Ordered Conducting Polypyrrole Doped with Sulfopropyl Ether of β-Cyclodextrin

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Received March 22, 2002
Revised Manuscript Received August 4, 2002

Introduction. Cyclodextrins (CDs) are cyclic oligosaccharides built up from 1,4-glucopyranose units that exhibit a torus-shaped structure with a hydrophobic cavity and a hydrophilic exterior. They can form inclusion complexes only with guest molecules of the proper sizes.[1] This has led to considerable interest in using CDs in the synthesis of conducting polymers. It has been found that CDs bound to the electrode acted as molecular templates to restrict the growth sites of polypyrrole within the β-CDs cavities.[2] Inclusion compounds using CDs as host molecules have been used to electropolymerize some hydrophobic organic compounds in aqueous medium.[3] Sulfonates or organosulfonic acids have been widely used in in-situ doping polymerization to afford PPy with high conductivity and special morphology.[4,5] Gerard Bidan et al. have successfully immobilized sulfonated calixarenes into PPy film to make an ion-sensitive layer.[6] However, as far as we know, there has been no reports on the preparation of conducting polymer by using sulfonated cyclodextrin as a dopant, which in fact has a great impact on the properties of the resulting polymer. In this paper, we try to prepare polypyrrole doped with $CDSO_3$ because pyrrole is a very useful starting material to obtain conducting polymer. Besides, it has been reported that pyrrole can form a stable host−guest complex with CD, and after forming an inclusion complex, polypyrrole could be obtained as dark powder in the oxidized state by using ammonium peroxide sulfate as oxidant in aqueous medium.[7]

In this work, we report how to perform the chemical synthesis and electrosynthesis of PPy in the presence of $CDSO_3$ as a dopant. We carried out our study to explore the possibility of preparing well-ordered conducting polymer by choosing proper dopant and to see whether $CDSO_3$ with a hydrophobic cavity can induce self-assembly properties that allow molecular organization. The morphology and physicochemical properties of the prepared PPy−$CDSO_3$ samples were examined by means of transmission electron microscopy (TEM), scanning electron microscopy (SEM), UV−vis absorption and FT-IR absorption spectroscopies, thermogravimetric analysis (TGA), and conductivity measurements. We found thereby that $CDSO_3$ strongly affected the morphology, thermostability, and conductivity of PPy. Moreover, the effects of $CDSO_3$ in the polymerization on the physical properties and molecular structure of PPy are discussed.

Experimental Section. Pyrrole was purified by distillation before use. $CDSO_3$ was prepared according to the reported method.[8] Ammonium peroxide sulfate (A.R.) was used as received.

The PPy−$CDSO_3$ was prepared by adding 0.036 mol of pyrrole to 0.18 mol of $CDSO_3$ in 20 mL of deionized water under ultrasonic stirring. 20 mL of 0.36 M ammonium peroxide sulfate solution was then added into the above mixture under magnetic stirring. The polymerization was continued for about 24 h in ice bath to limit the dissociation of the inclusion complex. The resulted solution was poured into a sufficient amount of water to wash out the remaining $CDSO_3$ and ammonium peroxide sulfate. Finally, the precipitate was collected and dried under a vacuum atmosphere for more than 48 h.

Electrochemical polymerization was performed in a one-compartment three-electrode cell with the use of a PARC M273 potentiostat under the control of a computer at room temperature. The electrosynthesized PPy films were obtained by galvanostatic method in a current 1 mA cm^{-2} using a gold plate as working electrode and a stainless steel plate as counter electrode. An Ag/AgCl (0.1 M KCl) electrode was used as reference electrode. The synthesis system consisted of 0.1 M pyrrole and 0.1 M $CDSO_3$ in deionized water.

The conductivity of PPy was measured by using the standard four-probe method. FT-IR spectra were measured on an IFS 66V vacuum FTIR spectrophotometer. All spectra were taken from KBr pellets and with 4 cm^{-1} resolutiom. The morphology of PPy was examined on an X-650 scanning electron microscope or a JEM-200CX transmission electron microscope. UV−vis spectra of PPy in *m*-cresol were recorded on an UV-240 spectrometer (Shimadzu, Japan). Elemental analysis was taken on a Perkin-Elmer 240C elemental analysis apparatus. Wide-angle X-ray diffraction was taken with a Rigaku d/Max-Ra diffractometer using Ni-filtered Cu Kα radiation. A SDT 2960 thermogravimetric analyzer investigated thermal stability of the PPy with nitrogen as pure gas at a flow rate of 50 mL/min. The heating rate was 10 °C/min.

Results and Discussion. The morphologies of PPy samples prepared in the presence and in the absence of $CDSO_3$ successively are quite different. Figure 1 represents TEM micrographs for the resulting PPy samples prepared from chemical polymerization and SEM micrographs for the electrosynthesized PPy doped with $CDSO_3$ and $NaBF_4$, respectively. Figure 1a shows clearly the formation of polymeric tubules of outer diameter equaling about 200 nm and internal diameter equaling 50−60 nm, while the PPy prepared in the absence of $CDSO_3$ only resulted in a spherical morphology, as shown in Figure 1b. In our experiment, both the films of PPy electropolymerized in aqueous medium have a thickness of about 20 μm. The PPy film doped with $CDSO_3$ has a better ordering surface structure than that doped with $NaBF_4$. As shown in Figure 1c,d, the former has a relatively flat and compact surface with stripes about 200 nm in width while the latter only has a rough and irregular globular surface. This indicates that the morphology of synthesized PPy is strongly affected by $CDSO_3$.

The mechanism of oxidative polymerization of pyrrole may be described as follows: a neutral pyrrole monomer yields upon its oxidation cation radical species, which then recombine, yielding consecutively a dihydro dimer dication as an intermediate product, and after its disproportionation, a neutral bipyrrole molecule. The bipyrrole molecule undergoes further oxidation, recombination, and deprotonation steps, leading to PPy as the end product of oxidative polymer.[9] In our work, however,

10.1021/ma025521g CCC: $25.00
Published on Web 12/28/2002

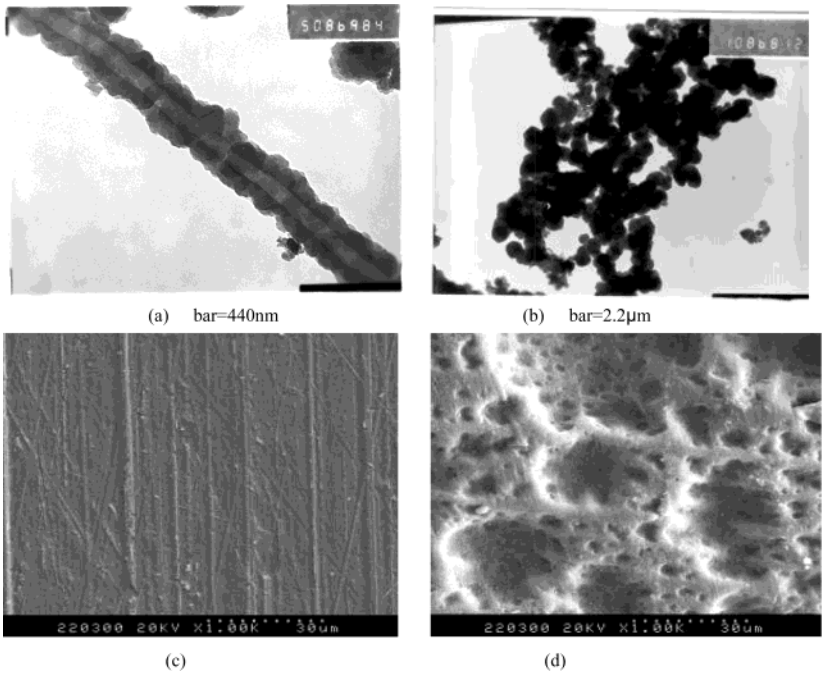


Figure 1. Typical TEM image of the PPy nanotube prepared in the presence of $CDSO_3$ (a), PPy particles prepared in the absence of $CDSO_3$ (b), and typical SEM image of the electrosynthesized PPy−$CDSO_3$ (c), and PPy doped by $NaBF_4$ (d).

although the original monomer was the pyrrole−$CDSO_3$ inclusion complex, the produced cation radical was not associated with the cyclodextrin and was rapidly expelled from the host after its formation.[10] The mechanism suggested in this work is different to what mentioned above only in the expelling of pyrrole cation radical from $CDSO_3$; however, $CDSO_3$ also can be threaded on the PPy backbone since it is possible for $CDSO_3$ to form an inclusion complex with pyrrole dimer or trimer.[11]

The structure of PPy−$CDSO_3$ was characterized by UV−vis and FT-IR spectroscopies. Because PPy samples oxidized by ammonium peroxide sulfate in aqueous medium had some solubility in *m*-cresol, UV−vis spectra were recorded in *m*-cresol solution at room temperature. PPy−$CDSO_3$ exhibits a more intense absorption band at 461 nm which is a characteristic absorption band of PPy, corresponding to $\pi-\pi^*$ transition.[12] Compared with the PPy sample synthesized in the absence of $CDSO_3$, this band has a red shift from 455 to 461 nm. That means PPy−$CDSO_3$ has a better coplanar characteristic. This phenomenon suggests that the existence of $CDSO_3$ could introduce ordering structure in the material. The FT-IR spectra of the resulting PPy−$CDSO_3$ in both the doped state and the reduced state, as shown in Figure 2, are similar to that of PPy formed in the absence of $CDSO_3$. But the peak at 1637 cm^{-1} suggests the existence of $CDSO_3$. On the other hand, the lack of a peak at 1261 cm^{-1} indicates the stronger coplanar characteristic of the pyrrole units in the PPy−$CDSO_3$.[13] This is in accordance with the result of UV−vis spectra. The good coplanar structure of PPy−$CDSO_3$ may be attributed to the formation of an inclusion complex consisting of $CDSO_3$ and pyrrole, which decreases the defect in the PPy main chain by including the monomer into the cyclodextrin cavity, leading to less β-position overoxidation of the pyrrole ring. That is, although pyrrole and $CDSO_3$ are likely to separate from each other after forming pyrrole oxidation cation radical species, the existence of the pyrrole−$CDSO_3$ inclusion complex can introduce self-assembly properties that allow molecular organization during the polymerization. Preliminary X-ray experiments were also performed. The results indicate that there is no microcrystallinity for PPy−$CDSO_3$. However, the intensity of the broad peaks at 24.3° and 12.4° is stronger than the corresponding PPy samples prepared in the absence of $CDSO_3$, which also indicates better structure ordering in PPy−$CDSO_3$.[14]

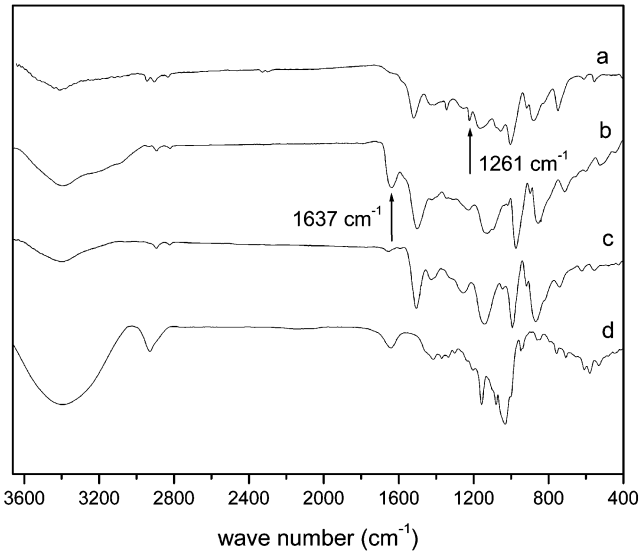
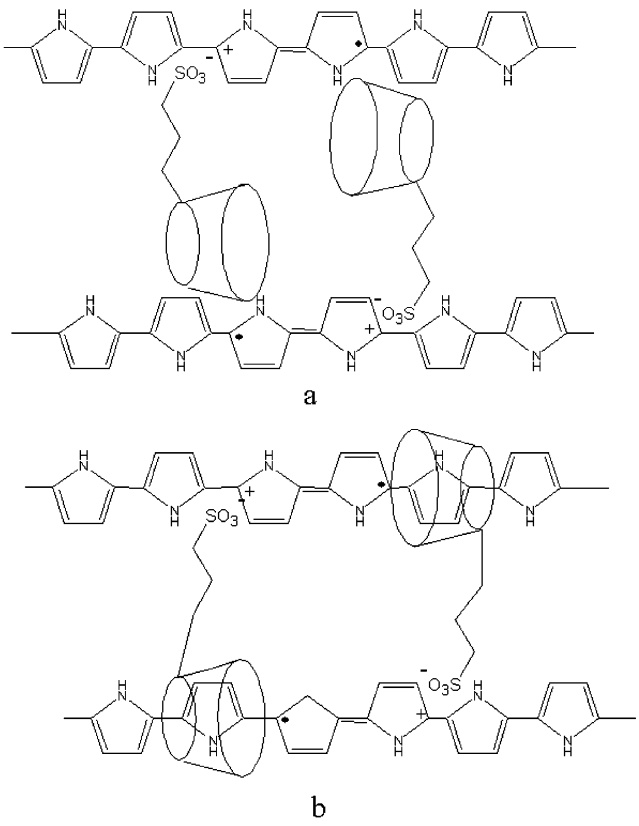


Figure 2. FT-IR spectra of the of chemical synthesized PPy in the absence of $CDSO_3$ (a), PPy−$CDSO_3$ (b), PPy−$CDSO_3$ after reduction (c), and $CDSO_3$ (d).

To get rid of the $CDSO_3$ absorbed in PPy backbone, the PPy−$CDSO_3$ sample was extracted by water in an extractor for 3 days. The FT-IR spectrum of the resulting polymer is the same as that of the original sample. This result indicates $CDSO_3$ is compactly combined with PPy backbone. Besides acting as doping anions, some $CDSO_3$ molecules include the PPy chain into their cavities. Accordingly, a possible structure of the PPy−$CDSO_3$ could be thought of as illustrated in Scheme 1.

Scheme 1. Possible Structure of the PPy−$CDSO_3$: (a) $CDSO_3$ Acts as Dopant in PPy Backbone; (b) $CDSO_3$ Threaded on the PPy Backbone Besides Acting as Dopant



The amount of $CDSO_3$ inserted in PPy was determined by elemental analysis. The doping lever assigned as [S]/[N] is about 0.25, which is among the normal range.[4] However, the PPy−$CDSO_3$ sample in the reduced state has a [S]/[N] value of about 0.05. This indicates that about 20% dopant is threaded on the PPy backbone.

The spatial order in conducting polymer is determined by the order of the polymer backbone, dopant anion, and their mutual interaction. The process of charge conduction in conducting polymer is affected by interchain parking. The counterion is indispensable for charge compensation of conducting PPys, and at the same time, the size, shape, and structure of the counterion are expected to influence the electrical conductivity.[15] In our work, the conductivities of PPy−$CDSO_3$ samples at room temperature are in the range from 0.21 to 2.02 S cm^{-1}, which are higher than those of the corresponding PPy samples prepared in the absence of $CDSO_3$ (with conductivities in the range from 0.05 to 0.20 S cm^{-1}). It has been reported that sulfonates can introduce a short-range order in PPy backbone.[15] This indicates that better ordering in PPy backbone is favorable for the interchain charge transition.

The thermogravimetric curve of PPy−$CDSO_3$ is shown in Figure 3, and PPy synthesized in the absence of $CDSO_3$ is compared. The PPy−$CDSO_3$ sample suffers only about 60% loss of its original weight when heated from room temperature to a temperature as high as 1000 °C in nitrogen. The thermogravimetric analysis

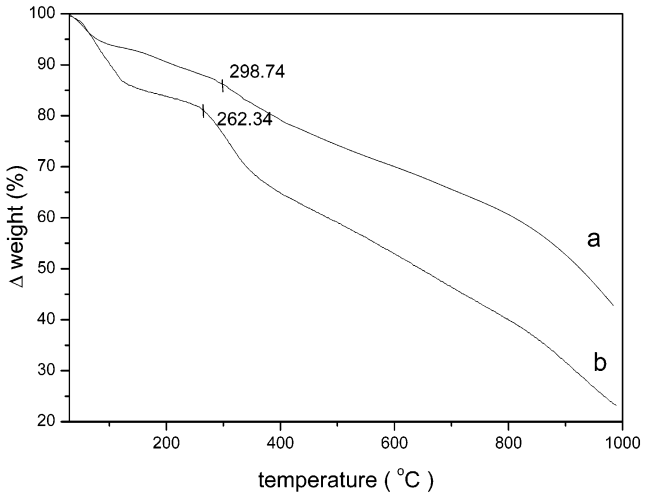


Figure 3. TGA spectra of chemical synthesized PPy−$CDSO_3$ (a) and chemical synthesized PPy in the absence of $CDSO_3$ (b).

patterns clearly indicate a better thermal stability of PPy−$CDSO_3$ than the compared sample. The decompose temperature of PPy shifted from 262 to 299 °C. This should be attributed to the relatively compact structure in PPy backbone by introducing $CDSO_3$.[16]

In summary, we synthesized ordered conducting polypyrrole by chemical and electrochemical methods in the presence of $CDSO_3$ as a dopant. $CDSO_3$ seems to play an important role in forming PPy's ordered structure. Besides acting as a dopant, it partially includes the polymer chain in CD cavity, which leads to enhanced coplanar characteristic of the PPy backbone and improves the conductivity as well as thermal stability of the resulting PPy.

Acknowledgment. The authors are grateful for the support from the National Natural Science Foundation of China (No. 50133010).

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MA025521G