

The catalytic microwave synthesis of biodegradable polyester polyols based on castor oil and l-lactide

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Abstract. Various strategies for achieving a functional poly(lactic acid) (PLA) have been developed such as ring-opening copolymerization with a functional monomer, the use of functional initiator and various post polymerization modifications. It is possible to obtain the star shaped polymer using natural oil with at least three OH groups as an initiator. It was estimated that despite of low-molecular mass of star-shaped PLA, the hydrophobic castor oil central core influenced the slow degradation rate in the case of injectable biomedical application. The star-shaped polymers with low-molecular-mass have a lower melt viscosity correlated with linear counterparts. In soft tissue reparation the polymer viscosity increases with fluid body contact and the solid implant can be formed. To ensure liquid state at injection temperature the low molar mass polymer is favorable. There is a particular size for each macromolecular chains at which chain entanglement occurs. In this work the influence of the l-lactide (LA) and the castor oil (CO) contents on the size of biodegradable branched polyester polyols was studied. The average molecular masses of synthesized polymers were estimated by GPC procedure. In sample formulations the [LA]/[CO] ratios were from 113 to 533. Mn values for obtained polymers were from 5000 to 20000 Da. The molecular mass distribution for the resulting polymers was between 1.09 and 1.37.

1. Introduction

The polymer materials derived from non-petrochemical resources have commercial and academic importance. Over the last decade, there has been explosive growth in the renewable polymer fabrication, culminating with the manufacturing of polymers such as glucose-derived poly (lactic acid) (PLA) and natural oil-based polyurethanes. Now, with the ecological focus on sustainability, there is a direction to build the polymeric materials from agricultural resources [1].

PLA is thermoplastic aliphatic polyester that can be derived from inexpensive corn and sugar beets. This polymer is fully biodegradable and has good mechanical properties, including a high tensile strength. However, the industrial applications of PLA are limited at present due to the undesirable properties such as low heat resistance, low impact strength, low injection –crystallization rate, high



brittleness, and a low barrier to gases. The low impact strength and high brittleness are the result of large crystal presence.

Different procedures have been made to enhance its flexibility by mixing with low-molecular-mass plasticizers or other polymers. The use of branched polymer will reduce the greenhouse gas emissions compared with PLA products containing commercially available petroleum-based plasticators. Materials based on natural resources have influenced the significant progress in medicine [2]. Nonlinear copolymers exhibit different characteristics in comparison with their linear counterparts. Biobased polyesters have a hydrophobic backbone with hydrolytically labile anhydride and/or ester bonds that may hydrolyze to monomers when placed in a physiological medium [3].

The main feature of star-shaped polymers is the compact structure and the multiple functionality convenient for some applications. PLA is an aliphatic polyester mainly used for packaging, pharmacy, medical devices, and tissue engineering applications. The injectable biodegradable polymers (liquid or pastes) are used for soft tissue repair procedures. In a preferred embodiment, the polymer composition contains liquid or pasty hydroxy fatty acid-based copolyesters, polyester-anhydrides, or some combinations. The viscosity of the polymers increases upon contact with body fluid to form a solid implant suitable for soft tissue repair. To ensure that the polymer is a liquid at temperatures for injection application, it must have a low molar mass.

There exists a particular size for each polymer at which chain entanglement occurs (the critical entanglement length). Below this value the melt viscosity is typically Newtonian. Thus it is important to ensure that the size is below critical value to ensure a low viscosity during flow through a needle. Molecular mass also influences the melting point of polymer (melting point is decreasing as macromolecular size increases). For PLA, branching is determined to influence rheological properties such as complex viscosity and elastic modulus and its melt processing [4]. If the polymer is semi-crystalline, macromolecular size can also be designed to ensure that it is amorphous at operating temperature (37° C). To ensure that star-shaped polymer can pass through a needle, the material have a low glass transition temperature [5]. Various strategies for achieving a functional PLA have been developed, such as ring-opening copolymerization with a functional monomer, the use of a functional initiator, and various post polymerization modifications.

One interesting aspect of the ring-opening reaction procedure is the flexibility in different topology designing using multifunctional initiators. It is possible to obtain the star shaped polymer using natural oil with at least three OH groups as an initiator. It was estimated that despite low-molecular mass of star-shaped poly(lactic acid), the hydrophobic castor oil central core influenced the slow degradation rate in injectable materials application. The viscosity of polymer can be regulated by the initiator type. Star-branched polyester polyol can be synthesized using the oil with at least three OH groups in molecule (castor oil is convenient). Hydroxyl groups at castor oil can initiate ring opening polymerization of lactide. The microwave polymerization provides a new procedure for enhancing economic advantages through energy saving. Chemically homologous chains with linear and branched structures may reveal different properties. The increase of castor oil content (hydrophobicity) decreased the polymer degradation rates. It was estimated that despite low-molecular mass of star-shaped poly(lactic acid), the hydrophobic castor oil (triglyceride of ricinoleic acid) central core influenced the slow degradation rate in injectable materials application. Branched polyester polyol bearing a castor oil core is also using for plastification of poly (lactic acid) [6],[7].

The fabrication of multiphase polymers from renewable resources faces many challenges. Self-assembling polymers such as copolymers are produced by controlled polymerizations, such as anionic, cationic or living radical polymerizations. It can be quite difficult to apply these techniques to many of the available renewable resource monomers due to the lack of appropriate functionality for polymerization, the presence of functionality that is incompatible with these techniques, or the heterogeneity of the feedstock. The majority of all-renewable block and graft copolymers found contain the aliphatic polyester polylactide as one component, largely due to the relative ease of the controlled syntheses of such thermoplastic materials. Macroinitiators containing hydroxyl groups used for thering-opening polymerization of lactide, copolymerization of lactide with other cyclic monomers

(or alternatively of lactic acid with other monomers through condensation polymerizations), and coupling procedures to fabricate polymers of various architecture are studied in ref [8]. The microwave-irradiated reactions are influenced the higher polymer purity. To develop a technique of microwave-assisted polymerization of L-lactide and castor oil, to efficiently and easily prepare star-shaped polyester polyol the ring opening polymerization of L-lactide using microwave irradiation was investigated. The lactic acid oligomers are polar molecules, thus they can absorb microwave energy.

In this study the goal was the synthesis of a branched poly(lactic acid) in the presence of stannous octoate as catalyst in a bulk.

2. Experimental part

2.1. Materials

Monomer (3S)-cis-3,6-dimethyl-1,4-dioxane-2,5-dione (L-Lactide) was used in the ring-opening polymerization (purchased from Sigma-Aldrich). Castor oil with the hydroxyl number 170 mg KOH g⁻¹ and acid value 1.27 mg KOH g⁻¹ was purchased from Merck Chemical Co and used as received. Tin(II) 2-ethylhexanoate (95%) from Aldrich was used as polymerization catalyst. All solvents were obtained from Merck Chemical Co. Castor oil content for samples with desired molar mass for star-like architecture was calculated according [9].



Figure 1. The picture of used "Single-mode" microwave reactor

2.2. Polymerization method

The polyester polyol was prepared by "core-first" method which involves the L-lactide polymerization using multifunctional initiator natural castor oil. Polymerization was carried out in microwave reactor. The molar feed ratio [LA]/[CO] was from 113 to 533. To dry L-lactide (pre-crystallized from methanol) the catalyst tin(II) 2-ethylhexanoate mixed with toluene was added. The mixture was homogenized. The evaporation of toluene was managed during 12 h at 60 °C in vacuum. After that appropriate amounts of castor oil were added in reaction mixture. The reactants mixture was placed to glass ampoule. The synthesis procedure was performed in a conventional microwave oven (Figure 1). The frequency and the power applied were 2.45 GHz and 150 W, respectively. Final product was the polymer with OH groups ended poly(L-lactide) chains. The prepared polymer could be transformed into other end-groups chains (e.g. the more stable ones) or used for different polymer architectures.

2.3. Characterization of obtained polymers

The molecular masses of obtained polymers were determined by GPC method using Agilent 1100 Series system. The column ZORBAX PSM 300 was used. Tetrahydrofuran was used as eluent. Poly(styrene) standards were used for instrument calibration. Fourier transform infrared spectra, FTIR, were obtained using Bomem Hartmann & Braun MB-series. Samples were milled with KBr and tablets were prepared using vacuum press. Thermal properties of samples was investigated by differential scanning calorimetry (DSC, TA Instruments Q20). Hermetically sealed aluminium pans containing 3-5 mg of sample were used for measurements. The non-isothermal melt-crystallization was scanned from 20 to 220 °C with heating rate 5 °C min⁻¹.

3. Results and discussion

Co-polyester based on lactid acid and castor oil was synthesized. The conversion of 90% under the applied synthesis procedure was attained. The structure of prepared material is given in Figure 2. Molecular masses and molecular mass distribution are known as the main characteristics of polymers, since they have significant effects on different properties. For small sized polymers the mass of initiator comprises a significant portion content of the overall mass. The polymer molar masses and molar mass distributions Q assessed by GPC measurements are given in the Table 1 for samples prepared during different reaction times. For prepared samples the feed ratio [LA]/[CO] was varied from 1 to 533 influenced different polymer size (M_n values from 5000 g mol⁻¹ to 20000 g mol⁻¹). It was determined that the size of obtained star-shaped polyesters increased with increase of feed ratio. The molecular mass distribution of the resulting polymer was between 1.09 and 1.37. The chemical structure of obtained samples was estimated by FTIR spectroscopy. In Figure 3 are the FTIR spectrum of synthesized materials. The vibrations at 1189 cm⁻¹ (asymmetrical valence) and symmetrical valence vibrations (C-O-C) of the aliphatic chain at 1093 cm⁻¹ were shifted, compared with L-lactide bonds at 1276 and 1099 cm⁻¹. The peak at 1759 cm⁻¹ was due to the aliphatic ester group (valence vibration of C=O), while the peak at 1454 and 1382 cm⁻¹ originated from asymmetric and symmetric banding vibration of C-H from CH₃. Bond at 1269 cm⁻¹ showed the overlapping C-H bending vibration and C-O-C stretching vibration (C-O-C). Existence of that peak confirmed L/lactide polymerisation.

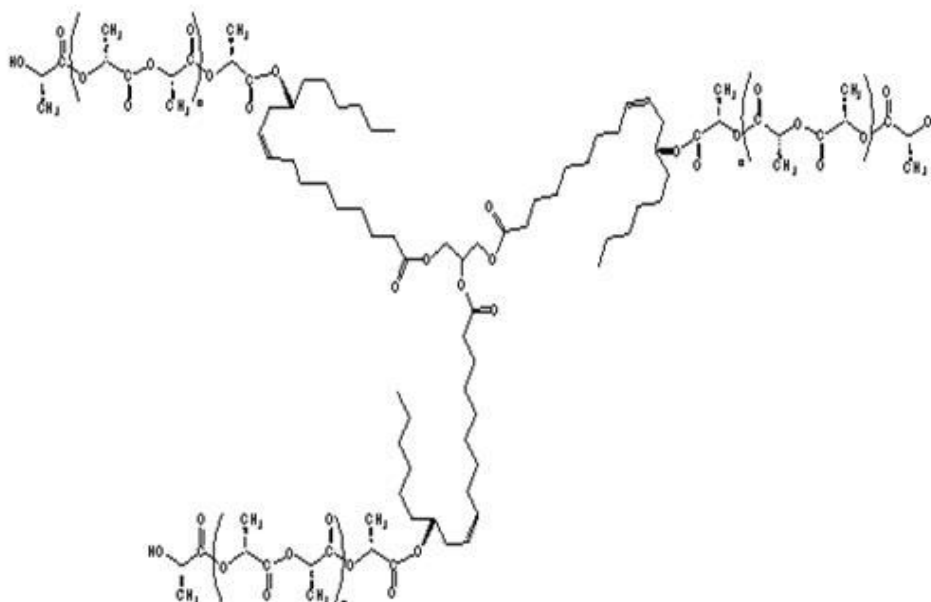


Figure 2. The structure of star-shaped polyester polyol prepared from castor oil as initiator and monomer L-lactide via ring-opening polymerization

The valence vibration bond (C=O) of aliphatic ester are splitted into two bonds (at 1759 cm^{-1} in PLA chains, and at 1748 cm^{-1} in the initiator castor oil). Bonds from asymmetric (2943 cm^{-1}) and symmetric (2856 cm^{-1}) νCH_2 vibrations with additional weak shoulder around 2993 cm^{-1} from νCH_3 , are consequences of terminal methyl group of castor oil fatty acid. Strong absorption at 3480 cm^{-1} originated from terminated hydroxyl groups, νOH , at poly(L-lactide) chains, which confirmed our presumption about polymerization mechanism. By regulating star-shaped polyester synthesis time and feed ratio of reactants it was possible to obtain the appropriate molecular mass of obtained polymer (very important for its degradation kinetics in the human body). However, before such product can reach the market, pharmaceutical-grade material quality and the fabrication costs must be estimated. In Figure 4 are given DSC curve of samples with molar feed ratio [LA]/[CO]s 533,1 synthesized in microwave reactor for different reaction time. In Table 2 are given all DSC data assessed for samples of polyester based on different feed ratio of monomer L-lactide and initiator castor oil.

Table 1. The number average molar mass (Mn) and polydispersity values (Q) for samples based on different feed ratio of monomer L-lactide and initiator castor oil

Sample name	Mass feed ratio	Molar feed ratio [LA]/[CO]	Reaction time (min)	Q	Mn (Da)
PLA-CO-I10	4,53	113,8	10	1.24	4567
PLA-CO-I15	4,53	113,8	15	1.37	5012
PLA-CO-I20	4,53	113,8	20	1.31	5588
PLA-CO-II15	6,85	168,8	15	1.02	6981
PLA-CO-II20	6,85	168,8	20	1.07	7358
PLA-CO-II25	6,85	168,8	25	1.09	7068
PLA-CO-III25	15,62	406,5	25	1.10	13598
PLA-CO-III30	15,62	406,5	30	1.09	14638
PLA-CO-III40	15,62	406,5	40	1.17	14687
PLA-CO-IV30	21,25	533,1	30	1.14	19876
PLA-CO-IV40	21,25	533,1	40	1.12	20933
PLA-CO-IV50	21,25	533,1	50	1.18	21692

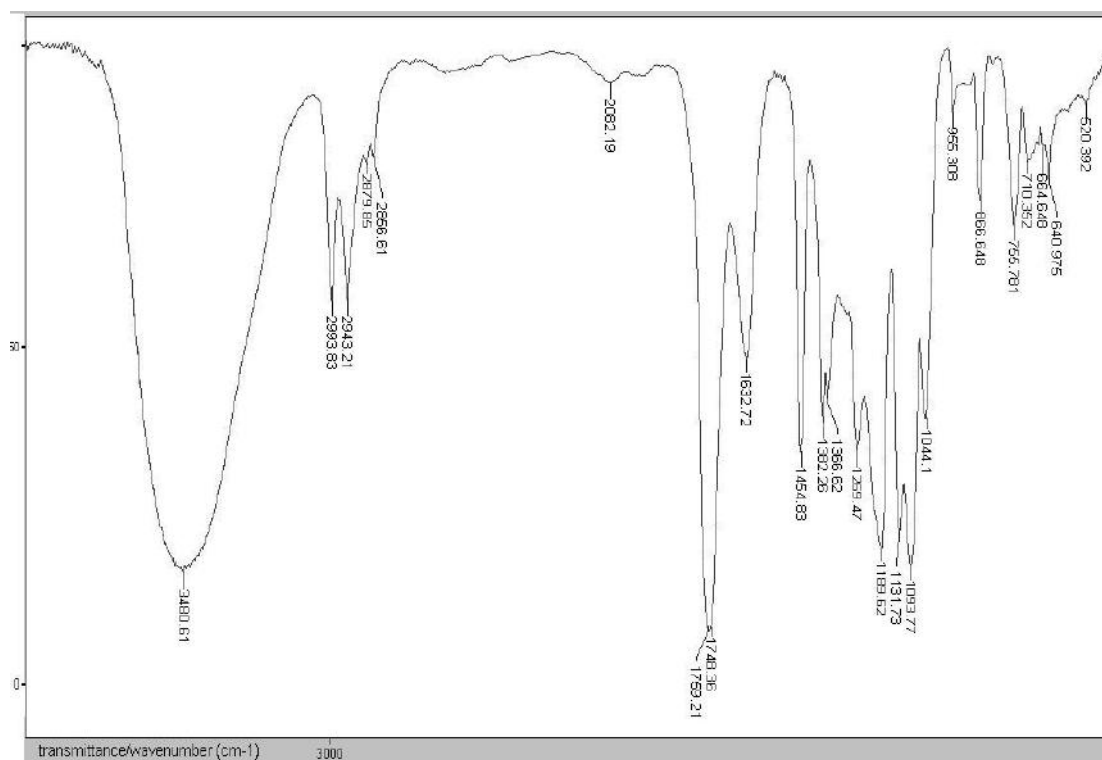


Figure 3. FTIR spectrum of synthesized samples based on lactic acid and castor oil

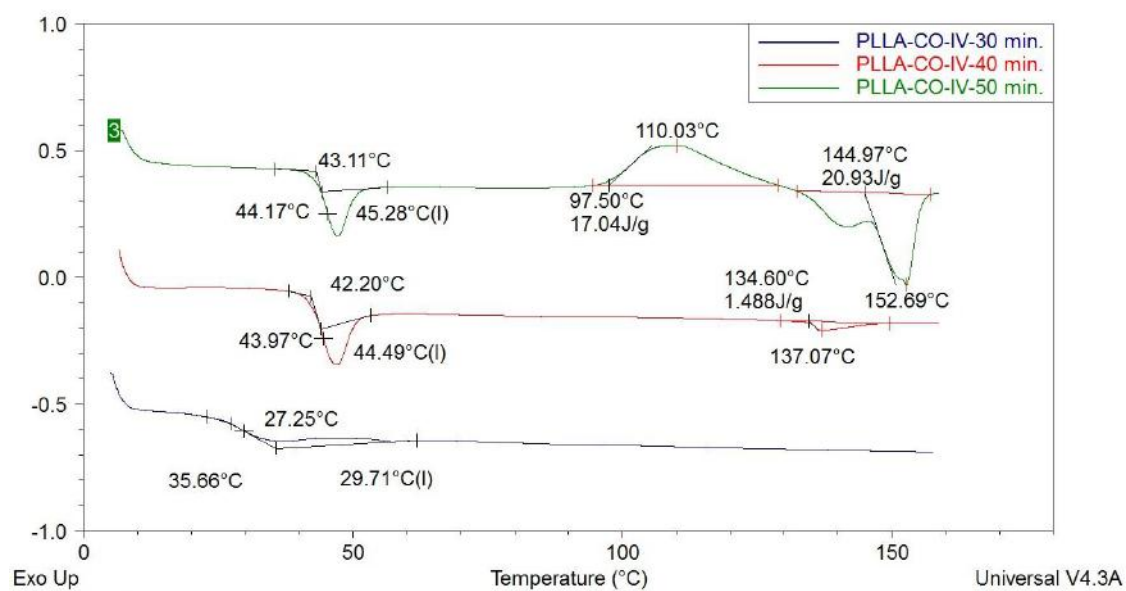


Figure 4. DSC curve of samples with molar feed ratio [LA]/[CO]s 533,1 synthesized in microwave reactor for different reaction time

Table 2. The DSC data assessed for polyester based on different feed ratio of monomer L-lactide and initiator castor oil

Sample name	Reaction time (min)	Molar feed ratio [LA]/[CO]	Tg [°C]	Tc [°C]	Tm [°C]
PLA-CO-I10	10	113,8	40.64	/	/
PLA-CO-I15	15	113,8	38.37	74.99	130.69
PLA-CO-I20	20	113,8	40.81	74.95	138.12
PLA-CO-II15	15	168,8	15	39.63	133.9
PLA-CO-II20	20	168,8	20	38.95	/
PLA-CO-II25	25	168,8	25	40.47	/
PLA-CO-III25	25	406,5	45.35	-	147.34
PLA-CO-III30	30	406,5	46.30	-	147.28
PLA-CO-III40	40	406,5	44.13	-	147.01
PLA-CO-IV30	30	533,1	35.66	/	
PLA-CO-IV40	40	533,1	43.97	137.07	
PLA-CO-IV50	50	533,1	44.17	152.69	

4. Conclusion

Using renewable feedstock for the production of new polymers can have both environmental and economic benefits. To design biodegradable branched polyester polyols based on L-lactide monomer and the castor oil initiator we developed a bulk synthesis microwave procedure using tin(II)2-ethylhexanoate as a catalyst. The star shaped structures of prepared materials was analysed using FTIR spectroscopy. Using the gel permeation chromatography method it was assessed that the size of prepared polyesters was affected by the reactant feed ratio. Obtained materials can be used for injection application if the molecular mass is below critical value to ensure a low viscosity for flowing through a needle. The feed ratio of the monomer and the initiator [LA]/[CO] from to 113 to 533 influenced number average molal mass from 5000 Da to 20000 Da. The polydispersity values were between 1.09 and 1.37. Obtained star-shaped polymers with smaller molar mass can be used for injection application if the molecular mass is below critical value to ensure a low viscosity for the flow through a needle.

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