

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

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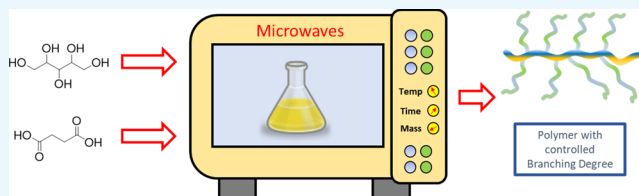


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ABSTRACT: Copolymerization of xylitol usually yields cross-linked materials. In this work, microwave-assisted polyesterification of xylitol and succinic acid produced materials with diverse molecular weights and different branching degrees, and more importantly, no cross-linking was observed, as supported by the solubility behavior 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.



1. 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.^{1–7} 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.⁸ 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.^{9–13}

Degradability and biocompatibility are green properties that have led to the use of renewable diols and diacids in polyester synthesis.^{14–16} Recently, Liz-Andela *et al.* synthesized poly(xylitol succinate) by refluxing toluene for about 80 h.⁸ Polyesters from sebacic acid have been synthesized showing both promising degradation and biocompatibility.^{17,18} Velmathi *et al.* reported the synthesis of poly(butylene succinate) in bulk via microwave irradiation in 30 min using tin(II) chloride as the catalyst at 200 °C and 200 W.^{19,20} More recently, Orozco *et al.* reported the polymerization of *trans*-aconitic acid

via microwave irradiation yielding exclusively cross-linked materials.²¹

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 ¹H-NMR, their thermal properties were explored by DSC and TGA, and their surfaces were studied by contact angle measurements.

2. RESULTS AND DISCUSSION

In research settings, polyesterification can be achieved in solution while in industrial production of polyesters using molten monomers over long (hours) polymerization periods to avoid solvent evaporation and further material purification.²² Polyesterification using microwave irradiation is an alternative that increases formation of high molecular weight polymers.²³ More importantly, regulation of temperature and time of exposure to microwave irradiation allows control over molecular weight.¹⁵ While conventional heating by convection is a lengthy and expensive process, the use of microwave

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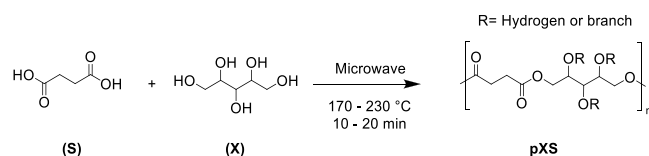
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irradiation for polyesterification is more efficient and economical.¹⁶

Polymerization of diols and diacids can be easily carried out in solution; for example, a series of polymerizations of xylitol and succinic acid were previously performed in toluene from 36 to 80 h.⁸ A greener methodology for obtaining a series of branched poly(xylitol succinates) without the use of solvents in short reaction times ranging from 10 to 20 min is presented here. Scheme 1 shows the polyester (pXS) obtained by microwave polymerization of succinic acid (S) and xylitol (X).

Scheme 1. Synthesis of Poly(xylitol succinate) via Microwave Polymerization of Succinic Acid and Xylitol



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. A series of different materials with diverse properties were obtained in yields from 60 to 81%, as summarized in Table 1.

All polymers in Table 1 are soluble in water at 60 °C and insoluble at room temperature in most organic polar solvents, such as methanol, ethanol, and dimethylformamide. It is expected that the degree of polymerization increases with increasing temperature and irradiation time. While five materials of the series are solid, only 230-10pXS1.0 is a viscous liquid, suggesting that its degree of polymerization must be the lowest of the series. Table 1 shows the viscosity average molecular weight for all polyesters, proving that 230-10pXS1.0 is in fact the material with the lowest molecular weight. As expected, extending the time of exposure to microwave irradiation while controlling the polymerization temperature at 230 °C from 10 to 15 and 20 min increases the molecular weight from 2 to 22 and 32 kg/mol, respectively. A much more dramatic effect on the molecular weight is observed by varying the polymerization temperature while fixing the time of irradiation at 15 min. Polymers obtained at 170, 200, and 230 °C show molecular weights of 3, 45, and 53 kg/mol, respectively. Although it is clear that the effects of time

and temperature over the degree of polymerization play an important role, the monomer ratio seems to be much more important. Keeping the polymerization temperature at 230 °C for 15 min while varying the monomer ratio (X/S) from 1 to 0.8 yields polymers with molecular weights of 22 and 45 kg/mol. Thus, excess succinic acid favors the formation of highly branched polymers with around 2 times the molecular weight.

A simple way to follow the polymerization progress is by ATR-FTIR, in which a direct comparison of the pure monomers with the resulting polymer shows that some characteristic bands from the monomers disappear, while new bands appear in the polymer material. Figure 1a shows the IR spectra of xylitol, succinic acid, and 230-10pXS1.0. Xylitol exhibits a broad vibration around 3500 cm⁻¹ due to the stretching of the hydroxyl groups, while succinic acid shows a stretching band at 1683 cm⁻¹, which belongs to the carbonyl group. Polymer 230-10pXS1.0 shows a weak band from the hydroxyl groups around 3500 cm⁻¹ and a stretching vibration around 1722 cm⁻¹ from the ester carbonyl group. However, the main signal that proves the formation of a new ester functionality is the band at 1154 cm⁻¹, which corresponds to the ester group stretching (C–O–C), thus confirming polymer formation.

The viscosity average molecular weight for polymers obtained at 230 °C increases when extending the time from 10 to 15 and 20 min, but small changes are also observed in their FTIR spectra. Figure 1b shows the effect of varying the time of microwave irradiation, where a change in the intensity of the OH band at 3400 cm⁻¹ indicates that there are fewer free hydroxyl groups and that the polyester is less linear, i.e., more branched, with higher molecular weight. Figure 1b shows a systematic decrease of the band intensity at 3400 cm⁻¹ for polymers 230-10pXS1.0, 230-15pXS1.0, and 230-20pXS1.0. The same behavior is observed in Figure 1c when increasing the reaction temperature from 170 to 200 and 230 °C; all molecular weights and consequently the OH band intensities for polymers 170-15pXS0.8, 200-15pXS0.8, and 230-15pXS0.8 decrease as well. The biggest change in molecular weight is observed while varying the monomer molar ratio from 1.0 to 0.8. In Figure 1d, this effect is observed by a decrease of the OH band intensity at 3400 cm⁻¹ for 230-15pXS1.0 compared to 230-15pXS0.8. Although IR spectroscopy does not follow the Beer–Lambert law, a comparison of the normalized absorbances of the OH stretching band for the polymer and xylitol gives a relative idea of the degree of branching in the polymer compared to the starting material, xylitol. Table 1 shows the calculated free OH index for each produced polymer. A higher index indicates that more free OH groups are present in the polymer with formation of a more

Table 1. Physical Properties of Polymers Obtained at Selected Reaction Conditions

polymer	T_g (°C)	ΔC_p (J/g °C)	T_d (°C)	M_v (kg/mol)	free OH index (pXS/X) ^a	branching degree ^b	contact angle (θ_c)	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

^aArea was measured from the normalized IR absorbance from 4000 and 3000 cm⁻¹. For xylitol, the normalized area was 805,060 (arbitrary units). For each polymer, the free OH index was calculated as the percentage of the OH area in the polymer relative to the OH area of xylitol. ^bCalculated by NMR from the ratio of the integrals of Z3/Z0.

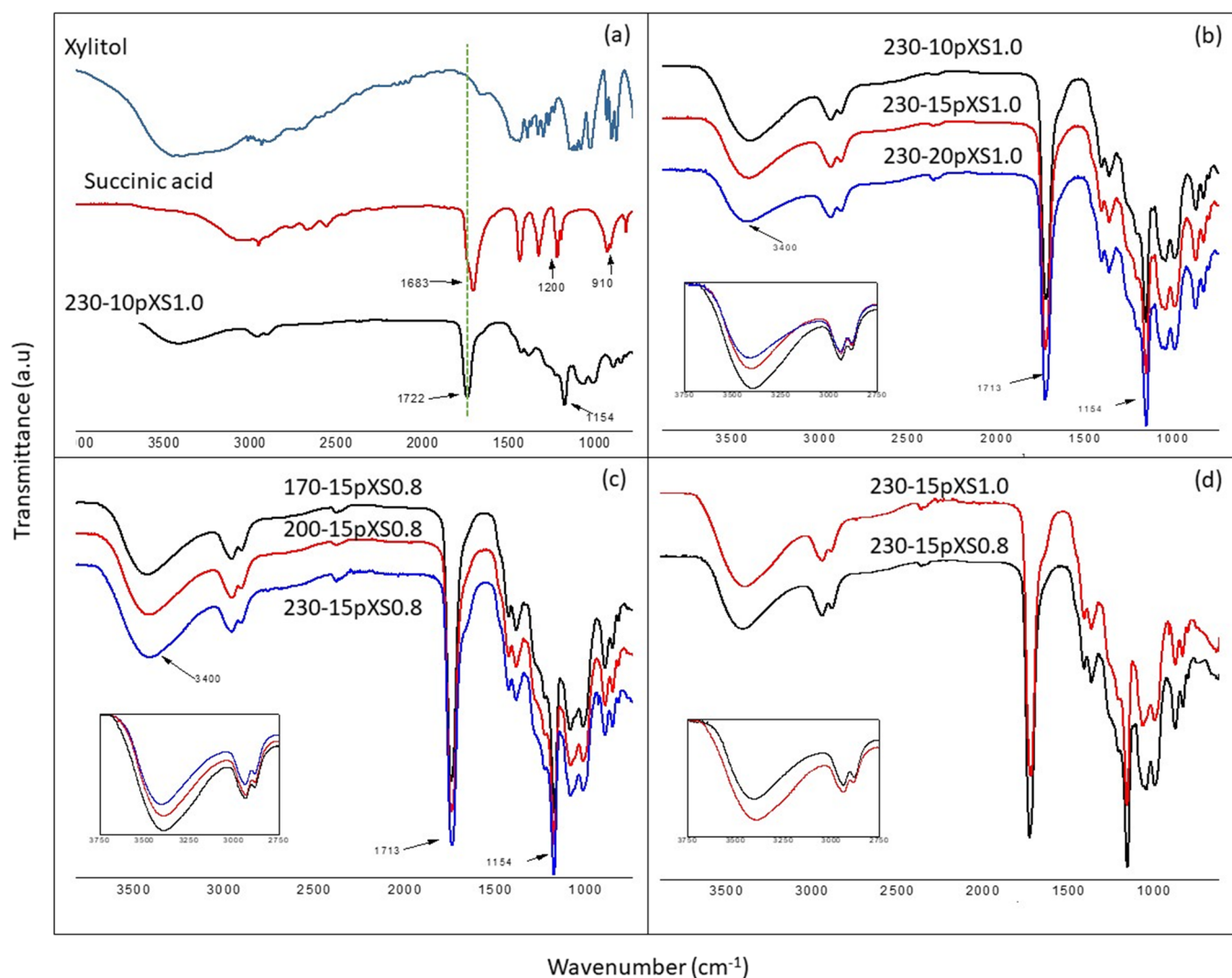


Figure 1. (a) FTIR of xylitol, succinic acid, and 230-10pXS1.0. (b) Effect of varying the time of microwave irradiation. FTIR of 230-10pXS1.0, 230-15pXS1.0, and 230-20pXS1.0. (c) Effect of varying the reaction temperature. FTIR of 170-15pXS0.8, 200-15pXS0.8, and 230-15pXS0.8. (d) Effect of changing the monomer molar ratio. FTIR of 230-15pXS1.0 and 230-15pXS0.8.

linear polymer of lower molecular weight. As expected, maintaining the polymerization temperature constant at 230 °C and varying the time of irradiation from 10 to 15 and 20 min decrease the index: 1.24 for 230-10pXS1.0, 1.10 for 230-15pXS1.0, and 1.01 for 230-20pXS1.0. On the other hand, polymer 230-10pXS1.0 possesses more available OHs and yields a less branched material, in comparison to 230-20pXS1.0 with fewer free OHs and a more branched material. The same trend is observed when varying the polymerization temperature; while polymer 170-15pXS0.8 presents a free OH index of 1.12, 200-15pXS0.8 gives 0.93, and 230-15pXS0.8 gives 0.91. Thus, the higher the temperature, the lower is the free OH index and the more branched is the polymer. An effect of stoichiometry on the OH index was also observed. While 230-15pXS1.0 showed an index of 1.10 (less branched), 230-15pXS0.8 showed an index of 0.91 (more branched), suggesting that, at higher concentrations of succinic acid, more OHs from xylitol react to yield a more branched polymer.

In addition to IR spectroscopy, characterization by nuclear magnetic resonance (NMR) was performed to understand the primary structures of the polymers and to calculate the

branching degree. Figure 2 shows the $^1\text{H-NMR}$ spectra for the materials in deuterated water. Figure 2a shows the effect of varying the time of microwave irradiation, and Figure 2b shows the effect of varying the reaction temperature. Representative zones are denoted in terms of the proton signals and their proportion. The NMR spectrum in Figure 2a is divided into three zones: zone zero (Z0) from 4.8 to 5.4 ppm shows two multiplets corresponding to methine protons from secondary carbons from xylitol, which are linked to the oxygen in the ester group. Zone one (Z1) from 4.0 to 4.5 ppm shows xylitol protons as follows: multiplets from methylene protons from primary carbons linked to ester groups, methine protons from the secondary carbons between two ester groups linked to a free OH index, and methine protons from the secondary carbons of the β -ester groups linked to a free OH index. Zone two (Z2) from 3.6 to 4.0 ppm shows multiplets for methylene and methine protons from primary and secondary carbons, respectively, linked to a free OH index from xylitol, and zone three (Z3) from 2.6 to 2.8 ppm exhibits methylene protons from succinic acid. Thus, Z0, Z1, and Z2 are related to protons from the xylitol moiety, while Z3 corresponds to protons from the succinic acid moiety. The branching degree was calculated

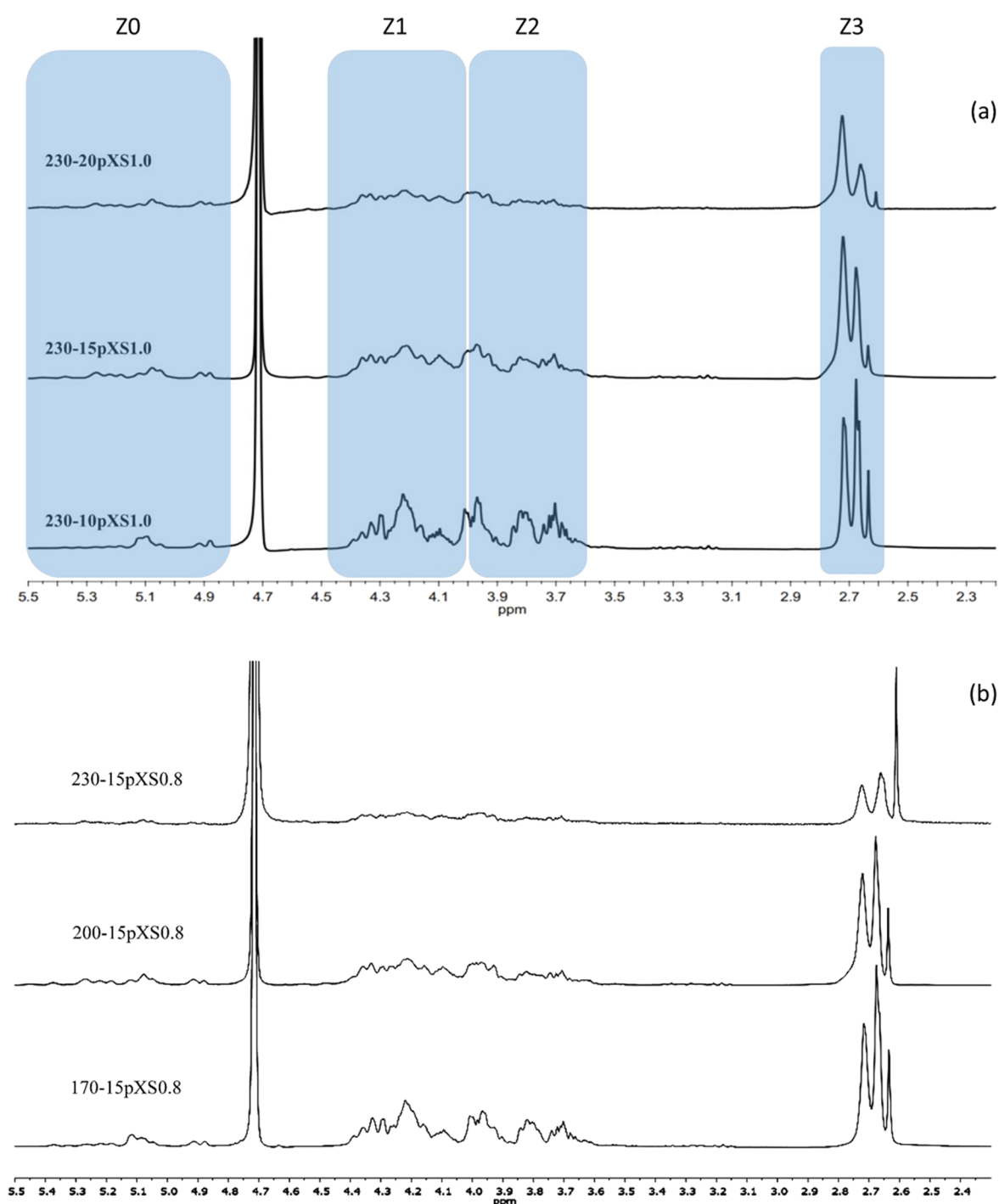


Figure 2. (a) ¹H-NMR of 230-10XS1.0, 230-15XS1.0, and 230-20pXS1.0. Effect of varying the time of microwave irradiation. (b) ¹H-NMR of 170-15pXS0.8, 200-15pXS0.8, and 230-15pXS0.8. Effect of varying the reaction temperature.

by dividing the integral of Z3 by the integral of Z0. Zones Z1 and Z2 were excluded from the branching degree calculation since they could include hydrogens from the hydroxyl groups. However, once the branching degree decreases, the integral in Z2 also decreases, maintaining the same trend since it includes hydrogens from primary and secondary carbons linked to free hydroxyl groups. The branching degree increases when Z0 tends to zero; for an ideal linear polymer, the ratio tends to infinite with the absence of ester methine protons, and for a totally branched polymer, the ratio will tend to zero. For example, the branching degree calculated for 230-10pXS1.0 is

$1/0.2 = 5.0$ (Figure 2a), indicating that the polymer, even with a low molecular weight (2 kg/mol), is not completely linear.

The effect of varying the time of microwave irradiation for 230-10XS1.0, 230-15XS1.0, and 230-20XS1.0 is shown in the ¹H-NMR spectra of Figure 2a. As the reaction time increases from 10 to 15 min, Z3/Z0 changes from 5.0 to 4.0, suggesting a reduction of the branching degree. With the further increase of the polymerization time from 15 to 20 min, Z3/Z0 changes from 4.0 to 2.6, suggesting a decrease in the branching degree, which follows the same trend of decreasing the intensity of the OH vibration in the IR free OH index, which changes from

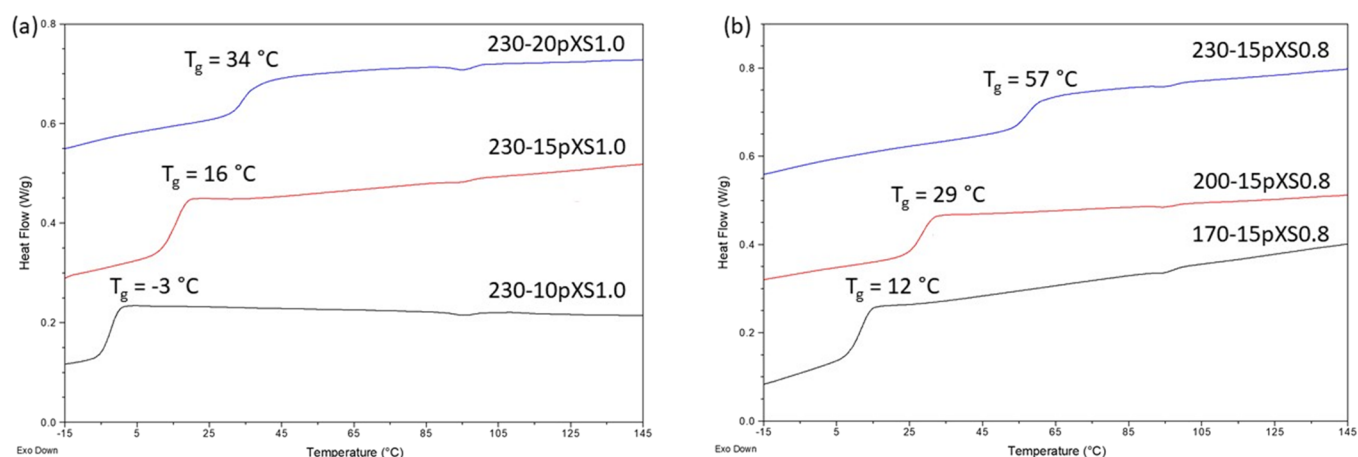


Figure 3. (a) DSC of polyesters 230-10pXS1.0, 230-15pXS1.0, and 230-20pXS1.0. (b) DSC of polyesters 170-15pXS0.8, 200-15pXS0.8, and 230-15pXS0.8.

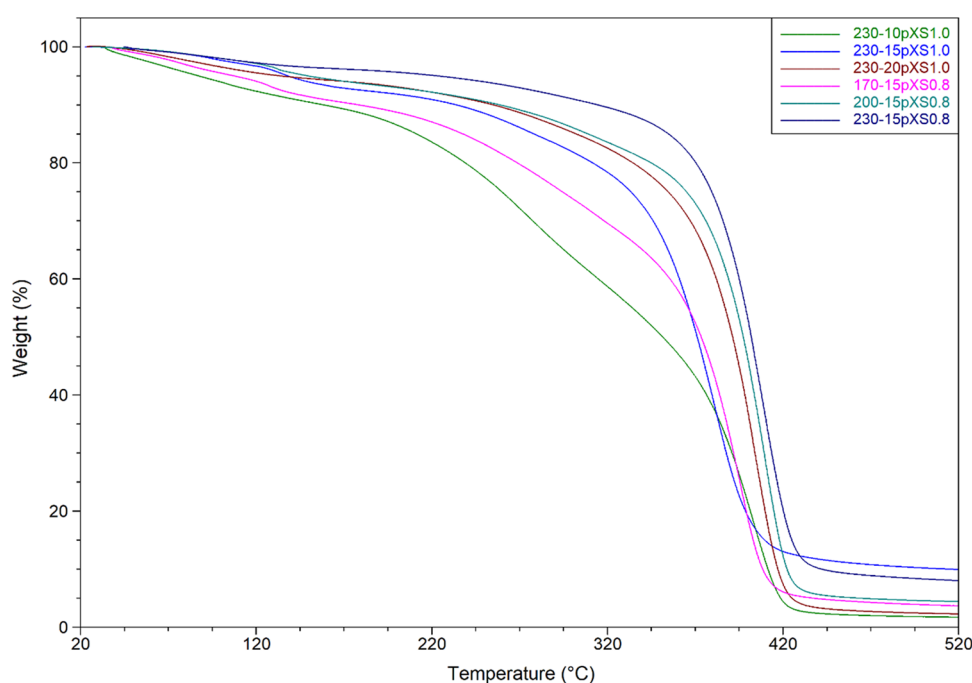


Figure 4. TGA thermograms for polyesters 230-10pXS1.0, 230-15pXS1.0, 230-20pXS1.0, 170-15pXS0.8, 200-15pXS0.8, and 230-15pXS0.8.

1.10 to 1.01 and the increment in the molecular weight from 22 to 32 kg/mol, suggesting less branching.

It is worth noting that the effect on the branching degree while changing the reaction temperature from 170 to 200 $^\circ\text{C}$ is insignificant, with 170-15pXS0.8 and 200-15pXS0.8 changing from 4.0 to 3.8. The branching degree is very similar for both polymers, but this does not mean that the molecular weights have to be the same, with values of 3 and 45 kg/mol, respectively. A different trend is observed after increasing the polymerization temperature from 200 to 230 $^\circ\text{C}$. The branching degree shows a large decrease from 3.8 to 1.9, and the change in molecular weight is dramatic, from 45 to 53 kg/mol. These data indicate that a higher molecular weight can be achieved by increasing the temperature while maintaining control over the branching degree. In terms of stoichiometry, increasing the amount of succinic acid is expected to produce a more branched polymer, which was observed when X/S was changed from 1 to 0.8, yielding branching degrees of 4.0 (less

branched) and 1.9 (more branched). It is important to mention that the calculated values for the branching degree and OH index are relative but not absolute; nevertheless, they provide useful information when controlling parameters such as time, temperature, and molar concentration.

Differential scanning calorimetry (DSC) was used to explore the thermal behavior of the polymers and their relationship to the branching degree and molecular weight. Figure 3 shows the DSC thermograms of all materials. Only a glass transition (T_g) is observed for all polymers, suggesting that the materials are amorphous. The effect of increasing the polymerization time while keeping the polymerization temperature constant is shown in Figure 3a. For 230-10pXS1.0, 230-15pXS1.0, and 230-20pXS1.0, the glass transitions are -3 , 16 , and $34\text{ }^\circ\text{C}$, respectively, with molar heat capacities (ΔC_p) of 0.69, 0.64, and $0.53\text{ J/g }^\circ\text{C}$, respectively. Increasing the time of exposure to microwave irradiation elevates the branching degree and the molecular weight, observed by DSC as an increase in T_g and a

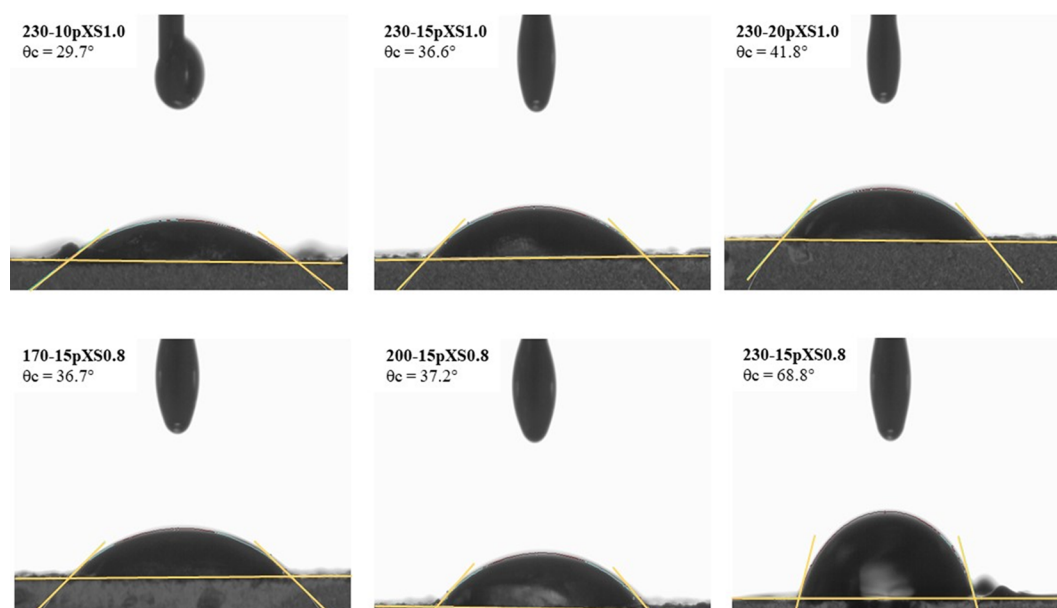


Figure 5. Contact angle (θ_c) measurements for polyesters 230-10pXS1.0, 230-15pXS1.0, 230-20pXS1.0, 170-15pXS0.8, 200-15pXS0.8, and 230-15pXS0.8.

decrease in ΔC_p , as shown in Table 1. The same trend is observed in Figure 3b when increasing the polymerization temperature; for polymers 170-15pXS0.8, 200-15pXS0.8, and 230-15pXS0.8, the T_g values are 12, 29, and 53 °C, while the ΔC_p values are 0.76, 0.58, and 0.50 J/g °C, respectively. When increasing the monomer molar ratio from 230-15pXS1.0 to 230-15pXS0.8, T_g increases from 16 to 57 °C, while ΔC_p decreases from 0.64 to 0.50 J/g °C. Thus, increasing the temperature, reaction time, or content of succinic acid increases the glass transition, suggesting that the materials are more amorphous, results that are validated by the higher degree of branching and the greater molecular weight. Thus, it is possible to control the branching degree, molecular weight, and glass transition by simple manipulation of polymerization temperature, the time of exposure to microwave irradiation, and the monomer content over short periods (minimum of 10 min and maximum of 20 min).

Thermal stability was determined by thermal gravimetric analysis (TGA) (Figure 4). All polymers are thermostable with decomposition temperatures (T_d) of 380–410 °C, all of which increase with increasing polymerization temperature, reaction time, and molar ratio. In summary, the high T_d values are related to a high degree of branching and increasing molecular weight. In addition to the structural and thermal characterization of the produced materials, surface analysis was achieved by contact angle measurements (θ_c), as shown in Figure 5 and Table 1.

The top row in Figure 5 shows polymer surfaces obtained after 10, 15, and 20 min of microwave polymerization while controlling the polymerization temperature at 230 °C. The above structural and thermal characterization suggested that the branching degree decreases while increasing the molecular weight and the time of microwave exposure, and the same trend was observed by contact angle measurements. The longer the exposure to microwave irradiation, the fewer free hydroxyl groups are present in the material, allowing polymers with more hydrophobic surfaces. The 230 °C pXS series showed contact angles of 29.7, 36.6, and 41.8° for 10, 15, and 20 min polymerization times, respectively. As expected, the

bottom row in Figure 5 follows the same trend when increasing the polymerization temperature while keeping the microwave exposure constant. Increasing the polymerization temperature from 170 to 200 and 230 °C yielded θ_c values of 36.7, 37.2, and 68.8°. The higher the polymerization temperature, the fewer free hydroxyl groups are present, which produces surfaces with increasing hydrophobicity. Although hydrophobicity increases with microwave irradiation exposure and temperature, all synthesized materials are way below the “impermeability” zone (higher than 90°), which is in agreement with the solubility of all polymers in water at 60 °C. These results ultimately demonstrate that none of the synthesized materials forms a strong rigid network, which is usually formed after cross-linking. Thus, the materials obtained are primarily branched polymers.

3. 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 cross-linked, 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.

4. EXPERIMENTAL SECTION

4.1. Chemicals and Materials. Succinic acid and xylitol ($\geq 99\%$ purity) were purchased from Sigma-Aldrich and used without any further purification.

4.2. Microwave-Assisted Polymerization. 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. In all cases in Table 1, a dynamic method was developed: conditions such as temperature and time were set as follows: 170, 200, and 230 °C for 15 min and 230 °C for 10, 15, or 20 min with a power set at 300 W. The reaction was stirred with the help of a magnetic stir bar during the course of the reaction until the increased viscosity stopped the bar motion.

4.3. Chemical Synthesis of Poly(xylitol succinate). Poly(xylitol succinate) was obtained in bulk without any solvent at different temperatures and reaction times, as shown in Table 1. 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.

4.4. General Methods. IR spectra for approximately 5 mg of pure solid samples were obtained in a Thermo Fisher Scientific Nicolet iS10 FT-IR spectrometer using an attenuated total reflectance (ATR) module; the background noise and atmospheric suppression were subtracted with OMNIC software. $^1\text{H-NMR}$ spectra were obtained in a Bruker instrument at 400 MHz (D_2O δ :4.71 ppm and TMS δ :0 ppm). Thermal transitions of the materials were obtained by differential scanning calorimetry (DSC) in a TA Instruments DSC Q2000. The temperature range was from -20 to 200 °C with a heating rate of 10 °C/min. Calibrations were made using indium and freshly distilled *n*-octane as the standards for peak temperature transitions and indium for the enthalpy standard. All samples were prepared in hermetically sealed pans (5–10 mg/sample) and were run using an empty pan as a reference and empty cells as a subtracted baseline. The samples were scanned for multiple cycles to remove recrystallization differences between the samples, and the results reported were of the third scan in the cycle. Thermogravimetric analysis was obtained in a TGA 2050 from TA Instruments with a heating rate of 20 °C/min. The viscosity average molecular weight (M_v) was determined following the Mark–Houwink–Sakurada equation using polymeric solutions at 1.0 g/mL in a $\mu\text{VISC-m}$ RheoSense Inc. viscosimeter, and the results were in agreement with gel permeation chromatography (GPC) and NMR data.^{24–28} Contact angle measurements (θ_c) were carried out in an OCA15EC Dataphysics Instrument. The measurements were performed on the surface of a freshly prepared tablet. The data capture was recorded using an IDS video camera in the

range of 400–800 frames as a reference point. The added drop volume was 0.05 mL at a rate of 5 $\mu\text{L/s}$.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.0c05875>.

More detailed FTIR data, a complete $^1\text{H-NMR}$ spectrum for 230-10pXS1.0, and DTGA of all samples as well as more in-depth information for the viscosity measurements (PDF)

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Notes

The authors declare no competing financial interest.

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