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Synthesis and characterizaton of block tercopolymer and degradation behavior of their nano-structured fibers via electrospinning

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ABSTRACT

Biodegradable block tercopolymers were synthesized by bulk ring-opening copolymerization of trimethylene carbonate (TMC), L-lactide (LLA) and ε-caprolactone (ε-CL) at different feed molar ratios. The molecular structure of the tri-block copolymer was confirmed by ^{1}H NMR, ^{13}C NMR and FT-IR analysis. Nano-structured fibers of the obtained tri-block tercopolymers were prepared by electrospinning technique. XRD spectra of the nanofibers showed that the polymer chain orientation enhanced and the crystallinity increased during the electrospinning process. The mechanical properties of the nano-structured fibers can be adjusted by changing the compositions of the copolymers. The biodegradability of the nanofibers was investigated by intrinsic viscosity change and SEM photos. The viscosity of the nanofibers, which derived from the tri-block copolymers, decreased gradually with degradation time. The SEM photos showed that the morphology change of the tri-block copolymers was related to the composition of the copolymer after the degradation time of 225 days.

1. Introduction

Electrospinning is an attractive approach for polymer biomaterial preparation in medical areas. Electrospinning produces nano-structured fibers with high porosity and surface areas [1], which make them have potential applications in medical areas such as tissue engineering scaffolds, immobilized enzymes, wound dressing articles, artificial blood vessels, nerve guides and so forth [2]. Biodegradable aliphatic polyesters, such as poly(ε-caprolactone)(PCL), poly(trimethylene carbonate)(PTMC), poly(L-lactide)(PLA), poly(glycolide)(PGA), as well as their copolymers have been widely studied for medical applications due to their biodegradability and good biocompatibility [3,4].

The properties of aliphatic copolyesters are influenced by the properties of monomers and their ratios, the sequence structure and the crystal structure, etc [5]. The properties of the aliphatic monomers are shown as follows. PCL is a semi-crystalline with low glass transition temperature (T_g) and has been widely used in tissue engineering scaffolding, but its poor hydrophilicity and long degradation time limits its applications [6]. PTMC is an amorphous or low crystalline polymer and exhibits good mechanical resistance and high chemical and thermal stability [7]. PLA is a semi-crystalline with high T_g and exhibits high tensile strength and low elongation. The copolymerization of these monomers is a promising way to tailor polymer properties to meet specific requirements. For instance, the degradability and mechanical properties of the copolyesters alter due to the changes in the copolymer composition and their sequence structure. The hydrolysis of PCL can be accelerated by the presence of a second monomer, such as LLA or TMC [8]. The mechanical properties of PLA can be modified by copolymerization with other monomers, such as ε-CL or TMC [9]. Schappacher et al. [10] reported that PCL is too hard while PTMC is too soft for nerve regeneration. They synthesized the copolymers of ε-CL and TMC as nerve guide material [11–13].

Encouraged by the advantages of copolymers, a series of random tercopolymers derived from ε-CL, TMC and LLA with different feed molar ratio were synthesized, with which the nano-structured fibers were obtained via electrospinning [14–16]. However, these random tercopolymers were sticky and its tensile strength was too low to be used in some biomedical field. Tri-block copolymerization should be an effectual approach for expending the application of aliphatic polyesters. Kricheldorf and Rost synthesized some A-B-A tri-block copolymers consisted of PLA as A-blocks in combination with random 1:1 copolymers of ε-CL and TMC as B-block, which resemble those of commercial thermoplastic elastomers [17]. Kwangsok fabricated nanofibers of PLA-based multi-component blends containing two bridging materials PLA-b-PEG-b-PLA tri-block copolymer and PLGA random copolymer [18]. To gain more details for application of ε-CL/TMC/LLA tercopolymer nanofibers in biomedical field, a series of tri-block of TMC, LLA and ε-CL were

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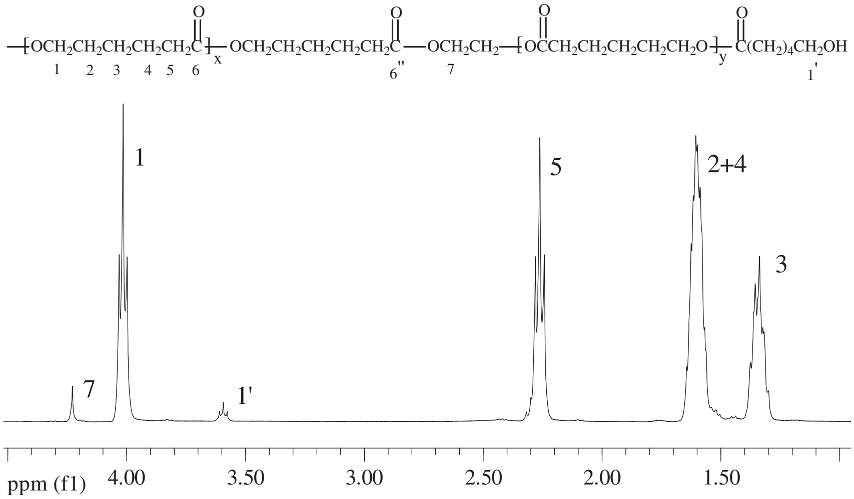

Fig. 1. ^{1}H NMR spectrum of the PCL pre-polymer.

synthesized. With the obtained tri-block copolymers, nano-structured fibers were prepared via electrospinning. The properties, especially the biodegradability, were investigated preciously in this work.

2. Experimental

2.1. Materials

Prior to use, ε-CL (Acros Organics, New Jersey, USA) was distilled over freshly powdered CaH_2. TMC was synthesized according to a previous study [19] and purified by recrystallization using acetone and diethyl ether as solvents, and then dried under vacuum before use. LLA purchased from Boeringer Ingelheim (Germany) was purified by recrystallization using alcohol as solvent, and then dried under vacuum before use. $Sn(Oct)_2$, methylene chloride (MC), N,N-Dimethylformamide (DMF), ethylene glycol and methanol were used as received.

Random tercopolymers with feed molar ratio of TMC/LLA/ε-CL of 10/50/40 (TP1), 20/40/40 (TP2) and 40/20/40 (TP4) were prepared in our previous work [15].

2.2. Synthesis of tri-block copolymer

2.2.1. Synthesis of the PCL pre-polymer

Specific amounts of ε-CL, $Sn(Oct)_2$ and ethylene glycol were charged into a flame-dried three-necked flask. The flame was evacuated and protected by nitrogen, and then heated to 130 °C for 24 h. The obtained raw products were dissolved in MC and precipitated in cold methanol. This process was repeated twice. The purified products were finally dried under vacuum at 28 °C for 2 days.

2.2.2. Synthesis of tri-block copolymer

Tercopolymers were synthesized according to the same procedure in Ref [15]. A flame-dried three-necked flask was charged with specific amount of TMC, LLA and ε-CL (feed molar ratio of TMC/LLA/ε-CL were 10/50/40(Q1), 20/40/40(Q2), 30/30/40(Q3), 40/20/40(Q4) and 50/10/40(Q5), respectively). After $Sn(Oct)_2$ (0.05 wt% of total monomer compositions) was injected into the flask, the polymerization was carried out at 160 °C for 25 h. The obtained raw products were purified and dried under the same process conditions as the PCL pre-polymer.

2.3. Nanofiber preparation

The various electrospinning parameters, such as solvent, the tercopolymer concentration, the voltage and the tip-collector distance (TCD) were investigated in previous work [16]. The obtained optimum condition for elctrospinning nanofibers were as follows: solvent DMF/MC molar ratio of 40:60, copolymer concentration of 30%, voltage of 12 kV and TCD 12 cm. Under the above mentioned conditions, nano-structured fibers were fabricated. Nanofibers of TP1, TP2, Q1, Q2, Q3, Q4 and Q5 were designed hereafter as TPE-1, TPE-2, QE-1, QE-2, QE-3, QE-4 and QE-5, respectively.

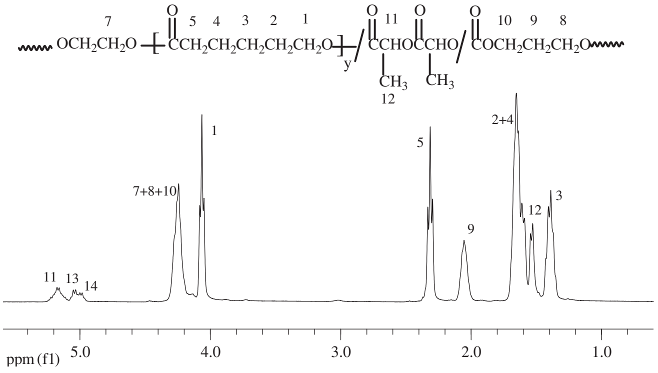

Fig. 2. ^{1}H NMR spectrum of the block tercopolymer of TMC, LLA and PCL pre-polymer.

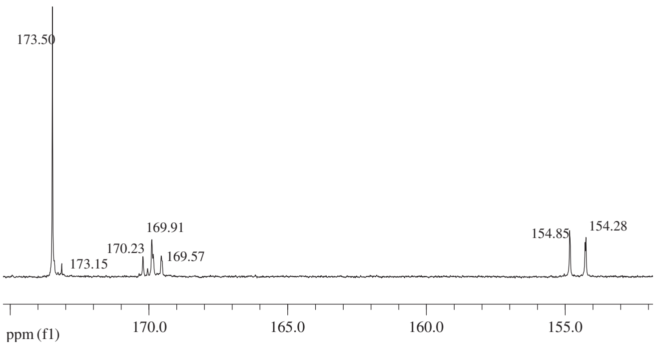

Fig. 3. ^{13}C NMR spectrum of the block tercopolymer of TMC, LLA and PCL.