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Controlled Branching by Step-Growth Polymerization of Xylitol and Succinic Acid via Microwave Irradiation

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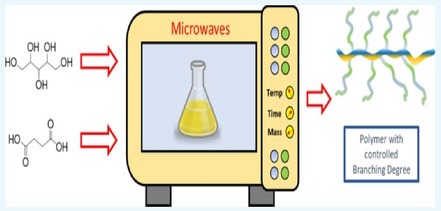
Abstract

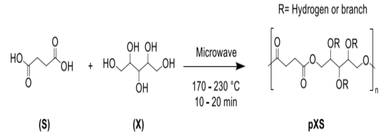
➢Copolymerization of xylitol usually yields crosslinked materials. In this work, microwave-assisted polyesterification of xylitol and succinic acid produced materials with diverse molecular weights and different branching degrees, and more importantly, no cross-linking was observed, as supported by the solubility behaviour and spectroscopic data. Reactions were carried out for short times, less than 20 min, which is not common for production of industrial polyesters. Control over the branching degree was achieved by tuning the reaction conditions, such as temperature, time of exposure, and monomer ratio, during microwave irradiation. No solvent or catalyst was employed during the step-growth polymerization.



Introduction

- Polymers derived from xylitol have gained great interest, especially because xylitol is very accessible, and the resulting materials are biocompatible and biodegradable. Different methodologies for polymerization of xylitol have been explored using catalysts and solvents, yielding materials with diverse properties and potential industrial applications. However, due to the multiple functionalities of xylitol, cross-linked materials are almost exclusively obtained, decreasing the potential applications because cross-linked materials are not post processable.
- Large-scale industrial production of polyesters is usually carried out by heating cycles, which involve hours or even days of reaction and significant energy consumption to achieve high molecular weights.
- The economic and environmental drawbacks of traditional polyesterification have generated the need to explore new methods using green chemistry, for example, polyesterification using enzymes and greener power sources, such as ultrasound and microwave irradiation.
- Polymerization via microwaves normally reduces the time necessary for achieving high molecular weights, optimizes energy consumption, and allows precise temperature control. More importantly, polymerization can be performed in bulk, with no solvent or catalyst.
- Degradability and biocompatibility are green properties that have led to the use of renewable diols and diacids in polyester synthesis. Recently, poly- (xylitol succinate) were synthetized by refluxing toluene for about 80 h. Polyesters from sebacic acid have been synthesized showing both promising degradation and biocompatibility.
- This paper reports the step-growth copolymerization of xylitol and succinic acid using microwave irradiation, without the need for a catalyst or solvent, in high yield in less than 20 min. More importantly, all materials were branched instead of cross-linked, thus potentially expanding their applications via industrial post-processing. The mild conditions used for this short polymerization contrast with hours using conventional heating for industrial processes. All materials were characterized by Fourier transform infrared (FTIR) and 1 H-NMR, their thermal properties were explored by DSC and TGA, and their surfaces were studied by contact angle measurements.

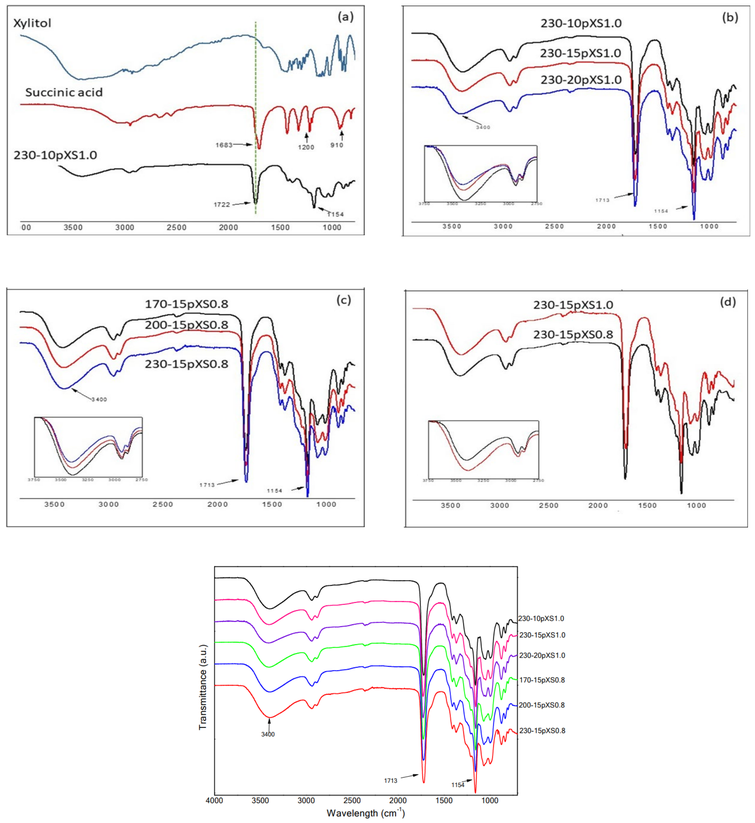
Synthesis



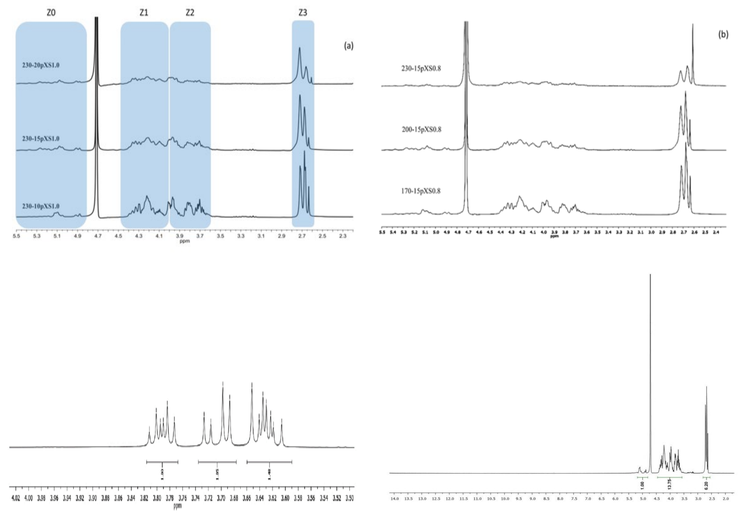
- Polymerizations were carried out while controlling the temperature from 170 to 230 °C, molar ratio of xylitol/succinic acid (X/S, 1 (equimolar) and 0.8 with succinic acid in excess), and reaction time from 10 to 20 min. All materials were coded in terms of temperature, reaction time, and molar ratio. For example, 230-10pXS1.0 corresponds to poly(xylitol succinate), pXS, synthesized at 230 °C for 10 min, with the suffix indicating a molar ratio of 1.0.
- Polymers were synthesized in a synthetic microwave reactor (Discover SP) from CEM Corporation, equipped with a camera for controlling the process. The reactor operates with standard vessels for different sample capacities, closed by septa for suitable pressure control. The temperature was controlled by an IR sensor to avoid risk of explosion. Reaction conditions, including the stirring rates, were set using preloaded methods from the software library.
- Poly(xylitol succinate) was obtained in bulk without any solvent at different temperatures and reaction times. A mixture of different amounts of monomers was strongly stirred and exposed to microwave irradiation at 300 W. After reaction completion, the product was purified by dissolving the polymer in deionized water at 60 °C followed by precipitation in cold ethyl acetate. The pure materials were filtered and dried in a vacuum oven for 1 day

Polymer	Temp (°C)	Time (min)	Xylitol (mg)	Succinic acid (mg)	Xylitol (mmol)	Succinic acid (mmol)	Ratio X/S
230-10pXS1.0	230	10	455.4	357.3	2.99	3.03	1.0
230-15pXS1.0	230	15	453.7	355.0	2.98	3.01	1.0
230-20pXS1.0	230	20	453.7	355.8	2.98	3.01	1.0
170-15pXS0.8	170	15	368.2	359.3	2.42	3.04	0.8
200-15pXS0.8	200	15	366.7	353.2	2.41	2.99	0.8
230-15pXS0.8	230	15	368.7	353.3	2.42	2.99	0.8

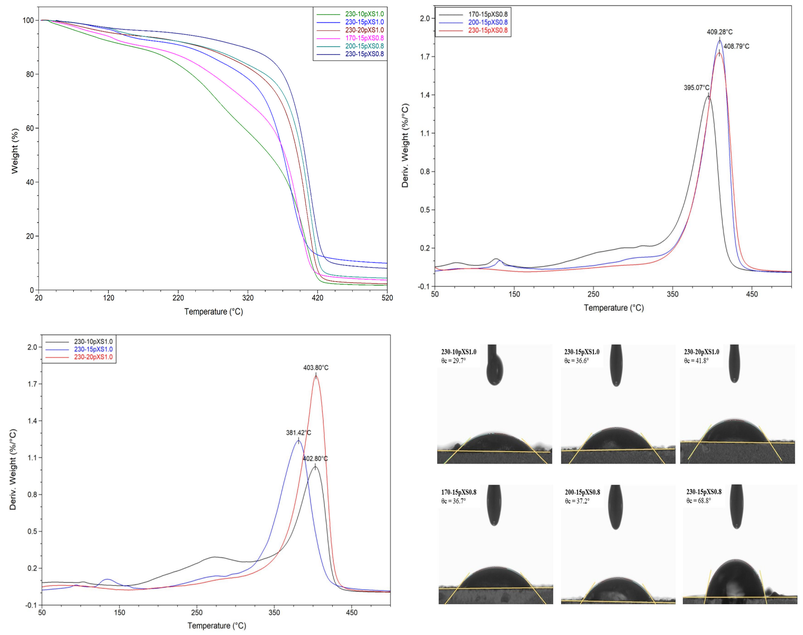
Characterization



Result and discussion



polymer	T_g (°C)	ΔC_p (J/g °C)	T_d (°C)	M_n (kg/mol)	free OH index (pXS/X)[a]	branching degree[b]	contact angle (θc)	appearance	yield (%)
230-10pXS1.0	−3	0.69	381	2	1.24	5.0	29.7	viscous	71
230-15pXS1.0	16	0.64	403	22	1.10	4.0	36.6	solid	81
230-20pXS1.0	34	0.53	404	32	1.01	2.6	41.8	solid	60
170-15pXS0.8	12	0.76	395	3	1.12	4.0	36.7	solid	76
200-15pXS0.8	29	0.58	409	45	0.93	3.8	37.2	solid	77
230-15pXS0.8	57	0.50	409	53	0.91	1.9	68.8	solid	71



Conclusions

- A series of branched polymers from copolymerization of xylitol and succinic acid were obtained by rapid microwave synthesis without the use of solvents or catalysts. Materials were rapidly obtained in less than 20 min, which is much faster than traditional industrial polyesterifications, which can require hours. The molecular weight, branching degree, and glass transition can be tuned by simply controlling the polymerization temperature, time of exposure to microwave irradiation, and monomer ratio, all conditions that avoid cross-linking and allow polymers with molecular weights as high as 53 kg/mol.
- The higher the polymerization temperature and the longer the exposure to microwave irradiation, the higher the molecular weight and the glass transition temperature of the material. All materials obtained were branched polymers instead of crosslinked, as demonstrated by NMR, solubility tests, and contact angle measurements. It is not clear why the reaction prefers to yield branched instead of cross-linked materials since the reaction occurs in bulk, and mobility must be an important factor along with steric effects.
- Currently, more reactions with diverse monomers are under study to understand these phenomena; however, this polymerization method offers new possibilities for the easy and rapid production of branched polymers of xylitol instead of cross-linked materials. This methodology could find use in the industrial fabrication of materials with a wide range of physical properties.

Acknowledgements

- National Institute for Materials Advancement
- Pittsburg State University

Reference

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