Water-soluble Poly(3,4-ethylenedioxythiophene) Nanocomposites Created by a Templating Effect of *β*-1,3-Glucan Schizophyllan

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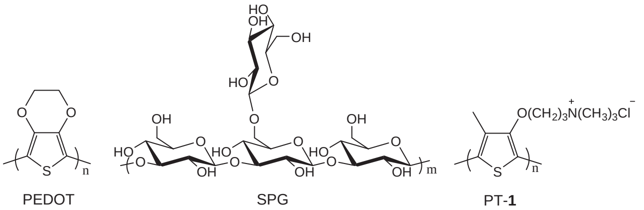
Chemical polymerization of 3,4-ethylenedioxythiophene (EDOT) in the presence of single-chain schizophyllan (s-SPG) gave water-soluble nanocomposites with the very uniform globular structure. The findings indicate that s-SPG is capable of acting not only as a one-dimensional host to create fibrous architectures but also as a neutral host to create nanoparticles. The mechanism is reasonably explained by the difference in the hydrophobicity of guest polymers or assemblies.

Poly(3,4-ethylenedioxythiophene) (PEDOT) (Scheme 1) has been widely investigated during the past decade owing to its low band gap, high conductivity, good environmental stability, and excellent transparency in its oxidized state.[1,2] More recently, the preparation and characterization of PEDOT nanostructures have become a topic of increasing interest due to their potential applications to electrical, optical, and sensor devices.[3–7] Several methods have been developed for the construction of these novel nanostructures, such as chemical or electrochemical polymerization of monomer using nanoporous membranes,[3] surfactant aggregates,[4] carbon nanotubes,[5] liquid crystals,[6] and silica or polystyrene latex particles[7] as templates.

Schizophyllan (SPG) (Scheme 1) is a natural β-1,3-glucan and is known to exist as a triple helix (t-SPG) in water but as a single random coil (s-SPG) in dimethyl sulfoxide (DMSO).[8] When water is added to its DMSO solution, s-SPG retrieves its original triple helix (renaturation). These specific structural characteristics make s-SPG form the stable water-soluble complexes with certain polynucleotides,[9] single-walled carbon nanotubes,[10] conjugated polymers,[11,12] silica,[13] porphyrin,[14] and Au nanoparticles[15] during its renaturation process. In the present work, our attention has been focused on extending this novel concept into the creation of PEDOT nanostructures. Herein, we report the preliminary results about the preparation of water-soluble PEDOT/SPG nanocomposites by chemical polymerization of EDOT in the presence of s-SPG based on a different mechanism. Being different from other systems which tend to give the one-dimensional architectures, the present system gives "nanoparticles" with the very uniform diameter.



Scheme 1.

As a typical experimental procedure, EDOT monomer and SPG ($M_w = 1.5 \times 10^{-5}$) were first dissolved in DMSO, and the solution was then added into water under stirring. Polymerization was initiated by the addition of an aqueous solution of oxidant ammonium persulfate (APS). The concentrations of the s-SPG/EDOT/DMSO and APS/water solutions were chosen so that, after mixing, the final concentrations of EDOT, s-SPG, and APS were 9.4 mM, 0.5 mg mL^{-1} (or 3.0 mg mL^{-1}), and 94 mM, respectively, and the volume fraction of water in the mixed solvent (V_w) was 0.95 unless specially stated. After polymerization (48 h at 35 °C), repetitive centrifugation (9000 rpm for 1 h each) and re-dispersion were performed to exchange the mixed solvent to water and to remove unreacted chemicals. These processes lead to homogeneous and stable aqueous dispersions with dark blue color, which exhibit a broad absorption peak centered around 750 nm (Figure S1). This peak is often present in the oxidized and doped conjugated polymers, and has been attributed to a polaron or bipolaron state.[6] To show the distinctive ability of s-SPG, three reference experiments were conducted for EDOT polymerization, in which all parameters and preparation procedures are the same as those used for s-SPG except (i) the absence of SPG, (ii) the presence of t-SPG (0.5 mg mL^{-1}), and (iii) the presence of amylose (0.5 mg mL^{-1}, $M_w = 1.6 \times 10^{-5}$) instead of s-SPG. The results indicated that only the reaction system including s-SPG resulted in a stable aqueous PEDOT dispersion whereas all reference experiments produced precipitates (Figure S2). It is clear, therefore, that s-SPG is playing an important role in stabilization of PEDOT in aqueous solution, thereby preventing self-aggregation followed by formation of precipitates.

The aggregated structures of water-soluble PEDOT/SPG

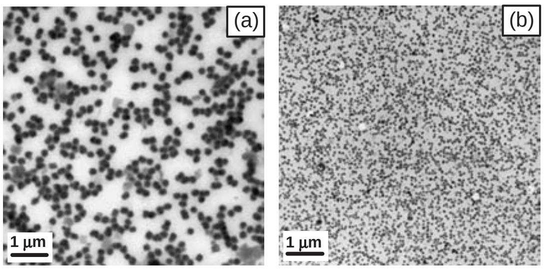


Figure 1. TEM images of PEDOT/SPG nanoparticles prepared by APS oxidant in the presence of s-SPG. (a) [SPG] = 0.5 mg mL^{-1}; (b) [SPG] = 3.0 mg mL^{-1}. [EDOT] = 9.4 mM; [APS] = 94 mM.

composites were detected by transmission electron microscopy (TEM, without staining). PEDOT was easily distinguished by TEM since it has a higher electron density than polysaccharide. Figure 1 shows the TEM images of PEDOT/SPG composites prepared by using APS as oxidant. It is clearly seen from this figure that PEDOT nanoparticles with the uniform size and the regular shape are formed in the presence of s-SPG, and with increasing SPG concentration, the diameter of nanoparticles decreases from 160 nm ($[\mathrm{SPG}] = 0.5\,\mathrm{mg\,mL^{-1}}$) to 70 nm ($[\mathrm{SPG}] = 3.0\,\mathrm{mg\,mL^{-1}}$). To further corroborate that s-SPG really acted as a template for the creation of PEDOT superstructures, the energy dispersive X-ray (EDX) analysis for the PEDOT/SPG nanoparticles were performed. It was confirmed that PEDOT and SPG coexist in the nanocomposites based on the fact that the O/S ratio (3/1) in the composites is significantly higher than the theoretical ratio in PEDOT (2/1). It is worthy to note here that the morphology of the PEDOT/SPG composites is entirely different from those of the supramolecular complexes formed between s-SPG and water-soluble (or hydrophilic) guests, which usually give the one-dimensional fibrous architectures.[9,11–15] These differences will be discussed in detail in the next section.

To elucidate the growth mechanism of PEDOT/SPG nanostructures, the absorption spectra of monomer EDOT in the absence and the presence of s-SPG were recorded (Figure S3). It is seen from this Figure that the absorption spectra are characterized by a broad band with a maximum around 255 nm, which is attributed to π–π^* electronic transitions, and that there is no distinct difference between the absence and the presence of SPG. The results indicate that no significant interaction occurs between SPG and monomer EDOT. This fact leads us to consider the bulk solution as a starting point for nucleation due to the good solubility of APS and EDOT in a $V_\mathrm{w} = 0.95$ DMSO–water mixed solvent.[16] After nucleation and growth, the more hydrophobic EDOT oligomer or polymeric PEDOT may interact with s-SPG to form PEDOT/SPG complex through hydrophobic interactions. Based on the experimental results presented here and reference reported previously,[17] a preliminary conceptual model for the formation of water-soluble PEDOT/SPG nanocomposites was proposed (Figure 2). We suggest that the two-component PEDOT/SPG supramolecular assembly may be regarded as a sort of amphiphilic block copolymers,[18] which can self-aggregate into nanoparticles under the present experimental conditions. This proposed model can be further supported by comparing the circular dichroism (CD) spectroscopic results of the PEDOT/SPG nanocomposites (not shown here) with those of the PT-**1**/SPG supramolecular complex reported previously (PT-**1** : poly[3-(4-methyl-3-thienyloxy)propyltrimethylammonium chloride]).[12] It was found that the PEDOT/SPG nanoparticles prepared by APS oxidant was CD-silent, whereas the PT-**1**/SPG supramolecular complex with the one-dimensional fibrous structure gave an intense split type induced CD (ICD) due to the interchain interaction between helical SPG and PT backbones. PEDOT is hydrophobic and insoluble in water–DMSO mixed solvent, being different from water-soluble PT-**1**. Once PEDOT is formed, the polymer chains intend to aggregate and the intermolecular π-stacking appears to be too strong to induce a conformational change upon the complexation with SPG, and therefore, no ICD is detected. On the other hand, water-soluble PT-**1** is characterized as an amphiphilic molecule, in which the substituted quaternary ammonium groups are hydrophilic and the polythiophene backbones are hydrophobic. Therefore, the water-soluble PT-**1** can exist in water as a single chain with random-coiled conformation, which makes it possible to form chiral supramolecular complexes with SPG.

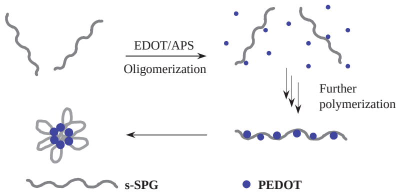


Figure 2. Schematic illustration of the possible growth mechanism of water-soluble PEDOT/SPG nanocomposites.

In conclusion, we have demonstrated that polymerization of EDOT in the presence of s-SPG can result in stable water-soluble PEDOT/SPG nanocomposites with the uniform size and the regular shape. The results presented here will not only confirm that SPG is a versatile neutral host in aqueous solution, but also open a way to construct water-soluble conjugated polymer superstructures.

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