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ORIGINAL PAPER

A facile synthesis of polyaniline/polyethylene glycol/polyaniline terpolymers: preparation of electrospun conducting nanofibers by blending of the terpolymers with polycaprolactone

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Abstract The water-soluble terpolymers were synthesized in two steps, containing esterification of polyethylene glycol (PEG) and 4-amino benzoic acid without protection of its amino group, then copolymerization of aniline from both end of amine-terminated PEG via an interfacial polymerization method. The chemical structure of triblock copolymers was determined by FTIR and ^{1}HNMR. The thermal behavior, morphology and electroactivity of terpolymers were also investigated by thermogravimetric analysis, field emission microscope (FESEM) and cyclic voltammetry (CV), respectively. Uniform nanofibers consisting of blends of $(PANI)_n$-*b*-PEG-*b*-$(PANI)_n$ terpolymers and polycaprolactone (PCL) were prepared using electrospinning technique. The FESEM was also used to investigate the electrospun nanofibers produced from different molecular weight of PANI/PEG/PANI terpolymers and PCL (30/70). The CV measurements of blends confirmed the preparation of electroactive nanofibers. The presence of terpolymers enhanced the spinnability of solution and significantly reduced the bead formation. This novel system opens up new and interesting opportunities for applications such as electroactive scaffold for tissue engineering.

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Introduction

Since 30 years ago, electrically conducting polymers, also known as ''synthetic metals'' are finding increasing number of applications in many areas of applied chemistry and physics, such as light emitting diodes [1]. Common classes of organic conducting polymers include polyacetylene, polypyrrole (PPy), polythiophene, polyaniline (PANI), and poly(*para*-phenylene vinylene). Some of these conducting polymers, especially PPy, have found some fascinating biomedical applications, for the synthesis of nanoparticles [2], immobilization of proteins [3], and coating devices with PPy materials [4]. But, also polyaniline (PANI) has attracted special attention because of its unique properties [5–7], including controllable electrical conductivity, excellent environmental stability, easy synthesis, reversible redox chemistry, and in vitro compatibility [8]. However, some practical problems related to the application of PANI still exist, such as poor solubility, hydrophobicity, and the lack of biodegradability. Therefore, it is very important to prepare electroactive materials with good solubility, biocompatibility, and biodegradability to be applied as tissue-engineering scaffold materials [9, 10]. A various range of polymers can be used for preparation of scaffold in tissue engineering especially polyesters. Among the polyesters, PCL is an incredibly versatile bioresorbable polymer and by way of its superior rheological properties it can be used by almost any polymer processing technology to produce an enormous array of scaffolds. The major scaffold fabrication technology in which PCL has been used extensively is electrospinning [11].

Recent studies demonstrated the usefulness of electrospinning as platform technology for generating fibrous structures with a high surface area. Various biodegradable synthetic polymers [12, 13], peptide copolymers [14], and natural proteins [15–17] have been electrospun into micro/nanofibers for a multitude of biomedical applications such as scaffolds used in tissue engineering [18–21], wound dressing [22], drug delivery [23], and vascular grafts [24]. 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 technique which can be further developed for mass production of one-by-one continuous nanofibres from various polymers. In addition, a great interest to synthesize conducting and biodegradable PANI is forcefully emerging. For example, PANI has been blended and electrospun with the natural polymers collagen [25] and gelatin [26, 27] or synthetic polymers like poly(lactic acid) [28], poly(l-lactide-co-ecaprolactone) [29] and polyethylene oxide [30]. In other researches, conducting heterocyclic oligomers have been joined together via degradable ester linkages [31, 32], synthesis of various branched copolymers of polylactide and conducting polymers with different architectures has been performed [33] and polylactide surface has been modified with aniline oligomers to create the electroactive and hydrophilic surface for biomedical applications [34]. Collectively, it remains a

considerable challenge to synthesize the ideal electroactive polymer which also exhibits tailored requisites of biocompatibility and biodegradability for use in biomedical field.

In this work, we used facile method for synthesis of novel electroactive triblock copolymers. First, the amine-terminated PEG was synthesized by esterification of PEG and 4-amino benzoic acid, secondly, terpolymers with appropriate molecular weight and electroactivity were obtained with polymerization of aniline in the presence of ammonium peroxydisulfate and amine-terminated PEG. PEG is well known for its good solubility and biocompatibility. With the introduction of PEG segment, the $(PANI)_n$-*b*-PEG-*b*-$(PANI)_n$ triblock copolymer showed good solubility in methanol and water.

We designed the nanofibers from blending of PCL and $(PANI)_n$-*b*-PEG-*b*-$(PANI)_n$ with electrospinning technique in new solvent system consisting of chloroform/2-chloroethanol. Blending the PANI with PCL is preferred because it improves the biodegradability and may assist the spinning of PANI fibers and also act as a support material for the nanofibers. Because of owning good electroactivity, solubility, and biodegradability, these blends have potential for a range of biomedical applications such as electroactive scaffold in tissue engineering.

Materials and methods

Materials

Polyethylene glycol (PEG $M_n = 6{,}000,\ 20{,}000$) from Fluka Co. and 4-amino benzoic acid and p-toluenesulfonic acid (PTSA, from Merck) were dried under vacuum before use. Xylene (Fluka) was dried completely and refluxed under an inert atmosphere by a constant flow of argon. Polycaprolactone (PCL $M_n = 70{,}000$–$90{,}000$) and Camphorsulfonic acid (CSA) were received from Aldrich. Aniline, diethyl ether, methanol, sulfuric acid, ammonium peroxydisulfate, chloroform were purchased from Merck, and used as received. 2-chloroethanol (Acros) was purchased.

Synthesis of amine-terminated polyethylene glycol benzoate (ATPEGB)

ATPEGB was synthesized from PEG (6,000 & 20,000) and 4-amino benzoic acid with PTSA in catalytic amount by refluxing it with xylene solvent [35]. The solid ATPEGB prepared from PEG of molecular weight 6,000 and 20,000 will be referred to as ATPEGB-1 and ATPEGB-2, respectively. These two were synthesized by the following procedure. PEG (10 g), 4-amino benzoic acid (2 equivalent of PEG mole) and xylene (70 mL) were taken into a two-necked reaction flask fitted with stirrer and a Dean and stark trap. The catalytic amount of PTSA (0.2 g) was added to the mixture. The mixture was heated to reflux temperature (140 °C). The water of reaction was removed as an azeotrope until the reaction was complete as indicated by no further liberation/formation of water. It needed refluxing at 140 °C for 5 h. The solvent then removed off under reduced pressure and the solid product was

dissolved in chloroform. Then, the unreacted 4-amino benzoic acid was filtered and the solvent of obtained solution was evaporated. The final solid product was dried in vacuum for 48 h.

Synthesis of $(PANI)_n$-*b*-PEG-*b*-$(PANI)_n$

The $(PANI)_n$-*b*-PEG-*b*-$(PANI)_n$ triblock was synthesized by an interfacial polymerization as described by Huang et al. [36]. Ammonium peroxydisulfate (5 mmol) was dissolved in 40 mL of 1 M sulfuric acid solution in a 200-mL beaker. To this was added, gently and with minimal agitation along the sides of the beaker a solution of 32 mmol aniline and each ATPEGB-1 or ATPEGB-2 in chloroform (40 mL) at 6 °C (in this part of work, because the molecular weight of ATPEGB-2 is too high and it needs high amount of it for polymerization, so we cannot select the same mole of both of ATPEGB in polymerization, for this reason, we choose two different mole ratio of aniline/ATPEGB. This feed ratio is 32 and 54 for ATPEGB-1 and ATPEGB-2, respectively). The aniline/ATPEGB/chloroform solution forms the lower organic layer and ammonium peroxydisulfate solution forms the upper aqueous layer. After a short induction period within 1 min, green polyaniline appears at the interface, migrating into the water phase, and finally filling the entire water layer. As the reaction proceeds, the color of the organic phase becomes darker and finally stops changing, indicating reaction completion. An overnight reaction time is generally sufficient. Then, the solid polymer that consist of aniline homopolymer and $(PANI)_n$-*b*-PEG-*b*-$(PANI)_n$ was filtered. The unreacted PEG from esterification step is soluble in chloroform and cannot enter in the structure of terpolymers. This precipitate was poured into methanol, the aniline homopolymer is insoluble in methanol, but $(PANI)_n$-*b*-PEG-*b*-$(PANI)_n$ is soluble in this solvent, the mixture was stirred for 12 h and then filtered. The solid aniline homopolymer is removed off and the resulting dark brown solution was poured into cold diethyl ether for precipitating of final polymer. The light brown color terpolymer washed with diethyl ether to remove oligomers (the filtrate is still brown that is originated from solubility of aniline oligomers in diethyl ether). The terpolymer isolated by filtration was dried thoroughly at 30 °C under vacuum.

Preparation of electrospun nanofibres of PCL, PCL/$(PANI)_n$-*b*-PEG-*b*-$(PANI)_n$(70/30)

Solution preparation

$(PANI)_n$-*b*-PEG-*b*-$(PANI)_n$ with two different molecular weight(0.26 g, 10^{-5} mol) and 0.0023 g (10^{-5} mol) of CSA were dissolved in a proper amount of 2-chloroethanol under magnetic stirring to obtain the polymer solutions doped with camphorsulfonic acid. The same procedure was used to prepare 20 wt % solutions of PCL in mixture of chloroform: 2-chloroethanol in ratio 2:1 (by volume). Then, the solutions of PCL and terpolymers were mixed in ratio of (70/30) and then stirred for 15 min.

The solution of pure PCL was also prepared in the same solvent ratio.

Electrospinning

The electrospinning apparatus was equipped with a high-voltage power supply (Gamma High Voltage Research E8-50P, Ormond Beach, FL, USA). The polymer solution was added to a 10-mL syringe with a 23G hypodermic needle used as the nozzle. The flow rate of the polymer solution was controlled with a precision pump (JZB 1800D double channel syringe pump from China) to maintain a steady flow from the capillary outlet. The experimental temperature was controlled at 25 °C. The solutions were injected at the rate of 0.5 mL h^{-1}, and the applied voltage was set to 20 kV. The collector was wrapped with aluminum foil and located at a fixed working distance of 15 cm from the needle tip, which was then removed from the drum after fiber deposition. The fiber mats were dried at room temperature until any solvent residue was completely removed before characterization.

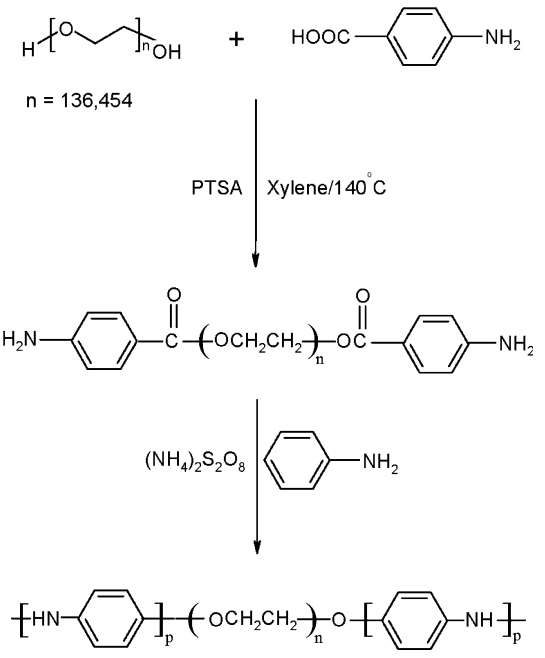
Characterization

FTIR spectra were recorded on Shimadzu FTIR-8400S Fourier transformation infrared spectrophotometer using KBr pellet technique. The spectra were measured at a wave number resolution of 4 cm^{-1} as single scan for a spectral range from 4,000 to 400 cm^{-1}. All the measurements were made at room temperature. ^{1}HNMR spectra were obtained on a Bruker spectrometer 400 MHz, using tetramethylsilane as internal reference for investigation of chemical structure of obtained polymers. The ATPEGBs were dissolved in $CDCl_3$ whereas the triblock copolymers were dissolved in D_2O. Also, the terpolymers and electrospun nanofibers samples were photographed by (FESEM HITACHI S4168) field emission microscope, coated by BioRad, ES200 Auto Sputter Coater. Cyclic voltammetry of terpolymers was performed using an AUTOLAB PGSTAT 30 electrochemical analysis system and GPES 4.7 software package (Eco Chemie, the Netherlands) in a three-electrode electrochemical cell using SCE as the reference electrode and platinum wire as counter electrode and a glassy carbon disk electrode as working electrode. The CV experiment was carried out in 1.0 M dodecylbenzenesulfonic acid solution that contains 30 mg of triblock copolymer. Although, cyclic voltammograms of the PCL/PANI terpolymer blends were measured in a acetone solution(that contain 0.05 mol of CSA in acetone) with a Stand Polarography 757 (Metrohm., Suiss) using a platinum wire counter electrode and an Ag/AgCl reference electrode. The thin films of blends were prepared on glassy carbon disk electrode by casting. The cyclic voltammograms were measured between the range of −0.2 and 1.0 V (vs. Ag/AgCl) at a scan rate of 50 mV/s. The thermal stability of block copolymers was investigated using a TGA/SDTA 851/Mettlear Toledo under nitrogen atmosphere at heating rate of 10° K min. The weight of samples was between 2 and 3 mg. The ultraviolet–visible spectra of the terpolymers were recorded on an Analytik AG, spectrophotometer SPECORD UV/vis 250 BU at the wavelengths of 200–1,000 nm with 2-chloroethanol as the solvent.

Results and discussion

In this work, we tried to prepare block copolymers of PANI/PEG/PANI by facile method, and use these terpolymers to prepare electroactive nanofiber. To achieve this goal, the esterification of PEG and 4-aminobenzoic acid should be performed first. In common method, three-step reactions involving phthaloylation of 4-aminobenzoic acid, esterification in the presence of dicyclohexylcarbodiimide and 4-dimethylaminopyridine and deprotection to regenerate amino groups should be carried out. But we used facile method for esterification that reduced the steps of reaction and augmented the yield without protection of amino groups. In brief, PEG (6,000, 20,000) and 4-amino benzoic acid were esterified with catalytic amount of PTSA by refluxing in xylene. The hydroxyls and carboxyls on the ends of PEG and 4-amino benzoic acid, respectively, were combined with each other by ester bonds (Scheme 1). This made it possible to polymerize aniline easily from the resulting amine-terminated polyethylene glycol benzoates (ATPEGB-1 and ATPEGB-2) with interfacial method to produce $(PANI)_n$-PEG-$(PANI)_n$ terpolymer.

These novel synthetic terpolymers bring two advantages; first is that the biocompatible triblock copolymers of polyaniline and PEG with different molecular weight can be dissolved in water and methanol in which it was impossible for PANI alone. The second is that the creation of electroactive property into these terpolymers which are capable to blend with other polymers, giving an electroactive property to the blends. With aim of biomedical application, PCL as a biodegradable and biocompatible polymer was chosen to blend with $(PANI)_n$-PEG-$(PANI)_n$ terpolymer. PCL and its blend with synthesized terpolymers were spun under an



Scheme 1 Schematic synthesis of $(PANI)_n$-*b*-PEG-*b*-$(PANI)_n$ with different molecular weight

applied electrical potential of 20 kV. For eletrcospinning the PCL and the blends with a certain ratio were dissolved in a new solvent system including chloroform/2-chloroethanol.

The chemical structure of ATPEGBs and $(PANI)_n$-*b*-PEG-*b*-$(PANI)_n$ has been characterized by FTIR and ^{1}HNMR. The FTIR spectra of ATPEGB-1, ATPEGB-2, $(PANI)_n$-*b*-PEG(6,000)-*b*-$(PANI)_n$ and $(PANI)_n$-*b*-PEG(20,000)-*b*-$(PANI)_n$ are shown in Fig. 1. From the Fig. 1a, b, it is seen that the –NH stretching frequencies of ATPEGBs which overlap with stretching bonds of unreacted PEG hydroxyl groups appear from 3,300 to 3,550 cm^{-1}. Peaks at 2,875 and 1,280 cm^{-1} are due to –CH aliphatic and C–N aromatic stretch, respectively for ATPEGB-1 and those stretching frequencies for ATPEGB-2 appear at 2,880 and 1,275 cm^{-1}, respectively. The –C = O stretch for aromatic ester in ATPEGB-1 and ATPEGB-2 at 1697and 1,710 cm^{-1}, respectively supports the esterification reaction. Here the –C = O stretches are shifted to lower frequency because of hydrogen bonds between carbonyls and amino groups. Compared with ATPEGBs, $(PANI)_n$-*b*-PEG-*b*-$(PANI)_n$ (Fig. 1c, d) exhibits several differences in stretching vibrations of carbonyl group and –CH aliphatic. The carbonyl bonds of $(PANI)_n$-*b*-PEG(6,000)-*b*-$(PANI)_n$ and $(PANI)_n$-*b*-PEG(20,000)-*b*-$(PANI)_n$ shift to 1,737 cm^{-1}. Also, the stretching bonds of –CH aliphatic shift to 2,930 and 2,887 cm^{-1} and the stretching bonds of –CH aromatic appear at 3,055 and 3,050 cm^{-1} for $(PANI)_n$-*b*-PEG(6,000)-*b*-$(PANI)_n$ and $(PANI)_n$-*b*-PEG(20,000)-*b*-$(PANI)_n$, respectively. Also, the elimination of stretching bonds of hydroxyl groups indicates the complete purification of terpolymers and separation of unreacted PEG in the polymerization process. A vibrational peak at 1,605 cm^{-1} can be assigned to the stretch of the quinoid (Q) ring and a peak at 1,500 cm^{-1} can be attributed to the stretch of the benzenoid (B) ring that confirm the polymerization of aniline and formation of block copolymers.

The ^{1}HNMR spectra for ATPEGB-1 (Fig. 2a) and ATPEGB-2 (Fig. 2b) clearly show a singlet peak at 3.6 ppm region. This peak is related to $–CH_2$ proton of PEG (c). But, in ATPEGB-2, two chemical shifts appear at around 2.6 and 4.8 ppm that can be assigned to hydroxyl group of unreacted PEG and the protons of NH_2 groups (d), respectively. The absence of these peaks in ATPEGB-1 may have two reasons:

-On considering the esterification of ATPEGB-1 and ATPEGB-2 (74 and 20 %, respectively), it is obvious that the percentage of unreacted PEG in ATPEGB-1 is low, but 80 % of polyethylene glycol chains of ATPEGB-2 are unreacted (that originated from the high molecular weight) which can support the appearance of hydroxyl group.

-Low molecular weight and high yield of esterification may enhance the accessibility of NH_2 and carbonyl groups with hydrogen bonds (ATPEGB-1), but, in ATPEGB-2, because of high molecular weight, amino and carbonyl groups act separately (low accessibility) that lead to appearance of amine signal in ATPEGB-2. The doublet signals at 6.6 and 7.8 ppm (Fig. 2a) and 7.2 and 7.8 ppm (Fig. 2b) are due to aromatic protons.

All protons a, a′ and b, b′ are chemically and magnetically equivalent. So each pair of them appears as doublet signals with ortho coupling. The protons b, b′ are magnetically deshielded (effect of neighboring carbonyl ester groups) in comparison to a, a′ protons (effect of neighboring amino group). From ^{1}H NMR spectra in

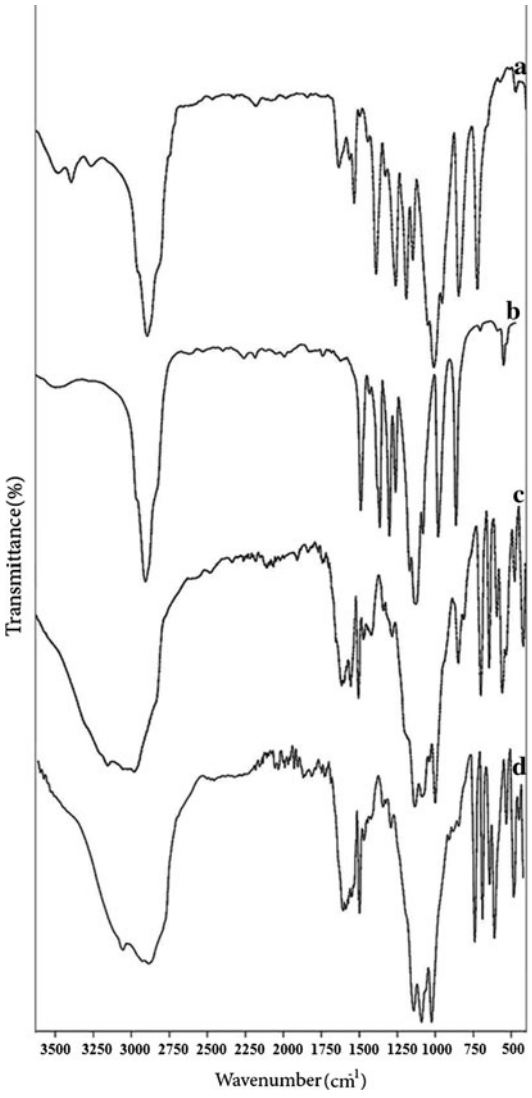


Fig. 1 FT-IR spectra of: *a* ATPEGB-1, *b* ATPEGB-2, *c* $(PANI)_n$-*b*-PEG(6,000)-*b*-$(PANI)_n$, *d* $(PANI)_n$-*b*-PEG(20,000)-*b*-$(PANI)_n$

Fig. 2c, d, compared with ATPEGB, some variations appear in triblock copolymer besides the proton signals of benzene ring at 7.2–7.4 ppm. Both of terpolymer shows a peak at 3.5 ppm that assigned to the protons in PEG and also the disappearance of hydroxyl proton was proved complete purification of unreacted PEG in the polymerization step. All these prominent peaks support the formation of expected products. Yields of esterification reaction were calculated from the intensities in NMR and were determined 74 and 20 % for $(PANI)_n$-*b*-PEG(6,000)-*b*-$(PANI)_n$ and $(PANI)_n$-*b*-PEG(20,000)-*b*-$(PANI)_n$, respectively. The molecular weight of terpolymers was calculated from the integral ratios of protons of benzene ring of polyaniline (7.2–7.4 ppm) and CH2 protons of PEG in 3.5 ppm. Based on

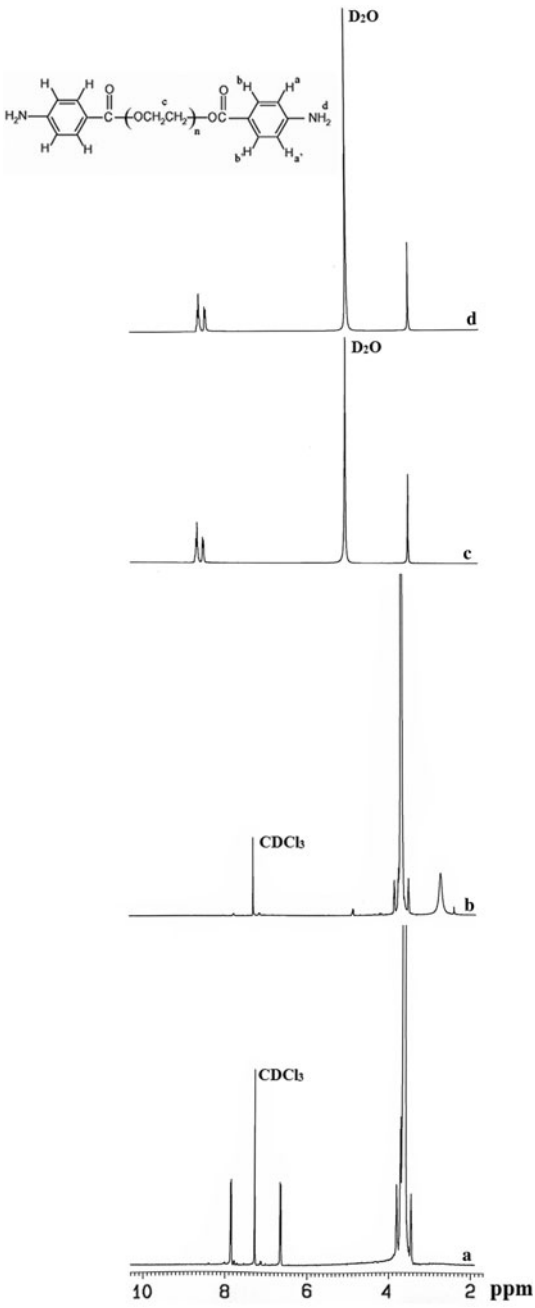


Fig. 2 ^{1}HNMR spectra of: *a* ATPEGB-1, *b* ATPEGB-2, *c* $(PANI)_n$-*b*-PEG(6,000)-*b*-$(PANI)_n$, *d* $(PANI)_n$-*b*-PEG(20,000)-*b*-$(PANI)_n$

these calculations, the units of aniline was determined 239 and 790 rings for $(PANI)_n$-*b*-PEG(6,000)-*b*-$(PANI)_n$ and $(PANI)_n$-*b*-PEG(20,000)-*b*-$(PANI)_n$, respectively and the terpolymers should be $(PANI)_{119}$-*b*-PEG_{136}-*b*-$(PANI)_{119}$ and

$(PANI)_{395}$-*b*-PEG_{454}-*b*-$(PANI)_{395}$ if we suggested that the both end of PEG chain own the same chance to take place polymerization with aniline [37]. Also the total molecular weight of terpolymers will be 28,226 and 92,918 g mol^{-1} for $(PANI)_n$-*b*-PEG(6,000)-*b*-$(PANI)_n$ and $(PANI)_n$-*b*-PEG(20,000)-*b*-$(PANI)_n$, respectively.

Thermal properties of obtained polymers were investigated by TGA thermograms. The TGA curve of the samples by heating them from room temperature to 700 °C is displayed in Fig. 3. The ATPEGB-1 and ATPEGB-2 have two decomposition paths. The first weight loss step that occurred in the temperature range 170–350 °C (ATPEGB-1) and 160–320 °C (ATPEGB-2) with a mass loss of about 93 % which could be attributed to the decomposition of PEG backbone. The subsequent weight loss step in the temperature range of 360–700 °C may be due to the decomposition of 4-aminobenzoic acid segments.

The thermal behavior of the terpolymers was also tested by TGA and is shown in Fig. 3c, d. As it is obvious, the decomposition of block copolymers took place in four stages. The weight loss occurred in the temperature range 150–250 °C for ($(PANI)_n$-*b*-PEG(6,000)-*b*-$(PANI)_n$) and ($(PANI)_n$-*b*-PEG(20,000)-*b*-$(PANI)_n$) may be related to the thermal degradation of PEG from the triblock copolymers(for the terpolymer with higher molecular weight, decomposition of PEG have two steps). There are also three another weight loss between 250 and 700 °C that are ascribed to the decomposition of polyaniline segments in three steps. It is notable that the decomposition of PANI blocks in terpolymers shifts to lower temperature as

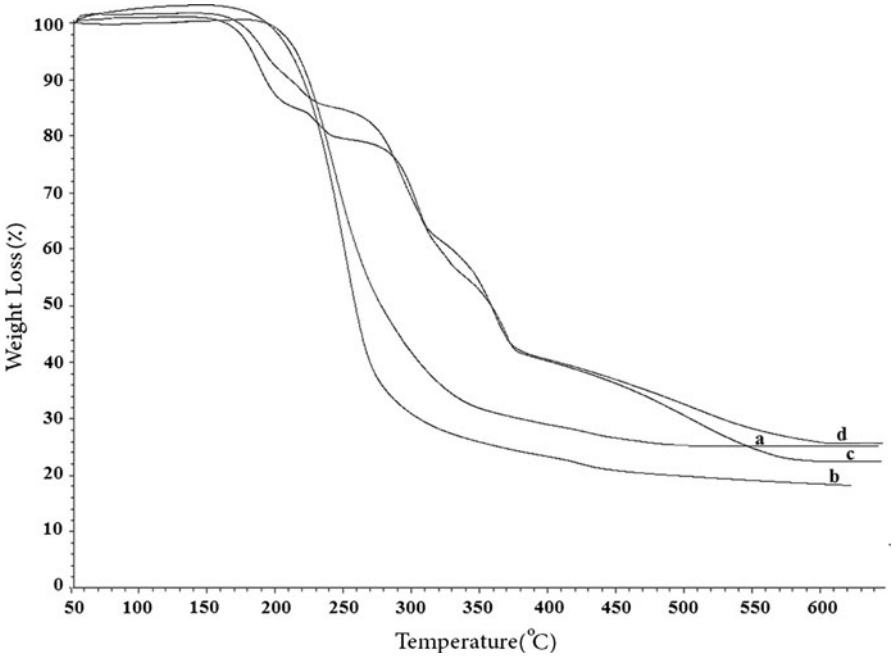


Fig. 3 TGA thermograms measured from: *a* ATPEGB-1, *b* ATPEGB-2, *c* $(PANI)_n$-*b*-PEG(6,000)-*b*-$(PANI)_n$, *d* $(PANI)_n$-*b*-PEG(20,000)-*b*-$(PANI)_n$

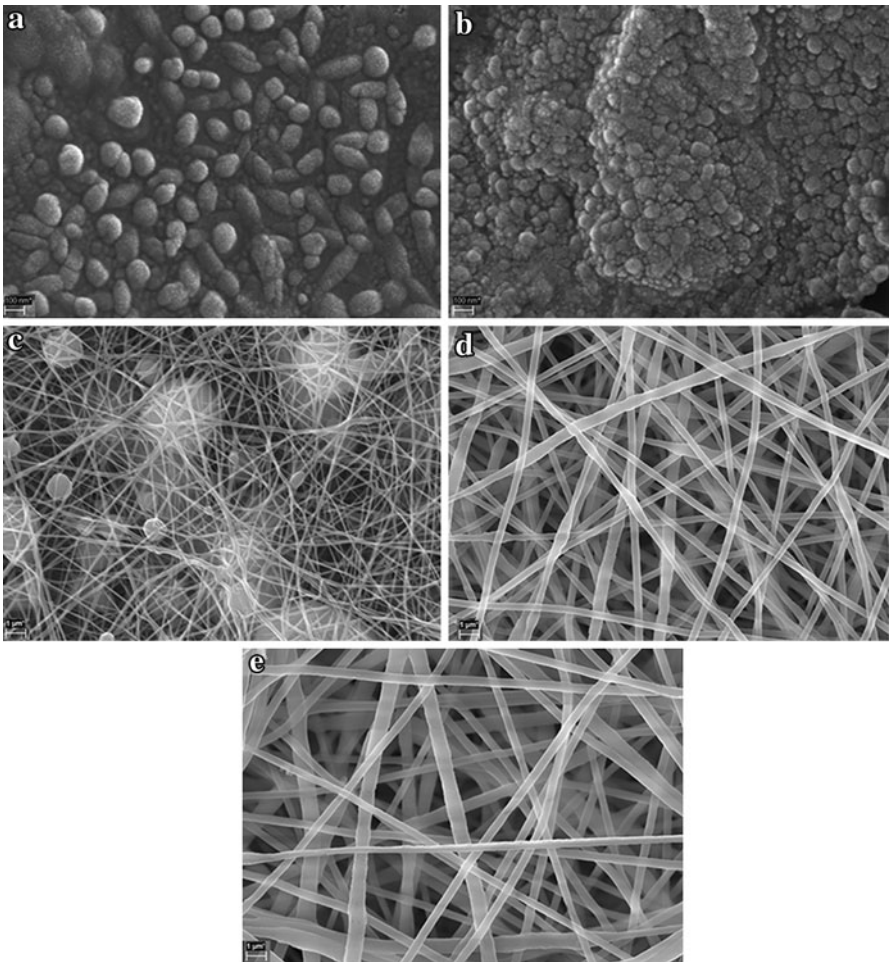


Fig. 4 FESEM micrographs of: **a** $(PANI)_n$-*b*-PEG(6,000)-*b*-$(PANI)_n$, **b** $(PANI)_n$-*b*-PEG(20,000)-*b*-$(PANI)_n$, **c** PCL, **d** PCL/$(PANI)_n$-*b*-PEG(6,000)-*b*-$(PANI)_n$ blend, **e** PCL/$(PANI)_n$-*b*-PEG(20,000)-*b*-$(PANI)_n$ blend

compared with pure PANI, probably due to the effect of PEG block on PANI chains [38]. The mass fraction of PANI blocks in the terpolymers is calculated and is about 80 and 75 % [for $(PANI)_n$-*b*-PEG(6,000)-*b*-$(PANI)_n$) and $(PANI)_n$-*b*-PEG(20,000)-*b*-$(PANI)_n$, respectively)], which is close to the calculated ones from NMR.

The FESEM micrographs were used to investigate the morphology and size of the triblock copolymers with different molecular weight and morphology of fibers obtained from electrospinning. Both of the block copolymer particles are in size of nanometer. Among them, small granular particles dispersed around surfaces in triblock copolymer of $(PANI)_n$-*b*-PEG(6,000)-*b*-$(PANI)_n$ (Fig. 4a), on the other hand, $(PANI)_n$-*b*-PEG(20,000)-*b*-$(PANI)_n$ terpolymer (Fig. 4b) had compact structure with more granular particles that revealed more growing of the aniline chain in

the further terpolymer. The difference in morphology for the terpolymers of PEG/polyaniline may be associated with different molecular weight of initial PEG and polyaniline in the block copolymers.

In addition, the morphology of fibers of PCL and PCL/$(PANI)_n$-*b*-PEG-*b*-$(PANI)_n$ blend were investigated. As it is obvious in Fig. 4c, the electrospun fibers of PCL has beads in its structure. But, the formation of beads could be influenced by the presence of synthesized terpolymers because of polyaniline segments in the terpolymers backbone.

The addition of terpolymers is almost equivalent to the addition of salts to electrospinning solutions, which affect not only the viscosity but also the ionic conductivity of the solutions. The increase in the ionic conductivity changes the dielectric constant of the medium and makes the movement of two equally charged species on the jet surface easier. Figure 4d, e presents SEM micrographs of PCL/$(PANI)_n$-*b*-PEG-*b*-$(PANI)_n$ blend fiber. The electrospun nanofibers of blends presented a single phase indicating good interactions between the blend components. Fibers containing polyaniline block copolymer presented a flat geometry and even for these fiber mats with higher average diameters, there was no formation of beaded structures.

The electrochemical properties of the terpolymers were investigated by UV spectrometry. 2-chloroethanol is a good solvent for block copolymers, and this makes it possible to study the UV spectrometry of these block copolymers. Figure 5 shows UV–vis spectra of (a) $(PANI)_n$-*b*-PEG(6,000)-*b*-$(PANI)_n$ and (b) $(PANI)_n$-*b*-PEG(20,000)-*b*-$(PANI)_n$ in 2-chloroethanol in the proton doping upon addition of camphorsulfonic acid. The UV spectra of both terpolymers show three absorbance peaks at about 375 and 377 nm, 440 and 447 nm, 634 and 639 nm for $(PANI)_n$-*b*-PEG(6,000)-*b*-$(PANI)_n$ and $(PANI)_n$-*b*-PEG(20,000)-*b*-$(PANI)_n$, respectively. The first and third peaks are ascribed to the π–π^* transition of the benzene ring and the benzenoid (B) to quinoid (Q) π_B–π_Q excitonic transition. As comparison to doped polyaniline with the peaks at about 430 and 810 nm, the doped terpolymers showed

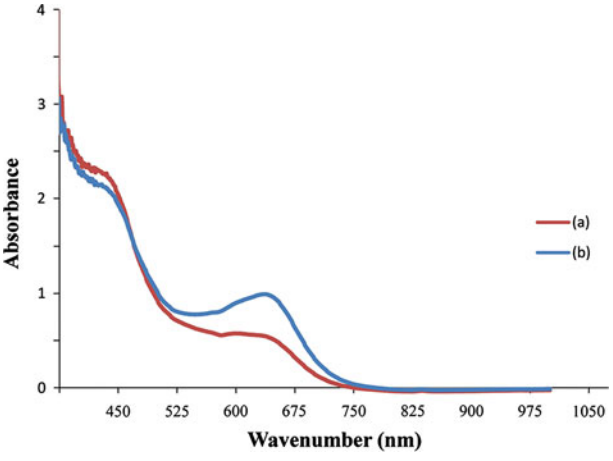


Fig. 5 UV–vis spectra of: (*a*) $(PANI)_n$-*b*-PEG(6,000)-*b*-$(PANI)_n$, (*b*) $(PANI)_n$-*b*-PEG(20,000)-*b*-$(PANI)_n$

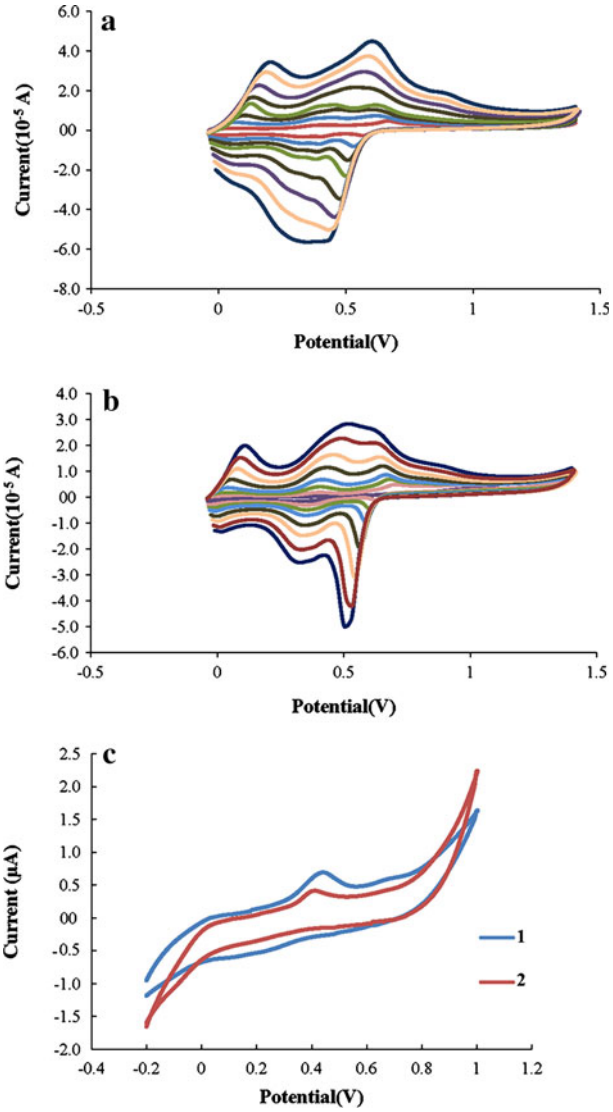


Fig. 6 Cyclic voltammetry curves of: **a** $(PANI)_n$-*b*-PEG(6,000)-*b*-$(PANI)_n$, **b** $(PANI)_n$-*b*-PEG(20,000)-*b*-$(PANI)_n$, (c1) PCL/$(PANI)_n$-*b*-PEG(6,000)-*b*-$(PANI)_n$ blend, (c2) PCL/$(PANI)_n$-*b*-PEG(20,000)-*b*-$(PANI)_n$ blend

only one peak at about 431 nm (Fig. 5a) and 436 nm (Fig. 5b), which can be probably originated from the affects of hydroxyl groups of solvent and oxygens of PEG in the block copolymer that deprotonate PANI chains.

Figure 6a, b show cyclic voltammetry data for $(PANI)_n$-*b*-PEG(6,000)-*b*-$(PANI)_n$ and $(PANI)_n$-*b*-PEG(20,000)-*b*-$(PANI)_n$, respectively. A three-electrode cell was employed using a glassy carbon disk electrode as working electrode, platinum wire

as counter electrode and SCE as reference electrode. Cyclic voltammetry measurements of terpolymer samples were recorded at different scan rates between −0.2 and 1.4 V versus SCE, show that they are electroactive polymers. 30 mg of samples were dissolved in 30 mL dodecylbenzenesulfonic acid (0.1 M) and then the cyclic voltammograms were recorded. Under these conditions, the cyclic voltammogram for both of terpolymers showed two pairs of redox peaks, similar to those of polyaniline. The first pair of the well-defined redox peaks at 0.22 ($(PANI)_n$-*b*-PEG(6,000)-*b*-$(PANI)_n$) and 0.2 V ($(PANI)_n$-*b*-PEG(20,000)-*b*-$(PANI)_n$) can be attributed to the reversible redox process from leucoemeraldine to emeraldine form. At higher potentials, a reversible redox peak at 0.6 and 0.57 V for $(PANI)_n$-*b*-PEG(6,000)-*b*-$(PANI)_n$ and $(PANI)_n$-*b*-PEG(20,000)-*b*-$(PANI)_n$, respectively was assigned to the oxidation/reduction of the emeraldine form to the pernigraniline state [39]. The oxidation peak of the $(PANI)_n$-*b*-PEG(20,000)-*b*-$(PANI)_n$ is somewhat lower than $(PANI)_n$-*b*-PEG(6,000)-*b*-$(PANI)_n$. This is attributed to the electronic effects of high molecular weight of PEG. Moreover, we can also see the decrease in the current at higher molecular weight of PEG block copolymer despite of high amount of polyaniline that obtained from ^{1}H NMR analysis. This also can be related to high molecular weight of PEG that prevents the high doping of polyaniline chains. All these spectroscopic and electrochemical results demonstrate the good electroactivity of the terpolymers.

We also analyzed the electrochemical properties of PCL/PANI terpolymers blends using cyclic voltammetry (Fig. 6c). Both of the blends exhibit significant peak at 0.4 V during the oxidation cycle, which corresponds to lecuoemeraldine/emeraldine transitions. But, in $(PANI)_n$-*b*-PEG(6,000)-*b*-$(PANI)_n$, we observed another oxidation peak at 0.63 V that originated from high doping state of this terpolymer in comparison of $(PANI)_n$-*b*-PEG(20,000)-*b*-$(PANI)_n$ (the molecular weight of PEG in $(PANI)_n$-*b*-PEG(20,000)-*b*-$(PANI)_n$ is high and this prevents the high doping of polyaniline chain as referred before).

Conclusion

The electroactive and biodegradable nanofibers were prepared from blending of PCL and (aniline/PEG/aniline) terpolymers. These soluble terpolymers were synthesized by esterification of PEG with 4-amino benzoic acid without protection of its amino group, then copolymerization of aniline from both end of amine-terminated PEG via an interfacial polymerization method. Their structure was also verified by FTIR and ^{1}HNMR spectroscopy. The molecular weight of these obtained terpolymers was determinate from ^{1}HNMR spectra. The terpolymers have good electroactive properties, indicated by their CV and UV spectra. Moreover, TGA investigation showed a good thermal stability of the block copolymers. Also, we prepared electroactive CPSA/$(PANI)_n$-*b*-PEG-*b*-$(PANI)_n$/PCL nanofibers by electrospinning technique in new solvent system consisting of chloroform/2-chloroethanol. The morphology of terpolymers and blends was also investigated with FESEM. FESEM analysis of the fibers showed that a nanoscaled structure was successfully formed with a uniform mean fiber diameter respective of PANI

terpolymers incorporation. Fibers containing of aniline block copolymers also showed morphology with no beads. Cyclic voltammetry also confirmed the electroactivity of blends. These novel electroactive and biodegradable system are favorable for using as scaffold in tissue engineering.

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