Soluble Conducting Polypyrrole Doped with DBSA–CSA Mixed Acid

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ABSTRACT: Soluble conductive polypyrrole (PPy) with room temperature conductivity (2–18 S/cm) has been synthesized by doping polypyrrole with mixed acid containing camphor sulfonic acid (CSA) and dodecyl benzene sulfonic acid (DBSA). The solubility and the room temperature conductivity of PPy doped with mixed acid were measured as a function of component of CSA–DBSA mixed acid, and the structure of PPy was characterized by Fourier transform infrared (FTIR), ultraviolet–visible (UV-vis) spectra, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). PPy doped with DBSA–CSA mixed acid is soluble in m-cresol although PPy doped only by CSA is completely insoluble in any solvent. The solubility of PPy doped with mixed acid increases with an increase in the fraction of DBSA in the mixed acid, while the room temperature conductivity of the PPy increases with increasing CSA molar fraction. The UV-vis spectra and electron spin resonance (ESR) measurements showed that both polaron and bipolaron are the charge carrier in the doped PPy with mixed acid. It was proposed that the contribution of CSA to the solubility of PPy doped with mixed acid is to decrease the interaction among PPy chains due to the large molecular size of CSA, while DBSA contributes to the solubility by its good solvating effect derived from its long alkyl chain. These may be a reason that both the solubility and conductivity of PPy are improved by the presence of CSA compared with those of PPy doped only with DBSA. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1277–1284, 1998

INTRODUCTION

Polypyrrole (PPy) is one of the most attractive conductive polymers among various conducting polymers due to various application potentials derived from its high conductivity and good environmental stability.[1–4] A lot of work has been carried out to investigate its synthesis, characteristics, and applications.[5–10] In general, PPy can be prepared by both chemical and electrochemical polymerization of pyrrole. Until now, electrochemical polymerization of pyrrole is the main method to synthesize polypyrrole because, by this method, freestanding film with good mechanical property and high conductivity can be easily prepared.[11–13] However, there are some limitations in this method. For example, the area of freestanding film is limited by the size of anode; thus the mass production of PPy by this method is difficult. Large-scale preparation of polypyrrole may be achieved by chemical polymerization of pyrrole. However, PPy powder obtained by the chemical polymerization of pyrrole is infusible and insoluble.[14] Therefore, synthesis of soluble conducting PPy is a key step to investigate its structure, physical, and chemical properties and applications in technology. Several methods, such as substitution on β-carbon or nitrogen of pyrrole rings, copolymerization, and doping with large-size counterions, have been proposed to improve the
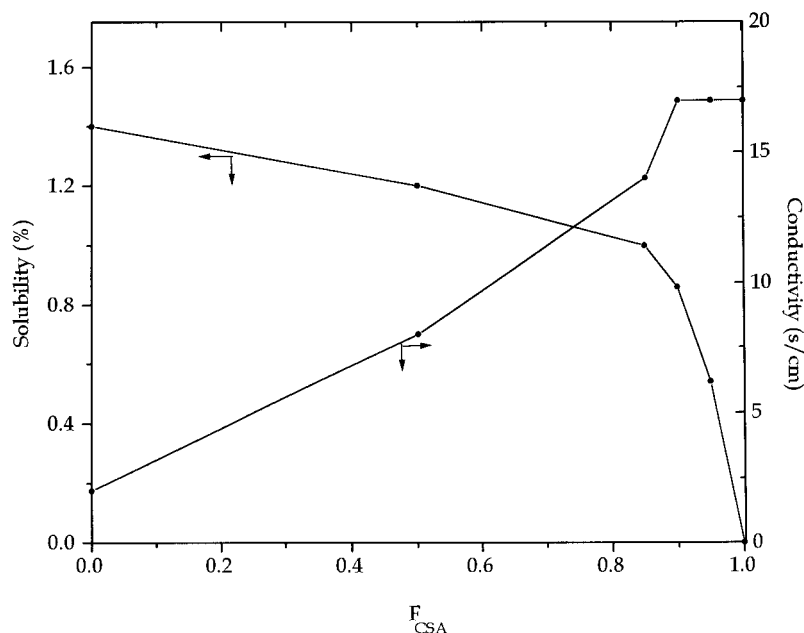
Figure 1 Relationship of the solubility in *m*-cresol and room-temperature conductivity of PPy(CSA–DBSA) to the composition of sulfonic acid: $[Py] = 0.5$ mol/L; $[H^+]$ $= 0.23$ mol/L; 0°C; APS as oxidant.

solubility of PPy. For example, poly(3-alkyl pyrrole) is soluble with conductivity ranging from 10^{-2} to 10^0 S/cm depending on the chain length of alkyl group.[15] However, β-substituted pyrrole monomer is not commercially available and its synthesis is very onerous.[15,16] In addition, poly(*N*-substituted pyrrole)[17] is soluble but has very low conductivity because the substituents on the pyrrole nitrogen disturb the conjugation of the polymer chain.

Compared with the substituting method, doping method for preparation soluble PPy is much more easy and effective. Lee et al.[18] found that PPy doped with dodecyl benzene sulfonic acid (DBSA) can be soluble in *m*-cresol or chloroform in the presence of another portion of DBSA. Our work showed that PPy *in situ* doped by β-naphthalene sulphonic acid (NSA) is soluble in *m*-cresol with high room temperature conductivity (27 S/cm) and interesting fibrillar morphology.[19]

In general, it has been proposed that the strong inter- and intramolecular interactions among PPy chains and weak interaction of PPy with solvent, as well as the crosslinking of PPy chain lead to the poor solubility of PPy,[11] and in order to synthesize soluble PPy by doping method, reducing the interaction among PPy chains and enhancing the interaction between PPy chains with solvent are required.[18,19] Recently, it was found that polyaniline

(PANI) doped with large CSA is soluble in *m*-cresol solvents and has high conductivity (300 S/cm).[20] Therefore, we first proposed that PPy doped with CSA may be soluble because large counterions of CSA can reduce the strong interaction among PPy chains. But our experiments indicated that PPy doped with CSA is completely insoluble in any solvent, although its conductivity is higher (18 S/cm) than that of PPy doped with DBSA. However, PPy doped with DBSA, which has long alkyl chain and thus a good solvating effect, is soluble in *m*-cresol and chloroform in the presence of another portion of DBSA.[18] This result indicates that in order to synthesize soluble PPy with doping method, not only is large molecular size of dopant necessary to reduce the strong interaction among PPy chains, but a strong solvating effect is also needed to enhance the interaction between PPy chains with solvent.

In this article, a soluble conducting PPy doped with mixed DBSA and CSA is reported and the role of sulfonic acid in the solubility of PPy is discussed.

EXPERIMENTAL

The conductive PPy is synthesized by the *in situ* doping polymerization method.[19] The typical pro-
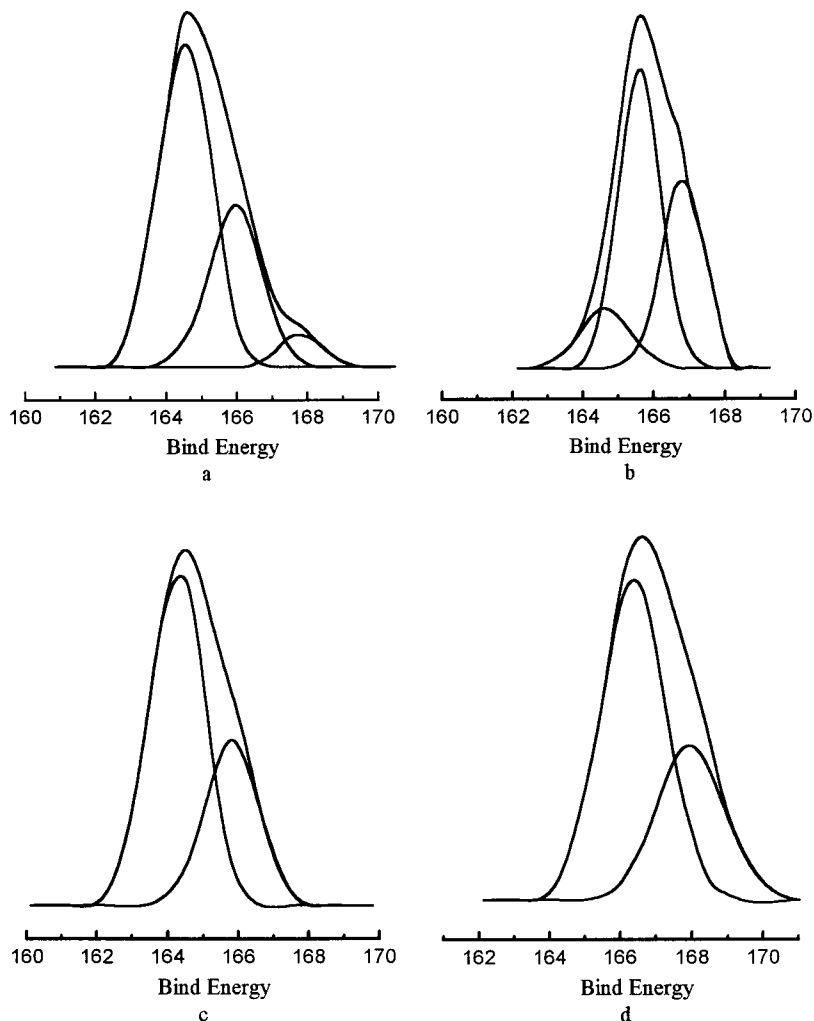
Figure 2 XPS spectra of sulfur element in PPy doped with DBSA, CSA, and DBSA–CSA mixed acid: $[Py] = 0.5$ mol/L; $[H^+] = 0.23$ mol/L; 0°C; APS as oxidant. F_{CSA} = (a) 0.90 and (b) 0.05; (c) PPy–CSA; and (d) PPy–DBSA.

cedure is as follows: 0.86 g CSA, 1.19 g DBSA, and 1.0 mL pyrrole monomer were dissolved in 20 mL deionized water with stirring vigorously at 0°C. 0.90 g ammonium persulfate (APS) (molar ratio Py/APS = 5) as oxidant dissolved in 10 mL deionized water was added slowly to the above solution. After 12 h, the reaction mixture was poured into a large excess deionized water and then filtered. The resulting CSA–DBSA doped PPy was washed with water and methanol for several times and dried in vacuum at 25°C for 2 days. The resulting PPy is designated as PPy(CSA–DBSA). 1 g, the resulting PPy, was added to 25 mL m-cresol by ultrasonification, filtered through a 1-μ filter. The solution was transferred to a glass plate, and the solvent was dried, thus, solubility was determined. The intrinsic vis-

cosity of PPy was determined in m-cresol at 25°C with a Ubbelohde viscosimeter.

PPy(CSA–DBSA) powder was molded into a disk by pressing for the measurement of conductivity. The conductivity of PPy was measured by using standard four-probe method using a Keithley 196 SYSTEM DMM digital mutimeter and ADVANTEST R6142 programmable DC voltage/current generator as current source. The Fourier transform infrared (FTIR) spectra were measured on a Perkin–Elmer System. UV-vis spectra of PPy(CSA–DBSA) in m-cresol were recorded on UV-3100 spectrometer. The morphology of PPy was examined on a Hitachi-530 scanning electron microscope (SEM). Electron spin resonance (ESR) experiments were carried out on a Bruker ER-200D. Thermal stability of the PPy was inves-
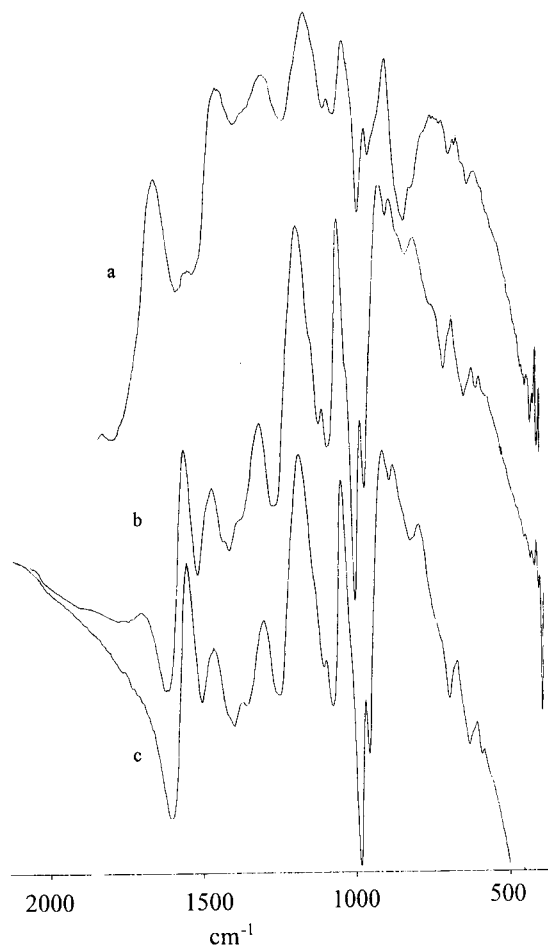
Figure 3 FTIR spectra of PPy doped with (a) CSA, (b) DBSA, and (c) the mixed acid (F_{CSA} = 0.5).

tigated by a thermogravimetric analyzer (Perkin–Elmer, TGA7) with nitrogen as a purge gas at a flow rate of 40 mL/min. The heating rate was 10°C/min.

RESULTS AND DISCUSSION

Solubility and Room-Temperature Conductivity of PPy Doped with Mixed Acid

It was found that PPy doped with CSA is completely insoluble but has high conductivity, although CSA-doped polyaniline has good solubility in CHCl$_3$ and m-cresol. The solubility of PPy doped with DBSA in m-cresol is about 1.4 g/100 mL with a room-temperature conductivity of 2 S/cm. Using CSA–DBSA binary acid to dope PPy can obtain soluble PPy with adjustable room conductivity. Figure 1 shows the relationship of solu-

bility and conductivity of PPy(CSA–DBSA) to the composition of CSA–DBSA mixed acid. As one can see that the solubility of PPy decreases with an increase of the molar fraction of CSA (F_{CSA}). When F_{CSA} is lower than 0.8, the solubility of PPy(CSA–DBSA) slightly decreases with increasing the F_{CSA} in the mixed acid, while it rapidly decreases after F_{CSA} is higher than 0.8. This means that DBSA plays an important role in the solubility of PPy(CSA–DBSA). It can also be noticed at the same concentration of DBSA, PPy(CSA–DBSA) has a higher solubility than that of PPy prepared only in the presence of DBSA. For example, the solubility of PPy(CSA–DBSA) prepared at F_{CSA} of 0.80 is 1.0 g/100 mL, but the solubility of PPy prepared only in the presence of the same amount of DBSA is 0.50 g/100 mL. Furthermore, no large difference was found in the intrinsic viscosity of the PPy doped with different acids. For example, the viscosity of PPy doped with CSA–DBSA mixed acid at F_{CSA} of 0.5 is 0.10 dL/g, in comparison with 0.12 dL/g of PPy only doped with DBSA. Therefore the difference in solubility should not be due to the difference in molecular weight. These results suggest that when using doping method to prepare soluble PPy, both CSA and DBSA contribute to the solubility of PPy(CSA–DBSA). It has been suggested that it is the strong interaction and crosslinking among PPy chains that give rise to the insolubility of PPy.[11] Thus, high concentration of sulfonic acid in the polymerization media may reduce the crosslinking reaction of pyrrole during the polymerization and decreases the interactions among PPy chains. So the large molecular size of CSA surrounding the PPy chains effectively decreases the interaction and crosslinking among PPy chains, while the strong solvating effect of DBSA derived from its long alkyl chain efficiently increase the interaction between PPy chains and solvent. Therefore, PPy prepared in the presence of binary acid has higher solubility than PPy prepared only in the presence of DBSA. The above results also suggest that the solvating effect of dopant is more important for the solubility of PPy doped with sulfonic acid.

The room temperature conductivity of PPy doped with CSA is 18 S/cm, while that of PPy doped with DBSA is only 2 S/cm. The conductivity of PPy(CSA–DBSA) lies between 2 and 18 S/cm and increases with increasing the amount of CSA in the mixed sulfonic acid, as shown in Figure 1. When F_{CSA} is higher than 0.90, there is no difference in conductivity between PPy(CSA–DBSA)
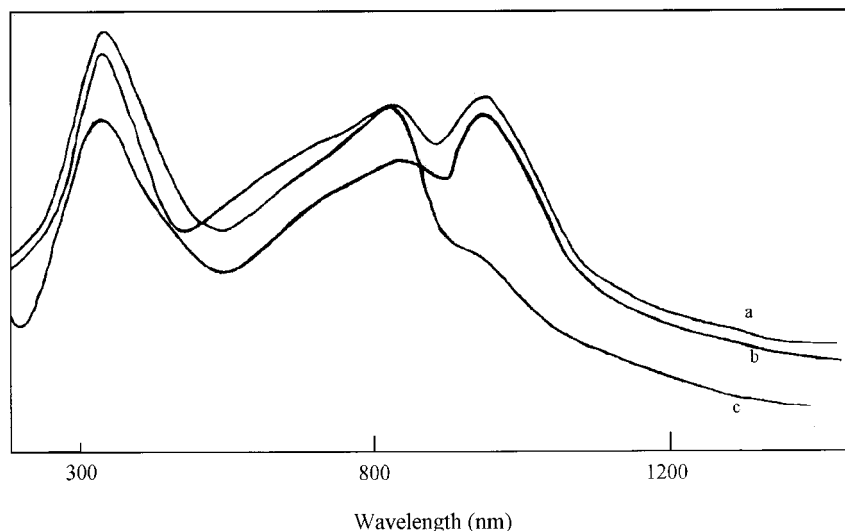
Figure 4 UV-vis spectra of m-cresol solution of PPy doped with DBSA–CSA mixed acid: (a) F_{CSA} = (a) 0.90 and (b) 0.95; (c) pure DBSA. [Py] = 0.5 mol/L; [H^+] = 0.23 mol/L; 0°C; APS as oxidant.

and PPy only doped with CSA. This is consistent with the results that the line width of ESR signal of PPy(CSA–DBSA) increases with increasing CSA fraction in CSA–DBSA mixed acid.

The Structure of PPy(CSA–DBSA)

In order to understand the role of CSA and DBSA dopant in the solubility and conductivity of PPy, the structure of PPy doped with mixed acid of CSA and DBSA was measured by X-ray photoelectron spectroscopy (XPS), FTIR, ultraviolet–visible (UV-vis) absorption, ESR, and SEM. The XPS
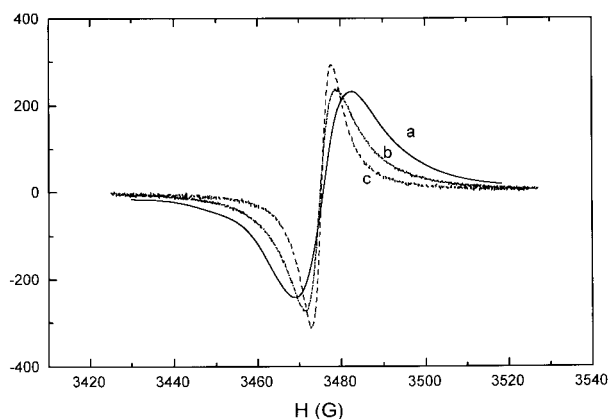

Figure 5 ESR curves of PPy doped with (a) CSA, (b) DBSA, and (c) DBSA–CSA mixed acid (F_{CSA} = 0.5). [Py] = 0.5 mol/L; [H^+] = 0.23 mol/L; 0°C; APS as oxidant.

spectra of sulfur element in PPy doped with CSA, DBSA, and their mixed acid are shown in Figure 2. It can be seen that XPS spectra of sulfur element in PPy doped with CSA or DBSA can be decomposed into two peaks, corresponding to the absorptions of $S_{1/2}$ and $S_{3/2}$. They are 164.2 and 165.9 eV for PPy doped with CSA and 166.4 and 167.9 eV for PPy doped with DBSA, respectively. On the other hand, the XPS spectra of sulfur element of PPy doped with mixed acid can be decomposed into three peaks at 164.6, 166.0, and 167.8 eV. The peak at 166.0 eV is the overlapped absorptions of $S_{1/2}$ of DBSA and $S_{3/2}$ of CSA because the bind energy of $S_{1/2}$ in DBSA (166.4 eV) and $S_{3/2}$ of CSA (165.9 eV) in PPy doped with binary acid are too close to be separated properly. This indicates that PPy(CSA–DBSA) is doped by both CSA and DBSA. It can also be found that the fraction of the two kinds acid doped in PPy(CSA–DBSA) is consistent with the molar fraction of the acid in polymerization media. The high concentration of CSA in the solution will give more CSA doped in PPy(CSA–DBSA) and vice versa.

FTIR spectra of PPy(CSA–DBSA) have no significant difference from other PPy doped with DBSA and CSA, respectively (Fig. 3). The strong absorption at 3400 cm^{-1} due to γ_{NH} and characteristic absorption bands of PPy at 1313, 1173, and 898 cm^{-1} are observed. Most absorption bands of DBSA and CSA are completely overlapped by those of PPy, but the CSA absorptions at 1647 cm^{-1} can be clearly seen. However, the UV-vis
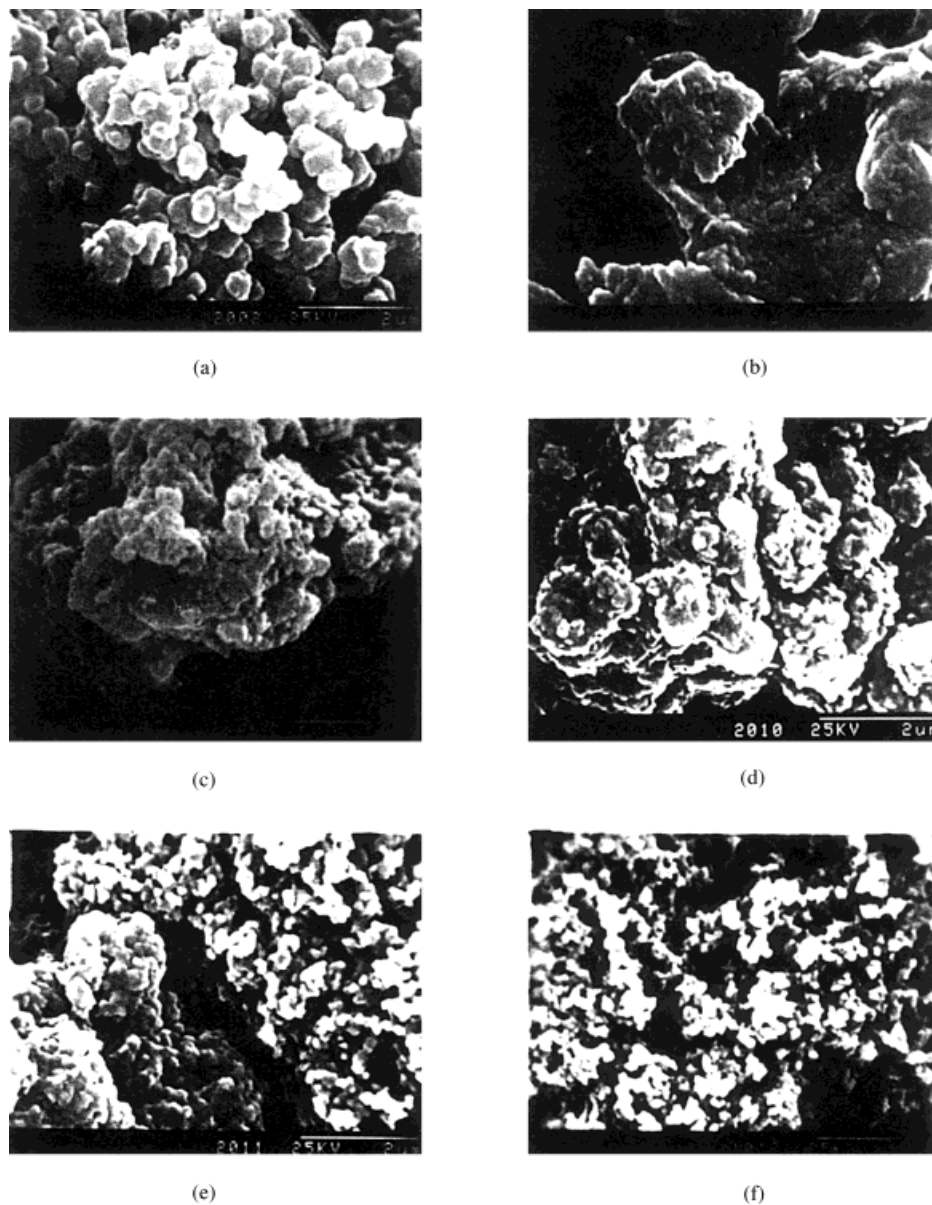
Figure 6 The morphology of PPy doped with (a) CSA and (b) DBSA and DBSA–CSA mixed acid F_{CSA} = (c) 0.5, (d) 0.60, (e) 0.80, and (f) 0.90. [Py] = 0.5 mol/L; [H$^+$] = 0.23 mol/L; 0°C; APS as oxidant.

spectra of PPy(CSA–DBSA) are very different from that of PPy doped with DBSA, as shown as Figure 4. It can be seen that besides the absorption band at 421 nm assigned as π-π^* absorption, a peak at 830 nm and a shoulder peak at 655 nm are present in the UV-vis spectra of both PPy(CSA–DBSA) and PPy doped with DBSA. It has been designated the absorption band at 655 nm as the polaron absorption produced by protonic doping.[19] But different from the spectrum of PPy doped with DBSA, PPy(CSA–DBSA) also has an absorption at 940 nm in the UV-vis spectrum. This suggests that the absorption of PPy(CSA–DBSA) at 940 nm is due to the doping by CSA, while peak at 830 nm is due to the doping by DBSA.

The presence of polaron in PPy can also be proved by ESR experiments, as shown in Figure 5. It can be seen that PPy doped with CSA, DBSA, or their mixed acid has a single ESR signal and its g-factor is 2.0030, indicating the presence of polaron as charge carriers. However, the line
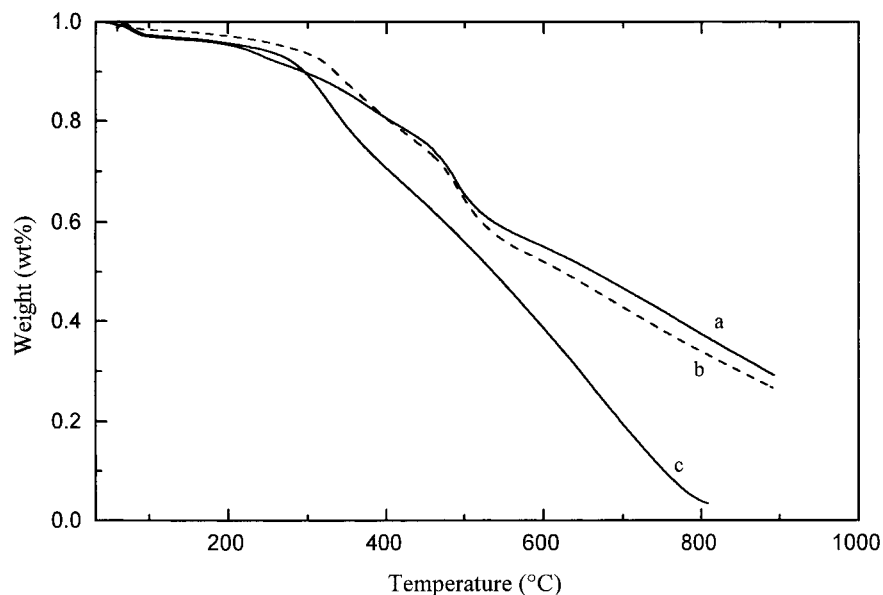
Figure 7 Thermogravimetric analysis of PPy doped with (a) DBSA, (b) CSA–DBSA($F_{CSA} = 0.50$), and (c) CSA.

width (ΔH) of PPy doped with CSA (11.6 G) is much broader than that of PPy doped with DBSA (3.8 G). The ΔH of PPy(CSA–DBSA) lies between 3.8 and 11.6 G and increases with an increase in the fraction of CSA. Furthermore, the ΔH of PPy(CSA–DBSA) also gets broader with increasing the acid concentration during the polymerization. For example, at F_{CSA} of 0.5, ΔH of PPy prepared at H^+ of 0.05 mol/L is 4.4 G, while it is 7.0 G at 0.23 mol/L, similar to the results of PPy *in situ* doped with NSA.[19] Therefore, the broader ΔH of PPy doped with CSA indicates that CSA counterions doped in PPy chains more efficiently decrease the interactions among PPy chains than DBSA due to the large molecular size of CSA, and the polymerization of pyrrole at higher F_{CSA} in DBSA–CSA mixed acid will give PPy having lower interaction among PPy chains. PPy prepared at high concentration of acid has a higher doping degree. This high concentration of counterions inserting among PPy chains greatly decreases the interactions.[19] These results of ESR experiments indicate that CSA mainly contributes to the solubility of PPy by decreasing the interaction among PPy chains, while DBSA is by its good solvating effect. Therefore, in order to synthesize soluble conducting polypyrrole by doping method, the selected dopant must have not only large molecular size to decrease the strong interaction among PPy chains but also a strong solvating effect to enhance the interaction be-

tween PPy chains and solvent. The UV-vis spectra and ESR experiment also prove that both polaron and bipolaron are the charge carrier of PPy(CSA–DBSA).

The Morphology and Thermal Stability of PPy(CSA–DBSA)

PPy doped with CSA is very loose powder, while PPy doped with DBSA is a hard solid. The morphology of PPy doped with CSA and DBSA is different, as shown in Figure 6. Under SEM, PPy-doped with CSA is typically granular while PPy doped with DBSA is lumpy. PPy doped CSA–DBSA binary acid is also granular but its granules are much smaller than those of PPy doped with CSA. The morphology of PPy(CSA–DBSA) is very similar to that of PPy–CSA at high F_{CSA}, while it is close to the morphology of PPy doped with DBSA when F_{DBSA} is high. Figure 7 shows the weight loss of PPy doped with DBSA, CSA, and their mixed acid. It can be found that the thermal stability of PPy(CSA–DBSA) is very similar to that of PPy only doped with DBSA. All the three kinds of PPy begin to decompose at about 260°C, but PPy doped with CSA decomposes more rapidly. CSA-doped PPy decomposes completely at about 800°C, while there is still 33% is left for PPy doped with DBSA or CSA–DBSA mixed acid. This may be due to the fact that CSA is more unstable than DBSA. CSA begins to de-

compose at 198°C, while DBSA is stable above 300°C.

CONCLUSION

PPy doped with DBSA–CSA mixed acid is soluble in *m*-cresol and the solubility increases with an increase in the DBSA molar fraction in the mixed acid, while the room temperature conductivity of the PPy increases with increasing CSA molar fraction. It has been concluded that both CSA and DBSA contribute to the solubility of PPy doped with the mixed acid, in which the CSA contribution decreases the interaction among PPy chains due to its large molecular size, while DBSA contributes to the solubility of PPy by its good solvating effect derived from its long alkyl chains.

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