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Biocompatible polyurethanes with thermally-induced shape memory properties derived from three-arm branched poly (ε-caprolactone-co-γ-butyrolactone)-b-poly(lactide) block copolymers

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ABSTRACT

A series of poly(lactide)-based polyurethanes with cross-linked network structure was synthesized through the chain extension of three-arm branched poly(ε-caprolactone-co-γ-butyrolactone)-b-poly(lactide) (3PBCL-b-PLA) block copolymers with various molecular weights and optical activities of PLA blocks. The structure of the synthesized poly(lactide)-based polyurethanes was analyzed, and it was confirmed that they contained the cross-linked network structure. Effects of the molecular weight and optical activity of PLA block on the various properties such as crystallization, mechanical property, shape memory performance, thermal stability and hydration ability were discussed. By simultaneously adjusting the molecular weight and optical activity of PLA blocks, the crystallization of flexible PCBL blocks and rigid PLA blocks in the synthesized cross-linked polyurethanes was effectively controlled, which was the basis for constructing poly(lactide)-based polyurethanes with a broad ranged mechanical property, excellent shape memory properties and controllable hydration ability. The synthesized polyurethanes exhibited adjusted tensile strength and elongation at break in the range of 11.2–32.4 MPa and 41–753 %, with the water content varying from 1.1 % to 20.1 %, respectively. The shape fixity ratio and shape recovery ratio of L-PU2.9 could reach 90.9 % and 96.0 %, respectively. The effect of stereocomplex-crystallization on the properties of poly(lactide)-based polyurethane was also analyzed. Stereocomplexed polyurethane based on 3PCL-b-PLA block copolymer enantiomers with short PLA block was constructed, which achieves fully stereocomplexation in a wide mixing ratio (20–50 %). It was found that the formation of a small number of stereocomplex-crystals can change the properties of poly(lactide)-based polyurethane in a wide range. Eventually, it was demonstrated by in vitro hemolysis test, cytotoxicity test and live/death staining that the synthetic poly(lactide)-based polyurethanes exhibited excellent biocompatibility. These results suggested that these biocompatible shape memory poly(lactide)-based polyurethanes with tunable mechanical properties and hydration ability demonstrated the promising potential as an excellent implantation for biomedical application.

1. Introduction

Poly(lactide) (PLA) is a biodegradable aliphatic polyester synthesized by polycondensation of lactic acid produced by plant-based starch fermentation [1–3]. It can also be synthesized by ring-opening polymerization of lactide, a dimer of lactic acid. PLA is considered the most potential substitute for petrochemical-based polymers due to its unique properties, such as high modulus, high strength, ease of processing, biocompatibility, and biodegradability [1–5]. At present, PLA has been used in a variety of fields, including food packaging [6], agriculture [7,8], tissue engineering [9], and drug carriers [10]. However, PLA performance has some drawbacks, such as poor toughness [11,12], low heat resistance [12], and slow crystallization rate [13], which limit its application. Thus, to improve the properties of PLA-based materials, physical and chemical modifications have been proposed [14,15]. Through physical modification, the properties of PLA can be improved by blending with nanoparticles [16], plasticizers [17], nucleating agents [18] and other biopolymers [19,20]. This method has the advantages of

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