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MICROWAVE SYNTHESIS OF NEW STAR SHAPED POLYESTER POLYOLS BASED ON L-LACTIDE

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Abstract
The molecular architecture of biodegradable polymers can be adjusted by incorporating multifunctional polyols into the polyester backbone to obtain branched polymers. The aim of our work was to prepare biodegradable polyester polyols based on L-lactide and castor oil in presence of tin(II) 2-ethylhexanoate as catalyst in microwave field. The polyester polyol was synthesized by core-first method which involves a polymerization of L-lactide from OH groups on castor oil. FTIR and ^{1}H NMR spectroscopy measurements were used to confirm the molecular structure of the synthesized products. DSC measurements were used to evaluate the crystallinity of obtained polyols. Thermal stability was investigated by thermogravimetric analysis, and results have shown the dependence of thermal stability on the arm length of the star shaped polyesters.

Introduction
Biodegradable polymers are useful materials for medical and pharmaceutical applications. They have a hydrophobic backbone with hydrolysable anhydride and/or ester bonds that may hydrolyze to monomers in an appropriate medium. Fatty acids are considered as suitable candidates for the preparation of biodegradable polymers, because they are natural body components. Manipulation of mechanical and physical characteristics of these polymers can be achieved by variation of polymer architectures. Star-shaped polymers consist of at least three linear polymeric chains radiating from one single multifunctional branched point [1]. The main feature of star-shaped polymers, make them different from the linear analogues of identical molar masses, is their compact structure and the multiple functionality. Final properties of the resulting star-shaped polymers may be adjusted by choosing the respective chemical structure of an arm and core, depending on the required application [2]. The aim of this work was the synthesis of star-shaped polyester polyol based on L-lactide arms and castor oil as core.

Experimental
Materials
Monomer *(3S)-cis*-3,6-dimethyl-1,4-dioxane-2,5-dione (L-Lactide), 98% *(*purity) was purchased from Sigma-Aldrich, Wisconsin. Initiator castor oil (CO) having the hydroxy number ($OH_{\#}$) 170 mg KOH/g and acid value 1.27 mg KOH/g was

supplied from Merck Chemical Co. Catalyst tin(II) 2-ethylhexanoate (purity of 95%, density 1.251 g cm^{-3} at 25 °C) was supplied from Sigma-Aldrich.

Microwave synthesis of polyester polyol

Microwave polymerization of L-lactide initiated by castor oil was performed according to our previous work [3]. This involves the addition of the dry monomer and castor oil in the glass ampoule, followed by the addition of tin(II) 2-ethylhexanoate. Very short polymerization times were 10, 20 and 30 minutes and carried out in microwave reactor.

Characterisation of prepared samples

The characterization of molecular structure of obtained materials was carried out by FTIR Bomem Hartmann & Braun MB-series, in the band ranged from 400 to 4000 cm^{-1}. ^1H NMR spectra were recorded on Bruker DPX-300 NMR (300 MHz). Samples were dissolved in deutereted chloroform and chemical shifts are given in δ from Me_4Si as an internal standard. Thermal properties of the samples were investigated by differential scanning calorimetry (DSC) using Setaram 151R instrument (heating rate 10 °C min^{-1}) and thermogravimetric analysis (TGA) on Setaram Setsys Evolution-1750 instrument in nitrogen atmosphere (heating rate 20 °C min^{-1}).

Result and Discussion

In the FTIR spectrum of polyester asymmetrical valence vibrations of C-O-C of the aliphatic polylactide chains were shifted at 1187 cm^{-1}, and symmetrical valence vibrations of C-O-C of the aliphatic chain at 1090 cm^{-1}, compared with bands at 1276 and 1099 cm^{-1}, which appeared in monomer L-lactide. Bands at 1455 and 1383 cm^{-1} originated from asymmetric and symmetric bending vibration of C-H from CH_3, respectively. Band from valence vibration of C=O of aliphatic ester splits at two bands, at 1758 cm^{-1} (in poly(L-lactide) chains), and at 1745 cm^{-1} (in castor oil). In the ^1H NMR spectrum peak H1 originated from proton of terminal methyl group in ricinoleic acid (in castor oil), Figure 1.

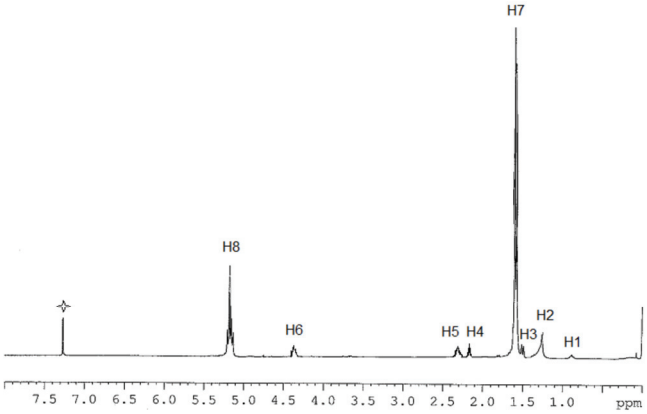

Figure 1. 1H NMR spectrum of obtained polyester polyol.

Peak H2 ascribed protons in methine groups from C4-C7 and C14-C17 in ricionoleic acid. When lactide polymerisation starts (from castor oil hydroxyl

groups) the peak related methylene proton attached to hydroxyl group (C***H***–OH) at 3.61 ppm [4] nearly disappeared, while a new peak at 4.32 ppm appeared, which represented the methylene protons connected to poly(L-lactide) chains. Peaks H3 and H5, due to chemical bonding between polylactide chains and castor oil, were shifted from 1.4 ppm and 2.21 ppm in crude castor oil [4] to 1.48 ppm and 2.42 ppm in polyester polyol. Peaks at 1.57 and 5.13 ppm (H7 and H8) were assignable to methyl and methine proton originated from lactic acid in main chain. Peak which noted with * originated from solvent.

The results of thermal property investigation were summarized in Table 1. For all synthesized samples was observed crystallization and melting from poly(L-lactide) arms. As expected melting temperature of samples increased as molecular masses of poly(L-lactide) arms increase. For star-shaped polyesters with the different arm length which was denoted by the molar mass of samples, the TGA curves show degradation temperature higher than 295 °C. Longer arms actually mean the higher molar mass of samples which can effectively enhance thermal stability.

Table 1. The DSC and TG data of different polyester polyol samples.

Sample name	T_g (°C)	T_c (°C)	T_m (°C)	T_{dec} (°C)
PE-ol-3000	45.5	86.4	130	295
PE-ol-4000	44.2	82.1	130.8	300
PE-ol-5000	43.8	91	133.2	324
PE-ol-6000	40.6	83.3	134.6	330

Conclusions

Star-shaped polyester polyol was obtained by polymerization of L-lactide, using, as an initiator, castor oil. Used polymerization method can be a fundamental technique for producing a low-melting polyol derived from renewable resources. FTIR and ^{1}H NMR spectroscopy confirmed presumed structures of obtained star shaped polymers. The polyester polyol has low crystallinity and a low melting point, so that its working properties is good when used in various medical and pharmaceutical applications. The investigation of thermal degradation by TGA method indicated that the novel star-shaped polyesters with higher molar masses have enhanced thermal stability.

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References

[1] S. Bywater, Adv. Polym. Sci., 1979, 30, 89–116.

[2] P. F. Rempp, P. J. Lutz, Polymeric materials encyclopedia, vol. 10. Boca Raton: CRC Press, 1996, 7880–7885.

[3] Lj. Nikolic, I. Ristic, B. Adnadjevic, V. Nikolic, J. Jovanovic, M. Stankovic, Sensors, 2010, 10, 5063-5073.

[4] E. Mistri, S. Routh, D. Ray, S. Sahoo, M. Misra, Ind. Crop. Prod., 2011, 34, 900–906.

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