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Different crystallinity of poly(d,l-lactide-co-p-dioxanone) copolymers acquired by control of chain microstructure

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Abstract

Poly(d,l-lactide-*co*-p-dioxanone) (P(LA-*co*-PDO)) copolymers with different chain microstructures were synthesized by one-step or two-step bulk ring-opening polymerizations of d,l-lactide (LA) and p-dioxanone (PDO) monomers using stannous octoate [$Sn(Oct)_2$]/n-dodecanol as the initiating system. The average sequence lengths of the lactidyl (L_{LA}) and dioxanyl (L_{PDO}) units were calculated from the ^{1}H NMR spectra. It was found that both L_{LA} and L_{PDO} values from the two-step syntheses were significantly longer than those from the corresponding one-step syntheses, indicating more blocky structure achieved for the two-step copolymers. Corresponding to this difference in microstructure, the two-step copolymers were semi-crystalline, while the one-step copolymers were completely amorphous. In conclusion, the crystallinity of P(LA-*co*-PDO) copolymers could be adjusted conveniently to meet specific applications by changing the microstructure of the copolymers via different polymerization routes.

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Keywords: Poly(d,l-lactide-*co*-p-dioxanone); Copolymerization; Chain microstructure; Crystallinity

Biodegradable polyesters have been extensively investigated for temporary therapeutic applications such as surgical sutures, medical devices, drug delivery systems as well as tissue engineering scaffolds [1–5]. To meet the demands for better healthy and improved clinical performance, there is a requirement to develop novel biodegradable polymers with controlled degradation rate, suitable mechanical properties as well as appropriate surface properties. The microstructure of polyester chains is an important factor to affect many properties of the polymer, such as degradation, crystallinity, solubility and mechanical properties. The microstructure of the polyester is influenced by the kind of applied initiator as well as by the transesterification occurring during the synthesis [6–8]. The transesterification results in the redistribution of the sequences along the polymer chains leading to changes in the chain structure and the lengths of microblocks.

In the present paper, we report first the synthesis of poly(d,l-lactide-*co*-p-dioxanone) copolymers with different chain microstructures by two polymerization routes (one- and two- step polymerization) (Scheme 1). The

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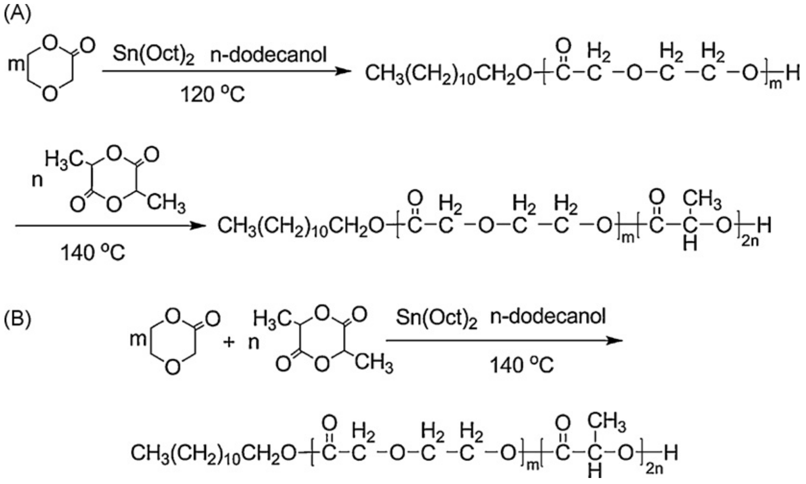

Scheme 1. The two-step (A) and one-step (B) copolymerization routes for P(LA-co-PDO) copolymers.

copolymerization was proceeded in bulk using stannous octoate ($Sn(Oct)_2$) and 1-dodecanol as the initiating system. Very recent pieces of evidence suggest that the actual initiator for the ROP of lactides or lactones by $Sn(Oct)_2$ is formed *in situ* in the interchange reactions between $Sn(Oct)_2$ and hydroxyl containing compounds present in the reaction medium [9]. Elementary chain-growth reaction consists of the concerted monomer insertion into the alkoxide oxygen-metal bond followed by the acyl-oxygen bond scission and reformation of the alkoxide species. The major side reactions in ROP of lactones or lactides are chain transfers with chain rupture, also called inter- or intra-molecular transesterification reaction. They contribute to redistribution of the sequences along the polymer chains leading to changes in the chain structure and the lengths of microblocks.

Table 1 shows the ^{1}H NMR and GPC data of the copolymers with various compositions obtained by the two different polymerization routes. In this paper, a copolymer notation such as P(LA50-*co*-PDO50) means that the initial comonomer feed consisted of 50 mol% LA and 50 mol% PDO. It is observed that the mole fractions of PDO monomer (f_{PDO} %) in the initial comonomer feeds are higher than those actual values (F_{PDO} %) in the copolymers determined by ^{1}H NMR. This is due to the unzipping depolymerization of PDO unit from the chain end occurring during the copolymerization process. From Table 1, we can also see that the copolymerization procedure shown little influence on F_{PDO}% value of the copolymers obtained with the same LA/PDO feed ratio. This indicates that for the two-step copolymerization, transesterification may occur on the PPDO prepolymer chain when the LA monomer was added and copolymerized.

The chain microstructure of the copolymers synthesized by one- and two-step copolymerizations was studied by ^{1}H NMR (Fig. 1). The peaks positioned at 4.14–4.18 ppm (a in Fig. 1) represent the ^{1}H NMR resonances of methylene a groups in the dioxanyl unit of the PDO-*PDO** sequence. It is worth to note that additional peaks at positions 4.19–4.22 ppm (a′ in Fig. 1) also emerge and correspond to the resonances of methylene a group in the dioxanyl unit of sequence LA-*PDO**, respectively. From Fig. 1, it is observed that the intensity of peak a is much higher than peak a′ for the one-step P(LA-co-PDO) copolymer, indicating a more blocky structure, while the intensities of peaks a and a′ are similar for the two step P(LA-co-PDO) copolymer indicating a more random structure. By comparison of peak intensities representing PDO-*PDO** and LA-*PDO** sequences, it is possible to

Table 1
Characterization of P(LA-co-PDO) copolymers synthesized by different copolymerization routes.

Copolymers	Procedure	f_{PDO}%	F_{PDO}%	L_{LA}	L_{PDO}	Mw	PDI
P(LA70-*co*-PDO30)	One-step	30	19.1	6.05	1.43	82,400	1.75
P(LA70-*co*-PDO30)	Two-step	30	22.2	12.07	3.45	62,300	1.61
P(LA50-*co*-PDO50)	One-step	50	38.3	3.11	1.95	64,200	1.69
P(LA50-*co*-PDO50)	Two-step	50	40.0	6.52	4.35	40,100	1.44

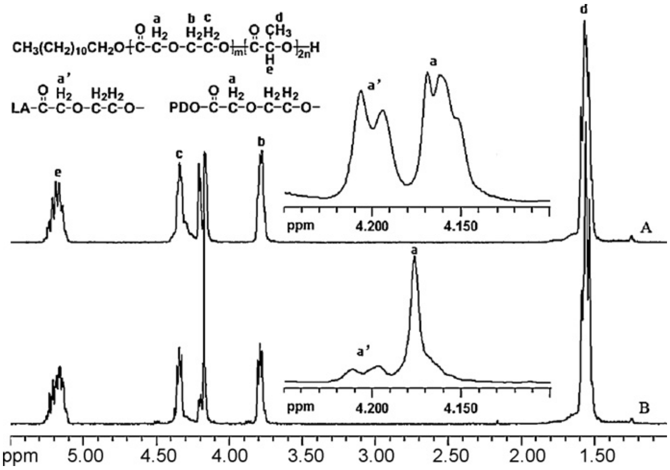

Fig. 1. Comparison of the ^{1}H NMR spectra of P(LA50-*co*-PDO50) from the one-step (A) and two-step (B) copolymerizations.

calculate the experimental number-average lengths of LA and PDO blocks, LLA and LCL, in the copolymers according to a literature method [4] and the results are presented in Fig. 1. It is interesting to note that the copolymerization procedure has played a critical role in the control of microstructure of the copolymers. For the same LA/PDO feed ratio, both L_{PDO} and L_{LA} values are much higher for the two-step copolymers as compared with those for the one-step copolymers. This difference in microstructure of the copolymers will have a profound effect on various properties of the copolymers.

The GPC chromatograms of the copolymers, both from the one-step and two-step copolymerizations, gave similar unimodal curves. This indicates that the PPDO prepolymer for the two-step copolymerization did indeed initiate the added LA. There is no evidence to suggest that the copolymer products contained any PLA or PPDO homopolymeric fractions. However, the microstructure analysis by ^{1}H NMR also ruled out the possibility of formation of PPDO–PLA diblock copolymer by the two-step reaction. This implies that transesterification reaction took place on the PPDO prepolymer chain during the second step copolymerization of LA.

DSC was used to study the influence of chemical composition and microstructure on thermal properties of P(LA-*co*-PDO) copolymers acquired by different copolymerization routes. The heating curves of the samples are shown in Fig. 2. The one-step copolymers show no melting transitions, indicate of their amorphous nature. However, for the two-step copolymers, multiple melting peaks at 70–100 °C are observed corresponding to the melting of crystals

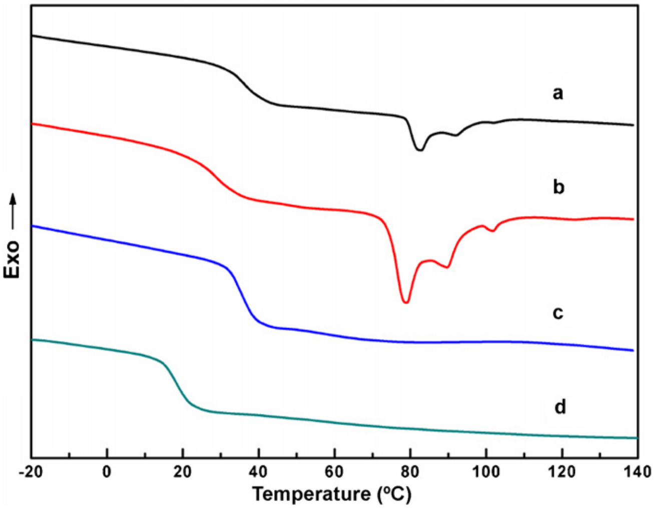

Fig. 2. DSC heating curves of P(LA-*co*-PDO) copolymers synthesized by different polymerization routes: (a) two-step P(LA70-*co*-PDO30); (b) two-step P(LA50-*co*-PDO50); (c) one-step P(LA70-*co*-PDO30); (d) one-step P(LA50-*co*-PDO50).

formed by PDO blocks, which is confirmed by WXRD. This difference in crystallinity is due to the longer PDO sequence lengths for the two step P(LA70-*co*-PDO30) (3.45) and P(LA50-*co*-PDO50) (4.35) copolymers, as compared with those for the one step P(LA70-*co*-PDO30) (1.43) and P(LA50-*co*-PDO50) (1.5) copolymers. When the L_{PDO} value is decreased below 1.5, the PDO blocks have lost the ability to crystallize. The values of crystallinity of PDO phase in the two-step P(LA70-*co*-PDO30) and P(LA50-*co*-PDO50) copolymers were calculated from the heat fusions as 22.2% and 30.5%, respectively.

In conclusion, we have acquired P(LA-*co*-PDO) copolymers with different crystallinity by controlling the chain microstructure via different polymerization routes.

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