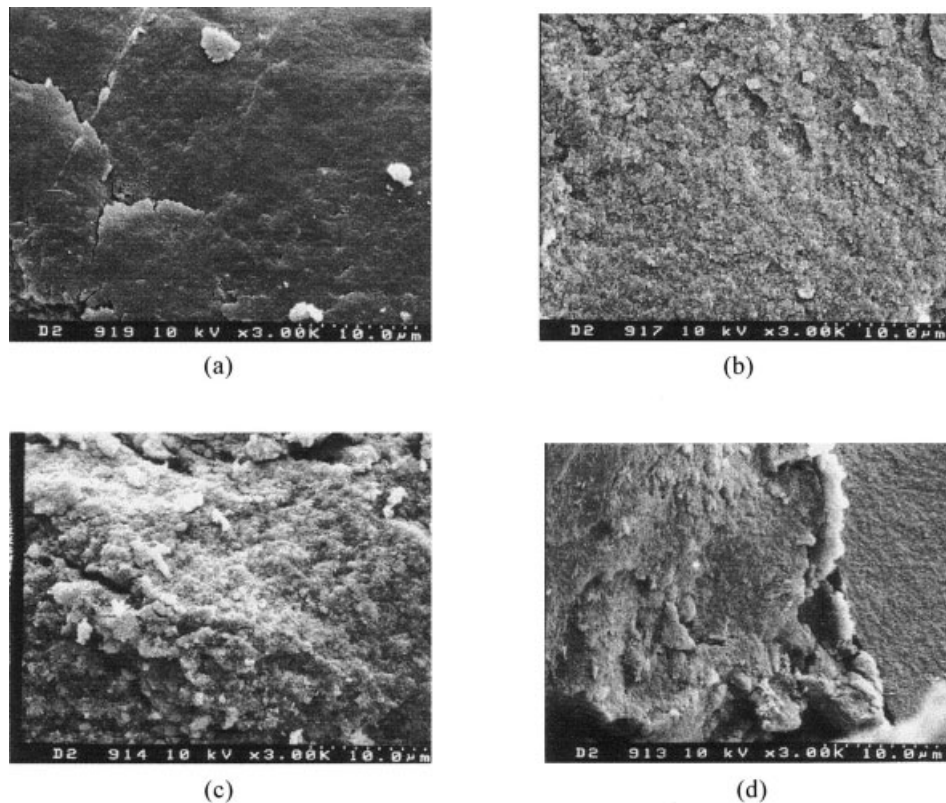


Figure 4 Morphology of soluble PPy-DBS-PEG samples: (a) 10:40, (b) 25:25, (c) 40:10, and (d) 50:0 (mol %) DBS/PEG with a constant pyrrole concentration of 100 mol %.

FTIR

Figure 2 shows the FTIR spectra of the KBr pellet PPy-DBS-PEG samples in the range of 2000–400

cm^{-1} . For the PPy-DBS-PEG samples, the N—H stretching vibration of the pyrrole ring does not appear at about 3400 cm^{-1} . It has been reported that it is

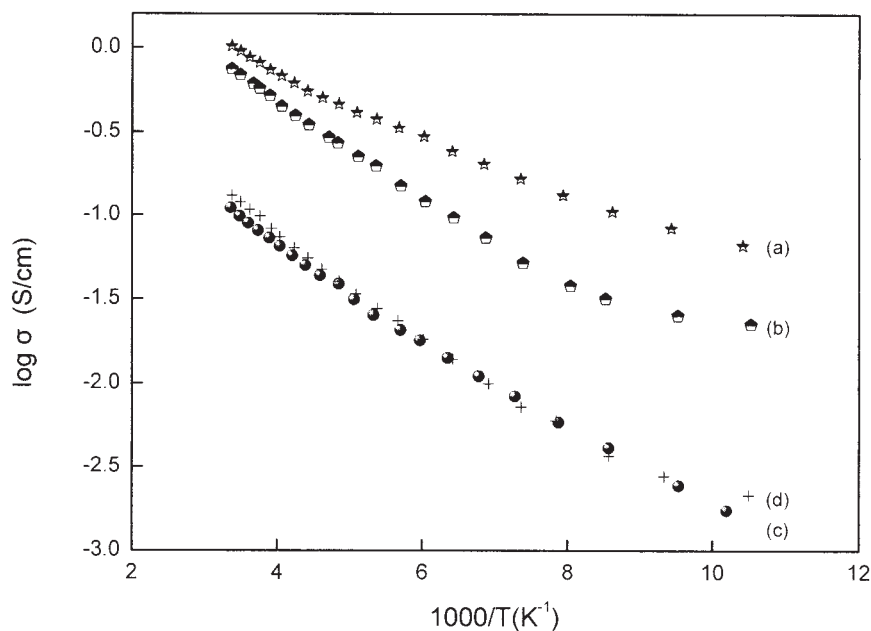


Figure 5 Temperature dependence of the electrical conductivity of soluble PPy-DBS-PEG samples: (a) 10:40, (b) 25:25, (c) 40:10, and (d) 50:0 (mol %) DBS/PEG with a constant pyrrole concentration of 100 mol %.

TABLE II
Electrical Conductivity of Soluble PPy-DBS-PEG
Samples at Room Temperature

PPy/DBS/PEG molar ratio (%)	σ (S/cm)
100/10/40	10.2×10^{-1}
100/25/25	7.0×10^{-2}
100/40/10	1.0×10^{-2}
100/50/0	1.0×10^{-2}

characterized by oxidized pyrrole.⁹ The C=C/C—C stretching vibrations of the pyrrole ring can be detected at $1500\text{--}1400\text{ cm}^{-1}$. The bending vibration of C—H appears at about 1300 cm^{-1} , and the absorption peak of about 1090 cm^{-1} was induced by the C—N stretching vibration. The absorption bands of the polaron and bipolaron appear at about $1045\text{--}1190$ and 900 cm^{-1} , respectively.^{10–12} All the features in the FTIR spectra are similar to those of pure PPy. However, in comparison with the spectra of pure PPy, those of PPy-DBS-PEG are shifted to small wave numbers. Because the dopant withdrew electrons of the pyrrole ring, all the band stretchings are weak.

ESR

ESR measurements were performed to examine the charge carriers in a nitrogen atmosphere at room temperature. The charge carriers in the PPy-DBS-PEG samples were proven by ESR spectra, as shown in

Figure 3. All the samples had ESR signals, which indicated the presence of a polaron as a charge carrier in the soluble PPy-DBS-PEG samples.³ Also, samples with good conductivity had low signals. It was confirmed indirectly that a bipolaron existed as another charge carrier.

SEM

The morphologies of pressed pellets of PPy-DBS-PEG samples were different, as shown in Figure 4. The morphologies were very aggregate. Comparing the conductivity, we found that the better the electrical conductivity was, the more crystalline the sample morphology was.⁴ Therefore, we think that the electrical conductivity of the PPy-DBS-PEG samples was related to the morphology of PPy-DBS-PEG.

Conductivity

We estimated the electrical properties of PPy-DBS-PEG by the temperature dependence of the electrical conductivity. Figure 5 shows $\log \sigma(T)$ versus $1000/T$ (where σ is the conductivity and T is the temperature) for PPy-DBS-PEG samples. All the PPy-DBS-PEG samples had a semiconducting property. For semiconductors, the higher the temperature is, the higher the electrical conductivity is.¹³ The values of the electrical conductivity at room temperature for all the PPy-DBS-PEG samples are presented in Table II. The con-

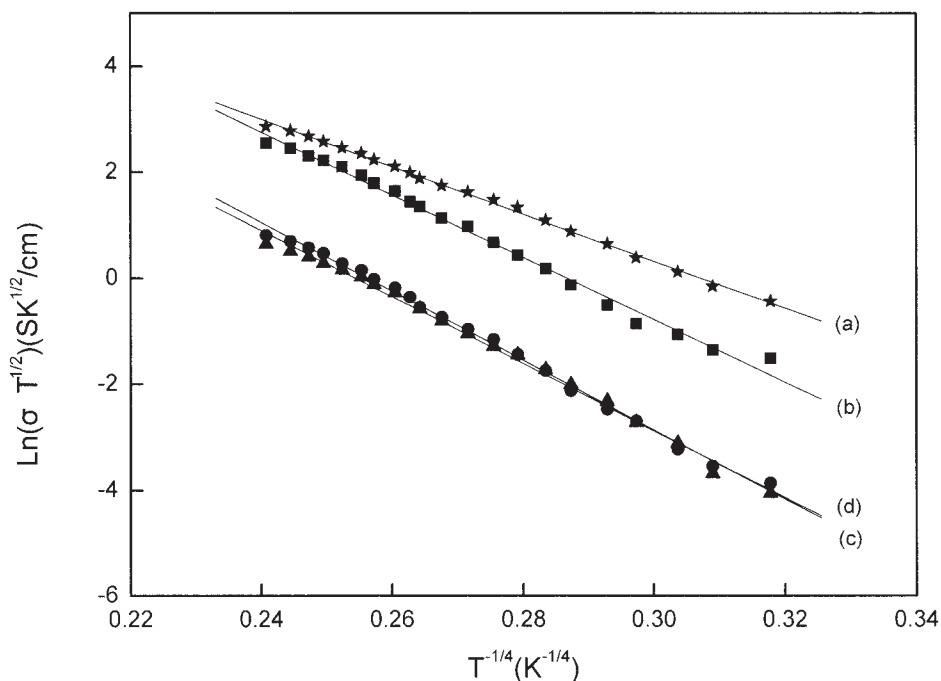


Figure 6 Temperature dependence of the electrical conductivity of soluble PPy-DBS-PEG samples in the Mott equation (3D-VRH): (a) 10:40, (b) 25:25, (c) 40:10, and (d) 50:0 (mol %) DBS/PEG with a constant pyrrole concentration of 100 mol %.

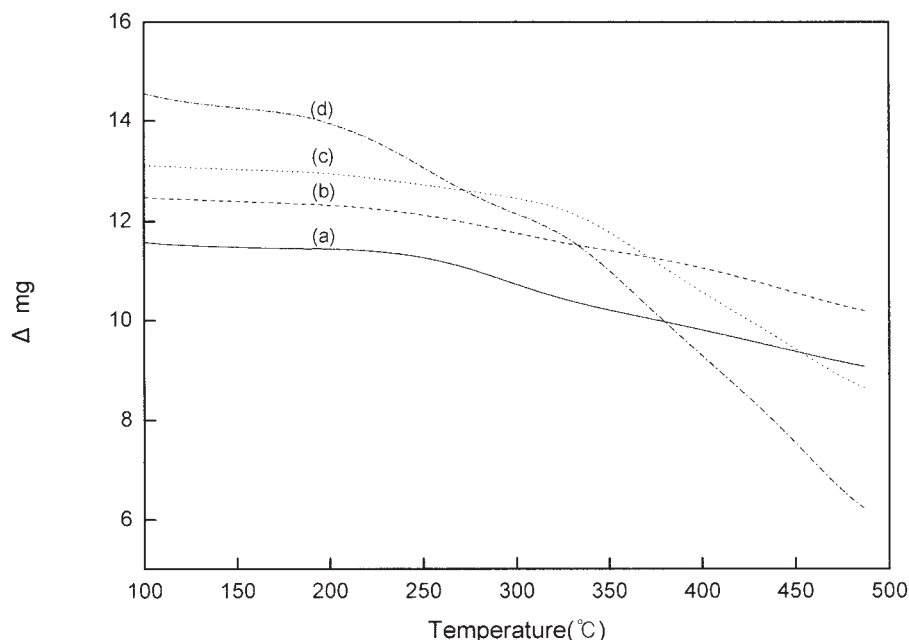


Figure 7 TGA thermogram of soluble PPy-DBS-PEG samples: (a) 10:40, (b) 25:25, (c) 40:10, and (d) 50:0 (mol %) DBS/PEG with a constant pyrrole concentration of 100 mol %.

ductivities of PPy/DBS with the same molar percentage ratios without the PEG additive were exactly the same as the values in Table II. The conductivity of the PPy-DBS-PEG samples increased as the molar percentage ratio of DBS decreased, on the whole. The maximum electrical conductivity of PPy-DBS-PEG at room temperature was 1.02 S/cm, which was in fact the true conductivity of 100/10 (mol %) PPy/DBS. The conduction mechanism for conducting polymers has been investigated with various models with respect to the temperature dependence of the electrical conductivity.¹⁴⁻¹⁶ The temperature dependence of the conductivity of all the PPy-DBS-PEG samples is shown in Figure 6. The linear plot of $\ln \sigma$ versus $T^{-1/4}$ is in agreement with the three-dimensional variable-range hopping (3D-VRH) model suggested by Mott where σ_0 is the conductivity at absolute zero temperature (T_0):¹⁵

$$\sigma(T) = \sigma_0 \exp[-(T_0/T)^{-1/4}] \quad (1)$$

Therefore, the transport properties of the PPy-DBS-PEG samples were dominantly characterized by hopping, which was due to microscopic-scale disorder.⁴

Thermogravimetric analysis (TGA)

Figure 7 shows the weight loss of the PPy-DBS-PEG samples. The thermal stability was higher than that of PPy-DBS. In comparison with the decomposition of PPy-DBS at about 230°C, PPy-DBS-PEG samples began to decompose at about 240–300°C.

CONCLUSIONS

PPy-DBS-PEG synthesized by chemical polymerization was soluble in *m*-cresol, and the solubility increased with an increase in the DBS molar percentage ratio. The maximum electrical conductivity at room temperature for PPy-DBS-PEG was 1.02 S/cm. This conductivity was in fact the true value of 100/10 (mol %) PPy/DBS. The conductivity decreased with an increasing molar percentage of DBS. The conduction mechanism was the 3D-VRH model.

References

- Chandrasekhar, P. *Conducting Polymers, Fundamentals and Applications: A Practical Approach*; Kluwer Academic: Boston, 1999.
- Lee, J. Y.; Kim, D. Y.; Kim, C. Y. *Synth Met* 1995, 74, 103.
- Shen, Y.; Wan, M. *Synth Met* 1998, 96, 127.
- Lee, G. J.; Lee, S. H.; Ahn, K. S.; Kim, K. H. *J Appl Polym Sci* 2002, 84, 2583.
- Lee, J. K.; Song, H. K.; Joo, J.; Lee, G. J.; Yo, C. H.; Kim, K. H.; Song, S. K.; Jang, K. S.; Oh, E. J. *New Phys* 1998, 38, 16.
- Kang, H. C.; Geckeler, K. E. *Polymer* 2000, 41, 6931.
- Shen, Y.; Wan, M. *J Appl Polym Sci* 1998, 68, 1277.
- Shen, Y.; Wan, M. *J Polym Sci Part A: Polym Chem* 1997, 35, 3689.
- Ribo, J. M.; Anglada, M. C.; Tura, J. M.; Anglada, N. F. *Synth Met* 1995, 72, 173.
- Davidson, R. G.; Turner, T. G. *Synth Met* 1995, 72, 121.
- Duchet, J.; Legras, R.; Champagne, S. D. *Synth Met* 1998, 98, 113.
- Song, K. T.; Lee, J. Y.; Kim, H. D.; Kim, D. Y.; Kim, S. Y.; Kim, C. Y. *Synth Met* 2000, 110, 57.
- West, A. R. *Solid State Chemistry and Its Applications*; Wiley: Singapore, 1989; p 497.
- Zeller, H. R. *Phys Rev Lett* 1972, 28, 1452.
- Mott, N. F. *Philos Mag* 1969, 19, 835.
- Greaves, G. N. *J Non-Cryst Solids* 1973, 11, 427.