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Spherulitic morphologies of the triblock Poly(GL)-*b*-poly(GL-*co*-TMC-*co*-CL)-*b*-poly(GL) copolymer: Isothermal and non-isothermal crystallization studies

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ABSTRACT

Crystallization of a biodegradable segmented copolymer constituted by polyglycolide hard segments and a middle soft segment constituted by a random disposition of glycolyl, ε-caproyl and trimethylene carbonyl units has been studied by means of optical microscopy, atomic force microscopy and time resolved X-ray diffraction techniques. This Poly(GL)-*b*-poly(GL-*co*-TMC-*co*-CL)-*b*-poly(GL) copolymer is widely employed as surgical suture and has similar characteristics than previously studied copolymers having a middle soft segment constituted by only two monomers (i.e. glycolide and trimethylene carbonate).

FTIR and NMR spectroscopies demonstrated that the middle segment had an amorphous character and a random microstructure as consequence of transesterification reactions that took place during synthesis. Nevertheless, polyglycolide segments were able to crystallize giving rise to peculiar positive birefringent spherulites with a morphology, which depends on crystallization temperature (i.e. flat-on and edge-on crystals) as verified by AFM and electron diffraction patterns.

Complete bell shaped curves that defined the temperature dependence of the crystal growth rate could be experimentally obtained from both, isothermal and non-isothermal crystallizations. Data from both analyses were in close agreement and pointed out a secondary nucleation constant ($2.42–2.88 \times 10^5$ K^2) which was clearly higher than that determined for the related system with two components. Lamellar morphologic parameters were similar for samples crystallized from the melt state and after the reordering process that took place on heating. Comparing to the bicomponent system, significant differences were again observed highlighting the influence of the soft segment on the crystallization behavior.

1. Introduction

Polyglycolide is a biodegradable polyester widely employed for biomedical applications, being specifically the development of bioabsorbable surgical sutures one of its first applications [1–8]. Polyglycolide has a distinctive crystalline structure

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that renders differentiated properties respect to similar aliphatic polyesters [9]. Thus, for example it has a melting temperature higher than 200 °C and a glass transition temperature in the 35–40 °C range that contrast with the low values found for the other members of the series (e.g. melting point of 55–60 °C and glass transition temperature close to −60 °C for poly(ε-caprolactone) [10]). In addition, polyglycolide is relatively hygroscopic and therefore exhibits a high degradation rate, shows a good biocompatibility and excellent fiber forming properties. These good properties can be extended to a wide range of copolymers differing on components and composition, being specifically degradation behavior and mechanical properties intensively investigated [11–15].

Bioabsorbable surgical sutures can be processed in monofilament and multifilament forms, being the former preferred due to advantages like more resistance to harbor microorganisms and higher facility to passage through tissue than conventional braided threads [16–18]. The high stiffness of polyglycolide makes its processing as a monofilament suture impossible, being therefore different formulations developed to get flexible materials while glycolide is kept as a predominant component. In this way, different segmented copolymers having two polyglycolide hard segments and a middle soft segment derived from glycolide and other monomers (e.g. trimethylene carbonate, ε-caprolactone or *p*-dioxanone) have been prepared to provide flexibility [19–21].

Maxon™ (Syneture) is one of the most simple monofilament synthetic sutures based on glycolide copolymers that has been employed. This copolymer is characterized by a 62 wt.% of polyglycolide hard segments and a middle soft segment constituted by a random disposition of 85 wt.% of trimethylene carbonate and 15 wt.% of glycolide [22]. The design of this Poly (GL)-*b*-poly(GL-*co*-TMC)-*b*-poly(GL) copolymer is relevant to meet the requirements of a bioresorbable suture. It should be also considered that processing affects crystallinity and hence mechanical properties and degradability. In this way, comprehension of the crystallization process in a polymeric system where amorphous (soft segments) and crystalline domains (hard segments) coexist is a highly interesting topic.

The crystallization process of Poly(GL)-*b*-poly(GL-*co*-TMC)-*b*-poly(GL) has been extensively evaluated under both isothermal and non-isothermal conditions for the commercial sample [23,24] as well as for copolymers with slightly different microstructure. Results demonstrated that small variations on the hard segment length and the soft segment content had a high influence on melting temperature, degree of crystallinity, degradation rate, crystallization kinetics and crystalline morphology [25–27]. For example, the crystalline lamellar thickness is higher for samples with a low polyglycolide hard segment content as a consequence of the incorporation of soft segments into the crystalline phase in such a way that imperfect crystals with a low melting point are developed [27].

Poly(GL)-*b*-poly(GL-*co*-TMC-*co*-CL)-*b*-poly(GL) has also been employed as a monofilament suture with properties (e.g. in vitro degradation) that covers a similar range than Maxon™. This segmented copolymer is synthesized following a two steps procedure (Fig. S1 in Supporting information (SI)), which renders a middle soft segment based on three components and two polyglycolide hard blocks [20]. With regard to Maxon™, it is significant the different constitution of the soft segment (three components instead of two), the lower hard segment percentage (57 versus 62 wt.%) and the slightly higher glycolyl content (72 versus 67.5 wt.%).

Studies about the crystallization process of the commercial Poly(GL)-*b*-poly(GL-*co*-TMC-*co*-CL)-*b*-poly(GL) suture are scarce and basically concern to isothermal and non-isothermal analyses from DSC calorimetric data [28]. These indicated a maximum overall crystallization rate around 131 °C and a secondary nucleation constant of 1.51×10^5 K^2 that became lower than reported for Maxon™ (1.86×10^5 K^2). This is an expected result taking into account the higher content of non-crystallizable soft segments with greater statistical monomer distribution. Therefore, a complementary study using optical microscopy data appears necessary. Furthermore, morphologic data concerning the lamellar structure are also interesting in order to improve comprehension of how small changes on the polymer architecture can affect microphase separation. In fact, fiber properties are governed by physical structures of different scales, including amorphous and crystalline domains as well as lamellar structures.

2. Experimental section

2.1. Materials

Commercially available sutures of Poly(GL)-*b*-poly(GL-*co*-TMC-*co*-CL)-*b*-poly(GL) (Monosyn™, USP 1) were kindly supplied by B. Braun Surgical, S.A. This triblock copolymer has a middle soft segment that constitutes a 43 wt.% of the sample and that is composed of 35 wt.%, 32.5 wt.% and 32.5 wt.% of glycolyl, trimethylene carbonyl and ε-caproyl units, respectively [20]. Diethylene glycol was used as a bifunctional initiator for the ring opening polymerization that leads to the soft segment (see the first synthesis step of Fig. S1 in SI). Therefore, a prepolymer having two hydroxyl terminal groups was obtained and consequently polyglycolide hard blocks could be incorporated at both ends in the second polymerization step (Fig. S1 in SI). Weight and number average molecular weights of Poly(GL)-*b*-poly(GL-*co*-TMC-*co*-CL)-*b*-poly(GL) samples were 71,000 and 41,000 g/mol, as previously reported [28].

2.2. Measurements

^{1}H NMR spectra were acquired with a Bruker AMX-300 spectrometer operating at 300.1 MHz. Chemical shifts were calibrated using tetramethylsilane as an internal standard. Dried dimethyl sulfoxide-d_6 (DMSO) was used as the solvent at a temperature of 90–95 °C to enhance solubility and resolution.