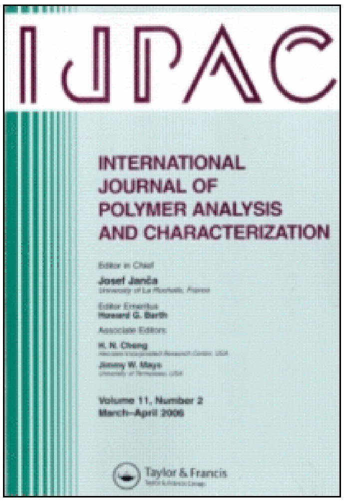

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Branched Fibers of Conducting Polypyrrole: Synthesis and Characterization

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Abstract: Three-dimensional network of branched fibers of conducting polypyrrole was synthesized by interfacial polymerization method in the presence of sulfonated β-cyclodextrin (SβCD) as the dopant. A high surface area of open-pore polypyrrole structure was obtained with the aid of SβCD, and the incorporation of SβCD units into the polypyrrole fibers was confirmed during the interfacial chemical polymerization. The effect of synthesis conditions such as the concentration of SβCD in the polymerization media, the type of oxidant, the reaction temperature, and the electrical properties of polypyrrole-SβCD was investigated. It was found that the concentration of SβCD strongly affects the morphology. The resulting polymer was characterized with SEM, UV-vis spectroscopy, FT-IR, EDAX, and ESCA measurements.

Keywords: Conducting polymer; Interfacial chemical polymerization; Polypyrrole; Sulfonated β-cyclodextrine

INTRODUCTION

Conducting polymers have attracted the interest of many researchers. The properties of these polymers have led to their use in various applications, such as sensors,[1,2] storage devices,[3] and microelectronics.[4,5]

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Conducting polymers could be an excellent choice as molecular wires due to their metal-like conductivity.[6,7] For instance, it was reported that poly(pyrrole), poly(3-methylthiophene) and polyaniline were synthesized by template synthesis[8–10] and self-assembly[11–14] with regular fibular morphologies, and these materials exhibited greater conductive properties. Submicrometer-sized tube junctions and dendrites of conducting polyaniline and polypyrrole were also synthesized through a self-assembly process.[11] Synthesis of polypyrrole fibers was carried out both chemically and electrochemically using templates such as alumina,[15] polycarbonate,[16] zeolite,[17] surfactants,[18] and self-assembled colloids.[19,20] A lamellar-structure crystalline polypyrrole supramolecular assembly was also prepared by surfactant templating.[21] When surfactant template is used, the micelles have been utilized as reactors and thus the spherical particles, microtubes, or fiber structures can be formed. The morphological transition of polypyrrole nanoparticles into fibers occurred over a critical micelle concentration.

Recently, Kaner and coworkers reported a chemical route to synthesize fibers under ambient conditions using aqueous/organic interfacial polymerization.[22,23] It is also important to produce large quantities of polymer, but by-products separation is needed to remove them from the product. In interfacial polymerization, the polymerization reaction is accomplished in an immiscible organic/aqueous two-phase system in which the water phase contains the conducting polymer, and the organic layer contains low molecular weight oligomers. The conducting polymer can be easily obtained from the aqueous phase. It was reported that the shape and size of the fiber does not appear to be affected by the solvent such as benzene, hexane, toluene, or carbon tetrachloride.[23,24]

Cyclodextrin (CD) cyclic oligosaccharides are used as complexing agents.[25] It is proven that CDs are good candidates for increasing the aqueous solubility of molecular templates.[26] There is considerable interest in the synthesis of conducting polymers by using CDs. Polymer films of CDs were prepared electrochemically on glassy carbon and platinum electrode using a pyrrole-derivatized CD. They can be also used as molecular templates.[26] Polypyrrole and polyaniline films were prepared electrochemically in β-CD templates.[27] In the design of selective electrodes, CDs have been used as host molecules.[28,29] The modified electrode showed molecular recognition for phenothiazine and naphthalene disulfonate.[30,31] Temsamami et al.[32] have reported the electrochemical synthesis of polymer films from pyrrole and sulfonated β-cyclodextrin complex. The electrochemical synthesis of polypyrrole/β-cyclodextrin film at a glassy carbon electrode has also been reported.[33] In the presence of sulfopropyl ether of β-cyclodextrin as a dopant, the ordered conducting polypyrrole was synthesized by chemical and electrochemical methods.[34] The role of 2,6-dimethyl-β-cyclodextrin molecules in the electrochemical polymerization of pyrrole and a simple electropolymerization of 1:1 mixture of γ-cyclodextrin and pyrrole monomer were also achieved in aqueous solution.[35]

In this article, the preparation of a three-dimensional network of branched fibers of a conducting polypyrrole network doped with sulfonated β-cyclodextrin through the interface polymerization process is reported for the first time. A high surface area of open-pore polypyrrole structure was obtained with the aid of SβCD, and the incorporation of SβCD units into the polypyrrole fibers was achieved during the interfacial chemical polymerization. The effect of the synthesis conditions on the morphology and electrical properties of the polypyrrole-SβCD (PPy-SβCD) three-dimensional network of fiber structure was investigated. The resulting polymer was characterized with SEM, UV-vis spectroscopy, FT-IR, EDAX, and ESCA measurements. The formation mechanism of network is also discussed.

EXPERIMENTAL SECTION

All chemicals were of analytical grade and used as received. SβCD as the dopant and ammonium persulfate and iron (III) chloride as the oxidant were used. Typically, the interfacial polymerization reaction was performed in a 50 mL beaker. The pyrrole monomer (100 mM) was dissolved in the organic phase (10 mL) toluene or carbon tetrachloride. Ammonium persulfate or iron (III) chloride was dissolved in 10 mL of 1 M $HClO_4$ acid solution. The SβCD concentration was studied in the range from 0.12 to 0.48 mM. In all reactions, the pyrrole-to-oxidant molar ratio was kept at 4:1. To remove the excess acid and by-products from the polymerization media, the obtained polypyrrole film was purified by filtration (Altech, nylon 66, 0,45 μm filter) and washed with distilled water and methanol several times. Dedoped PPy-SβCD film was obtained by washing with 15% NH_3 solution. The mixture was allowed to react for 1 h, and then dried in vacuum at room temperature for 24 h.

The morphologies of the PPy-SβCD films were examined by scanning electron microscopy (SEM). Scanning electron micrographs were obtained by a JSM-6400 electron microscope (JEOL), equipped with NORAN System 6 X-ray Microanalysis System and Semafore Digitizer. The Fourier transform-infrared (FT-IR) spectra of the polymer were obtained using a Bruker Vector 600 FT-IR spectrophotometer. Reduced polypyrrole-SβCD and polypyrrole-ClO_4^- dissolved in *N*-metyl-pyrrolidone solution and the absorption spectra were recorded with an UV-vis spectrophotometer (Spectronic). Electron spectroscopy for chemical analysis (ESCA) data were obtained using a Specs Esca (Berlin, Germany) system with a dual anode (Mg/Al) X-ray source and EA 200 hemispherical electrostatic energy analyzer equipped with multichannel detector (MCD) with 18 discrete channels. The X-ray beam was generated with a monochromatized Mg Kα source operated at 15 kV and 100 W, and the observed binding energies were calculated with reference to the saturated hydrocarbon peak at 284.6 eV.

The dry conductivity values were measured using a four-probe technique at room temperature. Gold-plate probes were used to avoid any errors that might arise from the ohmic contacts. At least 10 different measurements were used to calculate conductivity values. All data points reported in this work represent the average of three replicates. All conductivity experiments were run at room temperature.

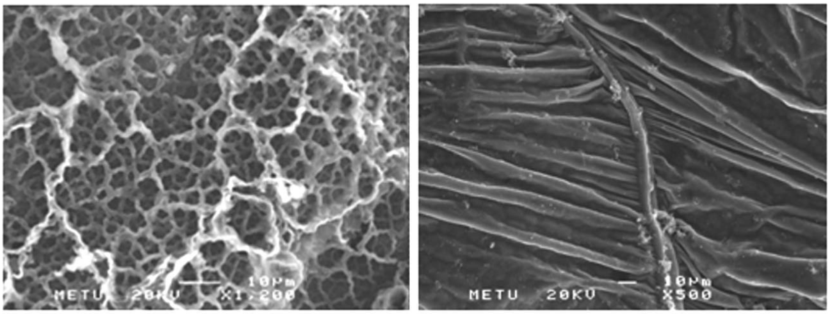
RESULTS AND DISCUSSION

Morphology

Recently, it is reported that the interfacial polymerization does not depend on any specific template or dopant and the quality/uniformity of the fibers seems to be affected only by acid concentration of the aqueous phase.[24] Interfacial polymerization of pyrrole resulted in blocks with a diameter about 200 nm and no tubular structures, and linear fibers were observed.[36] Surprisingly, however, we observed substantial effect of SβCD anion dissolved in the aqueous phase of interfacial polymerization.

The morphologies of PPy films obtained in the presence and in the absence of SβCD were found to be quite different. Figure 1 exhibits SEM images for the resulting PPy films prepared from interfacial polymerization process doped with SβCD and ClO_4^- anion, respectively. Figure 1(a) shows clearly the formation of a continuous 3-D network of branched segments, while the PPy prepared in the absence of SβCD anion resulted only in wrinkled texture, as shown in Figure 1(b). In general, wrinkled texture was observed in nonaqueous synthesis media.[37,38] This indicates that the morphology of synthesized PPy is strongly affected by SβCD. Highly uniform fibers are observed in samples prepared from the interfacial polymerization. The morphology of the films was also unaffected when the dopant was removed.

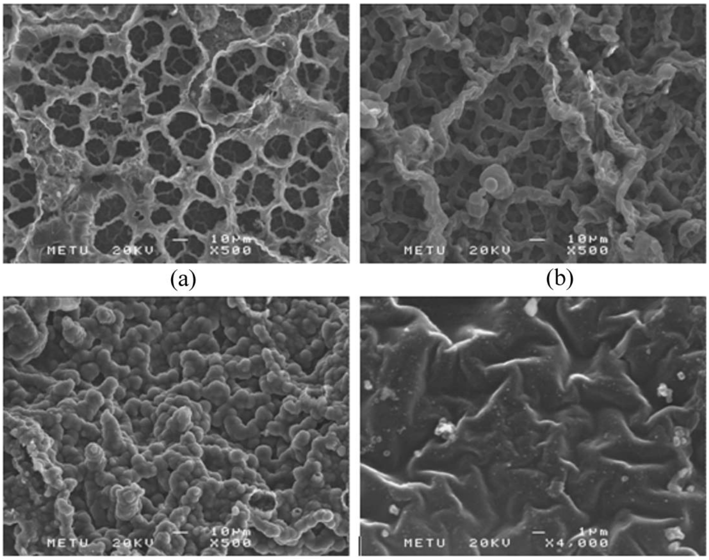
In order to find the optimal polymerization conditions, synthesis conditions of PPy-SβCD film were investigated. For instance, different molar ratios of pyrrole to SβCD monomer (pyrrole/SβCD = 833:1, 416:1, 277:1, and 208:1) were used under the same concentration of pyrrole monomer (100 mM). The uniformity of the fibers seems to be



(a) (b)

Figure 1. SEM images of (a) PPy-SβCD and (b) PPy-ClO_4^- synthesized via interfacial polymerization method.

substantially affected by SβCD concentration of the aqueous phase, as shown in Figure 2. When the pyrrole/SβCD ratio changed from 833 to 208, the open-pore structure formation was enhanced. The pyrrole/SβCD ratio is about 277, as shown in Figure 2(b). However, as can be seen in Figure 2(c), with the increase of SβCD anion, granular morphology was observed, and finally, when PPy-SβCD ratio reached



(a) (b) (c) (d)

Figure 2. SEM images of PPy-SβCD synthesized under different concentrations of SβCD: (a) 0.12 mm; (b) 0.24 mM; (c) 0.36 mM; and (d) 0.48 mM.

200, wrinkled texture took the place of open-pore structure of PPy-SβCD film. These results suggest that the pyrrole/SβCD ratio of about 400 is favorable for the formation of fiber structures when the interfacial polymerization is performed at room temperature.

Since the interfacial polymerization is performed in an aqueous/organic biphase system, before oxidation polymerization, SβCD and pyrrole are dissolved in water and in toluene, respectively. When the oxidant (persulfate) was added to the reaction solution, the polymerization started and took place at the water/toluene interface because the oxidant persulfate is water soluble. SβCD anion can self-assemble at the water/toluene interface due to its SβCD amphiphilic characteristics (hydrophilic-SO_3H group and hydrophobic O–C–O). At the interface, pyrrolium cation and SβCD anion may form a double layer, and the free pyrrolium can diffuse into the hydrophobic part of SβCD to form inclusion supramolecular complex. Formed supramolecular complexes may act as the templates in the formation of PPy/SβCD fibers.

We also performed interfacial polymerization in a water/carbon tetrachloride biphasic system. To investigate the surface morphology, the same experimental procedure was carried out. When the PPy-SβCD ratio changed from 833 to 208, the formation of 3-D network of polypyrrole fiber was again observed. It was found that the morphology of PPy-SβCD was strongly affected by the reaction temperature. When the reaction temperature was 20°C and PPy-SβCD ratio was 833 in toluene-water interfacial polymerization medium, wrinkled texture was observed. However, if the interfacial polymerization is performed at about 4°C the open-pore structure of polymer is again obtained. To investigate the effect of oxidant, the interfacial polymerization was also performed using $FeCl_3$ as oxidant. We observed the same network of polypyrrole as the PPy-SβCD ratio changed. In constrast, the granular morphology was observed in the reference experiment when ClO_4^- anion was used as dopant instead of SβCD anion.

Structural Characterization and Conductivity

The UV-vis spectra of reduced PPy-SβCD and PPy-ClO_4^- dissolved in *N*-methylpyrrolidone solution are shown in Figure 3. The PPy film synthesized with ClO_4^- anion in the reduced state shows an absorption band around 330 nm, which is attributed to the $\pi - \pi^*$ transition of the pyrrole moiety. It shows a broad absorption band around 830 nm, which is due to the bipolaron excitations.[35] In the reduced state, PPy-SβCD film shows an absorption band with a maximum at 370 nm, which is attributed to the $\pi - \pi^*$ transition. The reduced form also shows absorption band around 880 nm. As a comparison, PPy-ClO_4^- film shows

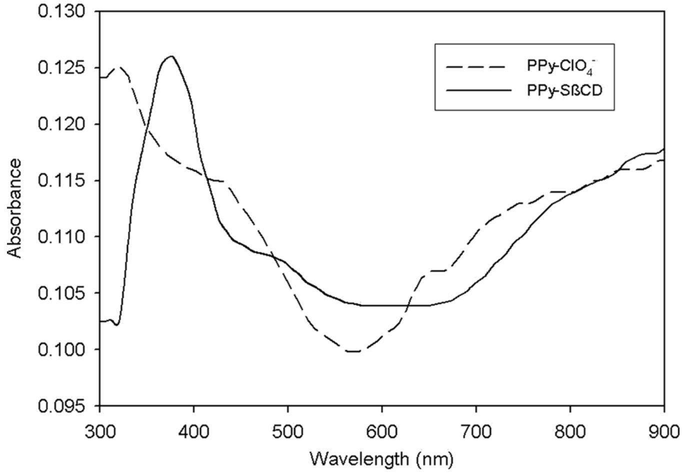


Figure 3. UV-vis spectra of reduced PPy-SβCD and PPy-ClO$_4^-$ dissolved in *N*-methylpyrrolidone solution.

red-shift upon addition of SβCD anion into the polymer matrix. The change in the spectra of PPy-ClO$_4^-$ and PPy-SβCD can be correlated to the amount of mobile charge carriers present in the system, and SβCD template results in growing polymer with longer conjugation length.[36]

To elucidate the presence of SβCD in chemically synthesized polymer film, FT-IR, energy dispersive X-ray (EDAX), and ESCA measurements of the reduced polymer film were performed. Characteristic infrared vibrations for PPy-ClO$_4^-$ and PPy-SβCD film are shown in Figure 4. Figure 4(a) shows the FT-IR spectrum of PPy-ClO$_4^-$. The bands at 1569 cm^{-1} and 1460 cm^{-1} are assigned to the typical polypyrrole ring vibrations. The C–H in-plane vibration and C–N stretching vibration appear at 1040 cm^{-1}. The band at 1188 cm^{-1} may be assigned to N–C stretching band.[39,40] Some typical characteristic absorption bands of PPy-ClO$_4^-$ were observed in the FT-IR spectrum of PPy/SβCD as shown in Figure 4(b). In the FT-IR spectrum of the PPy-SβCD film, the sulfate group in the chemical structure is demonstrated by the presence of the 1250 cm^{-1} and 1046 cm^{-1} bands, which are attributed to a symmmetric stretching vibrations of SO_2 and S–O, respectively.[41,42]

To obtain clear evidence of the presence of the SβCD in polymer films, we performed EDAX measurements on both pure PPy synthesized with ClO$_4^-$ and PPy synthesized with SβCD. Figure 5 represents the EDAX spectrum of the PPy synthesized with SβCD. It appears that the presence of a sulfur peak also confirms the incorporation of SβCD units into the polymer film during the chemical polymerization. We also confirmed the presence of SβCD group in the polymer network via this

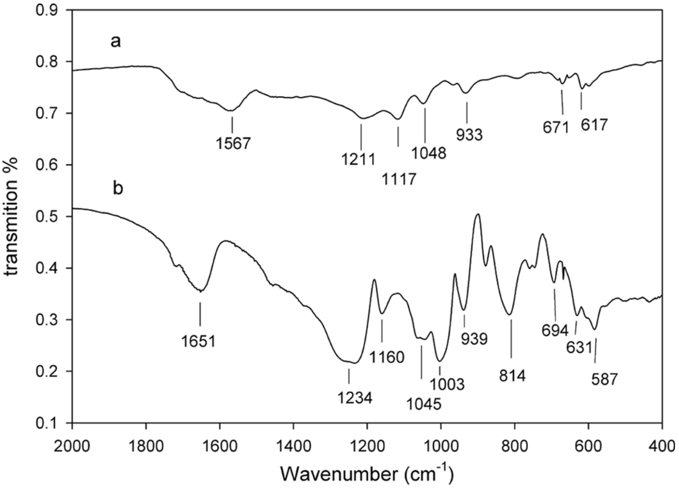


Figure 4. FT-IR spectra: (a) PPy-ClO_4^- and (b) PPy-SβCD.

interfacial polymerization method by ESCA. ESCA analysis indicates the presence of SβCD unit in the polymer matrix. The polypyrrole film synthesized with ClO_4^- anion contained carbon, oxygen, nitrogen, and chloride. The polypyrrole film synthesized with SβCD anion produced an additional peak attributed to the presence of sulfur. Wide-scan ESCA spectra for the reduced PPy-ClO_4^- and reduced PPy-SβCD film are given

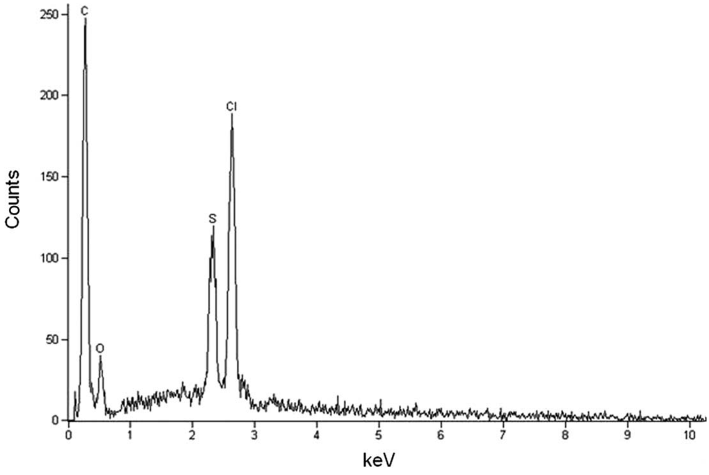
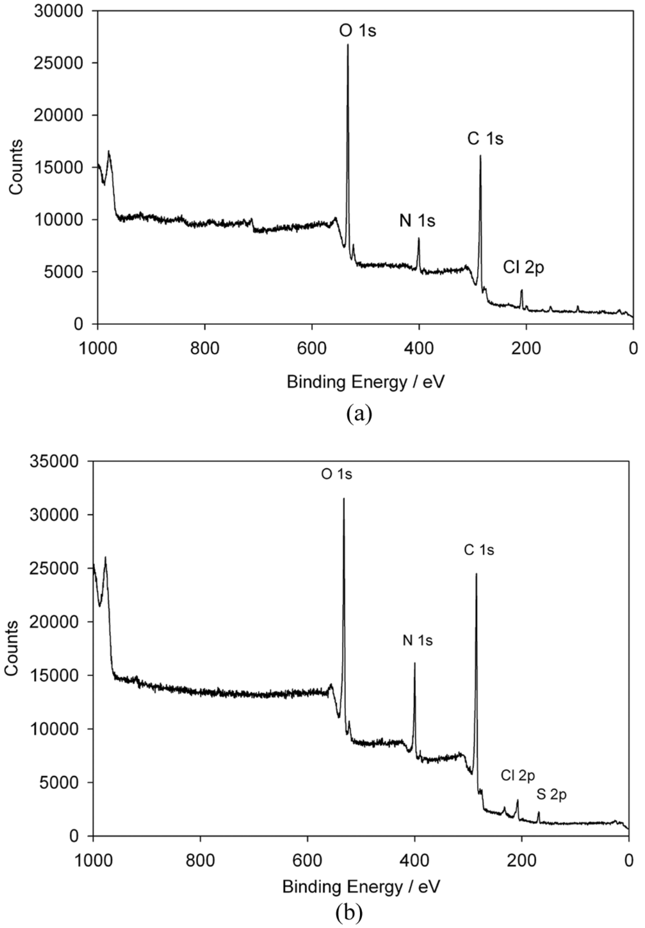


Figure 5. EDAX spectrum of PPy-SβCD polymer network.

in Figure 6, which clearly shows the presence of sulfur only in the reduced film surface of PPy-SβCD.

Dry conductivity values of PPy-SβCD films synthesized with different amounts of SβCD were also measured. The conductivities of PPy-SβCD film were between $2.9 \times 10^{-4}\,\mathrm{S \cdot cm^{-1}}$ and $1.5 \times 10^{-3}\,\mathrm{S \cdot cm^{-1}}$ depending on the initial SβCD concentration. The conductivity values increase with the incorporation of SβCD ring units into the polymeric structure, due to the increase of the doping level. For comparison, the room temperature conductivity value of PPy-$\mathrm{ClO_4^-}$ film was $2.7 \times 10^{-1}\,\mathrm{S \cdot cm^{-1}}$. The decrease in conductivity may be the consequence of a decrease in the number of charge carriers and conjugation length.[43,44]



(a)

(b)

Figure 6. Wide-scan ESCA spectra for (a) reduced PPy-$\mathrm{ClO_4^-}$ and (b) reduced PPy-SβCD film.

CONCLUSION

Three-dimensional network of branched fiber of polypyrrole was successfully synthesized through a self-assembly process in the presence of SβCD as the dopant. Substantial effect of SβCD anion dissolved in the aqueous phase of interfacial polymerization was observed. The micelles formed by SβCD and pyrrolium cations play the role of templates in the formation of open-pore structure of PPy-SβCD. The obtained open-pore structure polypyrrole may exhibit enhanced performance due to its high surface area, and SβCD functionalized three-dimensional network of branched fiber of polypyrrole could offer a wide potential range for developing smart materials such as sensors or support material for enantiomer separation. Studies showing the response to enantiomer separations of some drugs are in progress.

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