Micro/Nano-structured Conducting Copolymer from Aniline with 3,4-Ethylenedioxythiophene and their Property

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Abstract. Novel conducting copolymers from aniline (AN) with 3,4-ethylenedioxythiophene (EDOT) with different micro/nano-structures were synthesized by chemical oxidation. The influences of [EDOT]/[AN] molar ratios on morphology, structure, electrical conductivity, and solubility of copolymers are systematically studied. It is found that the copolymer’s morphologies as well as electrical conductivity vary with the change of [EDOT]/[AN], and the extremum exists during the conductivity variation. From the SEM photograph, we can know that the copolymer has a uniform nanofiber structure at [EDOT]/[AN]=1.5/1. It is shown in the infrared spectrum that the copolymer has both the macromolecular chain structure of PANI and PEDOT, indicating that the copolymerization effect of the two is very good. The UV absorption spectrum is non-monotonic with the change of [EDOT]/[AN] molar ratio, which also proves the copolymerization structure of EDOT and AN. Interestingly, the copolymers exhibit better solubility and partial crystallinity compare with each single homopolymer. Moreover, the copolymer presents good electrochromic properties with the reversible color change among blue, blue green, yellowish green, which combines the color variation range of PANI and PEDOT.

1. Introduction

Conductive polyaniline (PANI) has various structures, unique doping mechanism, excellent physical and chemical properties and good stability. It has been widely studied in the fields of chemistry, biochemistry, energy and functional materials[1]; especially when it is used as an electrochromic material, it has the characteristics of good optical quality, fast color conversion, good cycle reversibility, and low price. However, due to the presence of the benzene ring and the strong hydrogen bonding between adjacent molecules, its solubility in most organic solvents is poor, which limits its application in many fields. At present, copolymerization has proven to be an effective method to improve the performance of conductive polymer materials[2], compared with blended materials, copolymers are more likely to combine the advantages of both polymers and have more stable physicochemical properties. Especially in the research of conductive polymer electrochromic materials, in order to achieve color matching requirements, the study of copolymers between different monomers has attracted much attention. For example, Li Xingui et al. synthesized a binary conductive copolymer of red, green and blue primary colors of aniline and o-phenylenediamine at 70°C by chemical oxidative polymerization[3], and the copolymers were homopolymerized than their respective ones.
The material shows better film formation and film uniformity. The prepared polymer has excellent solubility and can be used for large-scale large-area film formation. Marley et al. [4] studied copolymers of aniline with o-methoxyaniline, anthranilic acid and o-methylaniline, and also obtained copolymers with improved electrochromic properties and physical properties.

Poly(3,4-ethylenedioxythiophene) (PEDOT) is the most widely studied conductive polymer in polythiophene derivatives as an electrochromic material. It has good electrical conductivity, stability, photoelectric properties and electroluminescence, and the film material has good transparency. Its oxidation (doping) and reduction (dedoping) states show black blue and transparent light blue [5]. In order to broaden the range of electrochromism, Pierre-Henri Aubert et al. [6] used Suzuki-Miyaura cross-linking reaction to prepare (3,4-dioxyethylenethiophene) (EDOT) and pyrimidine with alkyl hydrazine and phenylene, respectively. The precursors were copolymerized to synthesize four electrochromic conductive copolymers whose colors were changed between dark blue-yellowish green, blue-dark yellow, dark blue-yellowish green, and dark blue-yellow, respectively.

The aniline and (3,4-dioxyethylene thiophene) monomer raw materials are easy to obtain, simple in synthesis, and excellent in performance; if copolymerization is feasible, the application range of the two conductive polymers will be greatly broadened. In this paper, we obtained the conductive copolymer of AN and EDOT with micro/nanostructure by simple self-assembly method [7, 8]. The structure and properties of the copolymer were characterized and analyzed; the electrochromic effect of the copolymer was preliminarily studied, which laid a foundation for further practical application of the copolymer.

2. Materials and Methods

2.1 Materials

3,4-ethylenedioxythiophene (EDOT, A.R., Suzhou Industrial Yacoo Chemical Reagent Co. Ltd) and Aniline (AN, A.R., Beijing Mashi Fine Chem. Co.) was distilled under reduced pressure and kept refrigerated under nitrogen prior to use. Other reagents, such as sodium per-sulfate (Na2S2O8, Beijing Yili Fine Chem. Co.), ferric sulfate (Fe2(SO4)3, Tianjing Fuchen Chemical Reagent Co.), ethanol (Beijing Chemical Plant), Dimethylformamide (DMF, Beijing Yili Fine Chemicals Co.), Dimethyl sulfoxide (DMSO, Tianjin Yongda Chemical Reagent R&D center), trichloromethane (CHCl3, Beijing Chemical Plant), N-methyl-2-pyrrolidone (NMP, Beijing Chemical Plant ) and other reagents were all A.R. grade and used as received without further treatment. The water used is distilled water.

2.2 Synthesis Procedure

A certain molar ratio of Na2S2O8, Fe2(SO4)3 and glucose was weighed into 25 mL of 1 M HCl and dissolved sufficiently by electromagnetic stirring. Then 2.8 mmol of AN and 2.8 mmol of EDOT were added to the above mixed solution, and the solution quickly turned blue-green. The mixture was stirred under electromagnetic stirring at 20-25°C for 24 h, and filtered to obtain a blue-green precipitate, which was washed with deionized water, ethanol and anhydrous diethyl ether for 2 to 3 times, respectively, until the washing liquid was colorless. The obtained solid particles were vacuum dried at 60 °C for 24 h to obtain a product, which was represented by PANI-PEDOT. A series of copolymers of [EDOT] / [AN] = 1:1 to 2:1 were synthesized by changing the monomer molar ratio of EDOT and AN (indicated by [EDOT] / [AN]).

2.3 Structural characterization and performance testing

Field emitting scanning electron microscope (SEM, JEOL JSM-6360) was used to detect the morphology of the products. The molecular structure was characterized by FTIR spectra (KBr pellet, Perkin-Elmer System), ultraviolet-visible absorption spectrum (TU-1901) and X-ray diffraction (XRD, D/max-B wideangle goniometer). The thermal stability of the products was measured using a DuPont TG-63000 thermogravimetric analyzer at a heating rate of 10°C/min⁻¹, heating from 50 to 1100°C under
nitrogen with a flow rate of 40 mL/min, and the conductivity at room temperature was measured by a four-probe method with a Keithley 6221+2182A System.

The solubility of the products was measured in a way of half-quantitative analysis: 10mg sample is added into 1mL solvent, and the mixture was mixed by ultrasonic for 30min, and kept quiet for 24h for observing the solubility.

3. Results and Discussion

3.1 Morphology
Fig. 1 gives the morphology of pure PANI, PEDOT and the copolymer prepared at different molar ration of EDOT and AN(represented by [EDOT]/[AN]). It is found that [EDOT]/[AN] has an obvious effect on the morphology of the copolymers. The morphology of the obtained pure PANI is a kind of three dimensional micro/nano-structure piled up by one dimensional flake with average 50nm thickness as a certain degree, which is just like the rose in nature, therefore, we call it rose-like-structure(see Fig. 1a and 1b). The morphology of pure PEDOT is nano-particle structure with diameter of 300nm (Fig. 1c). The copolymer presents different morphology affected by [EDOT]/[AN]: when [EDOT]/[AN] is lesser, it is also nano-particles with lesser diameter, for example, when [EDOT]/[AN]=1, the particle diameter is 200nm(Fig. 1d). When [EDOT]/[AN] increase to 1.5, the copolymer take on uniform nanofibers with diameter of 100nm and length of 0.5~1μm(Fig. 1e). With the increase of [EDOT]/[AN], the diameter and length are decreased, when [EDOT]/[AN]=2, the copolymer appears nano-small fiber structure with diameter of 20~30nm, length of 30~50nm(Fig. 1f).

3.2 Conductivity
In addition to affecting the morphology of the PANI-PEDOT copolymer, the [EDOT]/[AN] ratio also has a large effect on its conductivity. Fig. 2 is a plot of the conductivity of the PANI-PEDOT copolymer as a function of [EDOT]/[AN].

![Figure 1. SEM image of both homopolymers and the copolymers prepared with different EDOT/AN molar ratios: (a): pure PANI; (b): single rose-shaped PANI architecture (c): PEDOT; (d), (e) and (f): PANI-PEDOT at [EDOT]/[AN]= 1, 1.5 and 2, respectively.](image-url)
Figure 2. Influence of [EDOT]/[AN] ratios on the electrical conductivity of PANI – PEDOT copolymers

As can be seen from Fig. 2, when [EDOT]/[AN] is between 1.0 and 1.5, the conductivity increases with the increase of [EDOT]/[AN], and when [EDOT]/[AN]=1.5, the conductivity reach to the maximum value of 0.75 S/cm, and thereafter, as the [EDOT]/[AN] is further increased, the conductivity begins to decrease. The conductivity of PANI and PEDOT monomer homopolymers synthesized by self-assembly method reached 8.89S/cm and 12.63S/cm, respectively, while the conductivity values of the two monomer copolymers are lower than the conductivity of their respective homopolymers. It is indicated that the increase of EDOT in the range of [EDOT]/[AN]=1.0-1.5 contributes to the increase of the doping degree of the copolymer, and is advantageous for intra-chain transfer and inter-chain jump of electrons. When [EDOT]/[AN] continued to increase from 1.5, we analyzed this because a large amount of dioxyethylene substitution resulted in electrostatic repulsion and steric hindrance, preventing polymer doping. Because PANI and PEDOT have different doping mechanisms: the former belongs to proton acid doping, the doping process has no electron gain and loss; the latter is redox doping. When the two are copolymerized, their doping levels affect each other, and thus the electrical conductivity decreases.

3.3 Structure

3.3.1 FTIR

Figure 3 shows the FTIR spectra of PANI, PEDOT and PANI-PEDOT copolymers.
In the FTIR spectrum of PANI (Fig. 3A.a), strong absorption peaks appeared in 1564, 1481, 1304, 1122, 815 and 505 cm\(^{-1}\), which belong to the C=C stretching vibration of the quinone ring and the benzene ring, CN stretching vibration, C=N stretching vibration and vibration of 1,4-substituted benzene ring, which is the infrared spectrum of typical doped polyaniline.

For the PEDOT spectrum (Fig. 3A.e), the stretching vibration peaks of C=C and CC bonds on the thiophene ring at 1519 and 1324 cm\(^{-1}\), the stretching vibration peak of the alicyclic chain CC bond at 1201 cm\(^{-1}\), and the COC bond at 1087 cm\(^{-1}\), the anti-expansion vibration peaks, the stretching vibration peaks of the CSC bonds in the thiophene ring at 975, 828, and 674 cm\(^{-1}\) were observed, those are characteristic absorption peaks of PEDOT[9]; the absorption peak at 1647 cm\(^{-1}\) reflects the doping degree of PEDOT[10]. The absorption peak of the copolymer varies with the change of [EDOT]/[AN], When [EDOT]/[AN]=1/1 (Fig. 3A.b), the copolymer and PANI have almost the same spectrum; When [EDOT]/[AN]=1.5/1 and 2/1 (Fig. 3A.c, d), there are absorption peaks at 1304, 1519, 1087, 975, 815, and 505 cm\(^{-1}\), they belong to the C-N stretching vibration of the AN unit, the stretching vibrations of C=C, COC and CS of CN and 1,4-substituted benzene rings and EDOT, which indicates that both PANI and PEDOT backbone structures are present in the copolymer, and confirms there is a copolymerization structure of EDOT/AN[11].

3.3.2 UV-Visible
The UV-Vis absorption spectra of different [EDOT]/[AN] were tested with N-methylpyrrolidone (NMP) as solvent (Fig. 3B). For the PANI spectrum (Fig. 3B.a), the peak at 300-330 nm is caused by the \(\pi-\pi^*\) transition between the conjugated bonds of the adjacent benzene ring, and the absorption peak at 623 nm is the electronic transition peak of the quinone imine structure. They are characteristic absorption peaks of doped polyaniline, and the trailing tail peak is caused by a polaron. For the PEDOT spectrum (Fig. 3B.e), there are two absorption peaks at 305 nm and 375 nm, and the weaker peak is the peak of the dioxyethylene pendant group on the molecular chain, which is the characteristic absorption peak of PEDOT; the peak at 780 nm corresponds to the polaron and bipolaron absorption in PEDOT, indicating that PEDOT is doped or partially doped. The absorption peak of the copolymer changes with the change of [EDOT]/[AN], and the absorption peak at 623 nm becomes weaker with the increase of [EDOT]/[AN]. The absorption peak at 300-330 nm increases with the increase of [EDOT]/[AN], and the strongest absorption peak is at [EDOT]/[AN]=2/1 (Fig. 3B.d) and there are UV characteristics absorption peaks at 305 and 422 nm which are respectively attributed to PEDOT and PANI. This change in peak shift may be due to the copolymerization effect of EDOT and AN monomers, i.e. the polymer synthesized by EDOT and AN chemical oxidation is the true two monomer copolymers.

3.3.3 XRD
Fig. 4 is an X-ray diffraction spectrum of PANI, PEDOT and copolymers thereof.

![Figure 4. XRD patterns of PANI (a), PANI-PEDOT at [EDOT]/[AN] = 1.5 (b) and PEDOT (c)](image-url)
It can be seen from the figure that PANI has a sharp diffraction peak at 2\(\theta\)=6.45° (d=13.799Å), which is the periodic distance between the nitrogen atom or oxygen atom and the dopant on the polymer backbone, indicating the anion of the dopant exhibits a short-range order in the polyaniline backbone. A broad peak appearing at 2\(\theta\)=19.4° (d=4.5 Å) and 26° (d=3.464 Å) due to the periodicity parallel to the polymer chain, which are typical doping Crystallographic peak of state PANI[12].

PEDOT has a diffraction peak caused by the periodicity parallel to its main chain at 2\(\theta\)=25.8° (d=3.64 Å), which is consistent with the literature report. The copolymers showed diffraction peaks at 2\(\theta\)=6.45° and 26°. The former indicates that there are doped AN units on the main chain of the copolymer, and the latter indicates the presence of EDOT units in the copolymer backbone, which further confirms Copolymer structure.

3.4 Solubility
Good solubility is the basis for film formation and device preparation after dissolution of conductive polymer. Thus, when the conductive polymer is dissolved in a suitable solvent, a dense film can be uniformly applied and spread on the electrode, thereby broadening the field of application thereof. We have semi-quantitatively tested the dissolution of EDOT/AN copolymers in common organic solvents such as N-methylpyrrolidone (NMP), dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and chloroform. The solubility of the copolymer was found to be strongly dependent on [EDOT]/[AN] and the type of solvent used (Table 1). The copolymerization of the two and the use of glucose dopants make the solubility of the copolymer much better than the monomer homopolymer. The copolymer has good solubility in NMP, DMF and DMSO, among which the solvent is the best in DMSO, all the polymers are only slightly soluble or even insoluble in chloroform. And when [EDOT] / [AN] = 1 / 1, the copolymer has the best solubility in DMF and DMSO. When [EDOT] / [AN] = 1.3 / 1, the copolymer has the most solubility in NMP.

|          | PANI | PEDOT | PANI-PEDOT copolymers prepared at different [EDOT]/[AN] ratios |
|----------|------|-------|-------------------------------------------------------------|
|          | 1/1  | 1.1/1 | 1.2/1 | 1.3/1 | 1.4/1 | 1.5/1 | 2/1  |
| NMP      | +    | +     | ++    | ++    | +++   | +     | +    |
| DMF      | +    | +     | +++   | +++   | +     | +     | +    |
| DMSO     | +    | +     | +++   | ++    | +++   | +     | +    |
| CHCl₃    | -    | -     | -     | -     | -     | -     | -    |

* -: insoluble; +: slightly soluble; +: partially soluble; + +: mostly soluble; + + +: completely soluble.

3.5 Thermal Stability and Electrochromism
Fig. 5 is the TG curves of PANI, PEDOT and their copolymer at [EDOT]/[AN] =1.5 / 1. As it can be seen in the Fig. 5, PANI is relatively stable at the beginning of temperature rising, and three inflection points appear near 180 °C, 340 °C and 550 °C, which are caused by evaporation of water or organic solvent, dedoping and decomposition of dopants, and decomposition of the main chain. It is consistent with the TG curve of typical doped polyaniline[13]. The initial loss of PEDOT is at about 60 °C. There are two inflection points near 140 °C and 350 °C, which are the decomposition of oligomers or dopants and the breakage of the main chain. When the temperature rises above 350 °C, PEDOT begins to decompose and lose weight obviously[14]. The copolymer has lost just only 3% of weight when the temperature reaches to 160 °C. The initial decomposition temperature of copolymer is lower than that of PANI, but the decomposition temperature of copolymer is higher than that of PEDOT. The
thermal stability of the copolymer is just between the two homopolymers which further demonstrates the presence of two molecular construction units in the copolymer.

Figure 5. TG curves of the copolymers and both homopolymers (heating rate is 10°C/min)
(a) PANI; (b) [EDOT]/[AN] =1.5/1; (c) PEDOT.

NMP used as a solvent, the polymer solution was spread on ITO conductive glass to form a film, and the electrochromic properties of PANI, PEDOT and their copolymers were tested by cyclic voltammetry. We found that PANI can change color between yellow green and green in the range of -0.5~1.5V vs SCE scanning potential, and PEDOT can change color in dark blue and light blue. The copolymer film obviously combines the color variation range of the two, and the reversible color change occurs among blue, blue green, yellowish green. Besides the response time is within 1 sec, and the expected color matching effect is initially achieved.

4. Conclusion
The copolymers of EDOT and AN synthesized by simple chemical oxidation self-assembly method have higher conductivity, and the structure and properties of the copolymer depend on the change of monomer molar ratio of [EDOT]/[AN]. The SEM photograph shows that the copolymer has a uniform nanofiber structure at [EDOT]/[AN] = 1.5/1. The infrared spectrum shows that the copolymer has both the macromolecular chain structure of PANI and PEDOT, indicating that the two have good copolymerization effects. The non-monotonic change of the UV absorption spectrum with the [EDOT]/[AN] molar ratio demonstrates the copolymerization structure of EDOT and AN. The copolymer also has good thermal stability and partial crystallization properties. PANI and PEDOT are electrochromic materials showing green and blue, respectively. The copolymer product is the intermediate color of the two, namely blue-green. The preliminary test of the electrochromic effect also combines the color variation of the two homopolymers.

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