Spontaneous stacking of electrospun conjugated polymer composite nanofibers producing highly porous fiber mats

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ABSTRACT

We produced novel composite nanofibers based on poly(6,6′-((2-methyl-5-((*E*)-4-((*E*)-prop-1-en-1-yl)styryl)-1,4-phenylene)bis(oxy))dihexanoic acid)/poly(lactic acid) (PDMP/PLA), using electrospinning technique. The composite nanofibers have a diameter in the range of 50–150 nm and present a novel morphology consisting of spontaneously stacked nanofibers creating a "wall-like" structure that then collectively form a "honeycomb" structure. As low as 0.5–1 wt% of the photoluminescent PDMP was able to produce this type of morphology. The pore size depends on the amount of PDMP incorporated in the nanofibers. The highly fluorescent and porous nanofibers mats provide good biosensing substrates. We provide evidence that the composite nanofibers can be used to construct a simple oligonucleotide (ODN) sensor, where capture probe ODNs (capODN) were covalently grafted onto the carboxylic acid functionalities of the composite nanofibers and the reporting ODN carries a reporting chromophore dye. The results indicate potential of such nanofiber mats as biosensor.

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1. Introduction

Conducting polymer (CP) nanofibers and their composites with conventional polymers have gained great attention due to the advantageous properties in applications such as electronic devices [1], scaffolds for tissue engineering [2–4] and sensors [5]. One of the promising approaches for producing CP nanofibers is electrospinning. Electrospinning is a simple but powerful technique which has gained enormous attention owing to its potential to fabricate very fine polymer fibers from micrometer to nanometer sizes [6]. Not only the fiber diameter, but also the orientation or shape of the produced fibers can be altered via electrospinning by using different collector geometries [7] or types of polymer [8]. For example, the electrospinning jet is influenced by the electrostatic field profile, when two parallel conducting electrodes are used as a collector, the electric field lines surrounding the electrodes are split into two fractions pointing toward the edges of the electrodes and as a result the electrospun fibers align themselves across the gap

[9]. Fibers with helical shape were produced from a mixed solution of poly(ethylene oxide) (PEO) and poly(aniline sulfonic acid) where the diameter of the loops was varied by changing the concentration of PEO in the mixture [8]. It was thought that the conductive poly(aniline sulfonic acid) played an important role as the helical fiber structure could not be produced from a pure PEO solution.

Poly(*p*-phenylene vinylene) is a well-known conjugated polymer discovered in 1990s [10,11]. PPV exhibits excellent photoluminescent and electroluminescent properties, which made it commonly used in electroluminescent devices such as organic light-emitting diodes [10,12–14]. Significant efforts have been made to fabricate PPV-based nanofibers [13–15]. These studies have shown that the solid state of PPV can strongly influence the nanofiber properties [16]. For example, Madhugiri et al. [17] have employed a dual syringe electrospinning method to prepare semiconducting and electroluminescent composite fiber networks using poly[2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylene vinylene] (MEH-PPV) and molecular sieve material, silica SBA-15. The resulting fibers were approximately 200 nm in diameter with many exhibiting a leaf-like structure and random orientation. The composite fibers exhibited a blueshift in the emission compared to the bulk, which is attributed to the non-aggregation of the MEH-PPV polymer chains in the composite fibers. The mesoporous silica in the fibers acted as a nanospacer, thereby lowering polymer interchain interactions, resulting in the blueshift in the emission.

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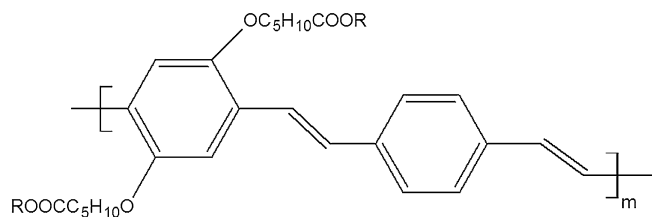
Fig. 1. Poly(6,6′-((2-methyl-5-((E)-4-((E)-prop-1-en-1-yl)styryl)-1,4-phenylene)-bis(oxy))dihexanoic acid) (PDMP); R=H. Poly(dimethyl 6,6′-((2-methyl-5-((E)-4-((E)-prop-1-en-1-yl)styryl)-1,4-phenylene)bis(oxy)))dihexanoate (PDMP-Me); R=CH$_3$.

Other electrospun nanofibers, prepared by Babel et al. [18] consisted of a binary blend of MEH-PPV with regio-regular poly(3-hexylthiophene) (P3HT) or poly(9,9-dioctylfluorene) (PFO). The resultant MEH-PPV/P3HT nanofibers were found to have diameters of ca. 100–500 nm with random orientation. The MEH-PPV/P3HT blend nanofibers had 30–50 nm phase separated domains, allowing efficient energy transfer from MEH-PPV to P3HT, thus showing enhanced red emission from P3HT in the MEH-PPV/P3HT blend nanofibers. In contrast, in the MEH-PPV/PFO blend nanofibers that had core–shell structures, a significant energy transfer was absent due to less interfacial surface area between two polymers (PFO and MEH-PPV), leading to reduced interaction between the blend components and less efficient energy transfer. Another research has demonstrated nanofibers of MEH-PPV and polyethylene oxide blends as conveniently formed by the co-electrospinning method [14]. The fluorescence spectra of the nanofibers indicated blueshift in the emission peak with a decreasing concentration of MEH-PPV in the nanofibers, suggesting that the MEH-PPV polymer chains were less aggregated in the electrospun nanofibers.

In this paper, we report the production of a novel luminescent nanoscale size polymeric fiber using the electrospinning technique that presents an unusual, interesting morphology that opens up new areas of application of these materials, such as in biosensing and filtration membranes. An anionic derivative of PPV, poly(6,6′-((2-methyl-5-((E)-4-((E)-prop-1-en-1-yl)styryl)-1,4-phenylene)bis(oxy))dihexanoic acid) (PDMP), with the structure as shown in Fig. 1, was used and blended with poly(lactic acid) (PLA) in the electrospinning experiments. The PDMP has free carboxylic acids that were utilized for creating an optical DNA sensor, but can be further modified with various chemicals or biological moieties to introduce additional functionality to the fibers. We also report the electrospun nanofibers of PDMP with ester groups for comparison of morphologies (using the same electrospinning parameters as PDMP), namely the poly(dimethyl 6,6′-((2-methyl-5-((E)-4-((E)-prop-1-en-1-yl)styryl)-1,4-phenylene)bis(oxy)))dihexanoate (PDMP-Me).

2. Experimental procedure

2.1. Materials

The poly(lactic acid), with $M_w = 160,631$ g mol^{-1} and $M_n = 73,289$ g mol^{-1} used, was a 2002D, purchased from Natureworks Co., Minnetonka, USA. Tetrabutylammonium chloride (TBAC, Fluka), N,N-dimethylformamide (DMF, Sigma–Aldrich), chloroform (CHCl$_3$, ECP), 1-ethyl-3-(3-dimethylaminopropyl), carbodiimide hydrochloride (EDC, Sigma–Aldrich) and N-hydroxysuccinimide (NHS, Sigma–Aldrich) were used as received. Custom oligonucleotides were obtained from Alpha DNA. The oligonucleotide (ODN) capture probes (denoted as capODN) were amino modified at their 5′ end with the sequence NH$_2$-ATA CTC ATC-3′. The sequences of complementary and non-complementary target ODNs used in hybridization experiments were 5′-GAT GAG TAT

TGA TGC CGA-3′ and 5′-TCG TCA CCA ACT CTG ATC-3′, respectively. HPLC purified 5′-end Cy3 modified signal probes (denoted as signal probe ODN-Cy3) with the sequence 5′-TCG GCA TCA-3′ were used. Stock solutions of capODN were prepared in a pH 5.6 phosphate buffer saline solution (PBS) while complementary, non-complementary ODNs and signal probe ODN solutions were prepared in a sodium citrate (SSC buffer). The oligonucleotide solutions were stored in a freezer until needed. All aqueous solutions were prepared using Milli-Q water. PDMP and PDMP-Me were synthesized as reported previously [19].

2.2. Electrospun PDMP/PLA and PDMP-Me/PLA nanofibers

The PDMP was a solution blended with PLA to form nanofibers using the electrospinning technique.

1 mL of PDMP solution in DMF with concentration of 0.5 mg mL^{-1} was blended with 1 mL of PLA solution in chloroform with different concentrations to obtain the solutions with weight percentages of PDMP in PDMP/PLA from 0.25 to 1 wt%. The blended solution was electrospun at 0.4 mL h^{-1}, 12 kV of potential applied and a 10 cm distance between the needle tip and the metal plate collector. The electrospinning was performed at room temperature with the humidity kept at 40–50% and duration of 2 h. The composition of the PDMP/PLA blend solutions producing the nanofibers is summarized in Table 1. The PLA$_{0.5}$ and PLA$_1$ fiber mats were prepared from solutions similar to those used for the PDMP/PLA 0.5 wt% and the PDMP/PLA 1 wt%, but without PDMP, where only 1 mL DMF was added to the PLA solution. The PDMP/PLA fiber mats obtained from a solution without the addition of tributylammonium chloride salt (TBAC) are denoted as "wo TBAC". The nanofibers of PLA$_{0.5}$, PLA$_1$ and PDMP/PLA wo TBAC were prepared with keeping the other parameters constant (0.4 mL h^{-1}, 12 kV, 10 cm distance between needle tip and collector, room temperature and 40–50% humidity), thus the effect of the PDMP and/or the TBAC on the fiber morphology can be studied. TBAC of 0.01 M was added to the PDMP/PLA solutions of varying compositions to increase the ionic conductivity of the solution.

The effect of TBAC concentration on the fiber morphology was investigated by varying the salt concentration in the PDMP/PLA 0.5 wt% solutions: 0 M, 0.0025 M, 0.005 M, 0.01 M, 0.02 M, 0.05 M and 0.1 M. All of the electrospinning parameters were kept constant (12 kV voltages, 0.4 mL h^{-1} pump rate and a 10 cm distance between needle tip and collector) and the duration of the electrospinning was fixed at 1 h. The same electrospinning parameters, except time, were used in the study of the effect of electrospinning times (30 s, 1 min, 10 min, 20 min, 45 min and 1 h were chosen), and the TBAC concentration was kept constant at 0.01 M.

The preparation of the PDMP-Me/PLA was similar to that of the PDMP/PLA. The PDMP-Me solution in DMF with a concentration of 0.5 mg mL^{-1} was prepared at room temperature and filtered. The PDMP-Me solutions were 1 mL of PLA solution in chloroform with different concentrations to obtain the solutions with weight percentages of the PDMP-Me in PDMP-Me/PLA ranging from 0.25 to 1 wt%. 0.01 M TBAC was added to the solution to increase the ionic conductivity.

The morphology of the PDMP/PLA nanofibers was studied using scanning electron microscopy (SEM). The nanofibers were electrospun on aluminum foil and left to air dry. The aluminum foil covered with nanofibers was placed on the SEM stub using conductive double sided adhesive tape and sputtered with Pt coating. More than 25 fibers were randomly selected from the SEM images to measure the mean diameter of the fibers. The ionic conductivity of the PLA and PDMP/PLA solutions were measured using a MeterLab conductivity meter model CDM210 at room temperature.