

Renewable Polymers: Synthesis and Characterization of Poly(4-ketopimelic acid-glycerol)

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ABSTRACT: Condensation polymerization of renewable resources-based monomers, 4-ketopimelic acid and glycerol, were studied using two different catalysts; *p*-toluenesulfonic acid and Sb_2O_3 . The highest polymer yield of 96% was achieved by using a 3:4 mole ratio mixture of 4-ketopimelic acid and glycerol, with Sb_2O_3 (0.5 mol% relative to 4-ketopimelic acid) as catalyst and heating at 23–210 °C, under N_2 for 1 h; then 210 °C, vacuum, 12 h. The poly(4-ketopimelic acid-glycerol) formed is insoluble in all common organic solvents and is shown to contain a branched polymeric structure with ketal and ester links by using FT-IR, ^1H and ^{13}C NMR spectroscopy.

KEYWORDS: 4-Ketopimelic acid, glycerol, antimony(III) oxide, polyketal, polyester

1 INTRODUCTION

The current interest in renewable resources-based polymeric materials has promoted the studies on a number of biomass-derived polyfunctional compounds, such as 5-hydroxymethylfurfural [1, 2], 2,5-furandicarboxylic acid or its derivatives [3, 4], lactic acid [5] and lignin-derived vanillin [6, 7], as monomers for the preparation of polymeric materials. Levulinic acid is also another key renewable feedstock and a potential monomer for the preparation of renewable generation polymeric materials [8, 9]. Furthermore, in 2011 we reported the synthesis of levulinic acid–glycerol ketal–ester oligomers by acid-catalyzed condensation of two renewable resources-based monomers, levulinic acid and glycerol, in 1:1 mole ratio [10].

In continuation of our efforts on the synthesis of renewable polymeric materials, we have studied the condensation reactions of levulinic acid related compound 4-ketopimelic acid (2, Figure 1) with glycerol as well. 4-Ketopimelic acid is a lesser known biomass-derived building block, structurally related to levulinic acid. This seven carbon symmetrical keto-diacid can be easily prepared by aqueous acid-catalyzed hydrolysis of β -2-furylacrylic acid (1), which is the product of the Knoevenagel condensation of furfural with acetic anhydride, as shown in Figure 1.

Even though 4-ketopimelic acid has been known for more than 70 years, this symmetrical diacid has been used in synthesis on only a few occasions [11]. Missio and Comasseto have used 4-ketopimelic acid as the key starting compound for the enantioselective synthesis of (-)- γ -jasmolactone [12]. In a handful of examples, 4-ketopimelic acid has been used in the preparation of polymeric materials, including bis(triorganotin(IV)) polyesters of 4-ketopimelic acid [13–17]. In addition, Wang and coworkers studied the condensation of 4-ketopimelic acid with aliphatic and aromatic diamines and found the formation of stable polymers based on a spirodilactam structure [18]. Furthermore, they reported the applications of these spirodilactam as thermoplastics and thermosets [18]. In contrast to 4-ketopimelic acid, familiar triol glycerol has a number of applications in pharmaceutical, food and personal care product industries [19]. Current interest in the utilization of this biodiesel production by-product has initiated a wide range of research efforts in converting glycerol to value-added products, such as acrolein, propylene glycol, and epichlorohydrin, that can be used with the existing polymerization methods [19]. In addition to conversion into other monomers or feedstocks, glycerol can be used directly as a monomer in applications like polyesterification [20, 21]. In one example glycerol has been used as the polyol in the polyesterification with adipic acid, where an immobilized *Candida antarctica* Lipase B (Novozym 435) catalyzed reaction gave dendritic polymers with moderate molecular weights [22]. Additionally, Gross and coworkers have recently reported the preparation

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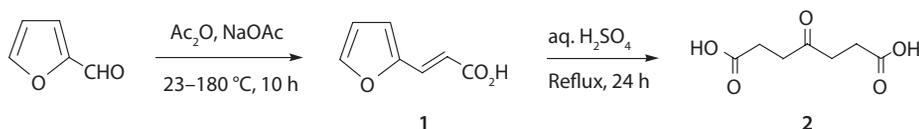


Figure 1 Synthesis of 4-ketopimelic acid (2) from furfural.

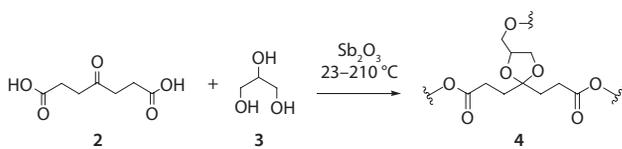


Figure 2 Synthesis of *poly*(4-ketopimelic acid-glycerol) (4).

of a biodegradable thermoset polymer by esterification of citric acid with glycerol [23].

The multifunctional 4-ketopimelic acid (2) can react with the triol glycerol (3) in two different reaction modes, where the keto group can form ketals with 1,2 or 1,3 hydroxyls and the carboxylic acid groups can undergo esterifications. In this communication, we report the first synthesis of all renewable feedstock-based *poly*(4-ketopimelic acid-glycerol) (4), as shown in Figure 2, and structural characterization of the new renewable polymer using spectroscopic methods.

2 EXPERIMENTAL

2.1 Materials and Instrumentation

Furfural, glycerol and antimony(III) oxide were purchased from Sigma-Aldrich Chemical Co., USA. The ^1H NMR spectra were recorded in $\text{DMSO-}d_6$ or CF_3COOD on a Varian Mercury Plus spectrometer operating at 400MHz, and chemical shifts are given in ppm downfield from TMS ($\delta = 0.00$). The ^{13}C NMR spectra in $\text{DMSO-}d_6$ or CF_3COOD were recorded on the same spectrometer operating at 100MHz; chemical shifts were measured relative to $\text{DMSO-}d_6$ and converted to $\delta(\text{TMS})$ using $\delta(\text{DMSO-}d_6) = 39.51$ and $\delta(\text{CF}_3) = 116.60$ ppm. Thermogravimetric analysis was carried out on a PerkinElmer Diamond TG/DTA system at 25–800 °C temperature range, 10 °C/min, in air and using Pt crucibles. FT-IR spectra were recorded on a Thermo Nicolet IR 200 spectrometer using KBr pellets.

2.2 Synthesis of β -2-Furylacrylic Acid (1)

β -2-Furylacrylic acid (1) was prepared by Knoevenagel condensation of furfural with acetic anhydride in the presence of sodium acetate as described in the literature; 70% yield, M.pt. 138–139 °C, Lit. 140–41 °C [24]. ^1H NMR ($\text{DMSO-}d_6$) δ 6.16 (1H, d, $J = 16$ Hz, $-\text{CH}=\text{C}$),

6.63 (1H, d, $J = 3.5$ Hz, C-4 Fu), 6.93 (1H, d, $J = 3.5$ Hz, C-3 Fu). 7.38 (1H, d, $J = 16$ Hz, $-\text{CH}=\text{C}$), 7.84 (1H, s, C-5 Fu), 12.20 (bs, 1H, COOH). ^{13}C NMR ($\text{DMSO-}d_6$) δ 113.1 (C-4 Fu), 115.9 (C-3 Fu), 116.3 ($=\text{CH}$), 131.2 ($=\text{CH}$), 146.1 (C-5, Fu), 150.7 (C-2 Fu), 167.7 (COOH). FT-IR (KBr) 756, 932, 973, 1231, 1271, 1314, 1416, 1627, 1636, 1668 (C=C), 1701 (C=O), 3060 (O-H) cm^{-1} . MS: (m/e) 138, 121, 110, 92, 65, 34.

2.3 Synthesis of 4-Ketopimelic Acid (2)

β -2-Furylacrylic acid [24] (2.00 g, 14.50 mmol) was suspended in 20 mL of 1.0 M aqueous sulfuric acid and refluxed for 24 h. The hot solution was treated with charcoal (0.50 g), filtered, and the filtrate was cooled to room temperature and then kept in a refrigerator for 2 days. The crystalline product was filtered and recrystallized with minimum volume of hot water to give 4-ketopimelic acid (2) as a white powder (2.04 g, 81% yield), M.pt. 139–140 °C, Lit. 142–44 °C [25]. ^1H NMR ($\text{DMSO-}d_6$) δ 2.37 (4H, t, $J = 6.4$ Hz, $2 \times \text{CH}_2$), 2.63 (4H, t, $J = 6.4$ Hz, $2 \times \text{CH}_2$), 3.60 (2H, bs $2 \times \text{COOH}$). ^{13}C NMR ($\text{DMSO-}d_6$) δ 28.2 (CH_2), 37.0 (CH_2), 174.2 (COOH), 208.3 (C=O). FT-IR (KBr) 610, 910, 1100, 1260, 1325, 1380, 1410, 1430, 1697 (C=O), 2900 (C-H), 3120 (O-H) cm^{-1} . MS: (m/e) 174, 156, 129, 101, 73, 55.

2.4 General Procedure for the Synthesis of *Poly*(4-ketopimelic acid-glycerol) (4)

A mixture of 4-ketopimelic acid (0.522 g, 3.00 mmol), glycerol (0.368 g, 4.00 mmol) and catalyst (0.5 mol% relative to 4-ketopimelic acid) was gradually heated from room temperature (23 °C) to 210 °C, under a nitrogen atmosphere during a period of 1 h. Then the reaction mixture was further heated at 210 °C under a vacuum (5 mmHg) for a specified period of time. The product was repeatedly washed with methylene chloride to remove any unreacted starting materials and dried in an oven at 90 °C for 24 h to give 4-ketopimelic acid-glycerol polymer as a transparent, solid material. The FT-IR spectrum, TGA-DTG, ^1H and ^{13}C NMR spectra of a typical 4-ketopimelic acid-glycerol polymer sample prepared are shown in the Figures 3, 4, and 5 respectively. The reaction conditions and percent yields in a series of polymer 4 synthesis experiments are shown in Table 1. The polymer is insoluble in all

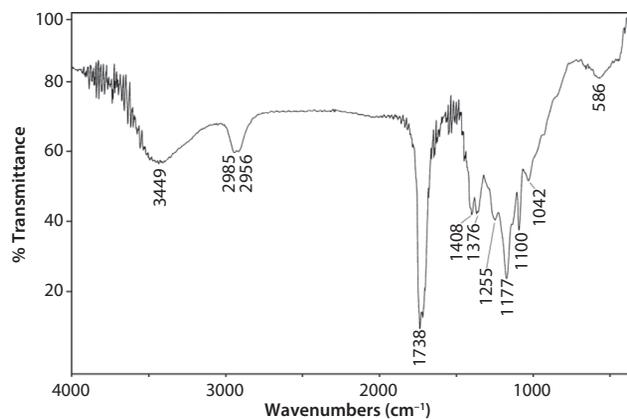


Figure 3 FT-IR spectrum of *poly(4-ketopimelic acid-glycerol)* (4) from entry 3, Table 1.

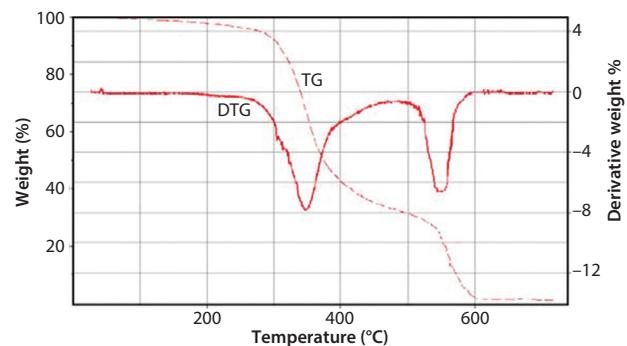


Figure 4 TG-DTG curves of *poly(4-ketopimelic acid-glycerol)* (4) from entry 3, Table 1.

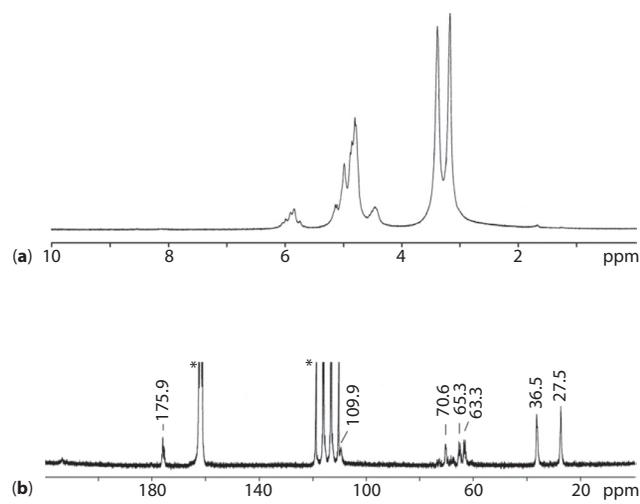


Figure 5 ^1H NMR (a) and ^{13}C NMR (b) spectra of *poly(4-ketopimelic acid-glycerol)* (4) entry 3, Table 1, in CF_3COOD , * = solvent.

Table 1 Catalyst, reaction conditions and percent yields in the preparation of *poly(4-ketopimelic acid-glycerol)* (4); 3.00 mmol of 4-ketopimelic acid (2) and 4.00 mmol of glycerol (3) were used in all reactions.

Entry	Catalyst	Reaction conditions	Yield (%) (4)
1	<i>p</i> -TsOH (0.5 mol%)	23–210 °C, N_2 , 1 h, then 210 °C, vacuum, 6 h	67
2	Sb_2O_3 (0.5 mol%)	23–210 °C, N_2 , 1 h, then 210 °C, vacuum, 2 h	80
3	Sb_2O_3 (0.5 mol%)	23–210 °C, N_2 , 1 h, then 210 °C, vacuum, 6 h	95
4	Sb_2O_3 (0.5 mol%)	23–210 °C, N_2 , 1 h, then 210 °C, vacuum, 12 h	96

common organic solvents, including CH_2Cl_2 , CHCl_3 , CH_3OH , ethyl acetate, and DMSO, and slightly soluble in warm trifluoroacetic acid. The attempts to measure molecular weight and degree of polymerization were not successful due to poor solubility.

3 RESULTS AND DISCUSSION

3.1 Synthesis of 4-Ketopimelic Acid (2)

As shown in Figure 1, 4-ketopimelic acid was prepared in two steps. First, β -2-furylacrylic acid (1) was prepared in 70% yield by Knoevenagel condensation of furfural with acetic anhydride, following the literature procedure [24]. Then hydrolysis of the β -2-furylacrylic acid in aqueous sulfuric acid gave 4-ketopimelic acid (2) in 81% yield.

3.2 Synthesis of *Poly(4-ketopimelic Acid-glycerol)* (4)

Polymerization of 4-ketopimelic acid with glycerol was studied in the presence of two different catalysts, Brønsted acid: *p*-toluenesulfonic acid and a Lewis acid: Sb_2O_3 , as shown in Figure 2. 4-Ketopimelic acid (2) can react with glycerol (3) in ketalization of the keto group as well as in the esterification of the two acid groups; therefore 3:4 mole mixtures of 4-ketopimelic acid and glycerol were used in all experiments in order to minimize the unreacted monomers. In all the experiments, 4-ketopimelic acid and glycerol were mixed with 0.5 mol% of catalyst and first heated from room temperature to 210 °C under a nitrogen atmosphere; then reaction mixture was further heated under a vacuum for 2–12 h. All polymer products were purified by repeated washing with

methylene chloride. The experiment using *p*-TsOH catalyst, 23–210 °C, N₂, 1 h, then 210 °C, vacuum, 6 h, gave polymer in 67% yield; whereas Sb₂O₃ catalyst, 23–210 °C, N₂, 1 h, then 210 °C, vacuum, 2 h, gave the polymer in 80% yield. Therefore, further experiments were carried out using Sb₂O₃ catalyst to improve the yield. In these experiments, increasing the 210 °C heating time to 6 h produced 95% yield; however, further increase of heating time to 12 h only produced a small increase in yield to 96%, as shown in entries 3 and 4 in Table 1.

3.3 Characterization of Poly(4-ketopimelic Acid-glycerol) (4)

3.3.1 FT-IR

A representative FT-IR spectrum of the sample from entry 3 in Table 1 is shown in Figure 3; all other poly(4-ketopimelic acid-glycerol) samples also showed similar FT-IR spectra. A strong absorption at 1738 cm⁻¹ indicated the ester group in the polymer and any unreacted terminal keto group absorption is probably masked by this strong ester absorption. The two strong absorptions at 1177 and 1376 cm⁻¹ could be assigned to the 1,3-dioxalane type ketal group in 4 and similar absorptions are reported for poly(levulinic acid-glycerol) at 1177 and 1378 cm⁻¹, supporting this structural unit in the polymer [10]. The broad absorption at 3449 cm⁻¹ can be assigned to unreacted terminal hydroxyl groups in the 4-ketopimelic acid-glycerol polymer.

3.3.2 TG-DTG

Thermogravimetric-derivative thermogravimetric (TG-DTG) analysis of the poly(4-ketopimelic acid-glycerol) sample from entry 3 in Table 1 is shown in Figure 4, and other poly(4-ketopimelic acid-glycerol) samples also showed similar TG-DTG curves. The polymers produced appear to be stable up to about 300 °C. These polymers decompose in two steps; the first with 65% weight loss and the second with 35% weight loss. The derivative thermogravimetric (DTG) curve showed two peaks at 350 and 555 °C.

3.3.3 ¹H and ¹³C NMR Spectroscopy

Proton and ¹³C NMR spectra of the representative poly(4-ketopimelic acid-glycerol) sample from entry 3 in Table 1 recorded in CF₃COOD are shown in Figure 5a and 5b respectively. The ¹H NMR showed two broad absorptions at 3.2 and 3.4 ppm, assigned to 4-ketopimelic acid unit methylene groups. The broad absorptions at 4.4–5.2 and 5.8 ppm are due to glycerol-derived hydrogens in the ketal function and ester groups.

The ¹³C NMR spectrum of poly(4-ketopimelic acid-glycerol) showed seven peaks supporting the proposed repeating unit shown in Figure 2. The signals at 27.5 and 36.5 ppm can be assigned to 4-ketopimelic acid-derived methylene carbons. The 1,3-dioxalane ring unit -O-C-O carbon is observed at 109.9 ppm, whereas the ester carbonyl carbons are observed at 175.9 ppm. The absorptions at 63.3, 65.3 and 70.6 ppm are due to glycerol-derived carbons in the 1,3-dioxalane ring unit of the polymer. Furthermore, these ¹³C NMR chemical shifts are comparable to the chemical shifts of 1,3-dioxalane ring unit carbons in poly(levulinic acid-glycerol) reported in the literature [10].

4 CONCLUSION

We have shown that Brønsted acid *p*-TsOH as well as Lewis acid Sb₂O₃ catalyzed condensations of 4-ketopimelic acid and glycerol can be used to prepare all renewable resources-based polymer poly(4-ketopimelic acid-glycerol). The highest polymer yield of 98% was achieved by using 3:4 mole ratio mixture of 4-ketopimelic acid and glycerol with Sb₂O₃ (0.5 mol% relative to 4-ketopimelic acid) as catalyst, heating at 23–210 °C under N₂ for 1 h, and then 210 °C, vacuum, 12 h. The poly(4-ketopimelic acid-glycerol) formed is stable up to about 300 °C in air and insoluble in all common organic solvents, except for being slightly soluble in trifluoroacetic acid. The new all renewable resources-based polymeric material is shown to contain a branched structure with ketal and ester links by using FT-IR, ¹H and ¹³C NMR spectroscopy.

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