

Biomimetic Synthesis of Water-Soluble Conducting Copolymers/Homopolymers of Pyrrole and 3,4-Ethylenedioxythiophene

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A novel biomimetic route for the synthesis of electrically conducting homopolymers/copolymers of pyrrole and 3,4-ethylenedioxythiophene (EDOT) in the presence of a polyelectrolyte, such as polystyrene sulfonate (SPS), is presented. A poly(ethylene glycol)-modified hematin (PEG-hematin) was used to catalyze the homopolymerization of pyrrole and EDOT as well as copolymerization of EDOT and pyrrole in the presence of SPS to yield homopolymers of polypyrrole/SPS and PEDOT/SPS as well as a polypyrrole-*co*-poly(3,4-ethylenedioxythiophene)/SPS complex. Spectroscopic characterization [UV–visible, Fourier transform infrared (FTIR), and X-ray photoelectron spectroscopy (XPS)], thermal analysis, (TGA), and electrical conductivity studies for these complexes indicated the presence of a stable and electrically conductive form of these polymers. Furthermore, the presence of SPS that serves as a charge-compensating dopant in this complex provides a unique combination of properties such as processability and water solubility.

Introduction

The rising concern of hazardous chemical wastes has led to increased interest in exploring alternatives for the synthesis of electronic/photonic polymers. Oxidoreductases such as horseradish peroxidase (HRP), obtained from natural and renewable sources, have been known to catalyze the polymerization of aniline and phenol-based monomers under benign conditions and in mixed solvent systems.^{1–3} The mechanism for HRP-catalyzed polymerization requires the interaction of the heme-iron active group of the enzyme with the hydrogen peroxide, generating an oxidized heme-iron complex.⁴ The oxidized heme-iron complex then reacts with the monomer, in a one-electron-transfer reaction, to yield a monomer radical and a modified iron-heme complex. The reaction of these monomer radicals leads to the formation of the polymer. Nevertheless, to date this procedure, based on “green chemistry”, could not be applied to polythiophenes or polypyrroles.^{5,6} This is due to the higher oxidation potential of monomers such as 3,4-ethylenedioxythiophene (EDOT) and pyrrole (PYR), compared to the catalyst HRP, thus proving to be inappropriate substrates for this enzymatic approach. The inactivity of HRP severely limits the prospects for the enzymatic synthesis of other conductive polymers such as polyethylenedioxythiophene (PEDOT), which exhibits important optical and electrical (antistatic/conductive) properties. Polymers based on PYR, currently used for organic batteries and display devices,⁶ are also of great interest. A synthetic route, based on green chemistry, for obtaining water-soluble electrically conducting polypyrrole (PPYR) or PEDOT has not been published.

Encouraged by a variety of reports based on the potency and effectiveness of Fe²⁺ catalysts, the use of cost-effective, “green”

biomimetic catalysts, which would reproduce the action of enzymes while imparting greater stability and more versatility in an analogous ecofriendly mode, has been examined. The use of poly(ethylene glycol)-hematin (PEG-hematin) and Hematin, which serves as a catalytic center of redox enzymes such as catalase, cytochrome *c*, etc., was also investigated. Previous efforts describe the use of different forms of hematin for catalysis in aqueous conditions. However, the catalytic activity was observed to be much lower than that reported for HRP.^{7–9} Moreover, Akkara¹⁰ has reported the synthesis of polyaromatic compounds catalyzed by hematin in mixed solvent systems or in buffered systems under basic pH conditions. Also previously reported was the use of the chemically modified hematin, PEG-hematin, as a “syn-enzyme” to catalyze the synthesis of conducting polyaniline in the presence of polyelectrolytic templates.¹¹ This synthetic enzyme has proved to be very appealing after being applied for the synthesis of polystyrene.¹²

Furthermore, a unique template-assisted approach for the synthesis of water-soluble polymers has been reported for the enzymatic polymerization of aniline and phenol with HRP as the catalyst in the presence of an anionic polyelectrolyte.¹³ Polyelectrolytes, such as SPS, performs several functions in these systems. In the case of anilines, the polyelectrolyte enables the electrostatic alignment of the monomer to promote a para-directed coupling, providing counterions for charge compensation in the doping process. The polyelectrolyte also complexes with the polymer to maintain water solubility. These templates have been reported to serve as nanoreactors for the one-pot enzymatic synthesis of conducting polyanilines.¹⁴

In this paper a novel synthesis of water-soluble PEDOT, PPYR, and PEDOT-*co*-PPYR using PEGylated hematin (PEG-hematin) as an effective catalyst in the presence of SPS as a template is reported. UV–visible, Fourier transform infrared (FTIR), and X-ray photoelectron spectroscopy (XPS), thermal

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gravimetric analysis (TGA), and electrical conductivity studies were carried out to characterize the polymers. To our knowledge this is the first report of a green chemistry approach for the synthesis of PEDOT, PPYR, and PEDOT-*co*-PPYR. Furthermore, the water-soluble copolymers showed an unusually high electrical conductivity in the range of 0.1–1.0 S/cm. This counterintuitive result indicates a possible synergic interaction between the two monomers.

Experimental Section

Hematin was purchased from Sigma Chemical Co. (St. Louis, MO). Pyrrole (PYR, purity 99.5%), 3,4-ethylenedioxythiophene (EDOT) monomer (purity 99.5%), polystyrene sulfonate (SPS), and hydrogen peroxide (30%) were purchased from Aldrich Chemicals Inc., Milwaukee, WI, and were used as received. All other chemicals were purchased from Aldrich and were of reagent grade or better. The esterification, yielding PEG-hematin, was carried out according to a procedure published earlier.¹⁵

The polymerization and the copolymerization of PYR and/or EDOT, in the presence of SPS, was catalyzed by PEG-hematin at 25 °C with hydrogen peroxide under ambient conditions. SPS (36.8 mg) was dissolved in deionized water (10 mL) at pH 1.0 for the polymerization of EDOT (18 mM) and at pH 2.0 for the polymerization of PYR (18 mM). A similar procedure was used for the copolymerization of EDOT/PYR (SPS/EDOT/PYR molar ratio 1:1:1) in the presence of SPS at pH 1. This was followed by the addition of 5 mg of PEG-hematin to this solution. The polymerization/copolymerization was initiated by the addition of several aliquots of 800 μ L of 0.03% hydrogen peroxide added in small increments. The reactants were stirred for 8 h to complete the polymerization, followed by dialysis with Centricon concentrators (10 000 cutoff; Amicon Inc., Beverly, MA). The samples were then dried under vacuum at 60 °C and used for further analysis. The gravimetric yield was typically 95%.

All UV-vis spectra were obtained on a Perkin-Elmer Lambda 9 UV-vis-near-IR spectrophotometer. The FTIR measurements were carried out on films cast on a ZnSe disk by use of a Perkin-Elmer FTIR spectrophotometer. Thermal gravimetric analysis (TGA) was conducted on a TA instrument 2950 (New Castle, DE). TGA was carried out in a nitrogen atmosphere, and a heating rate of 10 °C/min was used. To characterize the homo/copolymers catalyzed by the PEG-hematin, ESCA (electron spectroscopy chemical analysis) or X-ray photoelectron spectroscopy (XPS) was performed in a VG Escalab II with Al K α . Solid samples, after dialysis, were compressed in a disk and pasted on a sample holder. The copolymer does not charge during excitation since the C–C line appeared at 285 eV. The copolymer was highly conductive and maintained the C–C (cis) line at a binding energy of 285 eV.

Molecular weights of PEDOT-*co*-PPYR were assessed by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry (Waters MALDI-Micro MX MALDI-TOF) with dithranol as the matrix.

Conductivity measurements were performed on pellets by use of a standard linear four-point probe with a Keithley 619 electrometer/multimeter.

Results and Discussion

The polymerization reaction of EDOT with PEG-hematin was monitored spectroscopically in an aqueous solution at pH 1.0, and the spectral changes are reported in Figure 1. As seen in the figure, the monomer did not show significant absorption above 300 nm. However, initiation of polymerization by the addition of H₂O₂ led to the appearance of absorption from 600 to 1200 nm. This was also accompanied by the development of a dark blue color, with a simultaneous increase in the absorption

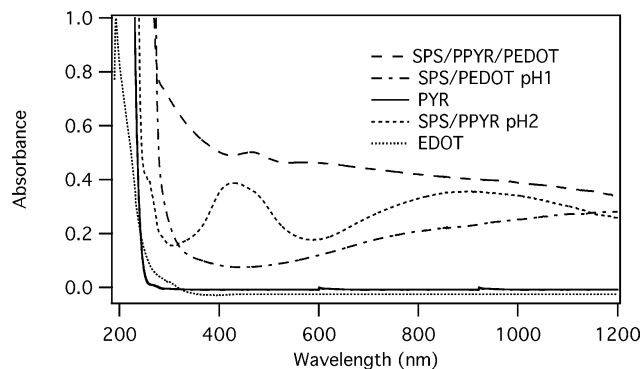


Figure 1. UV-Vis spectra of monomers EDOT and PYR and polymers PEDOT, PPYR, and PEDOT-*co*-PPYR.

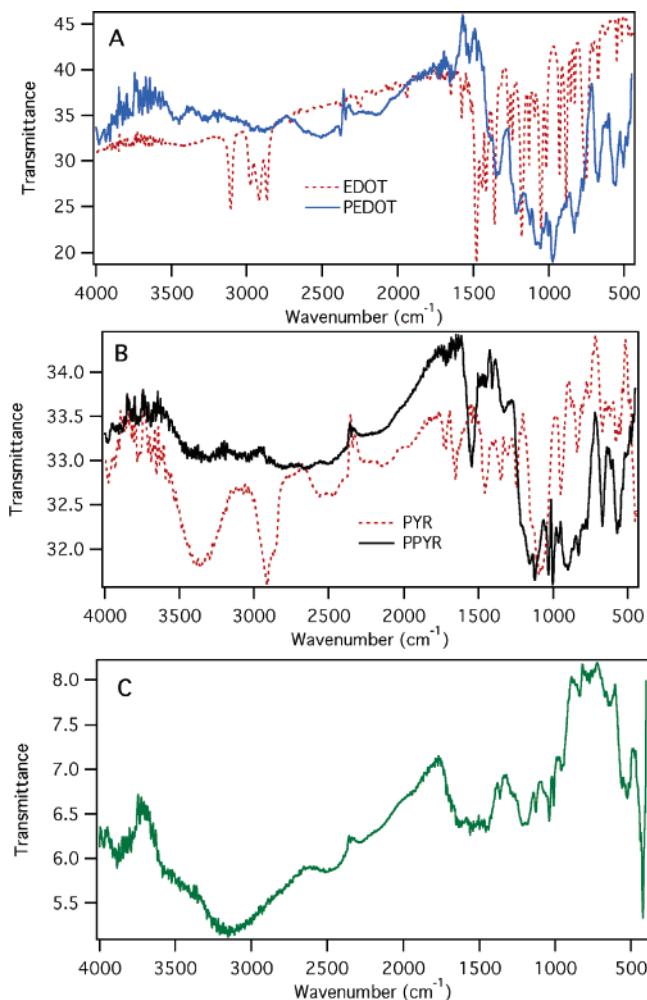


Figure 2. FTIR spectra of (A) monomer EDOT and polymer PEDOT in the presence of SPS, (B) monomer PYR and polymer PPYR in the presence of SPS, and (C) PEDOT-*co*-PPYR.

intensity of the peaks over time. The broad band at 700 nm, with a large absorption tail around 1200 nm, was attributed to the π - π^* transition in the polymer chain.

The FTIR spectrum (Figure 2) of the polymer showed absorptions at 1342, 1218, and 976 cm^{-1} , all assigned to doping interactions of SPS.¹⁵ The most significant feature, however, was the absence of bands at the range of 1600–1800 cm^{-1} , indicating that no overoxidation or ring opening had occurred.

PEDOT is stable over a fairly high range of temperatures as seen in Figure 3. Significant degradation is observed at 110 and at 250 °C. The initial decrease in weight percent is due to evaporation of bound water.

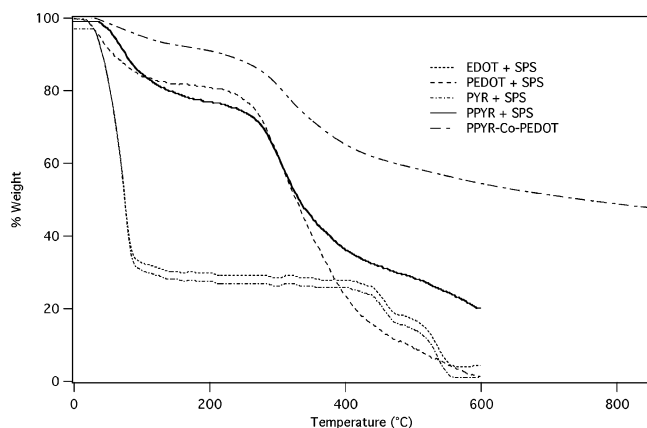


Figure 3. TGA of the different monomers and polymers.

The electrical conductivity data for the PEDOT (1×10^{-3} S/cm) is similar to the measured conductivity of the commercial PEDOT (Baytron).

The UV-vis spectrum of the water-soluble SPS/PPYR is also shown in Figure 1. The peak at 420 nm is assigned to an electron transition from the valence band state to an antibonding bipolaron state. The high absorption (900 nm and above) is related to an electron transition, to the valence band to the bonding bipolaron state. Moreover, conjugation was also confirmed by the FTIR spectrum of the polymer (Figure 2), wherein the peaks at $1480/1540\text{ cm}^{-1}$ are assigned to the symmetric and antisymmetric ring stretching modes, respectively.¹⁶

Similar to PEDOT, PPYR shows good thermal stability. The polymer exhibits two degradation temperatures. The first is due to bound water ($115\text{ }^{\circ}\text{C}$) and the second is assigned to polymer degradation ($273\text{ }^{\circ}\text{C}$). Conductivity for the PYR polymerized with PEG-hematin was measured with a four-point probe and found to be 1×10^{-4} S/cm. The low conductivity for this polymer is not a surprise. It is known that electrochemical polymerization, in water, of PYR yields a polymer with poor electrical conductivity.¹⁶ This is attributed to the formation of oxidized nonconjugated forms of PPYR that significantly lower the conductivity of the polymer.¹⁴ Nevertheless, this is the first water-soluble PPYR synthesized via synzyme.

In addition, copolymerization of EDOT and PYR was also carried out with PEG-hematin. The UV-vis spectrum (Figure 1) of this copolymer showed a large absorbance in the 400–900 nm range. Moreover, the conductivity of the copolymer was higher than that of the solitary homopolymers and was found to be in the range of 0.1–1.0 S/cm. This unusual result generated an increased interest in a thorough analysis of this copolymer. The FTIR spectrum of the copolymer (Figure 2) shows two important peaks. The first, centered at 3894 cm^{-1} , is due to intramolecular H-bonding, and a broad peak ($1384\text{--}1790\text{ cm}^{-1}$) is due to extended conjugation in the polymer backbone.

Thermal gravimetric analysis shows remarkable thermal stability. This counterintuitive result can be explained only by a synergic interaction of the two different monomers. MALDI-TOF mass spectrometry shows a prominent peak at an m/z value of 3120.84 g/mol.

Furthermore, ESCA studies were conducted on all polymers to further characterize this unique copolymer. It is evident from Figure 4 that the copolymer is not a mix of the two homopolymers. The binding energies for S 1s (163.5 and 167.5 eV) are different from the binding energies reported for PEDOT (164.4

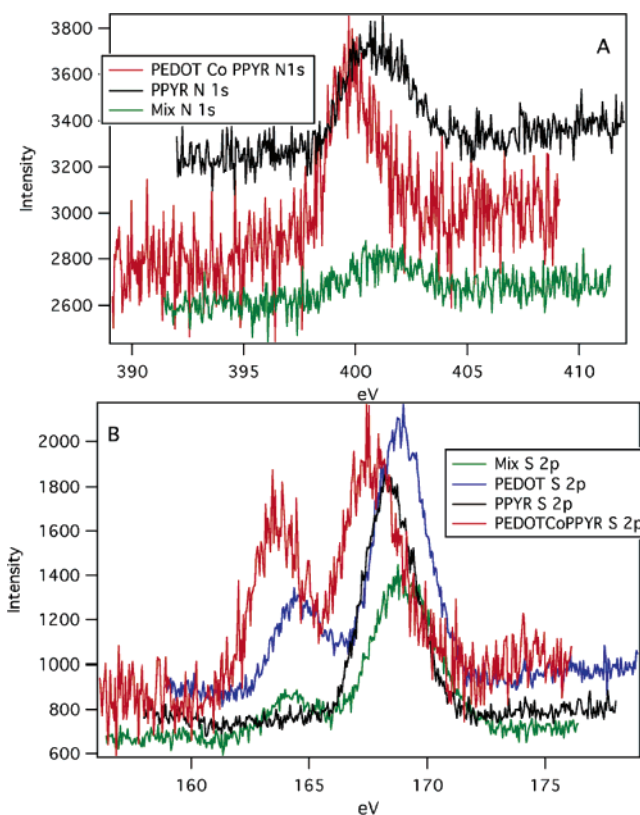


Figure 4. ESCA of N 1s orbital and S 2p orbital for PEDOT, PPYR, PEDOT-co-PPYR, and a mix of the two homopolymers.

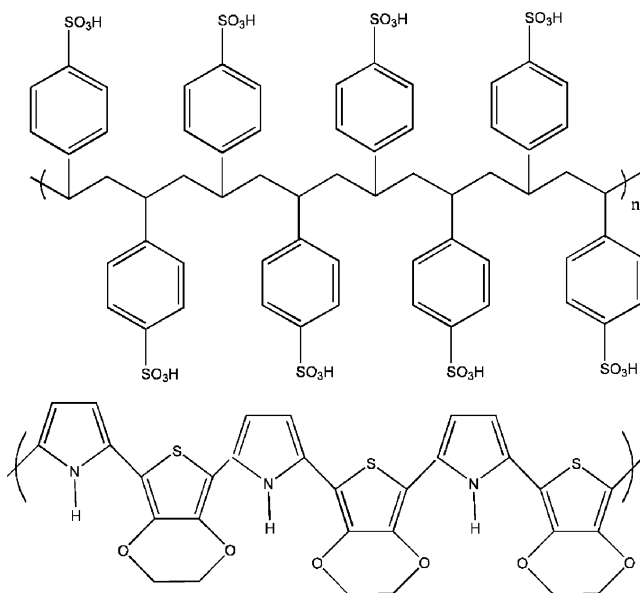


Figure 5. Proposed structure for the copolymer.

and 169.0 eV) and PPYR (168.4 eV). Similarly, the largest intensity peak for N 1s orbital for the PPYR is 399.7 eV . In contrast, the copolymer has a peak at 398.0 eV .

The proposed structure is reported in Figure 5. This structure will justify the high conductivity due to planarity of the final copolymer. Furthermore, the significant thermal stability can be attributed to the intramolecular hydrogen-bonding absorption observed in the FTIR that can arise only when PYR is adjacent to EDOT in the copolymer. Additionally, ESCA does not show presence of a block copolymer. Finally, modeling calculations show the lowest energies and a planar structure for the alternating copolymer.¹⁷ This evidence does not eliminate the

possibility of a statistical copolymer but is strongly suggestive that any blocks of PYR or EDOT are very short.

Conclusions

In summary, a novel biomimetic method for the synthesis of conducting molecular complexes of polypyrrole and of PEDOT in the presence of a polyelectrolyte, such as polystyrene sulfonate (SPS) is presented. A poly(ethylene glycol)-modified hematin (PEG-hematin) was used to catalyze the polymerization. UV-vis, FTIR, XPS, TGA, and electrical conductivity studies for all complexes indicate the formation of the electrically conductive form of these polymers. Copolymers of EDOT and pyrrole have also been synthesized and these novel materials have been shown to exhibit high electrical conductivity, with a unique combination of properties such as processability and water solubility.

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