



## Polymeric triglyceride analogs prepared by enzyme-catalyzed condensation polymerization



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### ABSTRACT

Unique crosslinkable unsaturated polyesters were prepared by a one-pot lipase-catalyzed copolymerization of crude linoleic acid (LA), glycerol (G) and 1,18-*cis*-9-octadecenedioic acid (oleic diacid, OD). The lipase used is *Candida antarctica* Lipase B (CALB) immobilized on Lewatit (N435). Experiments were conducted to assess N435's efficiency of forming poly(OD-co-G-co-LA) as a function of: (i) LA content in the co-monomer feed and (ii) reaction time. For comonomer feed ratio (OD:G:LA) 1:1:0.67,  $M_n$  reached ~9500 in 8 h, trisubstituted G-units increased to 64% and monomer was largely depleted. When LA and OD remained in products, a lower temperature thermal decomposition peak at about 280 °C was observed in addition to a higher temperature decomposition peak at ~475 °C. By increasing LA content in the comonomer feed from 1:1:1 to 1:1:1.33,  $M_n$  decreased from 11,000 to 6300 while trisubstituted G-units increased from 92 to nearly 100%. Thus, by varying the feed ratio of LA, polymeric triglyceride-type structures were formed with control of chain length and trisubstituted G-unit content. Since G-units may be substituted in various ways with OD and LA, calculations were performed that determined the relative proportion of different substitution patterns in products. A hypothetical structure showing general characteristics of the substitution at glycerol units for one such product is presented.

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### 1. Introduction

Research on bio-based polymers built from readily renewable resources continues to draw increased attention of academic and industrial scientists. Motivating forces to substitute current petroleum-derived plastics with bio-based alternatives include environmental pollution, climate change and a finite global supply of fossil fuel that is subject to disruptive price fluctuations [1,2]. Furthermore, by switching the manufacturing base to bio-renewable carbon from petro-fossil carbon feedstocks the

potential exists to achieve a zero material carbon footprint [3]. This paper describes building fully biobased polyol-polyesters from glycerol, 1,18-*cis*-9-octadecenedioic acid (oleic diacid) and crude linoleic acid from triglycerides using lipase-catalyzed condensation polymerizations.

Triglycerides from plant oils have been extensively studied and used in industrial processes as building blocks for polymer synthesis [4–12]. Their use in crosslinked polymers exploits the presence of natural occurring functionality such as unsaturation, hydroxyl and epoxide moieties as well as chemically modified plant oils. Examples of modifications such as epoxidation, acrylation, esterification with maleic anhydride by free radical grafting or esterification with free hydroxyl groups are all commonly employed

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to increase the number of crosslinking sites [12]. The polymers synthesized herein are polymeric triglyceride mimics that possess many of the above crosslinkable functionalities.

Fatty acid components of triglycerides have been chemically modified to form difunctional building blocks useful for synthesis of linear or branched chains having ester, amide and/or urethane links [6]. For example, Djigou and Meier [13] prepared unsaturated  $\alpha,\omega$ -diesters with chain lengths 12–20 carbon atoms by self-metathesis of methyl-10-undecenoate and its cross-metathesis with methyl acrylate. Warwel et al. [14] used a Grubbs catalyst to perform metathetical condensation converting 9-decenoic, 10-undecenoic, and 13-tetradecenoic acid methyl esters to their corresponding long-chain, symmetrically unsaturated  $\alpha,\omega$ -dicarboxylic acid methyl esters (C-18, C-20, C-26). Quinzler and Mecking [15] converted methyl oleate, by exposure to carbon monoxide and methanol catalyzed by  $\text{Pd}(\text{OAc})_2/1,2\text{-bis}[(\text{di-}t\text{-tert-butylphosphino)methyl] \text{-benzenemethanesulfonic acid}$ , to dimethyl-1,19-nonadecanedioate. Reduction of the latter gave nonadecane-1,19-diol. Turunc and Meier [16] demonstrated the utility of thiol-ene additions to methyl 10-undecenoate to prepare a series of  $\alpha,\omega$ -bisfunctional fatty acids. Kolb and Meier prepared malonate derivatives bearing long aliphatic chains [17]. Furthermore, biotechnological routes using different engineered *Candida tropicalis* to convert fatty acids to diacids (e.g. oleic diacid) [18,19] and  $\omega$ -hydroxyfatty acids have been reported [20]. In this work, we have adopted the *C. tropicalis* catalyzed conversion of oleic acid to oleic diacid as a building block for the preparation of a unique family of lipid functionalized polyol-polyesters.

Enzyme-catalysis has proved useful in building polymers by condensation polymerization methods from hydroxyl or  $\omega$ -carboxyl functionalized fatty acids. This work has been reviewed by us in 2010 [21]. Other examples are provided in a review by Kobayashi and Makino [22]. In one example,  $\alpha,\omega$ -dicarboxylic acid methyl esters (C-18, C-20, C-26) described above [14] were epoxidized and then copolymerized with 1,4-butanediol in diphenyl ether using *Candida antarctica* Lipase B (Novozym 435, N435) catalysis to give polyesters ( $M_w$  7900–11,600 g/mol) in which epoxy groups remained intact.

Historically, polyesters from diacids and polyols (e.g. glycerol and sorbitol) were prepared using chemical catalysts such as those based on titanium and tin alkoxides [23–27]. However, undesirable results such as crosslinking leading to gelation were encountered when high functional group conversions were desired. Crosslinking can be avoided by protection-deprotection chemistry but such approaches are tedious and, therefore, costly [28]. Other problems with chemical catalysts such as titanium and tin alkoxides are the need to conduct polymerizations at high reaction temperatures ( $\geq 150^\circ\text{C}$ ) that are energy intensive and lead to product discoloration. In contrast, lipases can provide better control over branching while avoiding cross-linking reactions due to steric constraints at enzyme active sites.

Reviews including extensive background on lipase-catalyzed synthesis of polyol-polyesters have been

published by us and others [21,29–33]. Examples of lipase-catalyzed routes to polyol-polyesters of high relevance to this study are as follows. Oleic diacid was synthesized in high conversion yields by whole-cell biotransformations catalyzed by *C. tropicalis* ATCC20962 [19]. The synthesis of poly(oleic diacid-co-glycerol) was performed using N435 and dibutyl tin oxide (DBTO) as catalysts. Relative to the metal catalyst, N435 was preferred due to its preference for forming linear chains, as well as its ability to catalyze branching without crosslinking (e.g. formation of a gel fraction) [28]. We attribute this behavior of N435 to its high activation energy barrier for catalysis of crosslinking reactions caused by steric constraints at the lipase active site. In contrast, DBTO catalysis resulted in rapid network formation at low functional group conversions. N435 catalysis with a molar ratio of oleic diacid to glycerol of 1.0:1.0, resulted in polyesters with  $M_n$  6000 g/mol at 6 h and 9100 g/mol at 24 h with low branching degree (13%–16 mol% trisubstituted glycerol).

Kobayashi and coworkers in two related papers studied lipase-catalyzed copolymerizations of glycerol, divinyl esters and fatty acids [34,35]. Primary variables explored was the lipase catalyst, the divinyl ester structure (terephthalic, isophthalic, adipic and sebacic), reaction temperature (45, 60, 70  $^\circ\text{C}$ ) and applied vacuum where reaction time was generally fixed at 24 h. After 24 h, reaction mixtures were added to large volumes of methanol/water (95:5 v/v) resulting in loss of oligomers soluble in the non-solvent. Insoluble product yields ranged from about 11 to 80%. Analysis by  $^1\text{H}$  NMR gave the ratio in copolyesters of fatty acid-to-diacid, an indication of glycerol substitution. Measurements of molecular weight were by size exclusion chromatography (SEC) relative to polystyrene samples. An exemplary result was a bulk polymerization of glycerol, sebacate divinyl ester and a fatty acid, in equimolar quantities, using N435 as catalyst at  $\sim 20$  mmHg, 60  $^\circ\text{C}$  for 24 h. The fractionated product (77% yield) had  $M_n = 8,500$  and, from  $^{13}\text{C}$  NMR, 13% residual 1,3-glycerol units (i.e. 87% trisubstituted units). The polymer obtained using linoleic or linolenic acid was cured using a cobalt naphthenate catalyst or by thermal treatment to give crosslinked, transparent, polymeric films with high-gloss. Crosslinked films placed in activated sludge reached 45% biodegradation in 42 d. In a subsequent publication by Kobayashi and co-workers [35], N435 catalyzed preparation of epoxidized polyol-polyesters from glycerol, sebacate divinyl ester and an unsaturated fatty acid was studied. Epoxidized products with  $M_n$  ranging from about 3 to 9 K were obtained and cured thermally to give transparent polymeric films with high gloss surfaces.

In this study, the enzyme-catalyzed synthesis of a unique series of bio-based polymeric triglyceride analogs, with the general structure shown in Scheme 1, was prepared. Synthesis of polymeric triglyceride analogs was enabled by *C. tropicalis* catalyzed  $\omega$ -carboxylation of oleic acid to give oleic diacid (OD). This molecular design benefits from the diverse family of natural fatty acid structures that are available via plant biosynthesis as well as established chemical methods to further elaborate these functionalities (see discussion above). Experiments were conducted to interrogate key variables that affect the

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