

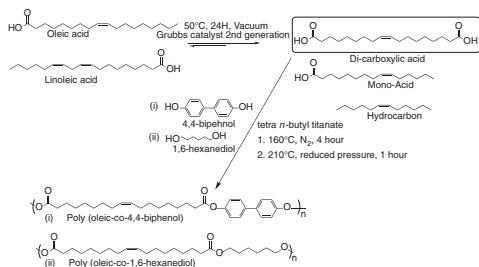
# Synthesis of Bio-based Monomer from Vegetable Oil Fatty Acids and Design of Functionalized Greener Polyester

Noor Farisha Abd. Rahim,<sup>1</sup> Kohtaro Watanabe,<sup>2</sup> Hidayah Ariffin,<sup>1</sup> Yoshito Andou,<sup>\*2</sup> Mohd Ali Hassan,<sup>1</sup> and Yoshihito Shirai<sup>2</sup>

<sup>1</sup>Department of Bioprocess Technology, Faculty of Biotechnology and Biomolecular Sciences, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

<sup>2</sup>Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology, 2-4 Hibikino, Wakamatsu-ku, Kitakyushu, Fukuoka 808-0196

(E-mail: yando@life.kyutech.ac.jp)



In order to provide greener materials with high potentials, we propose and design the reaction method and combination with useful counterparts for higher efficient green products using fatty acids as biomass. Herein, the proposal of fabrication for functional greener polymers is provided through reaction between green chemicals and petrochemicals for giving more control functionalities as additional values to greener polymer.

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<sup>1</sup>Department of Bioprocess Technology, Faculty of Biotechnology and Biomolecular Sciences, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

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In order to design sustainable materials from vegetable oil-based fatty acids, we propose herewith a method to obtain unsaturated dicarboxylic acids as a polymerizable monomer through metathesis reaction of oleic and linoleic acids with the 2nd generation Grubbs catalyst. Subsequently, functional green polyester was produced from dicarboxylic acids and aromatic diol. Dicarboxylic acid having similar structure i.e., octadec-9-enedioic acid was successfully obtained from metathesis of both oleic and linoleic acids. Condensation polymerization of octadec-9-enedioic acid with 1,6-hexanediol and 4,4'-biphenol was carried out and it was shown that polymer with aromatic backbone had higher glass-transition temperature than aliphatic polyester.

There has been increased interest in renewable resources from both academia and industry due to worldwide concern over the shortage of nonrenewable resources such as petroleum.<sup>1</sup> The huge demand for polymers and other chemicals has opened the potential of vegetable oils to be used as feedstock as it contains different composition of triglycerides.<sup>2</sup> Since vegetable oils are abundantly available, have various chemical structure due to the variety of triglyceride composition and are biodegradable, fatty acid derivatives from vegetable oils have been an attractive resource for the production of polyester materials.<sup>3</sup> Among all fatty acids, oleic and linoleic acids can be found in most vegetable oils.<sup>4</sup>

In recent years, studies on synthesis of polymer from fatty acids have made great progress. Metzger et al., (2009) reported that linear diacids derived from fatty acid can be valuable renewable monomers for polyesters, polyamides, and polyurethanes.<sup>5</sup> Though fatty acids as starting materials have been extensively employed to synthesize polymer materials, many researchers are concerned with the design of well-defined polymer from green materials only.<sup>6</sup> Recently, new routes for synthesis of diacid from unsaturated fatty acid through olefin cross-metathesis reaction in the presence of the second generation Grubbs catalyst (G2) have been proposed.<sup>7-9</sup> Dicarboxylic acids derived from fatty acid can be easily provided to design greener materials. Consequently, aliphatic homo- and copolyesters can typically be prepared by polycondensation of difunctional monomers such as diols and diacids.<sup>10</sup> Most often, the mechanical performance of these aliphatic polyesters can be improved by synthetic chain extension and addition of aromatic moieties to the polymer structure.<sup>11,12</sup> Herein, a proposal of fabrication for functional greener polymers is provided through reaction between green chemicals and petrochemicals for giving more control functionalities as additional value to greener

**Table 1.** Synthesis of dicarboxylic acids from vegetable oil fatty acids

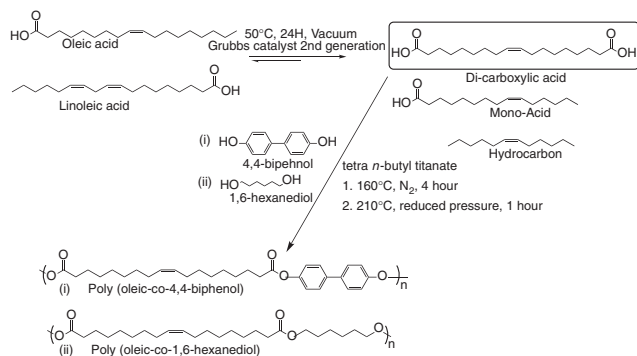
Entry	Fatty acid <sup>b</sup> /mmol	G2 /μmol	Reduced pressure <sup>c</sup>	Time /h	Temp /°C	Yield /%
1 <sup>a</sup>	OA (35.4)	3.2	×	24	50	43.7
2	OA (35.4)	3.2	○	24	50	62.0
3	LA (35.7)	3.2	×	72	50	27.5
4	LA (35.7)	3.2	○	24	50	35.9

<sup>a</sup>Control conditions. <sup>13</sup> <sup>b</sup>OA: oleic acid, LA: linoleic acid. <sup>c</sup>×: no reduced pressure applied, ○: reduced pressure applied.

polymer. Following these circumstances, we have attempted to provide functionalities in polymers that consist of green diacid and petro-diol having liquid crystalline properties.

Most studies on synthesis of diacid from unsaturated fatty acid using olefin cross-metathesis reactions have focused on the conversion of mono-olefinic fatty acid such as oleic acid, selenic acid, and erucic acid. However, the synthesis of diacids derived from multiolefinic fatty acids such as linoleic, linolenic, and  $\alpha$ -eleostearic acid has rarely been examined because of their complicated coupling reactions under various combinations. Thus, if metathesis of different fatty acids can produce the same structure of diacid, it is expected that the product would be a desirable monomer compound for design of greener polymer.

As starting materials for the synthesis of long-chain symmetrically unsaturated  $\alpha,\omega$ -dicarboxylic acid, oleic and linoleic acids were used as listed in Table 1. Though metathesis reaction of oleic acid has been extensively investigated, few reports have been conducted using linoleic acid for dicarboxylic acid production using G2 because the two double bonds on its structure may cause the formation of various different compounds. In this study, olefin metathesis of oleic acid led to the formation of octadec-9-enedioic acid when G2 was used in bulk. The conditions were based on the methodology of previous research<sup>13</sup> and has been used as control conditions for the other reactions, resulting in symmetrically unsaturated  $\alpha,\omega$ -dicarboxylic acid (Entry 1) with product yield of 44%. The diacid was isolated for further analyses by <sup>1</sup>H, <sup>13</sup>C NMR, and FT-IR spectra (Supporting Information).<sup>14</sup> In order to increase the yield, the reaction was carried out in vacuo. From the results (Entry 2), this condition was an effective method which gave higher yield than control conditions. Additionally, reactions were performed

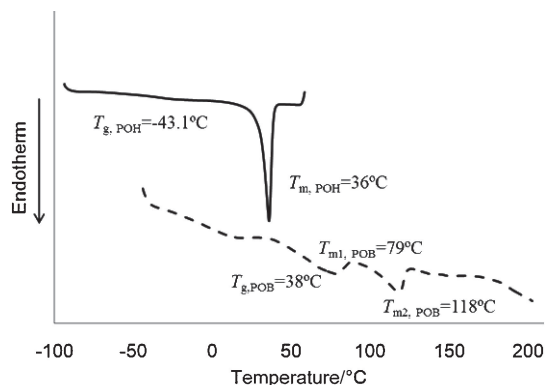


**Scheme 1.** Copolymerization of dicarboxylic acid derived from oleic or linoleic acid with 1,6-hexanediol or 4,4'-biphenol.

at 90 and 120 °C with yield of diacid at 28% and 32%, respectively. This attempt was to avoid solidification of the reaction mixtures and to enable a maximum removal of by-product.<sup>15</sup> However, the resulting yield of products was decreased because of suppression of the G2 activity at high temperature in spite of removed by-products.

Metathesis of linoleic acid was also carried out using a similar method to obtain  $\alpha,\omega$ -dicarboxylic acid. It was found that a similar structure of diacid product was obtained, i.e., octadec-9-enedioic acid.<sup>16</sup> However the yield was lower at 29% even when the experiment was prolonged to 72 h (Entry 3). There was no product formation at 24h of reaction. Thus, reaction was carried out under reduced pressure, and able to afford 34% of linoleic diacid after 24h of reaction time (Entry 4). This olefin metathesis reaction proceeded intricately because linoleic acid contains two cis-double bonds at positions 9 and 12.<sup>17</sup> In order to purify diacids from the by-products, the reaction mixture was dissolved in small amount of  $\text{CHCl}_3$  and precipitated in MeOH. The mixture was then filtered and the resulting solid was washed with hexane to give a white powder as diacids. The filtered solvent was evaporated under reduced pressure and the residue was purified by column chromatography using hexane and MeOH to obtain the by-products. Each segment of compounds was analyzed by  $^1\text{H}$ NMR spectra, respectively.<sup>18,19</sup> The separated crude products obtained with dicarboxylic acid (a), unsaturated aliphatic monoacids (b), and unsaturated aliphatic hydrocarbon (c) are shown in Figure S-2 and Figure S-3 (Supporting Information).

The synthesis of greener polyester using octadec-9-enedioic acid was tested by condensation polymerization with 1,6-hexanediol and 4,4'-biphenol in the presence of isopropyl titanate, respectively (Scheme 1). The polyesters with 1,6-hexanediol (POH) were soluble in common organic solvents such as chloroform and acetone because of their extended aliphatic soft structures whereas polyester with 4,4'-biphenol (POB) was insoluble in these solvents. Therefore, POH was confirmed by  $^1\text{H}$ NMR and FT-IR (Supporting Information).<sup>12</sup> POB was confirmed by FT-IR and TOF-MS (Supporting Information) because of insoluble compound. The thermal behaviors of POH and POB were investigated with DSC and conducted at a heating rate  $10\text{ }^\circ\text{C min}^{-1}$  after the 1st scan at heating and cooling under the same rate. For POH with long aliphatic spacer is seen a glass transition at  $-43.1\text{ }^\circ\text{C}$  and a sharp endotherm with a peak temperature at  $36\text{ }^\circ\text{C}$  corresponding to the



**Figure 1.** Differential scanning calorimetry data for POH (solid line) and POB (dotted line) recorded at a rate of  $10\text{ }^\circ\text{C min}^{-1}$ .

melting point. The rigidity of the backbone results in high  $T_g$  value at  $38\text{ }^\circ\text{C}$  for POB against POH. Interestingly, DSC thermogram of the POB shows some endothermic peak after a glass transition at  $38\text{ }^\circ\text{C}$  (Figure 1). The DSC thermogram of the POB shows an initial base line shift along with two broad endothermic peaks at about 79 and  $118\text{ }^\circ\text{C}$ . Bagheri et al., (2008) reported DSC thermogram of polyesters with a biphenyl unit in the main chain which indicates thermotropic liquid crystallinity.<sup>20</sup> The DSC thermogram behavior of the POB show a similar trend to their characterization. It is well known that the thermotropic liquid crystalline behavior of polyesters consists of aromatic moieties as stiff mesogenic units connected by soft linkages such as ether and ester.<sup>21</sup> This finding may indicate that POB can easily change from one conformation to another because each unit possesses a high degree of flexibility.

In conclusion, to provide greener materials with high potential, we proposed and designed a reaction method and combination with useful counterparts for higher efficient green products using fatty acids as biomass. The synthesis of unified diacid from oleic and linoleic acids was successfully obtained via olefin cross metathesis reaction. Eventually, we succeeded in preparing greener polyester through combination of petrochemicals and oleo chemicals. Further evaluation and combination of the characteristics of greener and hybrid polyester will be needed in order to clarify the potential as practical useful material.

Supporting Information is available electronically on J-STAGE.

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- 12 Polyester from octadec-9-enedioic acid and 1,6-hexanediol was isolated as white solid powder in 61% yield. <sup>1</sup>H NMR (10 mg in 0.7 mL CDCl<sub>3</sub>, ppm): 5.35–5.2 (2H, =CH–CH<sub>2</sub>–), 4.05 (4H, –(CO)–O–CH<sub>2</sub>–), 2.23 (4H, –CH<sub>2</sub>–CO–), 2.0–1.8 (8H, =CH<sub>2</sub>–CH<sub>2</sub>–(CO)–O–CH<sub>2</sub>–CH<sub>2</sub>–), 1.6–1.45 (4H, –CH<sub>2</sub>–CH<sub>2</sub>–CO–), 1.35–1.1 (20H, –CH<sub>2</sub>–). GPC (Sample from precipitation was measured using chloroform as eluent): *M*<sub>w</sub> 3500 g mol<sup>–1</sup>.
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- 14 Diacids from oleic acid (octadec-9-enedioic acid) was isolated as white solid powder product in 64.5% yield. FT-IR (KBr, cm<sup>–1</sup>): 1724 (s, C=O), 757 (m, C=C). <sup>13</sup>C NMR (10 mg in 0.7 mL CDCl<sub>3</sub>, ppm): 179.6 (C=O), 130.3 (=CH–), 34.0, 32.1, 29.1, 28.8, 28.6, 28.4, 24.6. <sup>1</sup>H NMR (10 mg in 0.7 mL CDCl<sub>3</sub>, ppm): 5.4–5.3 (2H, =CH–CH<sub>2</sub>–), 2.35 (4H, –CH<sub>2</sub>–CO–), 2.1–1.9 (4H, =CH–CH<sub>2</sub>–), 1.6 (4H, –CH<sub>2</sub>–CH<sub>2</sub>–CO–), 1.4–1.2 (16H, –CH<sub>2</sub>–).
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- 18 Carboxylic acid (pentadec-9-enoic acid) from linoleic acid was purified by column chromatography. <sup>1</sup>H NMR (10 mg in 0.7 mL CDCl<sub>3</sub>, ppm): 5.4–5.3 (2H, =CH–CH<sub>2</sub>–), 2.35 (2H, –CH<sub>2</sub>–CO–), 2.1–1.9 (4H, =CH–CH<sub>2</sub>–), 1.6 (2H, –CH<sub>2</sub>–CH<sub>2</sub>–CO–), 1.4–1.2 (14H, –CH<sub>2</sub>–), 0.9–0.8 (3H, –CH<sub>3</sub>).
- 19 Unsaturated hydrocarbon (dodec-6-ene) from linoleic acid was purified by column chromatography. <sup>1</sup>H NMR (10 mg in 0.7 mL CDCl<sub>3</sub>, ppm): 5.4–5.3 (2H, =CH–CH<sub>2</sub>–), 2.1–1.9 (4H, =CH–CH<sub>2</sub>–), 1.4–1.2 (12H, –CH<sub>2</sub>–), 0.8–0.9 (3H, –CH<sub>3</sub>–).
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