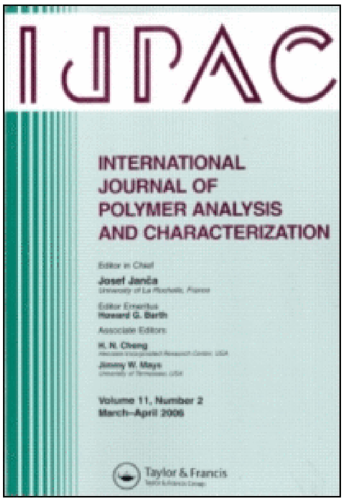

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PREPARATION AND CHARACTERIZATION OF CONJUGATED POLYPSEUDOROTAXANE POLY(PYRROLE/α-CYCLODEXTRIN)

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Conjugated polypseudorotaxane polypyrrole/α-cyclodextrin (PPy/α-CD) was synthesized by chemical oxidative polymerization of pyrrole in the presence of α-CD. The FT-IR spectra and wide-angle X-ray diffraction (WAXD) pattern showed that the pyrrole-CD (Py-CD) rotaxanes were presented in the polypyrrole (PPy) chains. The polypseudorotaxane wires composed of α-CD as the insulating cover and polypyrrole as the core were expected product in this study. The elemental analysis suggests that the molar ratio of α-CD to pyrrole is 1:5. Because of the discontinuous presence of Py-CD rotaxanes, the conductive behavior morphology and thermal stability of the polypseudorotaxanes are greatly different than those of the pure PPy. Moreover, this work analyzed the reaction mechanism in the microscopic view.

Keywords: Conjugate; α-Cyclodextrin; Polypseudorotaxane; Polypyrrole; Supramolecular

INTRODUCTION

Cyclodextrins (CDs) are a family of oligosaccharides composed of six or more D-glucopyranose residues attached by α-1, 4-linkages in the $^4C_1$ chair conformation. The most common CDs have six, seven, and eight glupyranose units, referred to as α-, β-, and γ-CD, respectively. Cyclodextrins exhibit a torus-shaped structure with a hydrophobic cavity and a hydrophilic exterior. CDs and their derivatives have been extensively studied as host molecules in supramolecular chemistry.[1,2] Either small molecules or linear polymers can serve as the guests interacting with CDs toward the formation of supramolecular complexes. However, the guest molecules and polymers incorporated into the hydrophobic cavity of CDs must have appropriate size and shape.[3,4] Since the 1990s it has been found that CDs are threaded onto many kinds of water-soluble and nonionic linear polymers to produce polypseudorotaxanes or polyrotaxanes, such as poly(ethylene glycol) (PEG), poly(proplene glycol) (PPG), and their block copolymers.[5–7] Since the

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specific structure of CDs can change the performance of guest polymers, CDs have seen dramatic growth in the field of novel functional materials.

Since its discovery, polypyrrole (PPy) has been considered an attractive conducting polymer due to good thermal stability, nontoxicity, and relatively high electrical conductivity.[8] Storsberg et al.[9] synthesized and characterized the 1:1 host-guest inclusion of cyclodextrin and pyrrole monomer for the first time, since then some reports about electro-preparation of polypyrrole in the presence of cyclodextrins appeared.[10,11] Michels et al.[12] described polyrotaxane insulating molecular wires synthesized by hydrophobic binding to promote threading of the cyclodextrin units. These polyrotaxanes have conjugated polymer cores based on poly(para-phenylene), polyfluorene, and poly(diphenylene-vinylene), threaded through 0.9–1.6 cyclodextrins per repeat unit.

In this study, conjugated polypseudorotaxane PPy/α-CD has been chemical oxidation polymerized and characterized. Polypseudorotaxane wire composed of α-CD as the insulating cover and polypyrrole as the core was expected in this study. It is focused on the morphology and molecular structure of PPy/α-CD thus obtained. We investigate and compare the conductivity, voltametric behavior, and thermal stability of pure PPy and polypsedorotaxane. The reaction mechanism in the microscopic view is also analyzed.

EXPERIMENTAL SECTION

Materials

Pyrrole (>97%) was purified by distillation before use. α-Cyclodextrin was purchased from Fluka Chemical Company (Switzerland). Other chemicals used were of analytical regent grade without further purification. Distilled water was used in this investigation.

Chemical Oxidative Synthesis of Poly(Py/α-CD) and PPy

Poly(Py/α-CD) was prepared by injecting 2 mL pyrrole to 28.0 g α-CD (pyrrole: α-CD = 1:1) in 250 mL of distilled water under constant stirring. The 57.7 mL of 0.5 M ferric trichloride aqueous solution was added dropwise into the above mixture under magnetic stirring. The polymerization was continued for about 8 h at 25°C. The resulting solution was filtered and washed by sufficient amount of hot water for one hour to wash out the remaining α-CD and ferric trichloride. The solid product was collected and dried at 60°C under a vacuum atmosphere for 48 h. The final product was small needle-shaped solids. Pure PPy was prepared as above in the absence of α-CD. Finally, the PPy was obtained as a platy solid. A physical mixture of PPy and α-CD (PPy + α-CD) was also made for comparison.

Characterization

The conductivity of PPy was measured by the standard four-probe method at 25°C. Cyclic voltammetry (CV) experiments were carried out in a standard three-electrode thermostated glass cell at 20°C with a PARSTAT 2273 Cornerstone electrochemical system (Ametek Inc., USA). In order to measure the CV, PPy or

PPy/α-CD was suspended in 20 mL of distilled water and sonicated for several minutes. This suspension of several drops was carefully transferred to the surface of the working electrode (Pt sheet of 2 mm diameter). After water evaporation (at room temperature) a uniform film was formed, then rinsed with distilled water. A Pt foil and a saturated calomel electrode (SCE) were used as the counter and referenced electrodes, respectively. CVs were recorded in 0.1 M NaCl. The scan speed was 50 mV/s, and the potential ranged from −0.5 to 1.8 V.

FT-IR spectra were measured on a Nicolet 5700 FT-IR spectroscope. All spectra were taken from KBr pellets and with 0.09 cm^{-1} resolution. The morphology of PPy was examined on a JSM-6360LV scanning electron microscope (JEOL, Japan) and a H-600 transmission electron microscope (Hitachi, Japan). Wide-angle X-ray diffraction was taken with a D/MAX 2550 VB/PC diffractometer (Rigaku, Japan) using Ni-filtered Cu Kα radiation. Elemental analysis was performed on a Vario EL III element analyzer (Germany). A WRT-2P 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

Conductivity and Voltametric Behavior of Poly(Py/α-CD) and PPy

Table I shows the conductivity of poly(Py/α-CD) was 0.3694 $S \cdot cm^{-1}$ at 25°C, and that of PPy synthesized in the absence of α-CD was 5.56 $S \cdot cm^{-1}$. The conductivity of poly(Py/α-CD) decreased by one order of magnitude as compared with pure PPy. This result implied that α-CD was threaded onto the main chain of PPy macromolecule, not only acting as a dopant in the conductive polymer, or else the conductivity wouldn't decrease so significantly. The conductivity of the mixture of PPy and α-CD (PPy + α-CD) also decreased by one order of magnitude as compared with poly(Py/α-CD), which means that the polypyrrole and α-CD of poly(Py/α-CD) was not just like a physical mixture. These results suggest that the existence of α-CD in poly(Py/α-CD) weakened the interchain charge transition, but it was different with the α-CD in the mixture PPy + α-CD, which totally hindered the charge transition.

The voltamograms of PPy and poly(Py/α-CD) were carried out in 0.2 M NaCl, and CVs after the thirtieth cycles are presented in Figure 1. Figure 1(a) shows a first strong oxidation peak around 1.46 V. Nevertheless, the first oxidation peak of poly(Py/α-CD) shifted to 1.32 V, and the current of the oxidation peak was apparently weaker than PPy. The slight negative shift of the oxidation peak and the lower current compared to PPy might be the results of the polypyrrole partly

Table I. Conductivity of PPy, poly(Py/α-CD), and the mixture of PPy and α-CD (PPy + α-CD) at 25°C

	Sample		
Conductivity	PPy	Poly(Py/α-CD)	PPy + α-CD
($S \cdot cm^{-1}$)	5.56	0.3694	0.02116

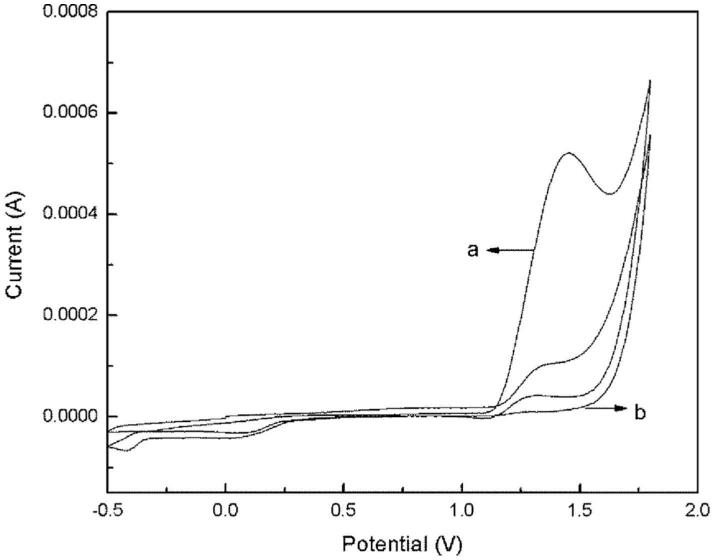
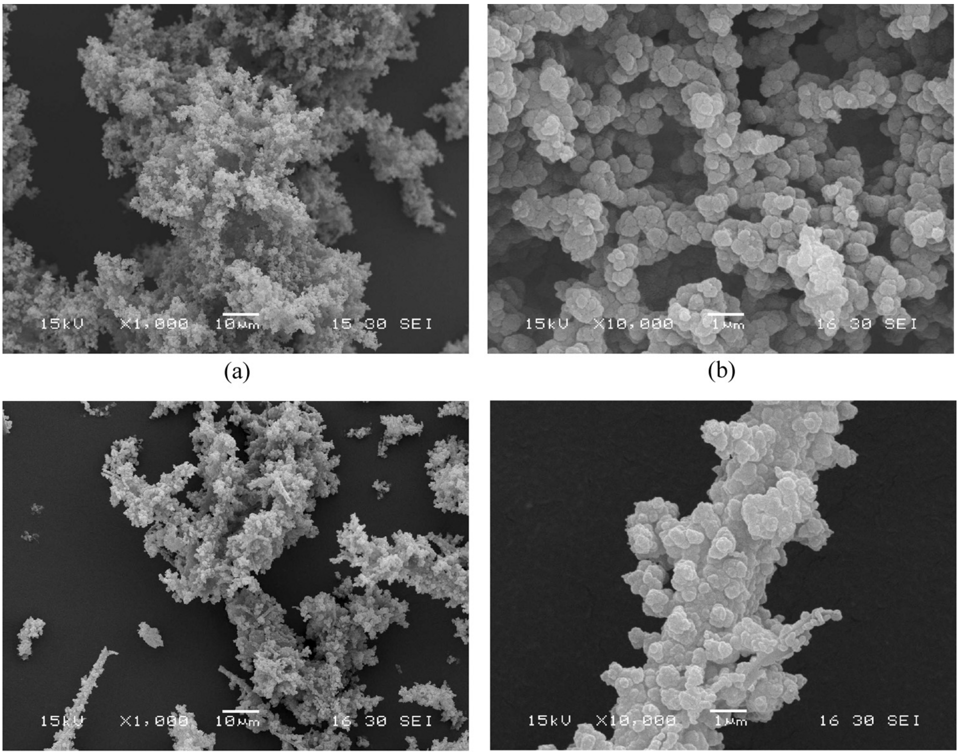


Figure 1. Cyclic voltamograms of PPy (a) and poly(Py/α-CD) (b); electrolytic solution: 0.2 M NaCl, sweep rate: 50 mV/s.

or entirely included in the α-CD hydrophobic cavity. It was also found that redox reversibility of poly(Py/α-CD) was much worse than that of PPy in comparison with Figures 1(a) and (b). This should be attributed to stereo-hindrance effect of α-CD, which decreased the contacts between the molecular chains of PPy.

Morphology of Poly(Py/α-CD) and PPy

Scanning electron microscope (SEM) experiments were performed on both poly(Py/α-CD) and PPy, as shown in Figures 2(a)–(d). When the amplification of SEM was ×1000, the morphologies of PPy (Figure 2(a)) and poly(Py/α-CD) (Figure 2(c)) were different. There were more rod-like substances in the bulk of poly(Py/α-CD) than PPy. When the amplification of SEM was ×10, 000, the pictures (Figures 2(b) and (d)) clearly show different organization modes. The PPy (Figure 2(b)) shows a cauliflower configuration with a large dimension, while the rod-like structure of poly(Py/α-CD) system (Figure 2(d)) could be seen more clearly. Samples for transmission electron microscopy (TEM) images (Figures 3(a) and (b)) were dispersed in aqueous solution undergoing sonication process. Figure 3(b) shows that poly(Py/α-CD) was fibrous with a diameter of about 250 nm, while PPy prepared in the absence of α-CD had the agglomeration morphology as shown in Figure 3(a). Apparently, the structure of poly(Py/α-CD) was more oriented and organized than that of PPy. It indicated that the α-CD molecules might slide along and rotate around the polymer chains, and some α-CD molecules formed the pseudopolyrotaxanes with the polymer axes. The interaction of α-CD and polypyrrole could strengthen the binding force between polymer chains and finally optimize the configuration of polymer. This result was in accordance with the electrochemical polymerization reported by Izoumen et al.[10]



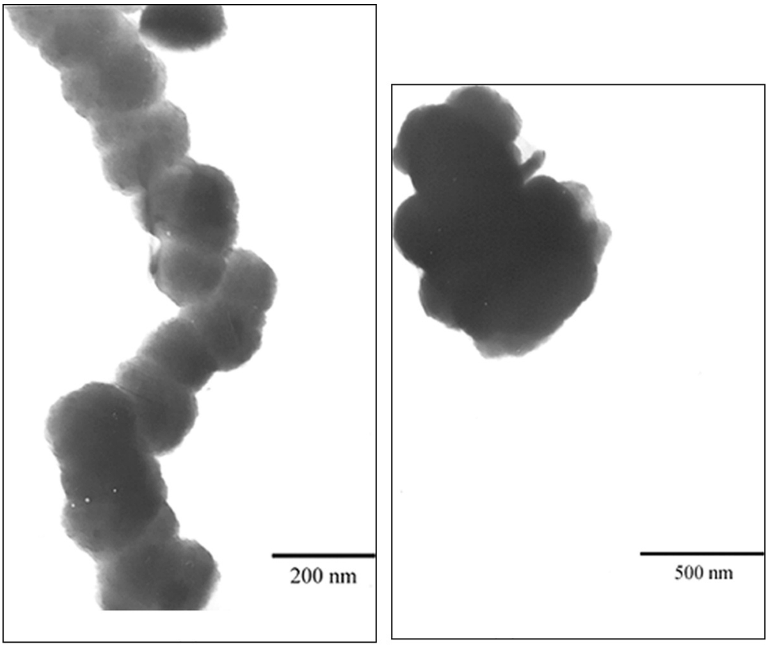
(a) (b)

(c) (d)

Figure 2. Scanning electron micrographs of: PPy, amplification ×1000 (a); PPy, amplification ×10, 000 (b); poly(Py/α-CD), amplification ×1000 (c); poly(Py/α-CD), amplification ×10, 000 (d).

Fourier-Transform Infrared Spectra

The structure of poly(Py/α-CD) was characterized by FT-IR and WXRD spectroscopies. FT-IR spectra of α-CD, the mixture of PPy and α-CD (PPy + α-CD), poly(Py/α-CD), and PPy are given in Figure 4. The spectra of PPy + α-CD (Figure 4(b)) and α-CD (Figure 4(a)) were nearly the same, except 1543 cm^{-1}, suggesting the main characteristic skeleton vibration band of the pyrrole ring. However, the spectrum of poly(Py/α-CD) (Figure 4(c)) was more similar to the spectrum of PPy (Figure 4(d)). On the spectrum of poly(Py/α-CD) (Figure 4(c)), 3364 cm^{-1} (intensive and wide absorption band of O–H stretching vibration), 2926 cm^{-1} (C–H stretching in saturated hydrocarbon), 1703 cm^{-1}, and 1154 cm^{-1} (intensive band of ether bond) suggested the existence of α-CD. However, comparing to PPy, the O–H stretching vibration band of poly(Py/α-CD) shifted to low field. Meanwhile, the corresponding N–H absorption band moved to 3430 from 3400 cm^{-1} and the band became wider and stronger, which was caused by the hydrogen band between hydroxyl of α-CD and the H of N–H on the backbone PPy. Also, 1089 cm^{-1} in the spectrum of PPy is the wavenumber of C–H nonplanar bending vibration. But the feeble peak at 1089 cm^{-1} disappeared in the spectrum of PPy/α-CD, which indicates that PPy/α-CD has the stronger coplanar characteristic of the pyrrole



(a) (b)

Figure 3. Typical TEM images of PPy (a) and poly(Py/α-CD) (b).

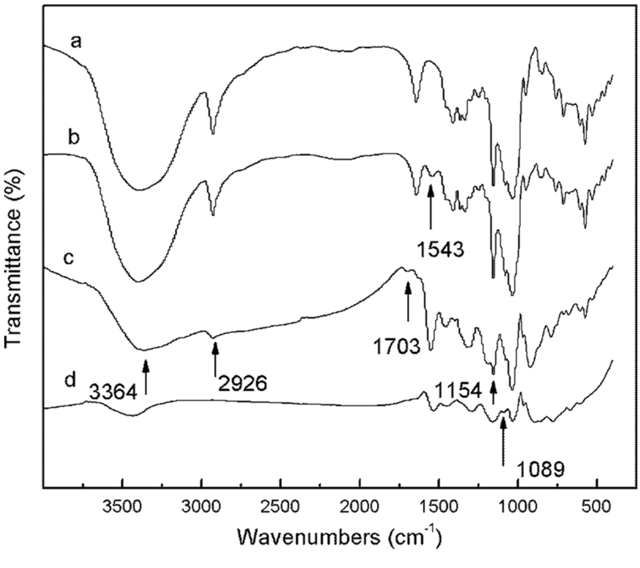


Figure 4. FT-IR spectra of α-CD (a), the mixture of PPy and α-CD (PPy + α-CD) (b), poly(Py/α-CD) (c), and PPy (d).

units. That means the α-CD affected the forming of the whole structure of PPy in the chemical oxidative polymerization. These results suggest that PPy/α-CD not only affects the structure of backbone PPy, but also interacts with the backbone PPy. PPy/α-CD is totally different from the physical mixture PPy + α-CD.

Wide-Angle X-Ray Diffraction Patterns and Elemental Analysis

Wide-angle X-ray diffraction patterns for α-CD, PPy + α-CD, poly(Py/α-CD), and PPy are given in Figure 5. As shown in Figure 5(a), α-CD has many sharply pointed crystallization peaks, especially at 11.8°, 14.2°, and 21.6°. Figure 5(d) shows that the amorphous region of pure PPy is dominant, and the diffraction pattern of PPy just exhibits a wide-spreading peak from 10° to 35°. In Figure 5(b), the wide-spreading peak of PPy is not very obvious, but characteristic peaks of α-CD at 11.8°, 14.1°, and 21.5° are nearly the same as in Figure 5(a). The result suggested that the XRD spectrum of the mixture was simple superposition of each phase. However, Figure 5(c) shows that the wide-spreading peak of PPy was obvious and the characteristic peaks of α-CD shifted to 12.3°, 13.3°, and 22°, which indicates that the crystallization peaks were affected by the PPy chains. This suggests that α-CD molecules were encapsulatings for PPy, and the degree of crystallinity of PPy-threaded α-CD was obviously enhanced. However, only a small part of PPy chains were encapsulated by α-CD, or else poly(Py/α-CD) would become holocrystalline.

Elemental analysis was performed on poly(Py/α-CD) to determine the amount of α-CD encapsulating PPy. The sample was dried at 80°C in a vacuum oven for

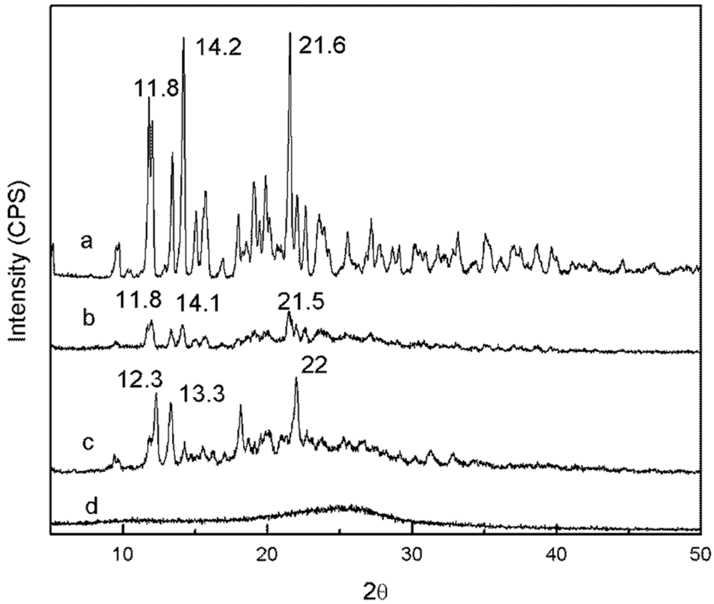


Figure 5. WAXD patterns of α-CD (a), the mixture of PPy and α-CD (PPy + α-CD) (b), poly(Py/α-CD) (c), and PPy (d).

Table II. Content of each element in poly(Py/α-CD) measured by elemental analyzer

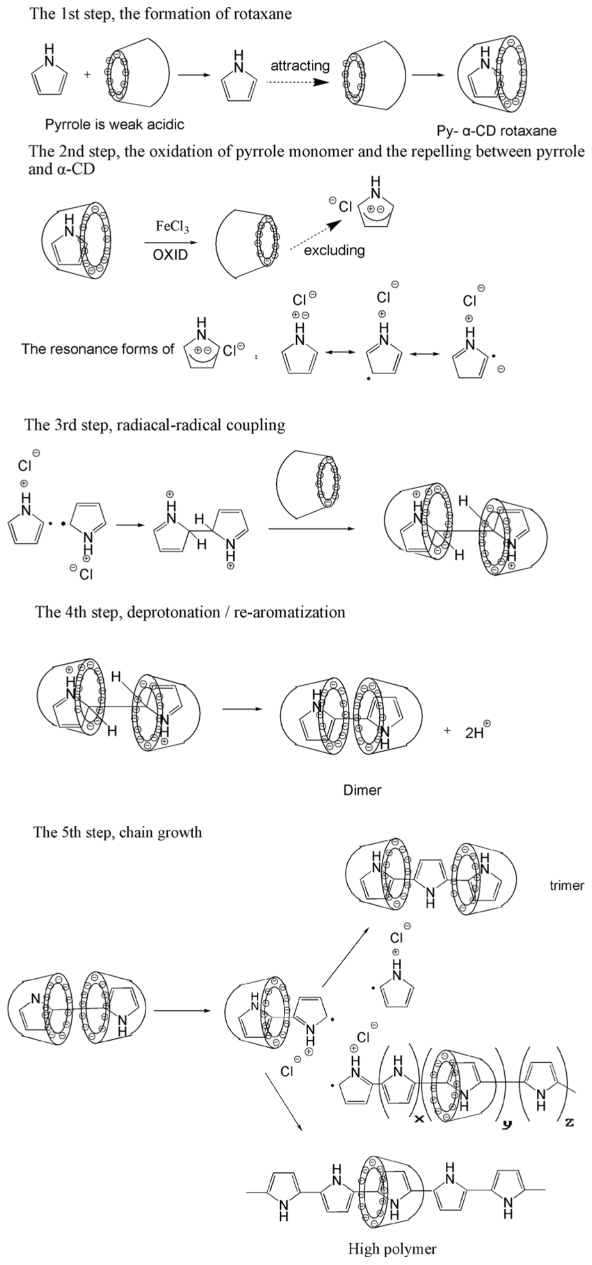
	Sample			
	N	C	H	O
Poly(Py/α-CD)	5.37%	47.65%	5.93%	41.05%

another 72 h to remove the residual water completely. The poly(Py/α-CD) sample had a [O]/[N] value of about 6.69 and a [C]/[N] value of about 10.35 (see Table II), so the molar ratio of α-CD to pyrrole was about 1:5. This result indicates that each of the five pyrrole molecules had one rotaxane structure with one α-CD molecule.

Reaction Mechanism Analysis

Scheme 1 illustrates the reaction mechanism of the oxidation polymerization. In the first step, the original pyrrole monomer and α-CD molecule formed the typical rotaxane structure Py-α-CD, and this had been characterized through X-ray structure by Storsberg et al. in 2000.[9] The proper size and shape of the pyrrole monomer are not the only reasons for forming the rotaxane Py-α-CD. Another important reason is that the non-shared electron pair in the nitrogen atom participates the conjugated system of pyrrole heterocyclic ring, therefore, the pyrrole monomer is weak acidic.[13] However, there are glycosidic oxo-bridged atoms arraying in the cavity of α-CD, and the nonbonding electrons of oxygen atoms point to the cavity center, so the cavity has quite high electron density and shows some of properties of Lewis bases.[14] So the pyrrole and the α-CD cavity attracted each other and could form the rotaxane structure easily. In the second step, when the pyrrole monomer was oxidized by $FeCl_3$, the pyrrole radical generated and was doped by Cl^-, meanwhile, the rotaxane disassembled. The pyrrole radical had three kinds of resonance forms, and we can see that the one end of the pyrrole radical had a negative charge.[15] Hence, the repelling interaction between the pyrrole radical and the electronegative cavity of α-CD destroyed the relatively stable rotaxane structure. Furthermore, the large volume of pyrrole radical might be another reason for excluding.

In the third step, two pyrrole radicals coupled, and the hydrogen protons (H^+) doped in the $1 - C$ of the backbone. Then the structure had positive charges and threaded into the α-CD cavities. The dimer rotaxane formed in the fourth step, where the deprotonation happened, and the H^+ divorced from the backbone, then the reaction solution became acidic. Choi et al.[7] had reported that the polypseudorotaxane formation of linear polyethylenimine (LPEI) with α-CD was pH dependent, and they found that no polypseudorotaxane was observed below pH 8.0.[7,16] Because the nitrogen atom N of the tertiary amine in the LPEI chain has quite high electron density and it can combine with H^+ easily, the tertiary amine shows basicity. Inversely, the tertiary amine in the pyrrole ring shows weak acidity, and it can barely bind with H^+. Therefore, the polypyrrole dimer didn't leave the α-CD cavity when pH was below 7.0.



Scheme 1. Possible reaction mechanism of the oxidation polymerization.

In the fifth step, the trimer and high polymer were generated, but not every pyrrole unit in the chain became rotaxane with α-CD, because the pyrrole-radical excluded from the α-CD cavity, which impeded the formation of the Py-α-CD rotaxane and degraded the speed of chain growth. Likewise, the space restriction of

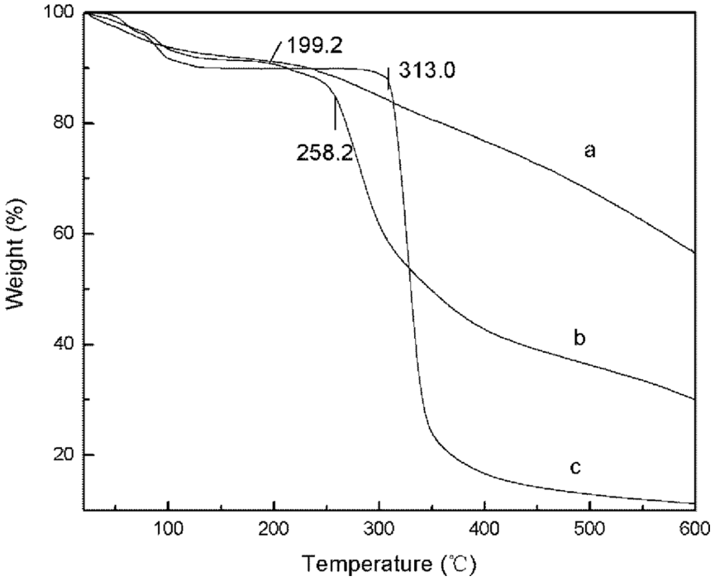


Figure 6. TGA spectra of PPy (a), poly(Py/α-CD) (b), and α-CD (c).

α-CD increased the polypyrrole sequence degree, which could be observed by SEM and TEM as above.

Thermal Stability

The thermal stability of poly(Py/α-CD) was evaluated by thermogravimetric analysis (TGA) and compared with free α-CD and the starting PPy. Figure 6 shows the weight loss curves for poly(Py/α-CD) and its precursors. Figure 6(a) shows that the starting decomposition temperature of PPy was 199.2°C, which was the lowest in the three curves. Because the PPy had some oligomers, such as dimers and trimers, the starting decomposition temperature was very low. However, the total weight loss of PPy was the highest in the three curves, because the high polymers of PPy had excellent thermal stability. The starting decomposition temperature of α-CD (Figure 6(c)) was 313°C, much higher than PPy, but the total weight loss was the highest. The thermogravimetric curve of poly(Py/α-CD) (Figure 6(b)) had colligated the features of PPy and α-CD, with a higher starting decomposition temperature than PPy and higher total weight loss than α-CD. Nevertheless, the course of weight loss was obviously slower than that of free α-CD. Therefore, both α-CD and PPy were stabilized by formation of rotaxanes.

CONCLUSIONS

The conjugated polypseudorotaxanes poly(Py/α-CD) were synthesized by oxidative polymerization of pyrrole in the presence of α-CD. The molar ratio of α-CD to pyrrole monomer is 1:5. Compared to polypyrrole, polypseudorotaxanes have obviously decreased conductivity, reduced redox reversibility, and better thermal stability in terms of the discontinuous presence of Py-CD rotaxanes in the PPy chain. This material needs a further exploration in the scope of molecular wire.

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