

© 2010 American Chemical Society

Synthesis and Characterization of "Hairy Urchin"-like Polyaniline by Using β -Cyclodextrin as a Template

Adhimoorthy Prasannan,[†] Tram Le Bich Truong,[†] Po-Da Hong,^{*,†,‡} Narayanasastri Somanathan,[§] Indrajit Shown,[†] and Toyoko Imae[†]

[†]Materials Technology Program, Graduate Institute of Engineering, and [‡]Department of Materials Science and Engineering, National Taiwan University of Science and Technology, Taipei-10607, Taiwan, and [§]Polymer laboratory, Central Leather Research Institute, Chennai 600020, India

Received August 27, 2010. Revised Manuscript Received November 24, 2010

A novel synthesis of "hairy urchin"-shaped polyaniline (PAni) and its surface coverage with nanospikes was achieved from a simple microemulsion polymerization technique in the presence of β -cyclodextrin (β -CD). The rodlike micelle phase was characterized, and the key factors affecting the formation of PAni nanostructures were systematically examined. Ferric chloride (FeCl₃) has played a role as a structural directing agent to fabricate the polymer as hairy urchin-like structure/nanorods via a cooperative interaction between FeCl₃ and DoTAC in an aqueous medium. Host–guest inclusion complex of β -cyclodextrin with aniline was used as a monomer. It has been revealed that the formation of the supramolecular complexes of polyaniline with β -CD due to host–guest interaction is indispensable for the fabrication of these unique PAni nanostructures, and a suitable β -CD to aniline molar ratio is essential to their exclusive formation. Different varieties of PAni nanostructures such as hairy urchin, branched particles consisting of rodlike branches, and regular rodlike particles were obtained in the presence of FeCl₃. Also, in the absence of FeCl₃, a predominant product of regular spherical particles and wirelike aggregation exhibiting faceted surfaces were obtained. The structures of polyaniline hairy urchin-like nanorods were analyzed using transmission electron microscopy (TEM). The synthesized polymer was characterized by Fourier-transform infrared spectroscopy and X-ray diffraction technique. Additionally, the relationship between the morphology and the conductivity of the PAni nanostructures was investigated as well.

Introduction

The nanosized particles have attracted the attention of the materials community due to their unique properties that are significantly different from their bulk materials. The dimensionality plays a key role to determine the properties of nanomaterials and synthesis of nanostructured materials with controllable morphology, size, chemical composition, and crystal structure.^{1,2} In current years, lots of one-dimensional (1D) nanomaterials have been extensively investigated because of their potential applications in electronics, optoelectronics, memory devices,^{3–6} and so forth. Conducting polymeric nanomaterials including nanofibers, nanorods, and nanotubes have been widely studied because of their advantages of both low-dimensional systems and organic conductors.^{7–9} Among the large family of conducting polymers, polyaniline is one of the most remarkable and has been used in

(1) Xia, Y.; Yang, P.; Sun, Y.; Wu, Y.; Mayers, B.; Gates, B.; Yin, Y.; Kim, F.; Yan, H. Adv. Mater. **2003**, 15, 353–389.

- (3) Shi, Y.; Zhou, B.; Wu, P.; Wang, K.; Cai, C. J. Electroanal. Chem. 2007, 611, 1–9.
- (4) Inguanta, R.; Piazza, S.; Sunseri, C. *Electrochem. Commun.* 2008, 10, 506-509.
- (5) Liu, Y.; Zhang, J.; Hou, W.; Zhu, J. J. Nanotechnol. 2008, 19, 135707-135714.

- (8) Marie, E.; Rothe, R.; Antonietti, M.; Landfester, K. Macromolecules 2003, 36, 3967–3973.
- (9) Huang, K.; Wan, M. Chem. Mater. 2002, 14, 3486-3492.
- (10) Hatchett, D. W.; Josowicz, M. Chem. Rev. 2008, 108, 746-769.
- (11) Haung, J.; Virji, S.; Kaner, R. B.; Weiller, B. H. Nano Lett. 2004, 4, 491-496.

many versatile applications,^{10–12} such as electrode materials in batteries, anticorrosion coatings, chemical sensors, superhydrophobic materials, and light-emitting and electronic devices. Recently, many efforts have been made on the synthesis of 1D or 2D polyaniline nanomaterials,^{12–14} but there are also several drawbacks known: they are insoluble, not meltable, and therefore difficult to process. They are sensitive to moisture, light, and oxygen; besides, they tend to cross-link. Each of these drawbacks limits their applicability. Therefore, it was a good idea to create so-called insulated molecular wires, in which cyclodextrins (CDs) shield polyconjugated monomer or polymers from the environment and prevent intermolecular cross-linking reactions.

CDs are cyclic oligosaccharides that are classified as α -, β -, and γ -CD according to the number of (α - 1, 4)-linked α -D-glucopyranose units six, seven, and eight, respectively. They are hallowing truncated cone shaped highly hydrophilic molecule with a nonpolar cavity. It is well-known to make inclusion complexes with a wide range of organic molecules through host–guest inclusion complex due to the hydrophobicity of their cavities. The inclusion ability of CDs has been studied extensively and applied to many fields including food sciences, cosmetics, and pharmaceutical industries.¹⁵ In addition, CDs have been utilized as potential templates for the synthesis of novel nanostructure materials.^{16,17}

- (14) Zhou, C.; Han, J.; Guo, K. J. Phys. Chem. B 2008, 112, 5014–5019. (15) Del Valle, E. M. M. Process Biochem. (Amsterdam, Neth.) 2004, 4, 1033-
- 1046
- (16) Storgberg, J.; Hartenstein, M.; Mueller, A. H. E.; Ritter, H. Macromol. Rapid Commun. 2000, 21, 1342–1346.
- (17) Hu, X.; Lu, Y.; Liu, J. Macromol. Rapid Commun. 2004, 25, 1117-1120.

^{*}Corresponding author. E-mail: poda@mail.ntust.edu.tw

⁽²⁾ Tang, C.; Bando, Y.; Golberg, D.; Ma, R. Angew. Chem., Int. Ed. 2005, 44, 576–579.

⁽⁶⁾ Zhang, L. Biosens. Bioelectron. 2008, 23, 1610-1615.

⁽⁷⁾ Huang, J.; Virji, S.; Weiller, B. H.; Kaner, R. B. J. Am. Chem. Soc. 2003, 125, 314–315.

⁽¹²⁾ Bhadra, S.; Khastgir, D.; Singha, N. K.; Lee, J. H. Prog. Polym. Sci. 2009, 34, 783–810.

 ⁽¹³⁾ Ding, H.; Wan, M.; Wei, Y. Adv. Mater. 2007, 19, 465–469.
(14) Zhou, C.; Han, J.; Guo, R. J. Phys. Chem. B 2008, 112, 5014–5019.

The complexation of CDs with aromatic compound can be polymerized to π -conjugated polymers. Harada et al. have obtained low molecular weight polythiophene included in macrocycles as β -CD and 2,6-dimethyl- β -CD by chemical polymerization of inclusion compounds: 2,2'-bithiophene/ β -CD and 2,2-bithiophene/2,6-dimethyl- β -CD in aqueous solution;¹⁸ moreover Dong et al. electrochemically polymerized an aniline/ α -CD complex to exclude a certain theory regarding byproducts formed during the electrochemical formation of polyaniline,¹⁹ and a more comprehensive review of the various types of insulated molecular wires was published.²⁰ However, the direct utilization of polymer nanomaterials.

Herein, we report the preparation and structural analysis of host–guest compounds of various amounts of β -cyclodextrins (β -CD) with aniline, and their polymerization in water using microemulsion polymerization. The rodlike micelle phase was characterized, and the key factors affecting the formation of PAni nanostructures were systematically examined. The polyaniline nanofibers were characterized by transmittance electron microscopy (TEM), Fourier-transform infrared (FTIR), and UV–vis spectroscopy (UV). The electronic transport behavior of the synthesized nanoparticles was discussed as well. In order to rationalize the effects of the β -CD concentrations with aniline, morphology would be extensively investigated from the viewpoint of polymer nanostructure formation in this work.

Experimental Section

Materials and Methods. The cationic surfactant dodecyltrimethylammonium chloride (DoTAC) was purchased from Tyoko Chemical Inc. (TCI). Aniline (Ani), β -cyclodextrin (β -CD), ferric chloride (FeCl₃), and ammonium persulfate (APS) were purchased from Aldrich. Methanol was dried by a common method.

Synthesis of Water-Soluble Complexes (Inclusion Type). For the synthesis of the water-soluble aniline/ β -cyclodextrin inclusion complex, first aniline (7.2 mmol) was separately added to various amounts of β -cyclodextrin (7.2, 9, 10.8, and 12.6 mmol are composition A, B, C, and D, respectively) in 100 mL of water. The mixture was stirred for 4 h at room temperature and then placed in a refrigerator for 24 h at 0 ± 2 °C. After that, the crystals were filtered off and washed with 20 mL of cold water. Then the water-soluble inclusion complex (IC) was dried at room temperature.

Synthetic Procedure of PAni Nanomaterials. In a typical synthesis procedure, first the surfactant (DoTAC) (7.2 mmol) was dissolved in distilled water (20 mL) and then 1 g of the presynthesized complex solution (25 mL of H₂O at 60 °C) was added dropwise to the micellar solution and stirred for 2 h. The initiator, APS (7.2 mmol) in 1 M HCl solution, was added to the above-stabilized solution. The polymerization reaction was carried out for 6 h. For selective fabrication of PAni nanorods, after aniline complex was polymerized for 15 min, FeCl₃ (7.2 mmol) was added to the polymer solution, and the resulting solution was stirred for an additional 6 h under ambient conditions. The PAni nanomaterials were precipitated in methanol (60 mL) and acetone (60 mL) respectively to remove the surfactants and initiators. Finally, the PAni nanomaterials were separated out by filtration and dried at 60 °C.

Measurements. To analyze the ICs compositions, ¹H NMR spectra of the IC complexes were recorded by using a Bruker Avance-500 MHz NMR spectrometer, using D₂O as solvent. A Nicolet 6700 (Thermo scientific) FT-IR spectrometer was used for



Figure 1. ¹H NMR spectra of β -CD and β -CD/aniline complex (D₂O).

the analysis of the synthesized ICs and PAni nanomaterials. UV-vis spectra were recorded with a Jasco V-970 spectrophotometer. Morphology of PAni nanomaterials was studied on a Hitachi H-7000 transmission electron microscope (TEM) equipped with a CCD camera attachment, operating at 100 kV. Samples for TEM were prepared by casting a droplet of the solution on a copper grid and a Hitachi (S-3400N) scanning electron microscope. Wideangle X-ray diffraction measurements of different dried ICs and PAni were carried out by using a BL17A (powder X-ray scattering end station) X-ray diffractometer of the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The incident beam is focused on a toroidal mirror and monochromated ($\lambda =$ 1.333 621 Å for BL17A) by a Ge double-crystal monochromator. The beam is mainly collimated by a 20 cm collimator of 1 mm diameter channel. The sample-to-detector distance is kept at 300 mm. X-ray diffraction data were collected using a mar345 imaging plate detector and corrected for background scattering. A fluorescence image of rodlike micelle was obtained with an Olympus BX51 cofocal laser scanning microscope. The dynamic light scattering measurements of the micelle solutions were studied at a scattering angle of 90° and a temperature of 30 °C using Malvern series 4700 apparatus equipped with the 7132 multiple- τ autocorrelator recording on 128 channels. An argon ion laser acts as light source, operating at a power of 20-50 mW with a wavelength of 514.5 nm. Impedance measurements of all PAni samples were performed using a Solartron 1260 frequency response analyzer applying a sinusoidal voltage of 10 mV amplitude over the frequency range of $1 \le f \le 10^6$ Hz at room temperature.

Results and Discussion

Formation of Aniline/ β -CD Complex. The synthesized water-soluble aniline/ β -CD complex was a stable white homogeneous crystalline. The crystalline nature of the ICs was studied using wide-angle X-ray diffraction (WAXD) analysis. They provide enough information to distinguish between herringbone packing of free CDs and the channel packing of inclusion complexes. The X-ray diffraction profiles of β -CD and aniline/ β -CD complex are shown in Figure S1 (Supporting Information). Structures of the inclusion complexes of CDs with low molecular weight compounds can be classified as "herringbone fashioned cage type" or "channel type". Pure β -CD shows the herringbone packing with lower symmetry and leads to a great number of reflections. CDs situated in inclusion complexes prove hexagonally symmetry and fewer reflection peaks. The patterns show that all of the complexes are crystalline, and the pattern of the β -CD/Ani complex is

⁽¹⁸⁾ Takashima, Y.; Oizumi, Y.; Sakamoto, K.; Miyauchi, M.; Kamitori, S.; Harada, A. *Macromolecules* **2004**, *37*, 3962–3964.

⁽¹⁹⁾ Dong, S. J.; Zhanf, D. B.; Li, Z. Chin. Chem. Lett. 1992, 3, 129–132.

⁽²⁰⁾ Frampton, M. J.; Anderson, H. L. Angew. Chem., Int. Ed. 2007, 46, 1028–1064.

Scheme 1. Schematic Diagram of the Overall Fabrication Procedure of PAni Nanorods and Nanosphere; Micelle after Addition of Aniline Monomer (β-CD/Aniline Complex) (a), after Polymerization (b), and PAni Nanomaterials Obtained after Washing (c)



different from that of pure β -CD and similar to that of the complex with channel-type inclusion complex. This result indicates that, in the aniline complex with β -CD, the β -CD exhibits packing different from that in pure β -CD and has channel structures as in the complex with aniline. The channel-type crystal structure of the aniline/ β -CD complex provides information on the inclusion complex, indicating the aniline is situated within the apolar cavity of the CD molecule. The solid host-guest inclusion complexes were stable under ambient conditions; after several months, the crystals remain unchanged whereas the uncomplexed aniline themselves change in color after a short exposure of the same conditions caused by partial oxidation. The ¹H NMR spectra of the aniline/ β -CD inclusion complex are shown in Figure 1. From the spectra we observed a clear upfield shift of the C3-H and the C5-H protons of the β -CD compared to the noncomplex β -CD. All aromatic and NH₂ protons of aniline are shifted upfield due to the inclusion of aniline inside the β -CD cavity. The FT-IR spectra of the aniline/ β -CD inclusion complex are presented in Figure S2 (Supporting Information); the characteristic bands at 1602 and 1332 cm^{-1} were attributed to the C=C stretching of the benzenoid rings and C-N stretching of the aromatic amine of aniline. The aromatic C-H in-plane bending vibration was also observed at 1156 cm⁻¹. The main characteristic bands at 3349, 1622, 1029, and 867 cm⁻¹ of β -CD were found in the aniline/ β -CD inclusion complex. The band at 1478 cm⁻¹ was shifted to higher wavenumbers due to the presence of β -CD host molecule. These results indicate that the backbone structure of aniline/ β -CD microstructures was obtained by the host-guest inclusion complex method.

Formation of Rodlike Micelle Phase. A typical fabrication process of polymer nanorods is given in Scheme 1. The DoTAC was dissolved in distilled water to make micelles as a nanoreactor. The micelle aggregation number and second critical micelle concentration (CMC II) of DoTAC surfactant were decreased with addition of metal salt into emulsion. CMC and the concentration for sphere-to-rod transformation are 0.016 and 0.35 m for DoTAC, respectively. Under these conditions, the strength of the hydrophobic interactions exceeds that of the electrostatic repulsions of the ionic head groups, which stabilizes the formation of micelles. The aniline/ β -CD complex monomer was added dropwise to the micelle solution. The monomer could be penetrating inside the micelles; hence, the micelles enlarged considerably. Consequently, the monomers inside the micelles were polymerized using APS as initiator (Scheme 1b). Polymerization of the aniline/ β -CD complex readily occurred due to the relatively high oxidation potential of APS. After 15 min polymerization, an amount of FeCl₃ was introduced, and the additional polymerization continued with stirring (Scheme 1c). FeCl₃ could be use as structural directing agent besides chaotropic agent. Chemical polymerization of PAni in the presence of surfactant at room/low temperature by adding inorganic salts avoids the aggregation of the micelle in water medium. However, FeCl₃ can act as an oxidant as well as easily interact with surfactant head groups and aid in the formation of rod-shaped micelles from spherical by decreasing the "second critical micelle concentration (CMC II)" value and increasing the solvent's ionic strength. Moreover, that can enhance the solubility of micelles, natural CDs, and its complex, a fact that could be directly connected with the self-assembly. FeCl₃ would weaken the strong intermolecular hydrogen bonds between the micelles and β -CDs. Accordingly, the polar headgroup of DoTAC extracts metal cations from the aqueous solution to the micellar phase. In other words, Fe³⁺ ions concentrated in the micelles were restricted by the polar head groups of DoTAC, so we used FeCl₃ purposely in this microemulsion system. Therefore, the introduction of salt promoted micelle growth from spherical to bigger rod or rodlike micelles because the addition of salt lowers the charge density around the micelle surface and hence will decrease the entropic penalty in transforming the micelles.^{21–23}

Rodlike micelle was analyzed by following several experiments. POM photograph of the DoTAC rodlike micelle phase (Figure S3, Supporting Information) with clear birefringent striations arises from the undulations of the rodlike micelles. The anisotropic refractive index of the DoTAC rodlike micelle phase alters the polarization of transmitted polarized light to blue and reddish-pink texture. The characteristic striations were comparable to the hexagonal liquid crystalline phase,²⁴ where it showed less random orientation due to some ordered arrangement of the cylinders compared with the hexagonal phase. Furthermore, using confocal laser scanning microscopy (CLSM), a surveillance photograph of the DoTAC rodlike micelle (Figure S4, Supporting Information) in the presence of rhodamine B was obtained. 10 wt % of aqueous solution of rhodamine B base (3.5 mmol) was used as a laser colorant, virtual to quantity of aqueous FeCl₃ contained, and added dropwise to the DoTAC rodlike micelle phase. The aqueous dye solution is instinctively entered into the aqueous core of the rodlike micelles due to its hydrophilicity. A CLSM image shows yellow rodlike emissions resulting from the

⁽²¹⁾ Carswell, A. D. W.; O'Rear, E. A.; Grady, B. P. J. Am. Chem. Soc. 2003, 125, 14793–14800.

⁽²²⁾ Wang, J.; Wang, J.; Yang, Z.; Wang, Z.; Zhang, F.; Wang, S. *React. Funct. Polym.* **2008**, *68*, 1435–1440.

⁽²³⁾ Hsieh, B. Z.; Chuang, H. Y.; Chao, L.; Li, Y. N.; Huang, Y. J.; Tseng, P. H.; Hsieh, T. H.; Ho, K. S. *Polymer* **2008**, *49*, 4218–4225.



Figure 2. Normalized intensity-intensity autocorrelation function obtained from DLS measurement of rodlike micelle solution at scattering angle of 90°.

dye molecules surrounded inside the rodlike micelles. DoTAC rodlike micelles are capable of assembling in a parallel way because of their unique anisotropic morphology. The aggregation of the DoTAC rods is encouraged by the evaporation of water during the observation, and the micelle solution became more concentrated. Then the DoTAC micelle would prefer to form a rodlike micelle (see upper portion of CLSM image). This above information confirmed the formation of DoTAC rodlike micelles like 1-D channels.

The dynamic light scattering (DLS) technique was performed to further authenticate the formation of rodlike micelles of the DoTAC in the presence of FeCl₃. Figure 2 shows the lightscattering autocorrelation functions of spherical and rodlike micelle solutions. In the correlation function of the spheres, one decay point is clearly observed. This may point out that the spherical micelles revealed only translational motion. Two decay points obtained in the case of rodlike micelles due to the change in molecular motions of micelles, which may be related to the rotational motion.^{25,26} While the spheres showed one peak attributed to the diameter of the micelle, the rodlike micelles shows two peaks associated with the radius and length of the micelle.²⁵ The hydrodynamic radii $(R_{\rm h})$ of micelles were calculated from the diffusion coefficients (D) by means of the Stokes-Einstein equation (Figure S5, Supporting Information), yielding the hydrodynamic radius $R_{\rm h}$. The $R_{\rm h}$ values of 112 and 15 nm were obtained for sphere and rod radius, respectively.

Fabrication of PAni Nanoparticles. The fabrication of PAni nanoparticles and nanofibers was further analyzed by FT-IR and UV-vis spectroscopy. Figure 3a shows the FT-IR spectra of various PAni nanoparticles (with and without FeCl₃) and aniline/ β -CD inclusion complex, respectively. The sharp peak at 1602 cm⁻ from the C=C stretching mode in the aniline/ β -CD complex monomers completely disappeared after polymerization. The characteristic bands at 1582 and 1494 cm^{-1} are attributed to the C=C stretching deformation mode of the quinoid and benzenoid rings, and the 1296 cm⁻¹ band is assigned to the C-N stretching of the secondary aromatic amine of PAni. The band at 1245 cm⁻ could be interpreted as a C-N-C stretching vibration in the polaron structure. Upon acid protonation of the emeraldine base,

Langmuir 2011, 27(2), 766-773



Figure 3. FT-IR (a) and UV-vis (b) spectra of PAni nanoparticles and nanorods were prepared from composition A.

the quinonoid units are considered to be switched to benzenoid units by a proton-induced spin-unpairing mechanism and have a small absorption band at 1373 cm⁻¹, and the intense broad band at about 1157 cm^{-1} has been associated with high electrical conductivity and a high degree of electron delocalization in PAni.²⁷ Bands at 1029 and 696 cm⁻¹ are the results of C–H out-of-plane bending of 1, 2, 4 ring and C–H out-of-plane bending of the 1, 2 ring, respectively. Out-of-plane deformations of C-H on 1,4disubstituted rings are located at 817 cm⁻¹, and the absorption peak at 610 cm^{-1} is caused by the deformations of the benzene ring.²⁸ The peaks observed at 800–900 cm⁻¹ are characteristic of para substitution of the aromatic ring and reveal that the polymerization has proceeded via a head-to-tail mechanism. These characteristic peaks are identical to those of PAni particles prepared via a common method, and main characteristic bands of CD were found in PAni despite bands shift, which were 3372, 1632, 1031, and 871 cm⁻¹. The results indicate that the backbone structures of PAni microstructures were obtained by the aniline/ β -CD complex polymerization method. The FTIR analysis demonstrates the successful polymerization into the β -CD cavity.

UV-vis absorption spectra of PAni microstructures dispersed in deionized water are shown in Figure 3b. The peaks at around 263 and 286 nm are attributed to the $\pi - \pi^*$ transition of PAni nanofiber and nanoparticle, respectively. The band at 375 nm is assigned to the transition from the valence band to the antibonding

⁽²⁵⁾ Schillen, K.; Brown, W.; Johnsen, R. M. Macromolecules 1994, 27, 4825-4832

⁽²⁷⁾ Lu, F. L.; Wudl, F.; Nowak, M.; Heeger, A. J. J. Am. Chem. Soc. 1986, 108, 8311-8313.

⁽²⁸⁾ Trchova, M.; Sedenkova, I.; Tobolkova, E.; Stejskal, J. Polym. Degrad. Stab. 2004, 86, 179-185.



Figure 4. WAXD pattern of PAni nanoparticles and nanorods were prepared from composition A.

polaron state. The absorption band of the PAni quinoid unit at 540 nm indicates that HCl-doped PAni products are in their conducting form (i.e., the emeraldine form of PAni) and is lower than that obtained by either chemical or electrochemical methods. The typical absorption of PAni emeraldine form maximum at 630 nm is completely shifted to the lower wavelength. This shift can be attributed to sometimes competing factors and PAni threaded by β -CDs. Both a change in the dielectric constant of the chain's surroundings and a deformation of the chain backbone may cause such changes in the spectrum. The observed shift in the spectrum might be the included molecule is in a different environment as compared to the molecule in pure solution. Cyclodextrin molecules are threaded with conducting polymer backbones, resulting in the pseudopolyrotaxanes.^{20,29} Pseudopolyrotaxanes are expected to exhibit different chemical, electrical, and optical properties compared to the base polymer because their chromophores were surrounded by a macrocyclic ring. Moreover, addition of FeCl₃ to polymer solution also may contribute to shorter wavelength due to charge transfer from the benzenoid to quinoid unit of PAni. This shift may be attributed to the complexation of Fe³⁺ with PAni molecular chain in a water medium.³⁰ The red shift of the polaron transition band from 532 to 539 nm is due to the longer conjugation length in the oriented PAni microsize fibers compared to the spheres. WAXD patterns for PAni samples synthesized with or without additive FeCl₃ are given in Figure 4, nanorods and nanosphere, respectively. The WAXD result proves the primarily amorphous character of the sticks. Some diffraction peaks at $2\theta = 3.2^{\circ}, 4.4^{\circ}, 7.4^{\circ}, 8.5^{\circ}, 11.6^{\circ}, 13.4^{\circ},$ and 14.1° are observed from the nanorods synthesized in the presence of the FeCl₃ as the additives, which are similar to that of PAni nanofibers oxidized by FeCl₃·6H₂O.³¹ The polyaniline nanorods have sharp lower angle peaks at $2\theta = 3.2^{\circ}$ and at $2\theta =$ 7.4°. These peaks are assigned to layered structural organization of polyaniline chains followed by the interdigitations and crystallization of the dopant tails on the comb-shaped polyaniline chains.³² Besides these peaks, there are broad peaks around 13.4° and 14.1°, which are ascribed to aromatic $\pi - \pi$ interactions between stacks of phenylene rings present in the polymer chains and may be ascribed to the periodicity parallel to the polymer chain.² For nanofibers, the lower angle peaks are very sharp, and the amorphous hollow region is very much suppressed with respect to higher crystallinity than nanosphere. The WAXD results show that the crystallinity of the nanofibers is higher than that without using FeCl₃ due to a low polymerization rate caused by adding inorganic salts as the additives. Besides, no peaks corresponding to aniline monomer were observed. Additionally, NMR analysis authenticated that PAni covered by β -CD due to guest-host complex formation between PAni and β -CD. The ¹H NMR spectrum (in DMSO- d_6) of the PAni is given in Figure S6 (Supporting Information). The multiplet signal at 6.9–7.5 ppm can be assigned to aromatic, and the singlet at 4.8 ppm is attributed to -NH- protons of PAni. The signals positioned at 5.65-5.8 ppm (O2-H, O3-H), 4.45-4.55 ppm (O6-H), and 3.0-4.0 ppm (C3-H, C6-H, C5-H, C2-H, and C4-H) are from β -CD. This may occur due to the aniline polymerized inside the β -CD cavity. ¹H NMR, FT-IR, and WAXD results also support that β -CD remains in the polymer, suggesting that encapsulation of the polymer chains occurs and polypseudorotaxane architecture is formed.

Furthermore, TEM was used to investigate the influence of FeCl₃ on the formation of PAni nanostructures; TEM micrographs of the PAni sample (7.2 mM β -CD, composition A) synthesized with or without FeCl₃ salt are shown in parts a and b of Figure 5, nanorods and nanosphere, respectively. Its corresponding SEM image is given in Figure S7 (Supporting Information), which resembled previously reported sea urchin structures.³³ TEM images of the PAni in the presence of FeCl₃ clearly show that the PAni exhibits the shape of "hairy urchin", and the surface is covered with nanospikes. The "hairy urchins" at low concentration of β -CD exhibit monodispersion, with a size distribution about 40 nm. On the other hand, globular spherical PAni structures were observed in the absence of FeCl₃ with a size distribution about 130 nm.

Electronic Transport Behavior. To investigate the electronic transport behavior of the material, the resistance of the material was measured by impedance spectroscopy. Figure 6 shows the typical impedance (Z = Z' + jZ'') plane plots between real (Z')and imaginary (Z'') parts of the impedance for pure PAni nanoparticles and PAni nanofiber samples. The impedance spectra of PAni nanoparticles shows a semicircle at high frequencies with an ohmic resistance of 152 Ω cm² (intercept on X axis (Z') normalized per unit area), while that of PAni nanorod is $18 \,\Omega \,\mathrm{cm}^2$ (intercept on X-axis (Z') axis normalized per unit area). Previously, it has been reported that in NMP plasticized PAni films, the peak at higher frequency to the relaxation of the phase with reduced repeat unit. It was also observed that the resistivity of the reduced repeat units is lower than that of the oxidized repeat units.^{34,35} On this basis it has been suggested that the arc at high frequency with low value of resistivity is due to the conductivity relaxation of the reduced repeat units, and the large arc at low frequency having high value of resistivity is because of the relaxation of the oxidized repeat units.³⁶A comprehensive decrease in the size of impedance plane plots has been observed with the FeCl₃ presence in PAni nanofibers. This decrease in the impedance can be attributed to the charge transfer between PAni and excess FeCl₃. With the amplification of frequency the imine

⁽²⁹⁾ Van den Boogaard, M. Ph.D. Thesis, University of Groningen, 2003.

⁽³⁰⁾ Yang, C.; Chen, C. Synth. Met. 2005, 153, 133-136.

 ⁽³¹⁾ Zhang, L.; Wan, M.; Wei, Y. *Macromol. Rapid Commun.* 2006, 27, 366–371.
(32) Dufour, B.; Rannou, P.; Fedorko, P.; Djurado, D.; Travers, J. P.; Pron, A. *Chem. Mater.* 2001, *13*, 4032–4040.

⁽³³⁾ Li, Y.; Wang, B.; Feng, W. Synth. Met. 2009, 159, 1597-1602

⁽³⁴⁾ Lee, H. T.; Chuang, K. R.; Chen, S. A.; Wei, P. K.; Hsu, J. H.; Fann, W. Macromolecules 1995, 28, 7645–7652.

⁽³⁵⁾ Calleja, R. D.; Matveeva, E. S.; Parkhutik, V. P. J. Non-Cryst. Solids 1995, 180, 260-265.

⁽³⁶⁾ Afzal, A. B.; Akhtar, M. J.; Nadeem, M.; Ahmed, M.; Hassan, M. M.; Yasin, T.; Mehmood, M. J. Phys. D: Appl. Phys. **2009**, 42, 015411–015418.



Figure 5. TEM images of PAni nanorods (a) and nanoparticles (b) were prepared through the chemical polymerization of the corresponding monomer complex (β -CD and aniline are equal moles) composition A.



Figure 6. Electrochemical impedance spectra of nanorods (a) and nanoparticles (b) were obtained from composition A.

nitrogen of PAni may donate electrons to FeCl₃. Consequently, the ferric ions become negatively charged, whereas PAni chains become more positively charged. Therefore, the electrical conductivity of PAni nanofiber significantly increases compared with that of PAni nanoparticles. Both resistances are in good agreement with the observed behavior in the morphological view. The impedance behavior of the PAni nanofiber is higher than that of PAni nanoparticles due to their dendritic structure with high charge conductivity along the fiber nature. However, a more detailed analysis requires an elaborate model and a full mathematical treatment, which is currently in progress. Similarly conducting nanomaterials are expected to show strong correlation between the solid state ordering (morphology) and the electronic properties. To study the effect of FeCl₃-assisted self-organization on the electrical conductivity, the samples were subjected to conductivity measurements for compressed pellets and used the following equation

Conductivity (S cm⁻¹) =
$$\frac{\text{Thickness (cm)}}{\text{Resistance }(R) \times \text{Area (cm2)}}$$
 (1)





Figure 7. TEM image of PAni nanorods prepared from (a) 9, (b) 10.8, and (c) 12.6 mmol of β -CD in the presence of FeCl₃.

where R was derived from the low intersect of the high frequency semicircle on a complex impedance plane with the Z' (real) axis (see Figure 6). The difference in conductance among the samples was correlated to the difference in morphology. The sample showed a higher order fiber nature and has high conductivity, whereas nanoparticles sample has 3 orders less conductance than ordered structures.

To study the effect of β -CD concentration on the fabrication of PAni, the weight ratio of β -CD relative to aniline was varied from 7.2 to 12.6 mmol and the change in morphologies are as shown in

Article

Article

Figure 7. Figure 7a shows the "hairy urchin"-like nanostructure of PAni, and the surface is covered with low nanospikes with preferential growth along certain directions. The "hairy urchin"like nanostructure of PAni was collected at the low concentration of β -CD and exhibited fair monodispersion, having a size distribution about 40 nm. In higher concentration of β -CD, the structures of PAni nanomaterials were changed from hairy urchin to irregular branched nanorod as shown in Figure 7b. On increasing β -CD concentration irregular nanorods shape changed to regular lengthy nanorod (Figure 7c) and similarly the β -CD



Figure 8. TEM image of PAni nanosphere prepared from (a) 9, (b) 10.8, and (c) 12.6 mmol of β -CD in the absence of FeCl₃.

influence on the morphology in PAni absence of FeCl₃. Figure 8a represents PAni in the absence of FeCl₃; the sample presented chainlike aggregates made up of a large number of small globular particles with a mean diameter of about 75 nm. These particles seem to interact and form branched structures obtained at higher concentration β -CD (Figure 8b). Wire-shaped aggregates were also observed (Figure 8c), and most of them appear to have a somewhat regular shape with a slightly multilateral outer profile, whereas their diameters range from 70 to 200 nm. Moreover, most of discoidal particles are overlapped through their edges. These discoidal particles interact through their surfaces, although they could merge completely in a homogeneous aggregate. This behavior may be consistent with the suggestion that the aggregates are made up of excess β -CD molecules and its complexes arranged in a columnar configuration, aniline block encapsulated by β -CDs, neighboring Ani/ β -CD complex molecules would form intermolecular hydrogen bonds between β -CDs threaded along PAni chains as proposed for β -cyclodextrin.^{37,38} This kind of structure for β -CD and its complex self-assembled aggregates in water would imply a rearrangement of the channel structure into a cage structure.

On the basis of the above experimental results, a tentative growth mechanism for the PAni nanostructures obtained at various molar ratios of β -CD to aniline is illustrated in Figure 9. The aqueous solution of the Ani/ β -CD complex is instinctively entered into the aqueous core of the micelles due to its hydrophilicity nature of complex. Resulting PAni/ β -CD complex molecules surrounded inside the micelles. In this case, the specific adsorption of the PAni/ β -CD inclusion complexes inside of the micelle core could considerably contribute to the formation of the PAni nanostructures. When the β -CD concentration to aniline was fixed at 7.2 mM (1:1), more β -CD and inclusion complexes on the micelle surfaces were replaced by the PAni/ β -CD inclusion complexes, which may lead to a delicate balance between the diffusion rate and the reaction rate under nonequilibrium conditions, thus favoring the formation of the "hairy urchin"-like nanostructure of PAni. If the β -CD to aniline molar ratio was increased to 1.25, inclusion complex would easily form between polyaniline and β -CD via the host-guest interaction, and the formed PAni/ β -CD complexes would replace more DoTAC molecules to adsorb on the micelle surfaces; it may be attributed to form "hairy urchin"-like nanostructure of PAni with preferential growth along specific directions. At a β -CD to aniline molar ratio of 1.5, branched particles were obtained, which could be ascribed to the weaker protection of the mixed adsorption of the



Figure 9. Schematic illustration of the formation of PAni nanostructures.

aniline molecules and the PAni/ β -CD complexes on specific surfaces of micelles. On further increasing the β -CD to aniline molar ratio to 1.75, rodlike particles became the predominant product, which could be partially attributed to the more effective capping of β -CD molecules to prevent further growth of PAni due to the high concentration of free β -CD in solution. Nevertheless, a detailed investigation on the structure of PAni/ β -CD inclusion complexes and the interaction between the PAni/ β -CD inclusion complexes in the presence of micelle solutions is needed to fully illuminate the formation mechanism of the unique PAni nanodendrites, which is currently in progress in our lab.

Conclusion

The PAni nanorod and nanosphere were synthesized selectively using β -CD-mediated microemulsion polymerization by using β -CDs as molecular host component. PAni nanorods were fabricated by using a sphere-to-cylinder micelle transformation process with the presence of FeCl₃ as a structure-directing agent. The rodlike micelle phase was developed through a cooperative interaction between aqueous FeCl₃ solution and aniline in an aqueous medium with β -CD. The DoTAC rodlike micelle template in the presence of β -CD was demonstrated as an efficient tool to architect conducting PAni nanorod. Average particle size of the PAni nanometerials was controlled by the amount of β -CD used to form an inclusion complex, and the impedance behavior of the PAni nanofiber is exceeding that of PAni nanoparticles caused by their dendritic structure with high charge conductivity along the fiber nature.

Acknowledgment. The authors thank the National Science Council of the Taiwan for financially supporting this research under Contract NSC 98-2923-M-011-002-MY2.

Supporting Information Available: Figure S1, wide-angle X-ray diffraction patterns of β -CD/aniline complex; Figure S2, FT-IR spectra of β -CD and β -CD/aniline complex; Figure S3, POM micrograph of the DoTAC rodlike micelle phase; Figure S4, CLSM image of the DoTAC rodlike micelle phase; Figure S5, micelle size calculation; Figure S6, ¹H NMR spectra of β -CD/PAni complex; Figure S7, SEM image of the PAni hairy urchin-like structure and spheres. This material is available free of charge via the Internet at http://pubs.acs.org.

⁽³⁷⁾ Hunt, M. A.; Rusa, C. C.; Tonelli, A. E.; Balik, C. M. Carbohydr. Res. 2005, 340, 1631–1637.

⁽³⁸⁾ Becheri, A.; Lo Nostro, P.; Ninham, B. W.; Baglioni, P. J. Phys. Chem. B 2003, 107, 3979–3987.