Enzyme-Mimetic Synthesis of PEDOT from Self-Folded Iron-Containing Single-Chain Nanoparticles

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ABSTRACT: Intrinsically conducting polymers (ICPs) such as poly(3,4-ethylenedioxythiophene) (PEDOT) have attracted significant interest for the development of flexible light-emitting diodes, electrochromic devices and solar cells, as well as for a variety of biosensing and regenerative medicine applications. Herein, we disclose the use of water-soluble self-folded metal-containing single-chain nanoparticles (SCNPs) as robust enzyme-mimic nanoreactors for the synthesis of ICPs *via* step-growth polymerization. As a proof of concept, we report the first enzyme-mimetic synthesis of PEDOT at room temperature (r.t.) *via* oxidative polymerization using self-folded iron-containing SCNPs as efficient artificial pseudo-enzymes. Remarkably, this work paves the way to the synthesis of other types of ICPs (*e.g.*, polyaniline, polypyrrole) using water-soluble metal-containing SCNPs as robust enzyme-mimic nanoreactors operating at r.t., and expands the use of SCNPs as bioinspired catalysts from chain-growth polymerization (*i.e.*, ring-opening polymerization and living radical polymerization) to step-growth polymerization (*i.e.*, polycondensation *via* oxidative polymerization).

Keywords: Nanoparticles; iron complexes; enzymes; biomimetic synthesis; PEDOT

1. Introduction

Intrinsically conducting poly(3,4-ethylenedioxythiophene) : polystyrenesulfonate (PEDOT : PSS) films prepared upon water removal from PEDOT : PSS dispersions have attracted significant interest for the development of transparent electrodes [1], as functional layers in light-emitting diodes [2], electrochromic devices [3] and solar cells [4], as well as for biosensing [5] and regenerative medicine [6] applications. The first enzyme-mediated synthesis of a PEDOT : PSS dispersion was reported only 11 years ago, through the use of horseradish peroxidase in the presence of PSS as both water-soluble template and charge-balancing dopant [7]. Traditional synthesis of PEDOT : PSS dispersions involves the use of iron-containing salts and oxidants such as ammonium persulfate. With the aim to introduce environmentally friendly alternatives over conventional chemical catalyst, a variety of enzyme-mediated synthesis of PEDOT : PSS have been developed in recent years by introducing proteins containing iron in a heme complex (horseradish peroxidase [1], soybean peroxidase [8], catalase and hemoglobin [9], cytochrome c [10]) and hydrogen peroxide as an oxidant. The properties of the resulting PEDOT : PSS films depend on the specific enzyme employed during the synthesis [11]. Interestingly, as demonstrated by Hira and Payne [12], even simple iron-binding proteins showing no enzymatic activity (*e.g.*, transferrin) can be used as oxidants for the synthesis of PEDOT : PSS dispersions. This fact significantly expands the library of biomolecular oxidants available for the synthesis of PEDOT-based films with a desired set of properties, since nowadays over 800 different heme proteins are known [13].

Recently, the use of single-chain polymer nanoparticles (SCNPs) as enzyme-mimic constructs has attracted significant interest [14-17]. It is worth mentioning that SCNPs endowed with enzyme-mimetic morphology and activity often show increased stability against thermal changes and reduced degradability when compared to natural enzymes [18].

SCNPs are constructed *via* self-folding of a single linear polymer chain by means of intra-chain covalent bonds or supramolecular interactions (*e.g.*, hydrogen bonding, dynamic covalent bonds, metal complexation) [19-29]. Two limiting morphologies have been observed in SCNPs depending on the particular synthesis route employed and the hydrophobic/hydrophilic balance of the SCNPs precursor chain. A sparse morphology resembling that displayed by intrinsically disordered proteins is often observed by means of intrachain folding/collapse of the precursor under good solvent conditions [30,31]. Conversely, a globular morphology more akin to that found in enzymes is typically obtained by single-chain self-folding in water of amphiphilic (neutral or charged) random copolymers of appropriate composition and molecular weight [32-36]. Recently, SCNPs have been used as enzyme-mimetic nanoreactors for the synthesis of a variety of chemical compounds [14], gold nanoparticles [37], quantum dots [38], and carbon nanodots [39], as well as for ring-opening polymerization (ROP) [40] and living radical polymerization (LRP) [41,42] processes. Hence, SCNPs containing entrapped $B(C_6F_5)_3$ molecules were found to display polymerase-like activity toward tetrahydrofuran *via* ring-opening polymerization in the presence of glycidyl phenyl ether that played the role of a co-catalyst [40]. Additionally, our group reported the metalloenzyme-mimic properties of copper (II)-containing SCNPs toward the controlled radical polymerization of water-soluble vinyl-type monomers under reductive conditions [41]. Very recently, efficient living radical polymerization of various alkyl methacrylate monomers using iron-containing SCNPs has been described by Azuma *et al.* [42].

However, to the best of our knowledge, the use of water-soluble self-folded metal-containing SCNPs as robust enzyme-mimic nanoreactors for the synthesis of intrinsically conducting polymers (ICPs) *via* step-growth polymerization has not been investigated yet. In this work, we report the first enzyme-mimetic synthesis of PEDOT : PSS dispersions at room

temperature (r.t.) *via* oxidative polymerization using self-folded iron-containing SCNPs as efficient artificial pseudo-enzymes. Remarkably, this work paves the way to the synthesis of other types of intrinsically conducting polymers (*e.g.*, polyaniline, polypyrrole) for a variety of potential applications using water-soluble SCNPs as robust enzyme-mimic nanoreactors operating at r.t. Moreover, it expands the use of SCNPs as bioinspired catalysts from chain-growth polymerization (*i.e.*, ROP and LRP) to step-growth polymerization (*i.e.*, polycondensation *via* oxidative polymerization).

2. Experimental part

2.1. Materials

Oligo(ethyleneglycol) methyl ether methacrylate (OEGMA) (average $M_n \sim 300$ g/mol), 2-acetoacetoxy ethyl methacrylate (AEMA) (95%), 3,4-ethylenedioxythiophene (EDOT) (97%), poly(sodium 4-styrenesulfonate) (PSS) (average $M_w \sim 77000$ g/mol), iron(II) acetate ($\text{Fe}(\text{OAc})_2$) (95%), 2,2-azobis(2-methylpropionitrile) (AIBN) ($\geq 98\%$), hydrogen peroxide (H_2O_2) (30 wt% solution in water, ACS reagent), and horseradish peroxidase (HRP) (type VI, essentially salt-free, lyophilized powder, ≥ 250 units / mg), 1,4-dioxane (anhydrous, 99.8 %), *N,N*-dimethyl formamide (DMF) (ACS reagent, 99.8 %) and deuterated chloroform (CDCl_3) (99.96 atom % D, containing 0.03 % (v/v) tetramethylsilane, TMS) were purchased from Aldrich. Tetrahydrofuran (THF) (GPC grade) and hydrochloric acid (extra pure, 37% in water) were supplied by Scharlau. 4-Cyanopentanoic acid dithiobenzoate (>97%) was purchased from Strem Chemicals. Deionized water obtained from a Thermo Scientific apparatus (Barnstead TII Pure Water System) was employed in this work. AIBN was recrystallized from methanol. OEGMA and AEMA were purified by passing through basic and neutral alumina, respectively.

2.2. Techniques

Size exclusion chromatography (SEC) measurements were performed at 30 °C on an Agilent 1200 system equipped with PLgel 5µm Guard and PLgel 5µm MIXED-C columns and triple detection: a differential refractive index (RI) detector (Optilab Rex, Wyatt), a multiangle laser light scattering (MALLS) detector (MiniDawn Treos, Wyatt), and a viscosimetric (VIS) detector (ViscoStar-II, Wyatt). Data analysis was performed with ASTRA Software (version 6.1) from Wyatt. THF was used as eluent at a flow rate of 1 mL/min. A value of $dn/dc = 0.115$ was used for the precursor and the single-chain nanoparticles. The freeze-drying system employed was a Telstar-Cryodos equipment. ^1H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker spectrometer operating at 400 MHz, using CDCl_3 as solvent. AEMA content was determined following the procedure described in Ref. [41]. Fourier transform infra-red (FTIR) measurements were performed at r.t. on a Jasco 3600 FTIR spectrometer. Dynamic Light Scattering (DLS) measurements were carried out at 25 °C in a Zetasizer Nano-ZS apparatus. Ultraviolet-visible (UV-vis) spectra were recorded on an Agilent 8453A apparatus equipped with a Peltier thermostatic cell holder (T-controller 89090A). Metal content was determined by inductively coupled plasma (ICP) atomic emission spectroscopy performed on an Agilent 7700X spectrometer. Atomic Force Microscopy (AFM) measurements were performed using a Multimode AFM, equipped with a Nanoscope V controller (Bruker). All images were taken in tapping mode, using Multi300Al-G probes (Budgetsensors). Samples for AFM were prepared by spin coating (3000 rpm, 2 min) the PEDOT : PSS dispersions at 100 mg/mL concentration onto glass slides, allowing to obtain thin films. Prior coating, the glass substrates were washed in soapy solution with deionized water, rinsed with acetone and finally dried under a N_2 flow. Conductivity of PEDOT : PSS thin films was measured using a 4-point probe setup (HFS600-P, Linkam) and a Alpha impedance analyzer (Novocontrol).

2.2. Synthesis of artificial iron-containing pseudo-enzymes

In a typical procedure, 1000 mg of an amphiphilic random copolymer of oligo(ethyleneglycol) methyl ether methacrylate (OEGMA) and 2-acetoacetoxy ethyl methacrylate (AEMA) prepared following the experimental procedures reported in Ref. [41] (**P**, M_w : 150 KDa, D : 1.33, AEMA content: 24 mol%) were dissolved in 1000 mL of THF at r.t. To this solution, 73.4 mg of $\text{Fe}(\text{OAc})_2$ dissolved in 1 mL of DMF were added under stirring to induce intrachain folding/collapse *via* iron(II)/(AEMA)₂ complexation. After 24h of reaction time, solvent exchange to water was performed and the mixture was dialyzed to remove unreacted $\text{Fe}(\text{OAc})_2$ and residual organic compounds. The concentration of the final single-chain nanoparticles (**NP**) solution in water was 0.96 mg / mL. Finally, a fraction of the **NP** solution was isolated *via* freeze-drying for characterization and other fraction was kept in solution to be used as artificial iron-containing pseudo-enzymes. The average number of iron atoms per individual single-chain nanoparticle was found to be 48 by ICP atomic emission spectroscopy.

2.3. Synthesis of PEDOT using artificial iron-containing pseudo-enzymes

In a typical reaction, 0.512 mL of artificial iron-containing pseudo-enzymes aqueous solution (0.49 mg of **NP**), 226.6 mg of poly(sodium 4-styrenesulfonate) (PSS) and 0.117 mL of 3,4-ethylenedioxythiophene (EDOT) monomer were dissolved in water (20 mL) at r.t. under an argon atmosphere. To this mixture, 0.112 mL of a hydrogen peroxide solution (30 wt% H_2O_2 solution in water) was added. The oxidative polymerization of EDOT was followed by UV-vis spectrometry by taken periodically samples from the polymerization medium. After reaction completion, conducting films (containing the artificial iron-containing pseudo-enzymes) were prepared from the resulting PEDOT : PSS dispersions *via* solvent casting.

3. Results and discussion

3.1. Synthesis of iron-containing self-folded single-chain nanoparticles as artificial pseudo-enzymes

Fig. 1 illustrates the synthetic approach followed in this work to produce iron(II)-containing SCNPs as artificial pseudo-enzymes. Based on our previous work [41], we synthesized a high molecular weight ($M_w = 150$ kDa, $\bar{D} = 1.33$) amphiphilic random copolymer (**P**) composed of OEGMA (76 mol%) and AEMA (24 mol%) units to guarantee the formation of single-chain core-shell globules in water with the hydrophobic AEMA units

Fig. 1. Schematic illustration of the synthesis of self-folded iron(II)-containing single-chain nanoparticles (**NP**) as artificial pseudo-enzymes.

placed in the core and the hydrophilic OEGMA moieties in the shell, by working at highly diluted conditions (1 mg **P** / mL). Metal complexation of AEMA units was carried out for 24h at r.t. The resulting single-chain nanoparticles (**NP**) were purified from unreacted Fe(OAc)₂ and residual organic compounds by dialysis after solvent exchange to water, and isolated for characterization *via* freeze-drying. The efficient formation of self-folded iron-containing SCNPs was confirmed by combined size exclusion chromatography (SEC) and dynamic light scattering (DLS) measurements. As depicted in Fig. 2A, the iron-containing SCNPs **NP** showed an increase in retention time (*i.e.* a reduction in hydrodynamic size) during SEC in

Fig. 2. A) Size-exclusion chromatography (SEC) traces in THF showing the typical reduction in hydrodynamic size of an amphiphilic random poly(OEGMA-*co*-AEMA) copolymer (**P**) (continuous red line) upon intra-chain iron(II) complexation to give single-chain nanoparticles

(NP) (broken blue line). B) Dynamic light scattering (DLS) results showing the different size of single-chain nanoparticles NP in H₂O, which is a good solvent for OEGMA units and a bad solvent for AEMA moieties (continuous blue line) and in THF, which is a good solvent for both OEGMA and AEMA repeat units (broken red line).

THF when compared to the amphiphilic random copolymer precursor **P** due to the formation of intrachain iron(II)/(AEMA)₂ complexes in the former case. The difference in hydrodynamic size of the iron-containing SCNPs when dissolved in water (good solvent for OEGMA units, bad solvent for AEMA moieties) and in THF (good solvent for both OEGMA and AEMA units) is shown in Fig. 2B, as determined by DLS measurements. The conformational change taking place on passing from THF to H₂O due to a modification in solvophilic / solvophobic balance promoting the self-folding of **P** to individual core-shell nanoparticles is illustrated schematically in Fig. 1. Further compaction is induced by intrachain iron(II)/(AEMA)₂ complexation. On average, self-folded iron-containing SCNPs were found to contain 48 Fe atoms per single-chain nanoparticle as determined by ICP atomic emission spectroscopy, which is a value similar to that found in copper-containing globular SCNPs prepared from amphiphilic random poly(OEGMA-*co*-AEMA) copolymers [41]. The above results support the efficient formation in water of individual SCNPs containing Fe(II)/(AEMA)₂ complexes placed in a hydrophobic core, which is stabilized by an external hydrophilic shell.

3.2. Synthesis and characterization of PEDOT using artificial iron-containing pseudo-enzymes

The enzyme-mimetic synthesis of PEDOT at r.t. using self-folded iron(II)-containing single-chain nanoparticles as artificial pseudo-enzymes is depicted in Fig. 3A. We follow a recipe similar to that used during the first reported enzymatic synthesis of PEDOT [7] but

Fig. 3. A) Schematic illustration of enzyme-mimetic synthesis of PEDOT : PSS dispersions at r.t. using self-folded iron(II)-containing SCNPs as artificial pseudo-enzymes. B) Evolution of the color of the reaction mixture with reaction time during the enzyme-mimetic synthesis of PEDOT.

totally replacing the horseradish peroxidase (**HRP**) enzyme by the self-folded iron(II)-containing SCNPs **NP** as artificial pseudo-enzymes, at a concentration of 0.96 mg **NP** / mL, (see Section 2.3 for technical details). As illustrated in Fig. 3B, the initially transparent reaction medium takes a deep blue color upon formation of the PEDOT : PSS dispersion at 3 h of reaction time, showing the ability of the self-folded iron(II)-containing SCNPs to perform as artificial pseudo-enzymes. It should be noted that by using neat $\text{Fe}(\text{OAc})_2$ instead of **NP**, the resulting PEDOT : PSS dispersion took a deep blue color only after 5 h of reaction time (see Supplementary material). A comparison of the performance of **NP** *versus* **HRP** for the preparation of PEDOT : PSS dispersions is shown in Fig. 4A, as determined by UV-vis spectroscopy. Although for the HRP-mediated synthesis of PEDOT : PSS dispersions the reported optimum temperature was 4°C [7], we found that the reaction temperature can be increased to r.t. by working under an inert argon atmosphere (Fig. 4A). Advantageously, the polymerization kinetics at r.t. is faster than at 4 °C. Remarkably, the characteristics of the

Fig. 4. A) Comparison of the UV-vis spectra corresponding to PEDOT : PSS dispersions prepared at r.t. by using self-folded iron(II)-containing single-chain nanoparticles as artificial pseudo-enzymes (**NP**) or horseradish peroxidase (**HRP**) enzyme (also the spectrum obtained by using **HRP** at 4°C is included for comparison). B) FTIR spectra corresponding to PEDOT : PSS films prepared from the dispersions described in A). C) Comparison of the UV-vis spectra corresponding to PEDOT : PSS dispersions prepared with **NP** in water, and **NP** in THF.

PEDOT : PSS dispersions and PEDOT : PSS films synthesized using **NP** or **HRP** at r.t. for 3 h were very similar, as determined by UV-vis (Fig. 4A) and FTIR spectrometry (Fig. 4B), respectively. Hence, the characteristic bipolaron absorption band around 800 nm was observed in both the PEDOT : PSS dispersion prepared with the artificial pseudo-enzymes **NP** and the PEDOT : PSS dispersion synthesized using the horseradish peroxidase, **HRP**, enzyme (Fig. 4A). Such bipolaron absorption band which is a signature of the conductivity of the resulting PEDOT was absent when the synthesis was performed using **NP** dissolved in THF instead of water (see Fig. 4C). Thin films prepared from PEDOT : PSS dispersions synthesized at r.t. for 3 h using **NP** as artificial pseudo-enzymes were examined by atomic force microscopy (AFM) as illustrated in Fig. 5. The bare glass slide showed a roughness of about 2.15 nm (Fig. 5A) that after coating with the PEDOT : PSS dispersion was significantly reduced to 0.35 nm (Fig. 5B). AFM images also showed that there were not any important presence of holes or discontinuities on the substrate after coating, indicating the homogeneous coverage of the PEDOT : PSS thin films. Using sharp tweezers, we performed a scratch on the PEDOT : PSS thin film and its thickness was quantified via AFM by the step height presented in Figure 5C, resulting in a film thickness of 250 ± 4 nm. Conductivity measurements on the PEDOT : PSS coated glass slide were performed using a 4 point probe setup. A mean electrical conductivity of $\sigma = 1 \times 10^{-4}$ S/cm was determined which is similar to

Fig. 5. AFM topography images (3 x 3 μm) of: (A) a bare glass slide, and (B) a PEDOT : PSS coated glass slide prepared from a PEDOT : PSS dispersion synthesized at r.t. for 3 h of reaction time by using self-folded iron(II)-containing single-chain nanoparticles **NP** as artificial pseudo-enzymes. (C) Film thickness determination *via* AFM step height method.

that typically reported for PEDOT : PSS films prepared from PEDOT : PSS dispersions synthesized using iron-containing proteins like catalase ($\sigma = 1.3 \times 10^{-5}$ S/cm).

4. Conclusions

This work establish the use of water-soluble self-folded metal-containing single-chain nanoparticles (SCNPs) as robust enzyme-mimic nanoreactors for the synthesis of intrinsically conducting polymers (ICPs) *via* step-growth polymerization. As a proof of concept, we performed the first enzyme-mimetic synthesis of poly(3,4-ethylenedioxythiophene) : polystyrenesulfonate (PEDOT : PSS) dispersions *via* oxidative polymerization using self-folded iron(II)-containing SCNPs as efficient artificial pseudo-enzymes. The synthesis, that can be easily carried out in water at r.t for 3 h under argon atmosphere, provides with a PEDOT : PSS dispersion displaying the characteristic bipolaron UV-vis absorption band at 800 nm from conducting PEDOT. Thin films prepared from this PEDOT : PSS dispersion showed a value of electrical conductivity of $\sigma = 1 \times 10^{-4}$ S/cm, similar to that typically reported for PEDOT : PSS films prepared from PEDOT : PSS dispersions synthesized using iron-containing proteins like catalase ($\sigma = 1.3 \times 10^{-5}$ S/cm). This work opens the door to the synthesis of other types of ICPs (*e.g.*, polyaniline, polypyrrole) using water-soluble metal-containing SCNPs as robust enzyme-mimic nanoreactors operating at r.t, and expands the use of SCNPs as bioinspired catalysts from chain-growth polymerization (*i.e.*, ring-opening polymerization and living radical polymerization) to step-growth polymerization (*i.e.*, polycondensation *via* oxidative polymerization).

Notes

The authors declare no competing financial interest.

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