



Linear and branched acetal polymers from castor oil via acetal metathesis polymerization

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ABSTRACT

Synthetic protocols to prepare new diols were developed to revalorize heptanal and 10-undecenoic acid castor oil derivatives. The Acetal Metathesis Polymerization of these diols yielded linear and branched renewable polyacetals and copolyacetals with number average molecular weights in the range 14,000–27,000 g mol⁻¹. Thermally robust semicrystalline or amorphous materials were obtained. Polyacetals were hydrolytically degradable down to parent diols under slightly acidic media and no significant differences on the degradation pattern were observed among them.

1. Introduction

Polymers are an indispensable component of our modern society and the major output of the chemical industry. Nearly all polymers are derived from non-renewable fossil resources and their disposal at their end of use brings about several environmental problems. The development of polymers that are sustainable from combined environmental, societal, human health and economic perspectives is a major challenge in polymer science [1]. The key to shifting to sustainable alternatives will be to obtain both existing and new low-cost polymers with competitive performance properties from renewable resources. Moreover, polymers that can be easily recycled, autonomously degraded to innocuous byproducts over reasonable time scales or safely incinerated to recover their embedded energy must be developed to address the end-of-life concerns.

The next generation of environmentally friendly commodity plastics will derive from sustainable feedstocks based on biomass. A particularly relevant option is to replace oil based resources by plant oils and their derived fatty acids, and castor oil is one of the most valuable choices. Their high versatility and exclusion of alimentary sector convert this material into a good candidate to explore new routes to obtain biopolymers. Castor oil derivatives have been employed in the synthesis of different kind of polymers such as polyesters, polyamides and polyurethanes among others [2]. However, the bioderived plastics suffer from the same end of life issues as fossil derived plastics and they persist in the environment long after their use. The design of durable products susceptible to rapid degradation at the end of their life plays a key role in sustainability.

Acetals are excellent candidates for facilitating degradation due to their acid-sensitive nature. The structural variations of the acetal moiety affect its sensitivity, thus allowing the fine-tuning of degradation [3]. Their incorporation in the main chain or as pendant group of a non-degradable backbone and their use in a variety of areas have been reported [4–9]. Hydrolytically sensitive polyacetals can be designed to degrade in aqueous environments [10]. Moreover, landfill leachate is slightly acidic and polyacetals should be degradable regardless of landfill depth and level of microbial activity, thus they are useful to improve the environmental degradability of commodity plastics. A more sustainable solution is the production of polyacetals from renewable resources and the use of plant oils [11,12], carbohydrates [13,14] and lignin [15,16] has been described.

The aim of this work was the synthesis of novel polyacetals sourced from castor oil as biorenewable feedstock that do not compete with food production. Its main constituent, ricinoleic acid, can be subjected to thermal cracking to obtain 10-undecenoic acid and heptanal. 10-Undecenoic acid has been widely used in polymer chemistry [17,18]. However, the use of heptanal as an intermediate in polymer chemistry is practically non-existent [19]. In this work, both starting materials have been used to synthesize biobased diols that were polymerized and copolymerized to obtain renewable polyacetals by acetal metathesis polymerization (AMP) [12]. Initial results on the hydrolytic degradability of the polyacetals are presented.

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2. Experimental section

2.1. Materials

The following chemicals were obtained from Aldrich and used as received: trimethyl phosphonoacetate (98%), 1,8-diazabicyclo-[5.4.0] undec-7-ene (DBU, 99%), 2-mercaptoethanol (98%), *p*-toluenesulfonic acid (*p*-TSA, 97%), 1,10-decanediol (**1**, 99%), 10-undecenoic acid (98%), 1-octene (99%), lithium aluminum hydride (powder, 97%), potassium *tert*-butoxide (98%), palladium on carbon (10% wt), methyl 3-mercaptopropionate (98%), 3-chloroperbenzoic acid (mCPBA, 70%), hydrogen peroxide (50% wt). Heptanal (96%) was obtained from Arkema. 10-undecen-1-ol was synthesized from 10-undecenoic acid using LiAlH₄ following a reported procedure [20]. Methyl 2-nonenolate was obtained from heptanal as previously described [19]. Diethoxymethane (DEM) from Aldrich was dried and distilled over CaH₂ and stored under inert conditions. THF was distilled from sodium and stored under inert conditions. Other solvents were used in technical grade as received.

2.2. Instrumentation

NMR spectra were recorded on a Varian VNMR400. The samples were dissolved in CDCl₃, and ¹H and ¹³C NMR spectra were recorded at room temperature with tetramethylsilane as an internal standard. ESI MS were run on a chromatographic system Agilent 1200 liquid chromatography coupled to 6210 Time of Flight (TOF) mass spectrometer from Agilent Technologies with an ESI interface.

Size exclusion chromatography (SEC) analysis was performed with an Agilent 1200 series system equipped with an Agilent 1100 series refractive-index detector. The analysis was performed at 35 °C on the three column system: 3 μm PLgel MIXED-E, 5 μm PLgel MIXED-D, 20 μm PLgel MIXED-A at a nominal flow rate of 1.0 mL/min and a sample concentration of 0.1% w/w in THF as solvent. The calibration curves for SEC analysis were obtained with polystyrene standards from Polymer Laboratories with molecular weights ranging from 500 to 400,000 Da.

Differential scanning calorimetry (DSC) measurements were carried out with a Mettler DSC822e thermal analyzer with N₂ as the purge gas and using heating and cooling rates of 10 °C min⁻¹. All data reported were collected from the second heating cycle. Thermal stability studies were carried out with a Mettler TGA/SDTA851e/LF/1100 with N₂ as the purge gas at a scanning rate of 10 °C/min.

2.3. Monomer synthesis and characterization

Diols **2**, **3**, **4** and **5** were obtained and characterized as described in the [supplementary information](#) (SI 1.1–1.7 and [Figs. S1–S12](#))

2.4. Polymer synthesis

Polyacetals **PA1**, **PA2**, **PA3**, **PA4** and **PA5** and copolyacetals **PA1-4** (1:1), **PA1-5** (1:1 and 3:1) and **PA2-5** (1:1) ([Scheme 3](#)) were synthesized according to the following general procedure. **PA1** was also obtained from 3,5,16,18-tetraoxaicosane (decanediol bis-acetal) (SI 1.8, [Fig. S13](#)).

General procedure: In a flame dried 50 mL Schlenk tube, 1.0 g of diol, 1.5% mol of *p*-TSA and DEM (6:1 mol DEM:mol diol) were charged under argon atmosphere. The reaction mixture was heated to 80 °C for 30 min and during the next 3 h, a 15 s argon flow was applied each 30 min. The temperature was then increased to 90 °C and dynamic vacuum was applied for 1 min at intervals of 30 min during 1.5 h to allow the removal of the volatile side product. Finally, additional 1.5% mol of *p*-TSA was added, the reaction was heated to 115 °C and was conducted under vacuum for 5 h. Once cool, the product was dissolved in the minimum amount of dichloromethane and 1 mL of aqueous 1 M

NaOH solution was added to quench the acid catalyst. The polymer was precipitated into 300 mL of cold methanol, filtered and washed several times with cold methanol, acetone and ether and dried under vacuum until constant weight.

2.4.1. PA1

1 (1.0 g, 5.73 mmol), *p*-TSA (15 mg, 0.08 mmol) and DEM (4.10 mL, 32.78 mmol) were used. The polymer was obtained as a white solid in a 82% yield.

Alternatively, a 100 mL round bottom flask was charged with 1.32 g (4.8 mmol) of 3,5,16,18-tetraoxaicosane and 26 mg (1.5 mol%) of (*p*-TSA). The mixture was stirred under inert atmosphere and the temperature was increased to 115 °C for 3 h. A 10 s argon flow was applied each 15 min during this period. Next, vacuum was applied, first 30 min at 115 °C and then 8 h at 150 °C. Once cool, the above mentioned work-up procedure was applied to give the polymer as a white powder in 80% yield. The overall yield over the two steps was 77%.

¹H NMR [CDCl₃, TMS, δ (ppm)] ([Fig. SI.22](#)): 4.64 (s, O-CH₂-O, 2H), 3.49 (t, O-CH₂, 4H), 1.53 (m, O-CH₂-CH₂, 4H), 1.37–1.27 (m, aliphatic chain, 12H).

¹³C NMR [CDCl₃, TMS, δ (ppm)] ([Fig. SI.23](#)): 95.1, 67.8, 29.5, 29.4, 26.2.

2.4.2. PA2

2 (1.0 g, 4.0 mmol), *p*-TSA (11 mg, 0.06 mmol) and DEM (2.8 mL, 23 mmol) were used. **PA2** was isolated as a slightly yellow solid (75% yield).

¹H NMR [CDCl₃, TMS, δ (ppm)] ([Fig. S24](#)): 4.72, 4.69, 4.67 (s, -O-CH₂-O-, 2H), 3.71 (q, O-CH₂-CH₂-S, 2H), 3.52 (q, O-CH₂-CH₂, 2H), 2.71 (t, O-CH₂-CH₂-S-CH₂, 2H), 2.53 (t, O-CH₂-CH₂-S-CH₂, 2H), 1.56 (m, O-CH₂-CH₂-S-CH₂-CH₂; O-CH₂-CH₂, 4H), 1.36–1.27 (m, aliphatic chain, 14H).

¹³C NMR [CDCl₃, TMS, δ (ppm)] ([Fig. S25](#)): 95.3, 95.2, 95.1, 68.0, 67.8, 67.2, 67.1, 32.5, 32.4, 31.8, 29.7–28.8 (8C), 26.2.

2.4.3. PA3

3 (1.0 g, 3.56 mmol), *p*-TSA (10 mg, 0.05 mmol) and DEM (2.54 mL, 20 mmol) were used. **PA3** was isolated as a solid. (84% yield).

Alternatively, 0.3 g (1.36 mmol) of **PA2** were dissolved in 9 mL of THF, followed by the addition of 20 mL of a mCPBA solution in THF (0.6 g, 2.72 mmol). The reaction mixture was stirred at room temperature for 2 h. After that, the reaction mixture was washed with Na₂S₂O₃ and NaHCO₃. The resulting organic phases were dried over MgSO₄ and concentrated. The resulting polymer, were purified by precipitation in cold methanol. **PA3** was isolated as a grey solid (88% yield).

¹H NMR [CDCl₃, TMS, δ (ppm)] ([Fig. S26](#)): 4.72, 4.69, 4.67 (s, -O-CH₂-O, 2H), 3.96 (q, O-CH₂-CH₂-SO₂, 2H), 3.52 (t, O-CH₂-CH₂, 2H), 3.22 (t, O-CH₂-CH₂-SO₂-CH₂, 2H), 3.06 (t, O-CH₂-CH₂-SO₂-CH₂, 2H), 1.78 (m, HO-CH₂-CH₂-SO₂-CH₂-CH₂, 2H) 1.58 (OH-CH₂-CH₂, 2H), 1.43–1.28 (m, aliphatic chain, 14H).

¹³C NMR [CDCl₃, TMS, δ (ppm)] ([Fig. S27](#)): 95.4, 95.2, 68.4, 67.8, 61.6, 61.13, 55.0, 54.8, 54.5, 29.3–28.4 (9C), 25.9, 22.6.

2.4.4. PA4

4 (1.0 g, 4.2 mmol), *p*-TSA (11 mg, 0.06 mmol) and DEM (3.05 mL, 24.4 mmol) were used. **PA4** was isolated as a yellow viscous liquid (80% yield).

¹H NMR [CDCl₃, TMS, δ (ppm)] ([Fig. S28](#)): 4.65 (s, O-CH₂-O, 2H), 3.67 (m, O-CH₂-CH₂-CH, 2H), 3.60 (t, O-CH₂-CH₂-CH₂, 2H), 2.71 (m, S-CH₂, 1H), 2.56 (t, S-CH₂, 2H), 1.81 (m, HO-CH₂-CH₂, HO-CH₂-CH₂-CH, 3H), 1.65 (m, HO-CH₂-CH₂-CH, 1H), 1.55 (m, S-CH-CH₂-(CH₂)₄, 2H), 1.45–1.28 (m, aliphatic chain, 8H), 0.88, (t, CH₃, 3H).

¹³C NMR [CDCl₃, TMS, δ (ppm)] ([Fig. S29](#)): 95.3, 66.3, 65.3, 42.6, 35.1, 34.8, 31.7, 29.9, 29.2, 26.8, 26.6, 22.6, 14.7.

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