

# Versatile synthesis of comb-shaped poly(lactic acid) copolymers with poly(acrylic acid)-based backbones and carboxylic acid end groups



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## ARTICLE INFO

### Article history:

Received 18 September 2016

Received in revised form 15 December 2016

Accepted 19 December 2016

Available online 21 December 2016

### Keywords:

Poly lactide

Poly(acrylic acid)

Comb

Triple SEC

Carboxylic groups

Polycondensation

## ABSTRACT

This paper focuses on preparing and characterizing nonlinear, highly carboxylic-functionalized poly(lactic acid) copolymer prepared through a reaction between poly(acrylic acid) and lactic acid. The resultant copolymer exhibits a comb architecture, in which poly(acrylic acid) creates the backbone and poly(lactic acid) its side arms. Thorough analysis was conducted on the molecular weight of polymers by gel permeation chromatography through triple detection of light-scattering and viscometry. Each copolymer property was studied in detail. Finally, cytotoxicity assay was also performed. Results showed that comb and multi-comb macromolecular architectures co-existed in the sample and that their size and amount are easily tuneable by ratio of the initial reactant.

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## 1. Introduction

Poly lactides (PLA) belong to the family of biodegradable and biocompatible polyesters, and are used in a wide range of commodity or biomedical applications, e.g. surgical sutures, drug delivery systems and bone fixation devices [1–3]. PLA can be synthesized through various approaches. The most important comprise (1) polycondensation of lactic acid [4–7] and (2) ring-opening polymerization (ROP) of the lactide dimer [8–12]. Similar to the majority of polymers, PLA require appropriate modification, depending on the presumed application, to tailor its properties effectively. Furthermore, it is possible to introduce completely new features or functionality of the polymer [13–16].

Modification of the PLA architecture is very useful in cases where specific properties are desirable. It is known that nonlinear macromolecules (e.g. long-chain branched, grafted, star-shaped, dendritic and/or cross-linked) differ from their linear counterparts significantly. They exhibit lower viscosity, higher molecular density and reduced crystallinity, with a faster hydrolysis rate [17–21]. Exhaustive reviews on the synthesis of nonlinear macromolecules can be found in [22–24].

Preparing nonlinear poly lactides is possible through both the above-mentioned synthetic routes—lactic acid polycondensation or ROP [25]. The former requires the presence of a multifunctional co-monomer, and molecular architecture is mostly limited to hyper-branched (e.g. LA + AB<sub>2</sub> monomer polycondensation) and star-shaped structures

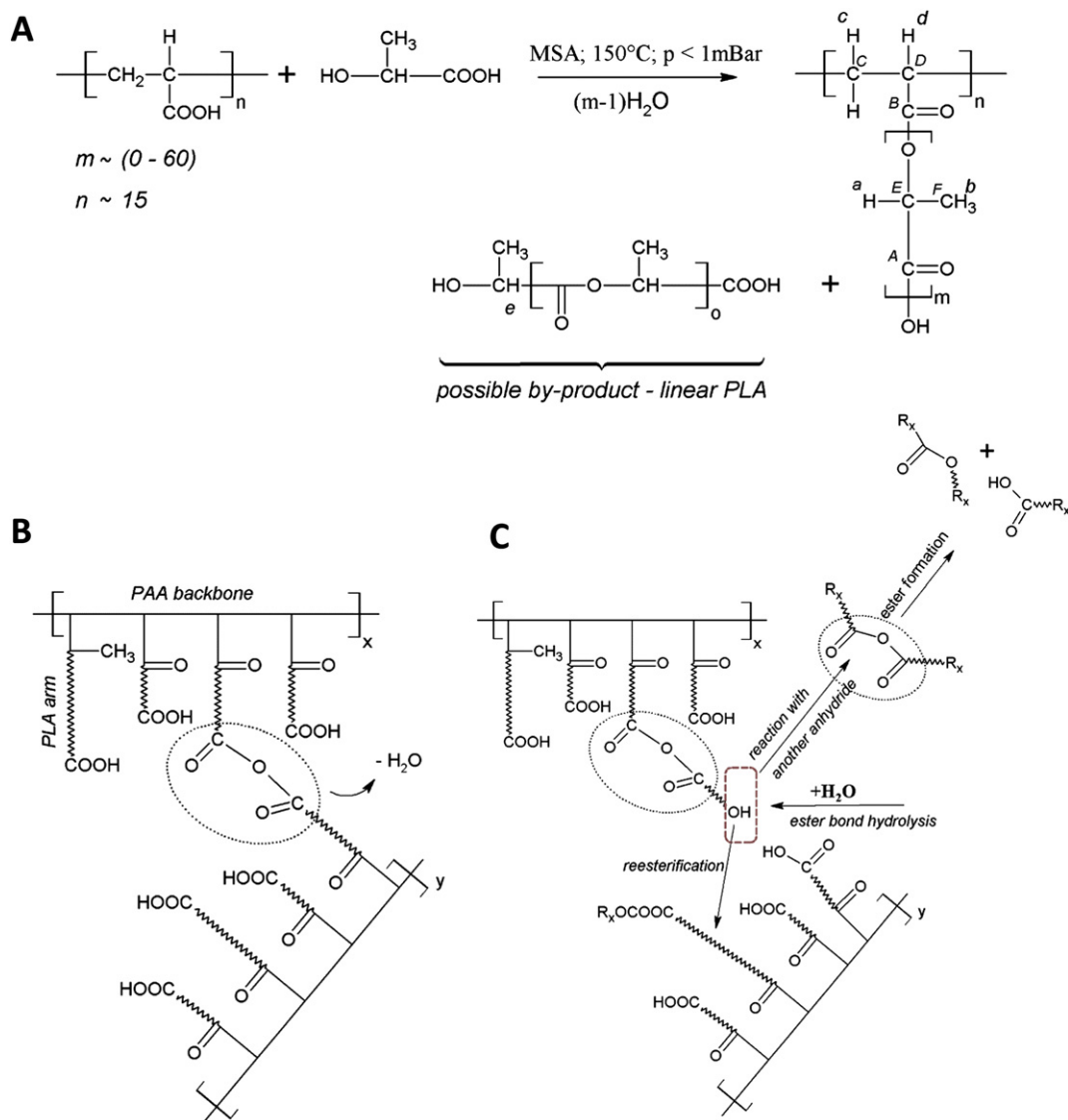
[26–39]. The ROP approach provides the opportunity to produce multiple, variable, nonlinear, polymeric architectures with a precisely controlled structure [40–50]. ROP, however, requires inert-reaction conditions, highly purified monomers and well-defined initiators. Furthermore, catalytic residues might result in the toxicity of the prepared polymers [51].

Traditional comb copolymers represent a special class of grafted polymers consisting of two parts. One of these is a linear polymer backbone, bearing suitable functional groups and facilitating bonding of the linear polymer side chains [52]. Such polymers combine the physical properties of a nonlinear architecture with high peripheral functionality. Synthesizing comb poly lactide copolymers was the chief domain of ROP [52–60]. Some findings on the lactic acid polycondensation approach (in particular with poly(vinyl alcohol) (PVA) as the linear backbone) have also been published [61–66].

In the present contribution, the synthesis of a comb copolymer with a poly(acrylic acid) (PAA) backbone and PLA arms through a simple one-pot polycondensation reaction is reported. The reaction proceeds through polycondensation of the carboxyl groups on the PAA main chain with L-lactic acid (L-LA), thereby forming a comb copolymer PAA/PLA (Scheme 1A) as expected. A side reaction between the terminal end-carboxylic groups (COOH) of the PLA arms through dehydration and anhydride formation also occurs (Scheme 1B). The consequent formation of a carboxylic anhydride bridged comb structure is described in this work. This investigation focused on the effect of the copolymer structure on PAA concentration. The following characterization techniques were used: gel permeation chromatography with triple

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**Scheme 1.** (A) Theoretical reaction scheme between lactic acid and poly(acrylic acid), in which a comb structure and linear by-product (PLA) are formed. (B) Scheme for reaction between the peripheral COOH groups of comb macromolecules – formation of a multi-comb structure. (C) Possible reactions in the PAA/PLA multi-comb structure, leading to further molecular weight redistribution.

detection (Refractive Index (RI)), viscometric and light-scattering ((LS) detectors), end group analysis, infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (NMR), differential scanning calorimetry (DSC), thermogravimetry (TGA) and solution rheology (SR).

Some specific properties of comb polymers were described in a previous report [17–21]. Mainly their possible functionality should be highlighted as the most interesting aspect. Combs with numerous side chains with high concentration of end groups exhibit much stronger interaction with the surrounding environment (e.g., living tissue or polymer-drug interaction). For example, it was revealed that the presence of COOH terminal groups can positively affect drug release and slow down the burst effect in PLA/chitosan nanosystems [68]. Furthermore, in the case of end groups of side chains offering further reactivity (such as the carboxylic group), there are possibilities for their easy conversion into other desired species by postpolymerization modification (e.g. through highly reactive acyl chlorides).

It is believed that the simple polycondensation approach described in this work has certain benefits over ROP in preparing the desired product, namely, in the reduced cost and complexity of the process. To achieve a similar polymeric architecture through ROP at least three steps must be performed: (i) comb polymer synthesis; (ii) conversion

terminal groups to COOH (e.g. through acetylation) and iii) linking the molecules of the combs through terminal COOH groups. Furthermore, the entire procedure would probably require the purification of intermediates during separate steps and the use of purified and dry solvents. All these steps can be avoided by conducting melt polycondensation.

## 2. Experimental section

### 2.1. Materials

L-LA (80% water solution) was purchased from Merci s.r.o., Czech Republic. PAA (50% water solution;  $M_w = 2000 \text{ g.mol}^{-1}$  according to the datasheet,  $M_n = 1050 \text{ g.mol}^{-1}$  as determined by end group titration), dimethyl sulphoxide (DMSO- $d_6$ ), chloroform ( $\text{CDCl}_3$ ) and methanesulphonic acid (MSA,  $\geq 95\%$ ) were all supplied by Sigma Aldrich, Steinheim, Germany. The solvents acetone, methanol, and isopropyl alcohol; the indicator phenolphthalein; and potassium hydroxide (all analytical grade) were purchased from IPL Petr Lukes, Uhersky Brod, Czech Republic. Tetrahydrofuran (HPLC grade) was purchased from Chromservis, Czech Republic. All chemicals were used as obtained without further purification.

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