

Functional electrospun nanofibres of poly(lactic acid) blends with polyaniline or poly(aniline-co-benzoic acid)

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ABSTRACT

Functionalised nanofibres of a controlled fibre diameter were electrospun from solutions of polyaniline (PANI) or poly(aniline-co-*m*-aminobenzoic acid) (P(ANI-co-*m*-ABA)) with poly(lactic acid) (PLA). Soluble copolymers of aniline (ANI) and *m*-aminobenzoic acid (*m*-ABA) were prepared and the average molecular weight of the copolymers, as determined by gel permeation chromatography, was found to decrease from 13,800 g mol⁻¹ to 1640 g mol⁻¹ with an increase of *m*-ABA content in the copolymer. By contrast, FT-MS results revealed that homopolymerisation of *m*-ABA formed oligomers rather than polymeric chains due to low reactivity of *m*-ABA monomer. ATR FTIR, Raman spectroscopy, and conductivity measurements confirmed incorporation of the conducting (co)polymers within the PLA based nanofibres. The conductivity of the nanofibres increased significantly with increased proportion of PANI or P(ANI-co-*m*-ABA) to 2.0 × 10⁻⁵ mS cm⁻¹ for PLA/PANI (3.27% of PANI) and 8.3 × 10⁻⁶ mS cm⁻¹ for PLA/P(ANI-co-*m*-ABA) (5.80% of the copolymer in the blend). The nanofibre diameter decreased from 640 ± 195 nm for pure PLA fibres to 141 ± 68 nm for PLA/PANI, and to 124 ± 31 nm for PLA/P(ANI-co-*m*-ABA). These fibres have potential for a range of applications, such as electroactive scaffold tissue engineering and sensing.

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1. Introduction

Conducting polymers such as polyaniline (PANI) and polypyrrole are commercially attractive in areas of sensing devices and as biocompatible tissue support structures. However, their utilisation in commercial applications is limited by poor processability and intractability [1,2]. A number of attempts have been made to improve the processability of PANI, including doping with functionalised protonic acids [3–5], preparing PANI composites with thermoplastic polymers [6], and synthesising copolymers of aniline and substituted anilines, e.g. with alkyl [7] (electron-donating), carboxylic acid [8] and sulfonic acid [9] (electron-withdrawing) substituents.

Acid functionalised polyaniline copolymers such as poly(aniline-co-*o*/*m*-aminobenzoic acid) (P(ANI-co-*o*/*m*-ABA)) and sulfonic acid ring-substituted polyaniline (SPAN) have been prepared chemically and electrochemically [10–16]. These copolymers show quite different properties from those of PANI homopolymer including lower conductivity, but improved solubility in common organic

solvents [10,11]. An interesting property of such copolymers is that the acid group in the polymer backbone can act as a “self dopant” instead of requiring an external dopant as is the case for polyaniline [11,17]. The advantage of self-doping is that the conductivity and electrochemical behaviour of the polymers show less pH dependence, and the polymers retain electroactivity even in basic solution [18,19].

PANI nanofibres and their blends with conventional polymers have excellent application potential in sensors [20], gas separation [21], electroactive scaffolds [22] and drug delivery [23], due to their characteristic nanostructure which provides a high surface area and conducting properties. One of the promising techniques for producing polymer nanofibres is electrospinning. Advantages of electrospinning as compared to other methods are that it requires a simple and inexpensive setup, as well as the fact that electrospinning is the only method which can be further developed for mass production of one-by-one continuous nanofibres from various polymers [24]. PANI has been electrospun with various polymers including poly(lactic acid) [25], poly(L-lactide-co-ε-caprolactone) [22], gelatin [26], polyethylene oxide [27] and polymethylmethacrylate [28]. Most of the studies used PANI doped with organic sulfonic acids such as camphor sulfonic acid (CSA) or *p*-toluene sulfonic acid (TSA) to improve the solubility of PANI. Few researchers have investigated electrospinning of aniline

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copolymers to form nanofibres. Aussawasathien et al. [29] demonstrated that poly(*o*-toluidine) can be electrospun and may have potential use as a sensing material for chemical vapour detection.

We have recently demonstrated that a conductive polymer nanofibrillar network of poly(lactic acid) can be electrospun with PANI, and its copolymers with *m*-ABA, from DMSO/THF solutions [30]. The obtained material showed interesting honeycomb-like nanofibrillar morphology and were found to be compatible with fibroblast cells. In this report, we have fully characterised the poly(aniline-*co*-*m*-aminobenzoic acid) copolymers and produced well-defined nanofibres by electrospinning PANI or P(ANI-*co*-*m*-ABA) solution blends with poly(lactic acid) (PLA) in DMF/THF mixed solvent.

2. Experimental

2.1. Reagents and materials

Aniline (Scharlau) was distilled under vacuum prior to use. *m*-Aminobenzoic acid (*m*-ABA; Sigma–Aldrich), ammonium persulfate (APS; Sigma–Aldrich), *N*-methyl-2-pyrrolidone (NMP; Sigma–Aldrich), *N,N*-dimethylformamide (DMF, Sigma–Aldrich), tetrahydrofuran (THF, Sigma–Aldrich), lithium bromide (LiBr; BDH), and triethanolamine (Sigma–Aldrich) were used as received. Poly(lactic acid, with $M_n = 73,289 \text{ g mol}^{-1}$ and polydispersity of 2.19 as determined by GPC versus polystyrene standards with THF as solvent and RI as detector, was a NatureWorks 2002D material.

All aqueous solutions were prepared using Milli-Q water.

2.2. Synthesis of polyaniline and copolymers

Polyaniline, P(ANI-*co*-*m*-ABA) copolymers and P(*m*-ABA) were synthesised in 1 M hydrochloric acid (HCl) at 10 °C, with APS as the oxidizing agent; the mole ratio of APS to monomer was kept constant at 1:1. The mole ratio of aniline to *m*-aminobenzoic acid (*m*-ABA) in the comonomer mixtures was varied from (90/10) to (20/80). A typical synthesis, of P(ANI-*co*-*m*-ABA) (50/50), for example, was as follows: 50 mL of 1 M HCl containing APS (3.65 g, 16 mmol) was slowly added with constant stirring to 100 mL of 1 M HCl containing aniline (0.75 g, 8 mmol) and *m*-ABA (1.1 g, 8 mmol) at 10 °C. A dark green colour developed immediately and the polymeric product started to precipitate from the solution. Polymerisation was continued with stirring for 24 h. The homopolymer P(*m*-ABA) was synthesised similarly except that the polymerisation time was 7 days. The polymer products were collected by filtration, washed with Milli-Q water until the filtrate was colourless, then vacuum dried at 40 °C. The percentage yield of polymer was calculated as $[\text{mass of the product}/\text{mass of the (co)monomer(s)}] \times 100$.

2.3. Preparation of electrospun nanofibres of PLA, PLA/PANI and PLA/P(ANI-*co*-*m*-ABA) (60/40)

30 mg emeraldine base (EB) of PANI or 50 mg P(ANI-*co*-*m*-ABA) (60/40) (EB) was mixed with 5 mL DMF and allowed to stand for 24 h at room temperature, to give solutions with concentration $3.38 \pm 0.03 \text{ mg mL}^{-1}$ or $6.16 \pm 0.06 \text{ mg mL}^{-1}$, respectively. The polymer solutions were filtered through regular qualitative filter paper (Whatman) to remove residues. The PANI or P(ANI-*co*-*m*-ABA) (60/40) EB solution was added to the PLA solution (10 w/v%) in DMF and an appropriate amount of THF was added to the mixture to give a DMF:THF ratio 1:1 (by volume). The mixed solutions were then stirred for 30 min.

The mixed PLA/conducting polymer solution was added to a 5 mL glass syringe with an 18G stainless steel needle used as a nozzle. A high voltage power supply (Bertan Hicksville, New York,

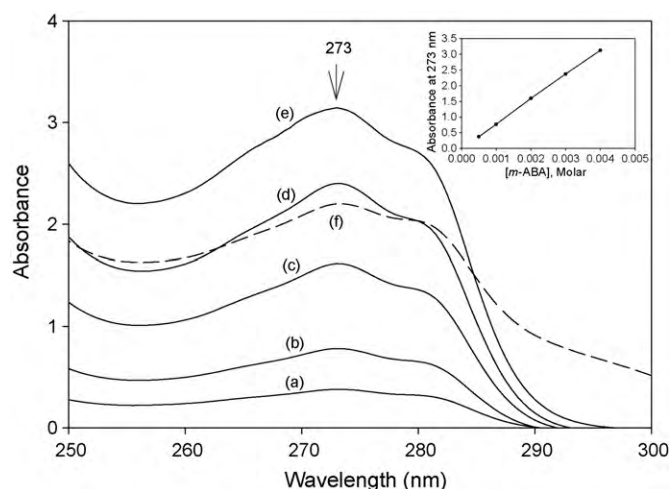


Fig. 1. UV–vis absorption of *m*-ABA solutions of different concentration in 1 M HCl: (a)–(e) 0.0005 M, 0.001 M, 0.002 M, 0.003 M, 0.0004 M and (f) absorption of unreacted *m*-ABA from polymerisation of P(ANI-*co*-*m*-ABA) (50/50) (for comparison). Inset: calibration graph of the absorbance of *m*-ABA at λ_{max} 273 nm vs. concentration of *m*-ABA.

series 230) was connected to the needle and collector. The collector was wrapped with aluminium foil and located at a fixed working distance of 10 cm from the needle tip. The flow rate of the polymer solution was controlled with a precision syringe pump (Cole-Parmer® Hz 50/60, cat# 789100C). The electrical field and flow rate were maintained at 16 kV and 0.4 mL h^{-1} . The resulting nanofibre mats were dried at room temperature, doped by treatment with 1 M HCl for 1 h, and vacuum dried at 25 °C for 2 days.

2.4. Characterisation

2.4.1. FTIR spectroscopy

Fourier transform infrared (FTIR) analysis of nanofibre samples was performed using the Smart Orbit Diamond Attenuated Total Reflection (ATR) Single Reflection accessory of a Thermo Electron Nicolet 8700 FTIR spectrometer.

2.4.2. Raman spectroscopy

Raman spectra were obtained with a Renishaw 1000 Raman spectrophotometer employing a 785 nm laser beam. A low laser power of 0.26 mW was used for pure polyaniline, P(ANI-*co*-*m*-ABA) (60/40), PLA/PANI and PLA/P(ANI-*co*-*m*-ABA) (60/40) nanofibres to avoid sample decomposition, and 26 mW was used for PLA nanofibres due to PLA showing a very weak Raman signal at low laser power.

2.4.3. Ultraviolet–visible spectrophotometry

UV–vis spectra of PANI and copolymers in emeraldine base form in NMP solution were recorded with a Shimadzu UV-2102PC spectrophotometer at room temperature.

The copolymer composition was determined by UV–vis spectrophotometry as follows. A set of standard solutions of *m*-ABA with a range of concentrations in 1 M HCl was prepared, and a calibration graph constructed based on the absorbance of *m*-ABA at λ_{max} 273 nm (Fig. 1). After polymerisation, each reaction mixture was immediately vacuum filtered and the filtrate (containing unreacted *m*-ABA) was diluted 20-fold for absorbance measurement. The absorption at 273 nm due to unreacted *m*-ABA monomer was used to calculate the amount of *m*-ABA that had reacted, and hence the copolymer composition.

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