

Renewable rosin fatty acid polyesters: the effect of backbone structure on thermal properties

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Two novel polyesters were prepared from renewable natural molecular biomass castor oil-derived fatty acid and rosin. Highly efficient monomer syntheses including thiol-ene click chemistry and condensation polymerization techniques including transesterification and acyclic diene metathesis were carried out. Their thermal properties were compared based on flexible and rigid structural motifs on the polymer backbone. Although linear polymer backbone led to the formation semicrystalline polymers, polymers with fused-ring structure in the backbone were amorphous. The presence of the rosin moiety in the backbone also resulted in higher glass transition temperature compared with the flexible linear counterpart.

1. Introduction

Fossil resources that are currently used for both energy and chemical production are of finite availability. The synthesis of plastics accounts for nearly 7% of the global fossil fuel production.^{1–11} Depleting oil reserves coupled with a rise in global energy demands has led to an increased interest in the development of energy and materials derived from renewable resources. A variety of green plastics have been derived from either abundant and low cost natural polymers such as cellulose, lignin and chitosan,^{12–18} or natural molecular biomass such as vegetable oil, lactic acid, fatty acid, terpenes and rosin.^{9,11,12,19,20} Usually obtained directly from forestry and agriculture products or by microorganism fermentation, these natural resources are important because their derived polymers could mimic plastics manufactured from petroleum chemicals.

Among natural molecular biomass, fatty acids have shown to be a prime resource for polymer chemistry.^{21–25} Derived from castor oil, 10-undecenoic acid is one of the most important fatty acids with a flexible, linear structure and can undergo a number of synthetic reactions to produce renewable monomers for polymer synthesis.^{24,26,27} In contrast, rosin that is obtained from pine resin is available with a more rigid fused-ring structure, and can also undergo a pyramid of reactions.^{20,28–36} Olefin metathesis and thiol-ene reactions are just a few examples of highly efficient reactions that take advantage of the unsaturated terminal olefins to produce

valuable monomers.^{37–40} With a range of renewable monomers, it is important to understand how monomers with different structural characteristics affect the properties of their corresponding renewable polymers. Herein we report the combination of castor oil-derived fatty acids and rosin to prepare novel polyesters. Our preliminary aim of this study is to compare rigid renewable polyesters derived from fatty acids and rosin with those linear flexible polyesters solely derived from fatty acids. Polyesters were analyzed by gel permeation chromatography (GPC), nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA).

2. Experimental section

2.1 Materials

10-Undecenoic acid, 1,2-ethanedithiol, triethylamine and Hoveyda-Grubbs second-generation catalysts (Sigma-Aldrich, USA), abietic acid and acrylic acid (Acros, USA), 10-undecen-1-ol (Alfa-Aesar, USA), titanium (IV) *n*-butoxide (Ti(OBu)₄), oxalyl chloride (Fisher Scientific, USA) and ethylene glycol (VWR, USA) were purchased from commercial sources and used as received. 2,2'-Azobisisobutyronitrile (AIBN, Aldrich) was recrystallized from methanol before use. Tetrahydrofuran (THF, Aldrich), dichloromethane (DCM, Aldrich) and methanol (MeOH, Aldrich) were refluxed with sodium and distilled under nitrogen atmosphere before use.

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2.2 Characterization

¹H-NMR spectra were recorded on Bruker ARX300 and ARX400 spectrometers. The chemical shifts were recorded in ppm (δ) relative to tetramethylsilane. GPC was performed at room temperature on a Varian system equipped with a Varian 390-LC multi detector and a Varian 290 pump injection module. The columns were PLgel MIXED-BLS (300 \times 7.5 mm, with capability to characterize molecular weight in the range of 500 to 10 000 000 g/mol) from Polymer Laboratories. HPLC-grade THF was used as eluent at a flow rate of 1 ml/min. Samples were filtered over a microfilter with pore size of 0.2 μ m (Nylon, Millex-HN 13 mm Syringes Filters, Millipore, USA). GPC was calibrated using polystyrene as standards. Fourier transform infrared spectrometry (FTIR) was conducted on a Shimadzu 8400 FTIR spectrometer. Thermal transitions were recorded using DSC on a TA Q200 calorimeter in a temperature range from -70 to 100°C at a heating rate of 10°C/min under continuous nitrogen flow. All the data were collected during the second heating process after cooling at 10°C min⁻¹ from 100°C. The average sample mass was about 5 mg, and the nitrogen flow rate was 50 ml/min. TGA was operated on a TGA Q500 apparatus (TA instruments), ramping from 30 to 600°C at a rate of 10°C/min, and maintained at 600°C for 5 min under nitrogen gas at a flow rate of 100 ml/min.

2.3 Synthesis of 6,6'-(ethane-1,2-diylbis(sulfanediyl))dihexanoic acid

To a 50 ml round bottom flask, 10-undecenoic acid (20.00 g, 1.09 \times 10⁻¹ mol), 1,2-ethanedithiol (3.0 ml, 3.62 \times 10⁻² mol) and AIBN (40 mg, 2.47 \times 10⁻⁴ mol) were added. While under a continuous flow of nitrogen, the flask was placed into a preheated oil bath set at 80°C. After 12 h the reaction was stopped and a white solid was observed. The final product was then recrystallized from THF and a white crystalline material (86% yield) was obtained. Mp 115°C; ¹H-NMR (300 MHz, DM F-d₇, δ): 2.9–3.0 (s, -SCH₂-); 2.7–2.8 (t, -CH₂S-); 2.4–2.5 (t, -CH₂CO), 1.3–1.8 (broad, -CH₂CH₂CH₂-). IR (neat): 3400–300 cm⁻¹ (OH stretching); 3020–2820 cm⁻¹ (CH stretching); 1720–1690 cm⁻¹ (C=O stretching).

2.4 Synthesis of diester monomer dimethyl 6,6'-(ethane-1,2-diylbis(sulfanediyl))dihexanoate

A solution of 6,6'-(ethane-1,2-diylbis(sulfanediyl))dihexanoic acid (33.90 g, 7.32 \times 10⁻² mol) in THF (200 ml) was introduced into a round bottom flask under nitrogen. Oxalyl chloride (20 ml, 2.30 \times 10⁻¹ mol) was slowly added to the above mixture at 0°C for 1 h. The mixture was allowed to react for 24 h at room temperature. After 24 h, the solvent and any unreacted oxalyl chloride were removed by vacuum distillation. The product was dissolved in THF (50 ml) and placed in a round bottom flask under nitrogen. A second mixture composed of triethylamine (25 ml, 1.79 \times 10⁻¹ mol), methanol (15 ml, 3.71 \times 10⁻¹ mol) and THF (300 ml) was placed in a separate round bottom flask under nitrogen. The diacid solution was

slowly added to this mixture at 0°C for 1 h. The reaction was run at room temperature for 24 h. The flask was opened and the final product was precipitated in MeOH as an off white crystalline material (92% yield). Mp 59°C; ¹H-NMR (300 MHz, CDCl₃, δ): 3.6–3.7 (s, CH₃O-); 2.9–3.0 (s, -SCH₂-); 2.7–2.8 (t, -CH₂S-); 2.4–2.5 (t, -CH₂CO), 1.3–1.8 (broad, -CH₂CH₂CH₂-). IR (neat): 3020–2820 cm⁻¹ (CH stretching); 1720–1690 cm⁻¹ (C=O stretching).

2.5 Synthesis of fatty acid- and rosin-based monomer

Acrylopimaric acid (APA) was synthesized according to the literature.³⁰ APA (2.5 g, 6.67 \times 10⁻³ mol) was mixed with THF (50 ml) and introduced into a round bottom flask under nitrogen. Oxalyl chloride (2.3 ml, 2.70 \times 10⁻² mol) was slowly added to the above mixture at 0°C for 1 h. The mixture was allowed to react for 24 h at room temperature. After 24 h, the solvent and any unreacted oxalyl chloride were removed by vacuum distillation. The product was dissolved in THF (50 ml) and placed in a round bottom flask under nitrogen. A second mixture composed of triethylamine (2.2 ml, 1.58 \times 10⁻² mol), 10-undecen-1-ol (5.5 ml, 2.75 \times 10⁻² mol) and THF (50 ml) was placed in a separate round bottom flask under nitrogen. The APA solution was slowly added to this mixture at 0°C for 1 h. The reaction was run at room temperature for 24 h. The monomer was purified by silica gel column chromatography (7:1 hexane: diethyl ether) to yield a colorless liquid (44% yield). ¹H-NMR (300 MHz, CDCl₃, δ): 5.7–5.8 (s, -CHCH₂-); 5.2–5.3 (s, -CCH-); 4.8–5.0 (d, CH₂CH-); 3.8–4.0 (d, -CH₂O), 2.4–2.5 (s, -CHCOO-); 2.4–2.2 (s, -CHC-); 1.9–2.0 (s, -CH₂CH-). 0.6–1.8 (broad, -CH₂CH₂CH₂-). IR (neat): 3080–3040 cm⁻¹ (CH alkene stretching); 3020–2820 cm⁻¹ (CH stretching); 1720–1690 cm⁻¹ (C=O stretching) 1640–1660 cm⁻¹ (C=C stretching); 1130–1190 cm⁻¹ (C–O stretching).

2.6 Melt polymerization of diester monomer

Before polymerization, the diester monomer was dried at 80°C for 2 h. The diester (8.08 g, 1.65 \times 10⁻² mol), ethylene glycol (1.09 g, 1.76 \times 10⁻² mol) and Ti(OBu)₄ (12.0 mg, 3.53 \times 10⁻⁵ mol) were placed in a three-neck round bottom flask. The flask was then equipped with a distillation arm, a nitrogen outlet and a stir rod. The stir rod was attached to an overhead mechanical stirrer and the stir rate was maintained at 60 rpm for the duration of the polymerization. A vacuum pump was connected to the distillation and several nitrogen purges were conducted using a Firestone valve. Once the reaction vessel had been purged, temperature was slowly increased until the monomers melted. A vacuum was applied and gradually increased throughout the polymerization until a final vacuum of 25-mm Hg was reached. Temperature was gradually increased throughout the reaction until a final temperature of 200°C was obtained. At this point, the reaction was stopped and the polymer solution was allowed to slowly cool to room temperature. The polymer was then dissolved in DCM and precipitated into MeOH. ¹H-NMR (300 MHz, CDCl₃, δ): 4.2–4.4 (s, -CH₂O-);

2.7–2.8 (s, -SCH₂-); 2.4–2.6 (t, -CH₂S-); 2.3–2.4 (t, -CH₂CO), 1.3–1.8 (broad, -CH₂CH₂CH₂-).

2.7 ADMET polymerization of rosin-fatty acid monomer

Rosin fatty acid monomer (0.2 g, 2.95×10^{-4} mol) was placed in a round bottom flask and purged with nitrogen for 10 min. Hoveyda–Grubbs catalyst (2.3 mg, 3.67×10^{-6} mol) was added to the flask and the temperature was raised to 80°C while under a constant flow of nitrogen. After 1 h, a 5 ml solution of ethyl vinyl ether in THF was added to the flask. The final polymer was obtained by precipitating in cold methanol. ¹H-NMR (300 MHz, CDCl₃, δ): 5.2–5.5 (d, -CHCH₂-); 3.9–4.1 (s, -CH₂O-); 2.4–2.5 (s, -CHCOO-); 2.4–2.2 (s, -CHC-); 0.6–2.1 (broad, -CH₂CH₂CH₂-).

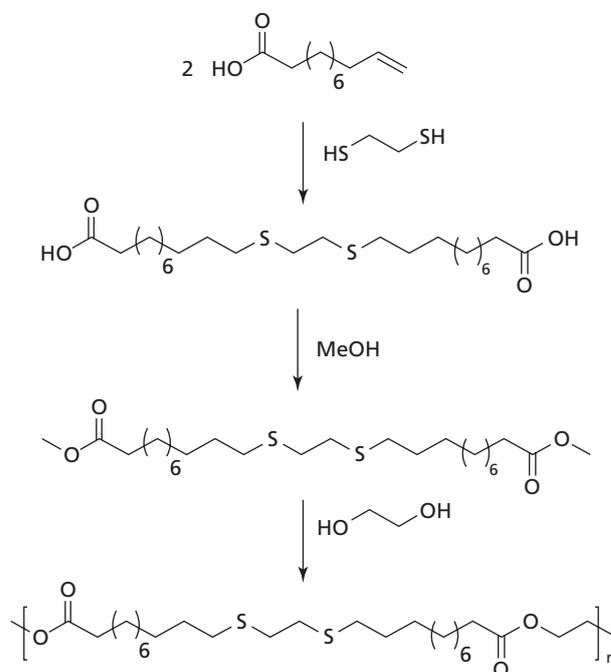
3. Results and discussion

3.1 Synthesis and polymerization of diester monomer

Scheme 1 shows the synthesis of castor oil-derived fatty acid-based monomer. The radical addition of thiols to terminal alkenes is a well-established and efficient click reaction.⁴¹ Using a slight excess of fatty acid to thiol, the intermediate diacid was obtained in high yield (86%) after recrystallization. The diacid was further converted to a diester by esterification with methanol.

The monomer was characterized by ¹H-NMR spectroscopy, as shown in Figure 1. The disappearance of the terminal alkene peaks confirmed a high conversion of alkene to thioether. In addition, the emergence of the thioether peaks at 2.5 and 2.7 ppm further indicated that the click reaction was highly efficient. The esterification of the diacid with excess MeOH produced the final diester monomer in high yield (92%) after recrystallization. The emergence of the methyl ester peak at 3.7 ppm was an indication of successful esterification.

The next step was to polymerize the diester monomer as shown in Scheme 1. Meier *et al.* polymerized vegetable oil based monomers by condensation polymerization.^{39,42,43} In the current work, ethylene glycol was chosen as a comonomer in order to produce polyesters by condensation polymerization. The catalyst utilized for the polymerization was Ti(OBu)₄ due to its commercial availability and high efficiency in polymerizing aliphatic polyesters.⁴⁴ The amount of catalyst was varied from 2 mol% to 4 mol%, while the 2 mol% produced the best results. ¹H-NMR analysis of the final polymers, shown in Figure 2, confirmed the successful polymerization, as indicated by the disappearance of the methoxy peak at 3.7 ppm and the appearance of the ethyl ester peak at 4.2 ppm. The number average molecular weights (M_n) of the polyesters were between 7000–26 000 g/mol, depending on the molar ratio of starting monomers (Figure 3). These polyesters were solid materials and had color ranging from light brown for the



Scheme 1. Synthesis and polymerization of castor oil-derived-based monomer.

low molecular weight to black for the high molecular weight. The color of the polymers is most likely because of the presence of the titanium based catalyst.

3.2 Synthesis and polymerization of rosin fatty acid-based monomer

Scheme 2 shows synthesis of a diene monomer derived from fatty acid and rosin. APA was synthesized and purified according to the literature.³⁰ The esterification reaction between the diacid and the unsaturated fatty alcohol was confirmed by ¹H-NMR (Figure 4). The disappearance of the -OH peak at 3.6 ppm and the emergence of a new ester peak around 4.0 ppm as well as the vinyl protons at 4.9 and 5.8 ppm indicated the successful esterification. Acyclic diene metathesis (ADMET) polymerization was used to prepare polymers.^{21,22,24,25} Both Grubbs second generation and Hoveyda–Grubbs second generation catalysts were used; however, the Hoveyda–Grubbs catalyst provided better results, including fast reactions and higher molecular weight. As shown in Figure 4, ¹H-NMR spectrum of the final polymer displayed a loss of the terminal alkene peak at 4.9 ppm, which was expected for an ADMET polymerization. The final polymer was a dark brown, sticky material with a molecular weight that varied from 4000 to 9200 g/mol, depending on the monomer to catalyst ratio (Figure 3).

3.3 Thermal properties of polyesters

DSC was used to examine the thermal properties of polymers with linear flexible backbone and polymers with bulky fused-

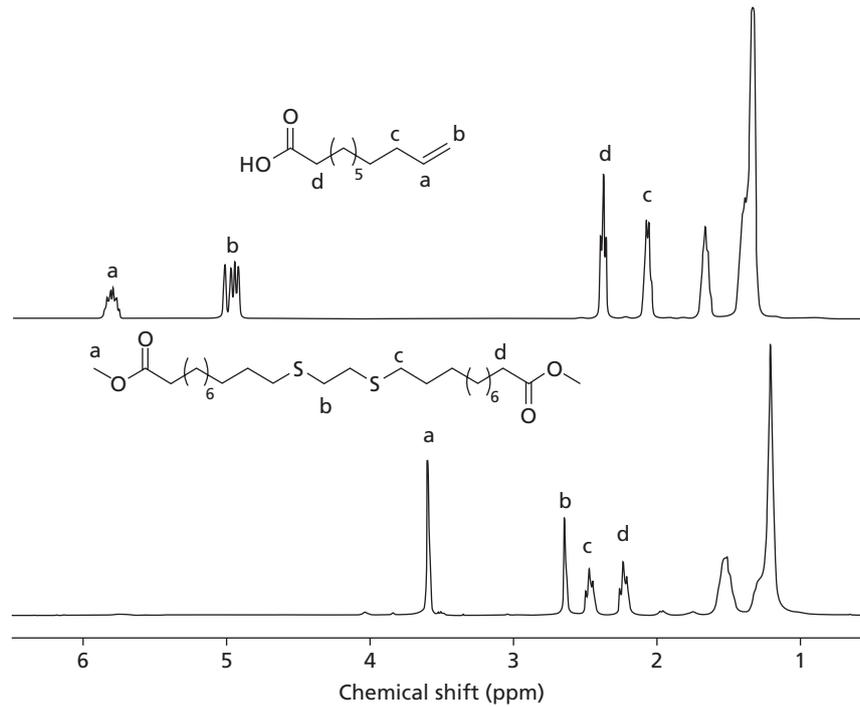


Figure 1. ¹H-NMR spectra of 10-undecenoic acid and dimethyl 6,6'-(ethane-1,2-diylbis(sulfanediy))dihexanoate monomer. NMR, nuclear magnetic resonance.

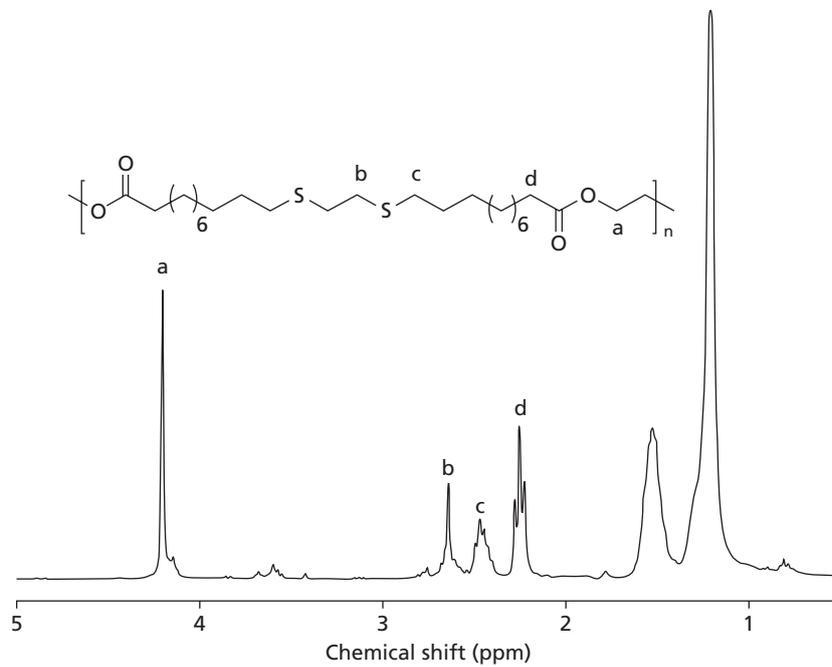


Figure 2. ¹H-NMR spectrum of fatty acid-based polymer. NMR, nuclear magnetic resonance.

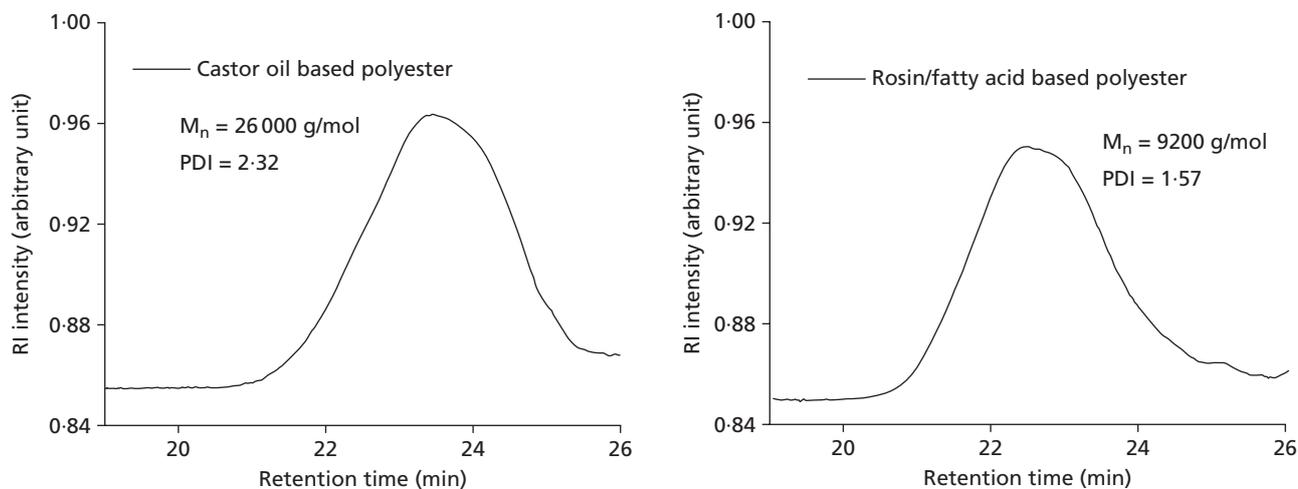
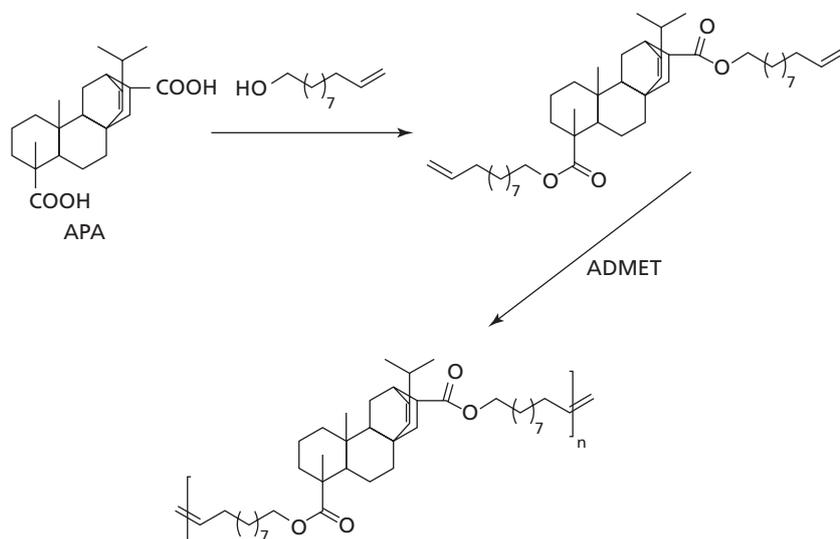


Figure 3. GPC traces of castor oil-derived polyesters and rosin fatty acid-based polyesters. GPC, gel permeation chromatography.



Scheme 2. Synthesis and polymerization of rosin fatty acid-based monomer.

ring backbone. As shown in Figure 5, three endothermic melting point (T_m) in the range of 30–70°C was observed for linear flexible polyesters. The presence of the T_m observed indicated the polyesters derived from castor oil are semicrystalline. This is consistent with previous reports.^{42,43} However, for the rosin fatty acid-based polyesters, DSC analysis revealed no melting transitions. The lack of melting transitions for these polyesters indicated that they are amorphous polymers. Our work suggested that the bulky fused-ring rosin moiety disrupts the packing of the linear alkyl group in the backbone, resulting in amorphous polymers. The glass transition temperatures (T_g) at -5°C were observed for the rosin fatty acid polyesters. Although no clear T_g was observed for linear

castor oil-derived polyesters, Meier *et al.* reported a T_g as low as -68°C for a branched polyester with the arm chains similar to our polymers. The sharp difference between these two polyesters indicated that the rotation barrier of bulky rosin moiety significantly increases the T_g .

TGA for the castor oil-based polyesters displayed thermal stability up to $\sim 250^\circ\text{C}$, above which rapid thermal degradation was observed, as shown in Figure 6. TGA of the more rigid rosin fatty acid-based polyesters showed thermal stability up to $\sim 300^\circ\text{C}$. This may indicate that thermal stability of polyesters can be increased by including more rigid naturally occurring structures. The thermal

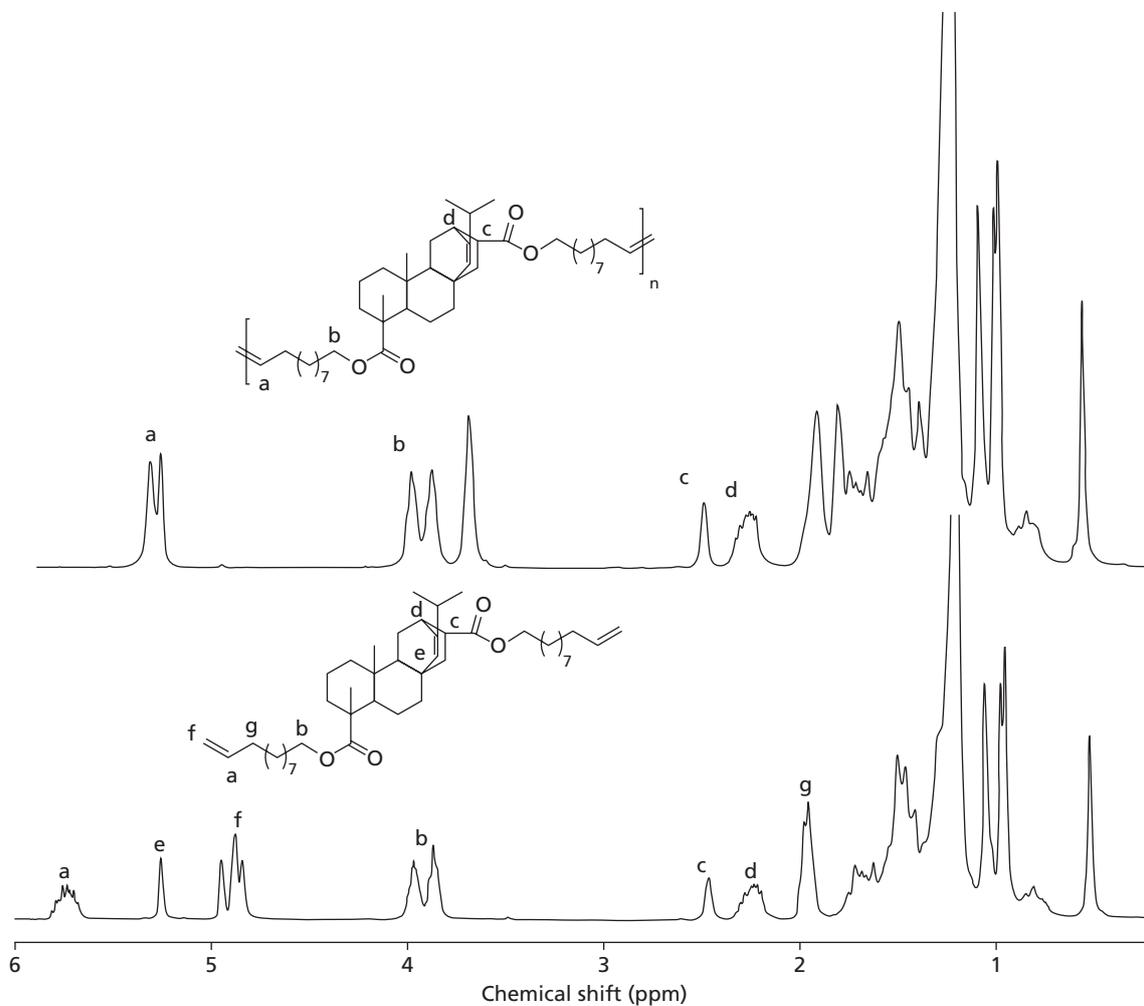


Figure 4. ¹H-NMR spectra of rosin fatty acid monomer and polyester.
NMR, nuclear magnetic resonance.

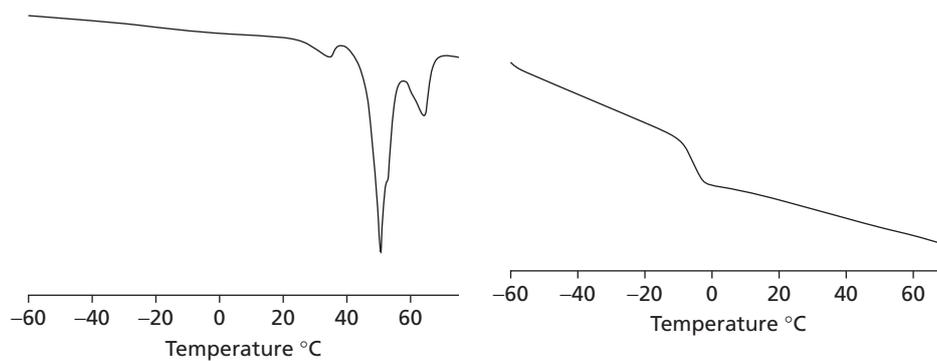


Figure 5. DSC thermograms (second heating cycle) of polyesters:
(left) castor oil-based polymer (M_n = 26 000 g/mol); (right) rosin fatty
acid-based polymer (M_n = 9200 g/mol). DSC, differential scanning
calorimetry.

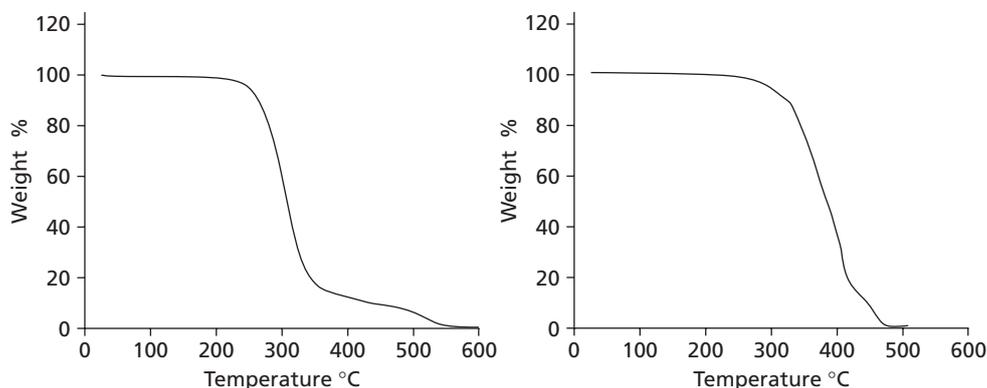


Figure 6. TGA thermograms of polyesters (left) castor oil-based polymer ($M_n = 26\,000$ g/mol) and (right) rosin fatty acid-based polymer ($M_n = 9200$ g/mol). TGA, thermal gravimetric analysis.

	M_n (g/mol)	T_m	T_g	T_{d5}	T_{d10}
Castor oil-based polyesters	26 000	50°C	N/A*	249°C	264°C
Rosin fatty acid-based polyesters	9200	N/A	-5°C	303°C	331°C

*Implies that this is typically observed for fatty acid-based polyesters.
 T_{d5} : Temperature at 5% weight loss; T_{d10} : Temperature at 10% weight loss.

Table 1. Properties measured for vegetable oil- and castor oil-based polymers.

properties obtained for both castor oil and rosin fatty acid-based polyesters are summarized in Table 1.

4. Conclusion

In conclusion, we developed a method for the conversion of naturally occurring castor oil-derived fatty acids and rosin into useful monomers for the preparation of polyesters. Thiol-ene chemistry was used for the castor oil based monomer synthesis with high yield. The resultant flexible castor oil-based polyesters prepared by condensation polymerization are semicrystalline polymers with moderate molecular weights. A more rigid rosin fatty acid-based monomer was synthesized in high yield and subsequently polymerized by ADMET technique. In contrast, these polyesters are completely amorphous with higher glass transition temperature and increased thermal stability. The incorporation of rigid natural biomass with linear flexible molecules could lead to polymers with different thermal properties, expanding potential applications for fatty acid-derived polymers.

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