Effect of β-Cyclodextrin on the Solid-State Synthesized Polyaniline Doped with Hydrochloric Acid

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ABSTRACT: Polyaniline (PANI) salts doped with hydrochloric acid were prepared by using solid-state polymerization in the presence of β-cyclodextrin (β-CD) at room temperature. The fourier transform infrared (FTIR) spectra, ultraviolet-visible absorption spectra, X-ray diffraction patterns were used to characterize the molecular structures of these polymers. Cyclic voltammetry study and conductivity measurements were done to investigate their electrochemical behaviors. The morphology of polymers was studied by the scanning electron microscopy and transmission electron microscopy. The results showed that PANI salts prepared in the presence of β-CD had different physicochemical characteristics compared with PANI salt prepared in the absence of β-CD. When the molar ratio of aniline to β-CD was 80/20, the obtained PANI salt displayed higher crystallinity, conductivity and electrochemical properties. However, these properties were opposite on condition that the molar ratio of aniline to β-CD was 50/50. The results also revealed that the morphology of PANI salt was affected by β-CD, especially at aniline/β-CD molar ratio in the feed of 50/50, in which PANI salt displayed rodlike structure morphology with a diameter of near 80–100 nm. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 3864–3870, 2008

Key words: conducting polymer; polyaniline; β-cyclodextrin; solid-state polymerization

INTRODUCTION

Among conducting polymers, polyaniline (PANI) is one of the most interesting polymers due to its environmental stability, ease in preparation, exciting electrochemical, optical, and electrical properties and possible applications in rechargeable batteries, microelectronics devices, biosensors, electrochromic displays, and chemical sensors.[1–4] Typically, PANI can be synthesized by either chemical or electrochemical oxidation of aniline in acidic solutions.[5,6] In addition, since the liquid monomer aniline will form solid salts with doping acids, room-temperature solid-state polymerization of aniline should be possible using a solid anilinium salt as the precursor. Gong et al. have reported solid state synthesis of PANI doped with $H_4SiW_{12}O_{40}$ under $-20°C$ by furbishing in a mortar.[7] Kaner and coworkers have reported solvent-free mechanochemical route to PANI in which the reaction was induced by ball milling an anilinium salt and an oxidant under ambient conditions.[8] Solid-state synthesis method is, however, advantageous; the reactant molecule will be put in order in solid-state synthesis reaction and the reaction happens on the surface of reactant molecule only, and this will bring some special properties of PANI material.

To improve some properties of PANI, it has been attracting a great attention to synthesize complex between PNAI and some chemicals with special structure recently.[9,10] Anitha and Subrammanian reported that the β-cyclodextrin (β-CD) could be as a dopant in the inclusion complex form, which could improve the properties of PANI.[11] β-CD is cyclic oligosaccharides consisting of seven α-(1,4)-linked D-glucopyranose units and a torus-shaped structure having a hydrophobic internal cavity and a hydrophilic outer side.[12] Because of this property, β-CD is able to form inclusion complexes with a wide variety of suitable hydrophobic guest molecules.[13–15] Yoshida et al.[16] have found that β-CD could be employed as an encapsule for conducting PANI, changing the conformation of PANI from a coil structure to a rodlike structure, where the conjugated structure could spread over the whole length of the conducting polymer.

In this report, we attempt to study the effect of β-CD on the solid-state polymerization reaction of PANI doped with hydrochloric acid (HCl), using ammonium peroxydisulfate (APS) as oxidant.

EXPERIMENTAL

Materials

Aniline was obtained from Xi'an Chemical Reagent Company (China). β-CD and APS were obtained from Tianjin Baishi Chemical Works (China). Aniline was purified by distillation before use. Besides, β-CD and APS were ground adequately in a mortar for about 1 h before use. Other chemicals used were of analytical reagent grade and used as received without further treatment.

Synthesis of PANI salts

Three different PANI salts were synthesized separately by solid-state polymerization. The detailed procedure adopted was as follows. An appropriate content of β-CD and 1-mL aniline in a mortar were ground adequately for 30 min at the room temperature (various aniline/β-CD molar ratio: 50/50, 80/20, 100/0). And then 1-mL 37 wt % HCl was put into the mortar. After grinding the reactant for about 10 min, 2.2 g APS was added by further grinding for 20 min until the color of solid changed to greenish black. The greenish black powder was isolated by filtration, washed with ether, ethanol, and hot distilled water until the filtrate was colorless, and then the powder was dried under vacuum at 50°C for 48 h.

Characterization

Fourier transform infrared (FTIR) spectra of PANI salts were obtained by using a BRUKEREUINOX-55 Fourier transform infrared spectrometer (Billerica, MA, USA) (frequency range 3500–400 cm^{-1}). Ultra-violet-visible (UV–vis) spectra of PANI salts in m-cresol solution were recorded by using a Shimadzu UV-2450 spectrophotometer (Tokyo, Japan) in the range of 300–1000 nm. The X-ray diffraction (XRD) studies were performed on a D/Max 2400 X-ray diffractometer (Tokyo, Japan) by using CuKα radiation source (λ = 0.15418 nm). The scan range (2θ) was 5–60°. The cyclic voltammetry (CV) were performed with a CHI 660A Electrochemical Workstation (CH Instruments, USA) in a conventional three-electrode cell. The working electrode was a PANI film electrode prepared by casting the DMF solution of respective PANI salts on platinum electrode. The reference electrode was SCE, and the counter electrode was a 1 cm^2 area Pt flag. The electrical conductivity measurements were made on 1-cm diameter pellets of PANI salts at 25°C by a SDY-4 four-probe instrument. The scanning electron microscopy (SEM) images of PANI salts were observed with a Leo1430VP microscope operating at 20 kV after the PANI salts were gold-coated. The transmission electron microscopy (TEM) studies of
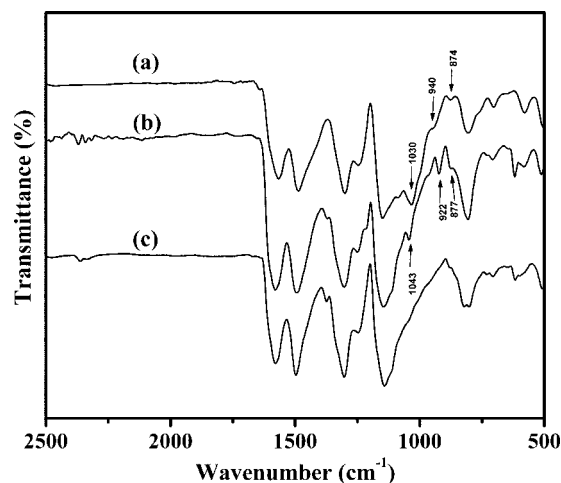
Figure 1 FTIR spectra of PANI salts prepared for various aniline/β-CD molar ratio: (a) 50/50, (b) 80/20, and (c) 100/0.

PANI salts prepared were carried out in a TEM apparatus (Hitachi, H-600). The inherent viscosity (η_i) of the obtained polymer was measured at 25°C in a 0.1 wt % solution in 96 wt % H$_2$SO$_4$ using an Ubbelohde viscosimeter.

RESULTS AND DISCUSSION

FTIR spectroscopy studies

FTIR spectra of PANI salts prepared for various aniline/β-CD molar ratio were given in Figure 1, and the major frequencies and assignment were summarized in Table I. The characteristic bands at ∼ 1563–1598 cm^{-1} arised mainly from both C=N and C=C stretching of the quinoid diimine unit, while the band at ∼ 1485–1498 cm^{-1} was attributed to the C=C aromatic ring stretching of the benzenoid diamine unit. The ∼ 1300–1304 cm^{-1} and ∼ 802–806 cm^{-1} bands could be assigned to C—N stretching of the secondary aromatic amine and an aromatic C—H out-of-plane bending vibration, respectively.[1,17] Figure 1(a,b) showed that the main characteristic bands of β-CD were found in PANI salts, which were ∼ 1030–1043 cm^{-1}, ∼ 922–940 cm^{-1}, and ∼ 874–877 cm^{-1}. This meant that there was still some β-CD in PANI salts prepared in the presence of β-CD.[18] And the intensity of ∼ 1030–1043 cm^{-1} in Figure 1(a) was stronger than that in Figure 1(b), which implied that there existed more β-CD in PANI salts prepared in the case of the molar ratio of aniline/β-CD of 50/50. In addition, these characteristic bands confirmed that these PANI salts contained the conducting emeraldine salt phase. The results indicated that the backbone structures of polymers obtained by this solid-state polymerization were identical to those of PANI

TABLE I
Frequencies and Assignments of the Major Transmittance Bands for PANI Salts

Aniline/β-CD molar ratio	νC—C + νQ—N (cm⁻¹)	νC—C (cm⁻¹)	νC—N (cm⁻¹)	δC—H (cm⁻¹)	γC—H (cm⁻¹)
50/50	1563	1485	1300	1149	804
80/20	1598	1492	1302	1145	806
100/0	1580	1498	1304	1142	802

Q, quinoid unit; ν, stretching mode; δ, bending mode; γ, deformation band.

salts synthesized previously in conventional chemical and electrochemical methods.[5,6]

On the basis of previous treatments of FTIR data in which the quinoid and benzenoid units were identified,[19,20] the intensity ratio of these two absorption bands at ∼ 1563–1598 cm⁻¹ and ∼ 1485–1498 cm⁻¹ was indicative of the extent of oxidation state of PANI, which reflected the content of the quinoid diimine and benzene ring structure. The ratio (R) is calculated as following:

$$R \text{ (intensity ratio)} = \frac{I_{\sim 1563-1598 \text{ cm}^{-1}}}{I_{\sim 1485-1498 \text{ cm}^{-1}}}$$

where I is absorption intensity.

Generally, the bigger the ratio (R) is, the more there is quinoid diimine, and the higher conductivity PANI may have.[20] The values calculated from the FTIR data were listed in Table II. From above results, PANI salts prepared at different aniline/β-CD molar ratio had different R (intensity ratio). These differences would be due to that a little amount of β-CD could reduce the probability of acid reacting with aniline to some extent, which would result that the highest ratio of relative intensity of quinoid to benzenoid ring modes occurred in PANI salt prepared at the aniline/β-CD molar ratio of 80/20.[21] But in the case of relatively high content of β-CD, it would strongly reduce the amount of oxidation of monomer, which is further supported by inherent viscosity measurements, where the η_i (0.90 dL/g) of PANI salt prepared at aniline/β-CD molar ratio of 50/50 was smallest, and PANI salts prepared at aniline/β-CD molar ratio of 80/20 and 100/0 had approximately equal value of η_i (1.21 dL/g). And therefore the extent of oxidation state in the case of aniline/β-CD molar ratio of 50/50 became smallest.

TABLE II
The Intensity Ratio (R) of Quinoid and Benzenoid Units in PANI Salts

Aniline/β-CD molar ratio	R (intensity ratio)
50/50	0.89
80/20	0.98
100/0	0.91

UV–vis spectroscopy studies

Figure 2 represented the UV–vis absorption spectra of PANI salts in *m*-cresol solution. These PANI salts showed three characteristic absorption peaks at ∼ 324–345 nm, ∼ 424–435 nm, and ∼ 884–892 nm (Table III). The absorption peak at ∼ 324–345 nm could be ascribed to π–π* transition of the benzenoid rings, while the peaks at ∼ 424–435 nm and ∼ 877–889 nm could be attributed to polaron–π* transition and π–polaron transition, respectively.[22,23] Figure 2 indicated that characteristic peak of PANI salt prepared at the aniline/β-CD molar ratio of 100/0 was different from those of others. In the case of high content of β-CD, β-CD would mainly play as a bulky dopant in inclusion complex form with Cl⁻ and SO_4^{2-} (from APS),[11] which increased the torsion angle between adjacent rings of the PANI chain, and decreased the degree of orbital overlapping between π electrons of phenyl rings with the lone pair of nitrogen atom. Consequently, the extent of conjugation diminished.[24] The π–polaron transition wavelength of PANI salt prepared at the aniline/β-CD molar ratio of 80/20 shifted to longer wavelength compared with that of aniline/β-CD molar ratio of 100/0. The red shift implied that β-CD as an encapsule during
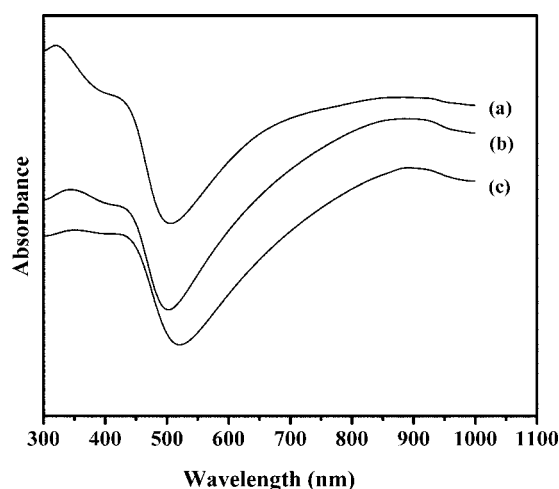
Figure 2 UV–vis spectra of PANI salts prepared for various aniline/β-CD molar ratio: (a) 50/50, (b) 80/20, and (c) 100/0.

Aniline/β-CD molar ratio	Wavelength of absorption peak			$A_{\sim 877-889}/A_{\sim 324-345}$
	$\pi-\pi^*$ transition (nm)	Polaron–π^* transition (nm)	π–Polaron transition (nm)	
50/50	324	424	884	0.74
80/20	341	424	892	1.46
100/0	345	435	889	1.45

polymerization would lead to enhanced coplanar characteristic of the PANI backbone, and that there existed interaction between PANI chains and β-CD, which made the energy gap of π–polaron narrower.[25]

Furthermore, according to the previous research that the level of doping could roughly be estimated from the UV–vis absorption spectra of PANI, in which the ratio of absorbances at $\sim$ 884–892 nm (π-polaron) and $\sim$ 324–345 nm (π–π* transition) indicated the doping level of PANI salts,[26,27] it was found that the intensity ratio ($A_{\sim 877-889 \text{ nm}}/A_{\sim 324-345 \text{ nm}}$) of PANI salt prepared in the case of aniline/β-CD molar ratio of 80/20 was the biggest (Table III), which meant that the doping level was the highest and the doping level of PANI prepared at the aniline/β-CD molar ratio of 50/50 was the lowest (Table III). This difference could also be resulted from the role of β-CD during polymerization. A little of β-CD as an encapsule could make doped PANI steadier. So the dedoping of PANI prepared in the case of low content of β-CD hardly occurred compared with PANI prepared in the absence of β-CD.[18] But in the case of relatively high content of β-CD, β-CD should mainly act as a bulky dopant leading the PANI more difficult to be doped by HCl.[18] This may be the proof that the largest intensity ratio ($A_{877-889 \text{ nm}}/$ $A_{324-345 \text{ nm}}$) occurs in PANI prepared at the aniline/β-CD molar ratio of 80/20 and the smallest intensity ratio occurs in PANI prepared at the aniline/β-CD molar ratio of 50/50.

XRD analysis

Crystallinity and orientation of conducting polymer have been of much interest, because more highly ordered systems could display a metallic-like conductive state.[28] Pouget et al. made the detailed and systematical study on PANI prepared through conventional methods and proposed a pseudoorthorhombic unit cell structure for PANI.[29] Wide-angle XRD patterns for PANI salts prepared were given in Figure 3 and the detailed data were presented in Table IV. The Bragg diffraction peaks of 2θ = $\sim$ 9°, $\sim$ 14°, $\sim$ 20°, and $\sim$ 25° could be found in the XRD patterns of PANI salts prepared at the aniline/β-CD molar ratio of 80/20 and 100/0. The peak centered at $\sim$ 20° may be ascribed to periodicity parallel to the polymer chain, while the peak at $\sim$ 25° may be ascribed to periodicity perpendicular to the polymer chain.[30] From Figure 3(b), the peaks were relatively sharper and stronger, which showed that the degree of crystallinity was a little better. However, some diffraction peaks disappeared in PANI prepared at the aniline/β-CD molar ratio of 50/50, which showed that crystallinity of PANI was the poorest. What is more, for PANI prepared at the aniline/β-CD molar ratio of 80/20, the peak of 2θ = 25.23° was stronger than that of 2θ = 20.49°, which was similar to that of highly doped emeradine salt.[29] Whereas, for PANI prepared at the aniline/β-CD molar ratio of 50/50, the peak of 2θ = 25.54° was weaker than that of 2θ = 20.36°, which was similar to that of less doped emeradine salt.[31] The reason may be that, when
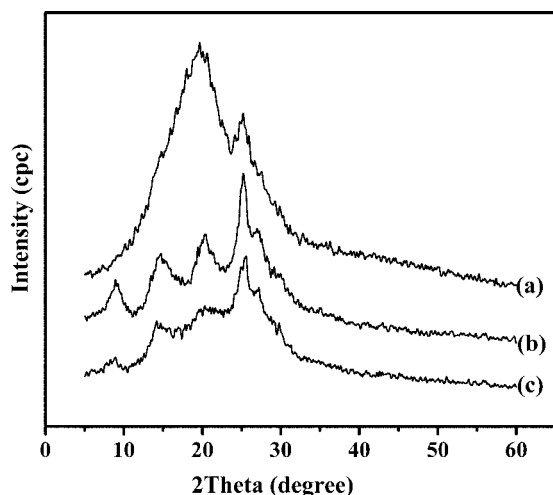

Figure 3 The XRD patterns of PANI salts prepared for various aniline/β-CD molar ratio: (a) 50/50, (b) 80/20, and (c) 100/0.

TABLE IV
XRD Data of PANI Salts

Aniline/β-CD molar ratio	2θ (Intensity)			
50/50			19.73° (s)	25.23° (m)
80/20	9.03° (s)	14.77° (s)	20.49° (s)	25.23° (s)
100/0	8.91° (w)	14.33° (m)	20.36° (w)	25.54° (s)

w, weak; m, medium; s, strong.
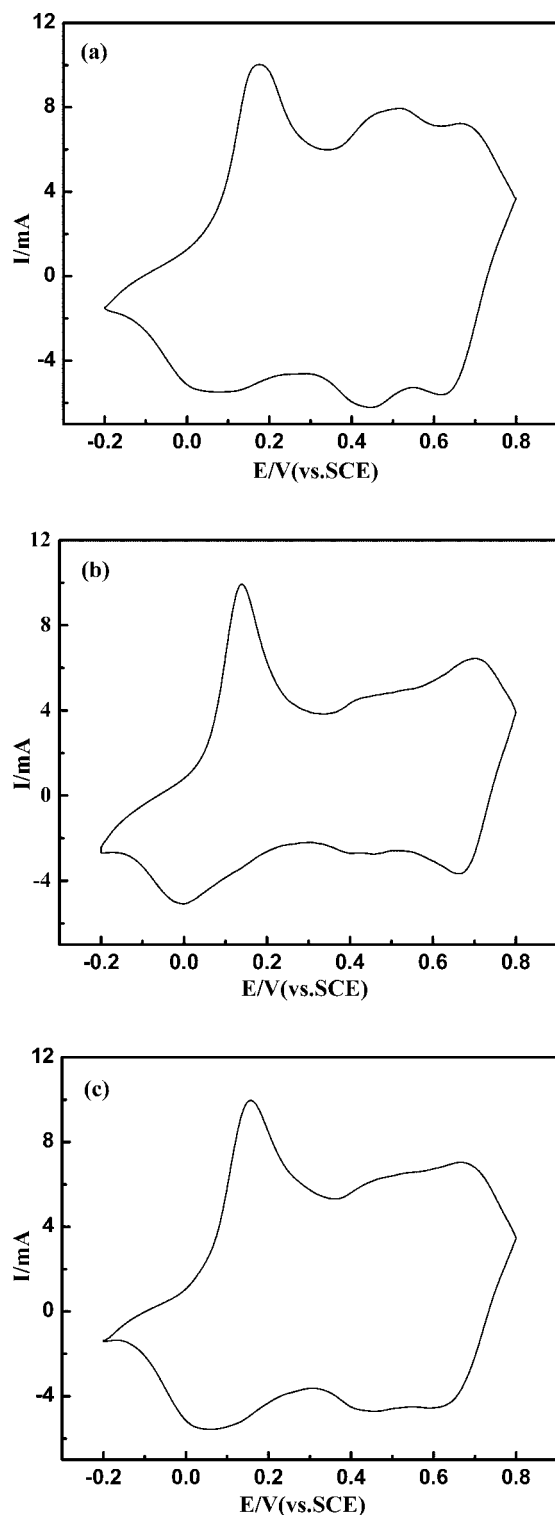
Figure 4 Cyclic voltammetry of PANI salts prepared for various aniline/β-CD molar ratio: (a) 50/50, (b) 80/20, and (c) 100/0 in 1 mol/L H₂SO₄ solution (Potential scan rate: 50 mV/s).

there existed a little of β-CD in polymerization, β-CD should mainly act as an encapsule for PANI, leading PANI to have better crystallinity and become easy to be doped by HCl. When there existed too

much β-CD in polymerization, β-CD should mainly act as a bulky dopant leading the PANI to have worse crystallinity and become difficult to be doped by HCl. This conclusion was agreed with the UV–vis spectroscopy studies.

Cyclic voltammetry and conductivity

CV of PANI salts films on Pt were carried out in 1 mol/L H₂SO₄, and CVs after the 30th cycles were given in Figure 4, and the anodic and cathodic potentials were listed in Table V. From Figure 4, it was seen that PANI salts prepared under the various conditions all showed three redox pair peaks, which were related to the typical inter-conversion reaction of PANI upon varying the potential. The first oxidation peaks in the CV (at $E_{SCE} = \sim 0.140–0.176$ V) had maximum peak current, which were assigned to the transition from leucoemeraldine form to emeraldine form, and the oxidation peaks at $E_{SCE} = \sim 0.677–0.702$ V were due to the transition from the emeraldine to the pernigraniline state. Between this two main pairs of peaks, a small peak located at $E_{SCE} = \sim 0.423–0.524$ V was observed, corresponding to the degradation products of PANI film. The products of degradation were usually identified as *p*-quinone/*p*-hydroquinone and *p*-quinoneimine/*p*-aminophenol redox couples.[32] In CVs of PANI salt prepared in the condition of the aniline/β-CD molar ratio of 80/20, the first redox peaks were relatively sharp and negative, and however, broad peaks and more positive potential in the first redox potential were observed in the CVs of PANI salt prepared in the condition of the aniline/β-CD molar ratio of 50/50, in which the degradation peak also became more obvious. These phenomena would be due to the crystallinity, extent of oxidation and doping level of PANI. It is well known that the electronic properties of aromatic polymeric systems are affected by the torsion angle between adjacent rings of the polymer chain.[24] And the voltanmmetric response of conducting PANI also depends strongly on the dopant used. During the polymerization in presence of a little β-CD, it acted as an encapsule, which would lead to better crystal-

TABLE V
The Redox Potentials of PANI Salts Prepared for Various Aniline/β-CD Molar Ratio

Aniline/β-CD molar ratio	E_{pa}			E_{pc}		
	A (V)	B (V)	C (V)	A (V)	B (V)	C (V)
50/50	0.176	0.516	0.677	0.058	0.446	0.628
80/20	0.140	0.423	0.702	−0.002	0.455	0.662
100/0	0.155	0.524	0.677	0.058	0.488	0.626

E_{pa}, oxidative potential; E_{pc}, reductive potential; A, first redox peaks; B, intermediate peaks; C, second redox peaks.
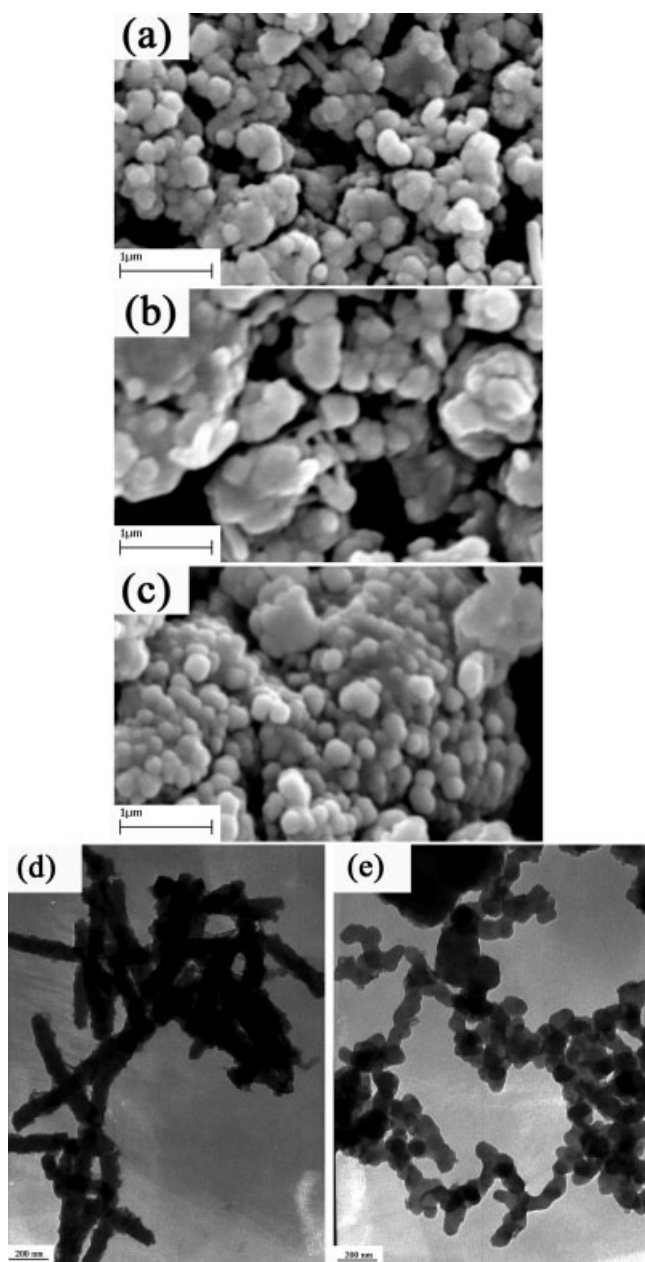
Figure 5 Morphology of PANI salts prepared for various aniline/β-CD molar ratio: (a) 50/50 (original magnification = 50,000×), (b) 80/20 (original magnification = 50,000×), (c) 100/0 (original magnification = 50,000×); and TEM of PANI salts prepared for various aniline/β-CD molar ratio: (d) 50/50 (original magnification = 80,000×), (e) 80/20 (original magnification = 80,000×).

linity. In presence of too much β-CD, the bulky inclusion complex as dopant increased the torsion angle, and decreased the extent of conjugation of PANI. Consequently, the energy of the transition from leucoemeraldine to emeraldine form increased, it became more difficult to oxidize the leucoemeraldine form of PANI. It was found that redox reversibility of PANI would become worse in the condition of aniline/β-CD molar ratio of 50/50.

The conductivity of PANI salts prepared for various aniline/β-CD molar ratio were 0.14 S cm^{-1} (50/50), 6.3 S cm^{-1} (80/20), and 5.1 S cm^{-1} (100/0), respectively at room temperature. The conductivity of PANI salts depends on the degree of doping, oxidation state, crystallinity, interior intrachain interactions, particle morphology, molecular weight, etc.[33] It is common that the ratio of the relative intensity of quinoid to benzenoid ring modes is related to the conductivity. The higher ratio is, the greater conductivity of PANI is. And a better crystalline structure can lead to higher conductivity. Therefore this would be explained by the results of FTIR spectra, UV–vis spectra, XRD analysis and CVs studies. These results showed that PANI salts prepared at aniline/β-CD molar ratio of 80/20 had higher doping level and crystallinity, these could be the possible reason that it had higher conductivity, while the lowest doping level and crystallinity leaded PANI to have the lowest conductivity.

Morphology

To obtain further insight into the variation of these characteristics, PANI salts prepared were characterized by SEM, and SEM images of PANI were given in Figure 5(a–c). As can be seen from Figure 5(c), PANI salt prepared without β-CD was mainly formed by particles of about 200 nm, which would be caused that the polymer growth orientation was random as a result of the flexible chain structure of PANI. And then in PANI salts prepared in the presence of β-CD there were a little of rodlike structure with a diameter of near 80–100 nm consisting of a lot of nanoparticles, TEM of which were shown in Figure 5(d,e). β-CD as template hydrogen bonds, via one of the lone pairs on its oxygen atom, with the sections of the PANI that were in the leucoemeraldine salt form, or the β-CD hydrogen also bonds directly to the emeraldine salt.[34] The effect of the hydrogen bonding was to push the polymer chains apart. But an increase in the initial content of β-CD did not monotonously enhance the extent of rodlike structure. On the contrary, it is concluded that, the role of β-CD would change from a template to a bulky dopant, which was in agreement with the results of FTIR, UV–vis, XRD, and CV.

CONCLUSION

In summary, in the presence of β-CD, we have synthesized PANI salts by solid-state polymerization successfully. Spectroscopic studies showed the ratio of the relative intensity of the quinoid to benzenoid unit in PANI salt prepared at the aniline/β-CD molar ratio of 80/20 was the highest. These results were further supported by CV and conductivity

measurements. A comparison indicated that in the condition of the aniline/β-CD molar ratio of 80/20, PANI displayed higher doping level, better crystallinity, which showed that β-CD mainly acted as an encapsule during polymerization, and therefore it had better electrochemical activity and higher conductivity. Whereas in the case of the aniline/β-CD molar ratio of 50/50, these properties were opposite, which showed that β-CD mainly acted as a bulky dopant during polymerization. Morphology studies also revealed that there was some rod-like structure in PANI salts prepared in the presence of β-CD. These results indicated that the role of β-CD would vary from an encapsule to a bulky dopant with the increase of content of β-CD. In addition, the characteristics of solid-state polymerization method, in which the reaction happens only on the surface of reactant molecule, would also affect the physicochemical properties of PANI salts. All these factors leaded the PANI in solid-polymerization to have different characteristics.

References

1. Kang, E. T.; Neoh, K. G.; Tan, K. L. Prog Polym Sci 1998, 23, 277.
2. Yang, C. H.; Chih, Y. K.; Cheng, H. E.; Chen, C. H. Polym 2005, 46, 10688.
3. Yang, C. M.; Chen, C. Y. Synth Met 2005, 153, 133.
4. Bienkowski, K.; Kulszewicz, I. B.; Francoise, G.; Oddou, J. L.; Adam, P. Mater Chem Phys 2005, 92, 27.
5. Guo, Q. X.; Yi, C. Q.; Zhu, L.; Yang, Q.; Xie, Y. Polymer 2005, 46, 3185.
6. Lv, R. G.; Zhang, S. L.; Shi, Q. F.; Kan, J. Q. Synth Met 2005, 150, 115.
7. Gong, J.; Cui, X. J.; Xie, Z. W.; Wang, S. G.; Qu, L. Y. Synth Met 2002, 129, 187.
8. Acquaye, J. H.; Moore, J. A.; Huang, J. X.; Kaner, R. B. Polymer Prepr 2004, 45, 147.
9. Vahid, M.; Geoffrey, M. S.; Gordon, G. W. Polymer 2006, 47, 4996.
10. Ding, S. J.; Zhang, C. L.; Yang, M.; Qu, X. Z.; Lu, Y. F.; Yang, Z. Z. Polymer 2006, 47, 8360.
11. Anitha, G.; Subrammanian, E. J Polym Sci Part A: Polym Chem 2006, 44, 281.
12. Szejtli, J. Cyclodextrins and Their Inclusion Complexes; Akademiai Kiado: Budapest, 1982.
13. Li, S.; Purdy, W. C. Chem Rev 1992, 92, 1457.
14. Connors, K. A. Chem Rev 1997, 97, 1325.
15. Yuan, Z. B.; Zhu, M.; Han, S. B. Anal Chim Acta 1999, 389, 291.
16. Yoshida, K.; Shimomura, T.; Ito, K.; Hayakawa, R. Langmuir 1999, 15, 910.
17. Tursun, A.; Zhang, X. G.; Ruxuangul, J. J App Polym Sci 2005, 96, 1630.
18. Li, X. W.; Zhao, Y. P.; Zhuang, T.; Wang, G. C.; Gu, Q. Colloids Surf A 2006, 295, 146.
19. Franco, C.; Paolo, M. Eur Polym J 2002, 38, 1791.
20. Huang, L. M.; Wen, T. C.; Gopalan, A. Mater Lett 2003, 57, 1765.
21. Morales, G. M.; Llusa, M.; Miras, M. C.; Barbero, C. Polym Commun 1989, 38, 5247.
22. Wei, Y.; Hsueh, K. F.; Jang, G. W. Macromolecules 1994, 27, 518.
23. Anjali, A. A.; Milind, V. K.; Vasant, V. C.; Athawale, A.; Kulkarni, M. V.; Chabukswar, V. V. Mater Chem Phys 2002, 73, 106.
24. Schemid, A. L.; Córdoba de Torrest, S. I.; Bassetto, A. N.; Carios, I. A. J Braz Chem Soc 2000, 11, 317.
25. Zhou, S.; Wu, T.; Kan, J. Q. Eur Polym J 2007, 43, 395.
26. Xia, H. S.; Wang, Q. J Nanoparticle Res 2001, 3, 401.
27. Kim, B. J.; Oh, S. G.; Han, M. G.; Im, S. S. Synth Met 2001, 122, 297.
28. Li, Q. M.; Cruz, L.; Philips, P. Phys Rev B 1993, 47, 1840.
29. Pouget, J. P.; Jozefowicz, M. E.; Epstein, A. J.; Tang, X.; MacDiarmid, A. G. Macromolecules 1991, 24, 779.
30. Moon, Y. B.; Cao, Y.; Smith, P.; Heeger, A. J. Polym Commun 1989, 30, 196.
31. Pouget, J. P.; Hsu, C. H.; MacDiarmid, A. G.; Epstein, A. J. Synth Met 1995, 69, 119.
32. Shreepathi, S.; Holze, R. Chem Mater 2005, 17, 4078.
33. Jiang, H.; Geng, Y. H.; Li, J.; Jing, X. B.; Wang, F. S. Synth Met 1997, 84, 125.
34. Tan, C. K.; Blackwood, D. J. Sens Actuators B Chem 2000, 71, 184.