

## PAPER

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## Cross-metathesis of technical grade methyl oleate for the synthesis of bio-based polyesters and polyamides†

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Fatty acid methyl esters (FAMES), despite being currently used mainly as a biodiesel, could be also a source of various building blocks. Their cross-metathesis allows the production of diesters—attractive bio-based monomers. However, most of the existing reports from academic research groups are mainly restricted to pure methyl oleate. With the goal of future industrial feasibility, a process for the self-cross metathesis of technical grade methyl oleate, which means containing a significant amount (20 wt%) of methyl linoleate, has been developed. The resulting dimethyl octadec-9-enedioate has been obtained with high selectivity and in good yield. Subsequent polycondensation with a co-monomer (diol or diamine) resulted in the formation of polymeric materials which were characterized using thermogravimetric analysis and differential scanning calorimetry.

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## Sustainability spotlight

The current situation demands an urgent transition towards sustainable and renewable sources of energy and materials to mitigate the environmental impact of the use of fossil fuels. Most polymers are currently made from fossil feedstocks, and they need to be replaced by renewable sources. Fatty acid methyl esters are derived from vegetable oil and currently used mainly as a biodiesel, but they hold promising use as a source of various building blocks. Their cross-metathesis yields diesters, monomers for the synthesis of polyesters and polyamides. However, pure fatty acid methyl esters are used for this process. The sustainable advancement of our work lies in the development of a process for the self-cross metathesis of technical grade methyl oleate, containing 20 wt% of methyl linoleate, derived from broadly available sunflower and rapeseed oil. Thus, it represents a real opportunity for making these polymers at large scale. Our work aligns with several United Nations Sustainable Development Goals: Industry, Innovation, and Infrastructure (SDG 9), Responsible Consumption and Production (SDG 12) and Climate Action (SDG 13).

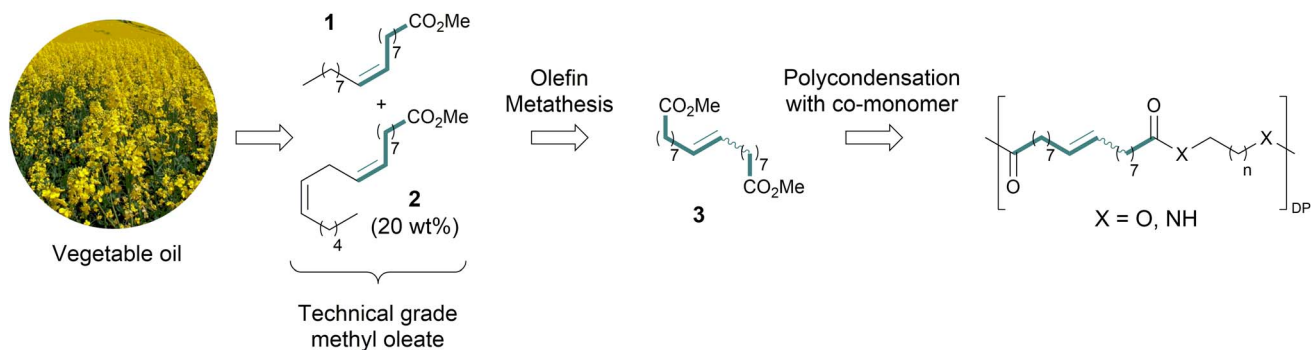
## Introduction

Fossil fuels are the main source of raw materials for the chemical industry.<sup>1</sup> However, as we move towards a net zero scenario, renewable feedstocks will take the place of fossil fuels as the starting material for the synthesis of chemicals. This transition is especially urgent in the case of polymers, which account for the largest volume of chemical industry products.<sup>1</sup> Biomass is currently the main source of renewable feedstocks, and among the different types of biomass, vegetable oils are the most widely used in the chemical industry,

due to their availability, affordability, and functionality.<sup>2–5</sup> Transesterification of vegetable oils with methanol yields fatty acid methyl esters (FAMES) with concomitant production of glycerol. Both feedstocks have already found applications in the production of cosmetics, detergents, plasticizers, and other products.<sup>2,6,7</sup>

Olefin metathesis (OM) has become a tool of prominent importance for C–C double bond formation, thus earning an outstanding position in the organic synthesis toolbox, and has already been proven useful in the synthetic modifications of FAMES.<sup>8,9</sup> Notably, the ethenolysis reaction (CM with ethylene) of FAMES has gained significant interest, since it gives access to valuable terminal olefins.<sup>10–12</sup> Moreover, the self-CM of pure methyl oleate (**1**, Scheme 1), which is the most abundant unsaturated FAME found in natural oil, affords dimethyl octadec-9-enedioate (**3**, Scheme 1) and internal alkene **5** (Scheme 2a)—both desirable products.<sup>9,13–16</sup> Diester **3** is an excellent monomer for synthesizing bio-based and potentially biodegradable polyesters (Scheme 1). A saturated analog of diester **3** was used to obtain long-spaced aliphatic

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Scheme 1 Outline of the concept: synthesis of polymers from diesters derived from vegetables oils.

Table 1 Results of catalyst screening<sup>a</sup>

Entry	Catalyst	Loading (ppm)	Conversion of 1(Z) + 2 (%)	Yield of 3 (%)	3/4 wt. ratio	E/Z ratio of 3
1 <sup>b</sup>	<b>Ru3</b>	100 <sup>b</sup>	<5	0	—	—
2		100	95	54	96 : 4	84 : 16
3		50	94	51	89 : 11	82 : 18
4		25	80	26	63 : 37	78 : 22
5	<b>Ru4</b>	100	94	45	90 : 10	82 : 18
6	<b>Ru5</b>		94	54	92 : 8	82 : 18
7	<b>Ru6</b>		95	49	96 : 4	82 : 18

<sup>a</sup> Reaction conditions: no solvent, pretreated technical grade methyl oleate, 50 °C, 3 h. <sup>b</sup> Non-pretreated, technical grade 1.

polyesters,<sup>17–19</sup> although reports featuring direct use of 3 in polymer synthesis are scarce.<sup>20</sup>

However, procuring pure methyl oleate is not a straightforward task.† Vegetable oils are triglycerides commonly composed of different fatty acids which lead to mixtures of FAMES after transesterification. Concerning OM transformation of FAMES, this can be particularly problematic when a mixture of unsaturated FAMES is formed. Historically, methyl oleate with a low content of polyunsaturated FAMES could be procured by selective hydrogenation of polyunsaturated fatty acids.<sup>21</sup> Nowadays methyl oleate with low content of polyunsaturated FAMES is produced from high oleic safflower oil (HOSO) raw material. HOSO is obtained from genetically modified crops, which are safflower plants into which one or several genes coding have been inserted through the process of genetic engineering.<sup>22,23</sup> So far, reports concerning self-CM of methyl oleate mainly focused on the use of pure, refined 1, but this cannot be a viable raw material for industrial scale due to high purification costs.<sup>13,24</sup> Moreover, to develop a process susceptible of potential future industrialization, raw material availability must be considered. Consequently, it is desirable to move from HOSO towards significantly more broadly available vegetable oil sources such as sunflower or rapeseed oils. This area has been largely unexplored and led us to embark on a search for a process utilizing technical grade methyl oleate,

which means containing a substantial amount (20 wt%) of methyl linoleate (2, Scheme 1), as starting material.§<sup>25,26</sup>

## Results

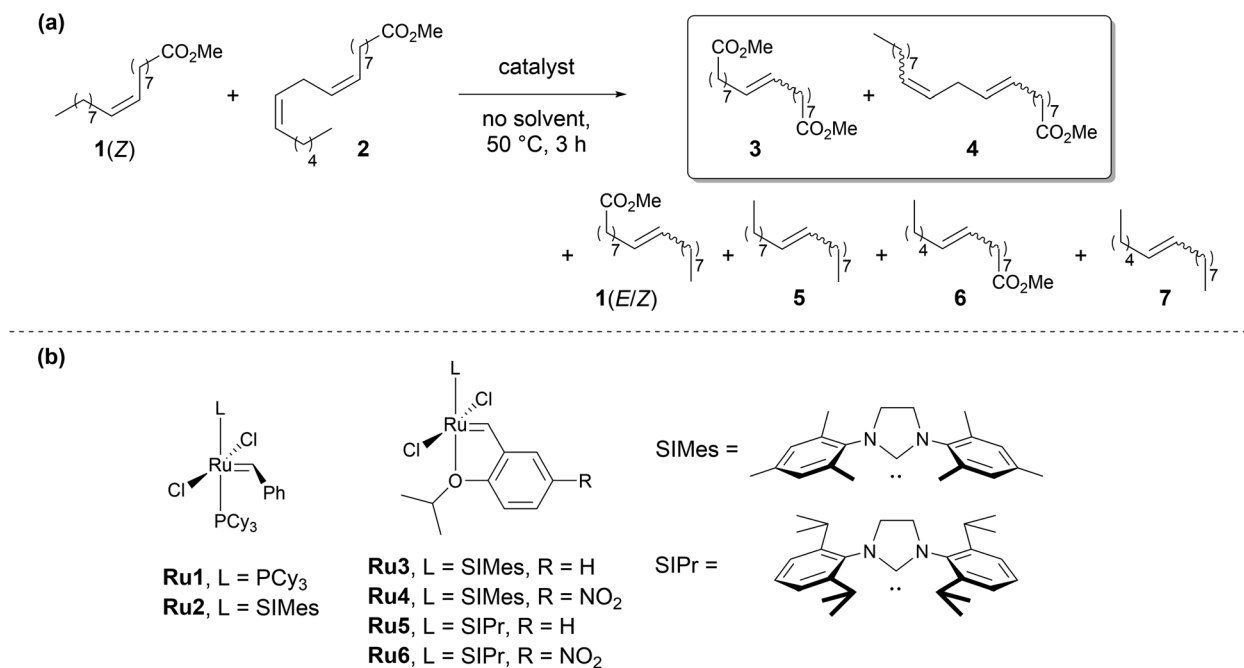
Owing to their relatively high activity and functional group tolerance, ruthenium alkylidene complexes are widely used, of which Grubbs 1st generation catalyst (**Ru1**, Scheme 2b) is a notable example. Exchanging the phosphine ligand to an *N*-heterocyclic carbene (NHC) ligand resulted in a more efficient second generation of the catalyst (**Ru2**, Scheme 2b). Furthermore, the installation of *o*-isopropoxybenzylidene ligand led to an even more stable and productive, phosphine-free second generation of Hoveyda–Grubbs catalysts (**Ru3–Ru6**, Scheme 2b).<sup>27</sup>

When anticipating a large-scale application of a homogeneous catalyst, it is paramount to have a high turnover number (TON) to render the process profitable. It was estimated that OM catalyst should give TON exceeding 50 000 to achieve an economically viable process<sup>10,28</sup> and this level of efficiency is achievable for contemporary catalysts.<sup>16,29,30</sup> However, TON is significantly dependent on the substrate quality which is connected to the content of catalyst poisons such as peroxides, phosphates, sulfates, soap, *etc.* Thus, several protocols to remove those poisons from methyl oleate have been developed and their impact on the overall economic viability of the process

† Extra-pure methyl oleate (>99%) is commercialized by Aldrich (79 €/5 g). Such reagent has been used in many academic research, for example in ref. 29.

§ OM of conjugated polyolefins (such as methyl lineolate) can cause issues of reaction selectivity (ref. 25) and catalyst efficiency (ref. 26).





Scheme 2 (a) Self-CM of technical methyl oleate (1) containing methyl linoleate (2). (b) Ruthenium catalysts used in OM.

has been discussed in the literature.<sup>¶</sup> Most commonly utilized method is 1 pretreatment with activated alumina combined with degassing.<sup>||</sup>

We started off with the self-CM of technical grade 1 after its prior simple distillation from activated alumina to decrease the content of catalyst poisons. 100 ppm of **Ru3** allowed to reach equilibrium in 3 h (50 °C, no solvent, Table 1, entry 2). Even though the reaction mixture contained a variety of products including several internal alkenes and monoesters (1(*E/Z*), 4, 5, 6, 7, Scheme 2a), we were pleased to find that the equilibrium mixture contained predominantly 3 as a diester species. Remarkably, when non-pretreated, technical grade 1 was used for the reaction (Table 1, entry 1) no diester 3 was formed with 100 ppm of **Ru3**. This highlights how substrate pretreatment can significantly impact catalyst efficiency.

Notably, although isomerization side reactions can be problematic for OM catalysts,<sup>31</sup> no significant formation of isomerization byproducts was observed. Such side reactions can be circumvented by a careful choice of reaction conditions which proved a good strategy in this case. Prolonged reaction time at higher temperatures promotes the undesired isomerization reactions,<sup>16</sup> presumably due to the formation of hydride species<sup>31</sup> and metal nanoparticles<sup>32</sup> during catalyst decomposition. Additionally, certain impurities derived from substrate or catalyst, such as alcohols,<sup>33</sup> metal nanoparticles,<sup>32</sup> can also contribute to lower selectivity due to increased formation of isomerized byproducts. To suppress those side reactions use of quinone additives was studied in the literature.<sup>34</sup> Moreover,

catalysts bearing unsymmetrical NHC ligands do not promote isomerization, however, at the cost of lower activity in OM.<sup>35,36</sup>

Upon decreasing the catalyst loading, we noticed that monoester 4 was also present in the reaction mixture and that the relation was inversely proportional (Table 1, entries 3–4). This suggests that at loadings lower than 100 ppm of **Ru3** the reaction equilibrium is not reached and 4 might only be a kinetically favored product. We wanted to avoid any monofunctional species such as 1, 2, 4, or 6 in the isolated product since they would lead to a lower molecular mass of the resulting polyester, as monoesters would terminate a polymer chain. From gas chromatography, we deduced that boiling temperatures of 3 and 4 would be very similar (Fig. S4, ESI<sup>†</sup>), which would make the purification of 3 challenging. Hence, we decided to focus on minimizing the formation of 4 as the primary objective of catalyst screening, rather than maximizing catalyst efficiency. All of the complexes gave reasonably similar conversions of substrates 1(*Z*) and 2, around 95%. All catalysts gave a ratio of 3 to 4 above 90 : 10, with **Ru3** and **Ru6**<sup>\*,37</sup> exceeding 95 : 5. **Ru3** gave a slightly higher yield of 3 than catalyst **Ru5** (54% versus 49% respectively, the maximal yield being approximately 50% resulting from the reaction equilibrium) and therefore it was chosen to continue with the development.

With the selected catalyst, self-CM of pretreated, technical grade methyl oleate was conducted with 300 g of substrate. After the reaction, product 3 was isolated by fractional distillation and subsequently purified by crystallization from methanol at −30 °C. Interestingly, this protocol gave pure 3 containing almost only *E* isomer (*E/Z* ratio of 97 : 3) in 36% yield.

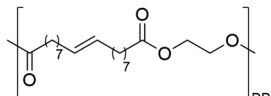
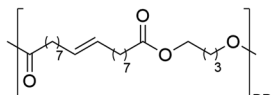
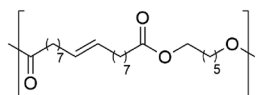
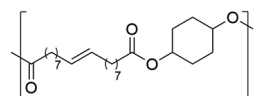
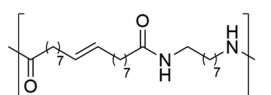
¶ For methods of methyl oleate pre-treatment to maximize catalyst efficiency consult ref. 30 and references cited therein.

|| For example, such pre-treatment protocol was utilized in ref. 29.

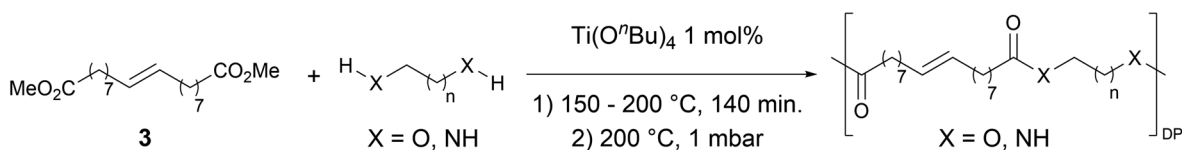
\*\* For effects of nitro and other electron withdrawing groups on catalyst activity and application see ref. 37.



Table 2 Polymerization of monomer **3** and characterization of obtained polyesters and polyamides<sup>a</sup>

Entry	Polyester	Vacuum time	Yield	DP <sup>b</sup>	$M_n$ (g mol <sup>-1</sup> ) <sup>b</sup>	$T_m$ (°C) <sup>c</sup>	$\Delta H$ (J g <sup>-1</sup> ) <sup>c</sup>	$T_d$ (°C) <sup>d</sup>	Mass loss <sup>d</sup>
1		30 min	51%	1.7	592	42	64	403	97%
2		19 h	52%	n.d	n.d	14	25	413	96%
3		225 min	76%	6.6	2238	34	72	395	98%
4		21 h	81%	n.d	n.d	11	55	398	97%
5		180 min	74%	7.5	2539	38	73	397	98%
6		21 h	88%	n.d	n.d	10	60	398	96%
7		19 h	24%	n.d	n.d	9	35	446 <sup>e</sup>	78% <sup>e</sup>
8		19 h	51%	n.d	n.d	152	55	443	82%

<sup>a</sup> Reaction conditions: Ti(O<sup>*n*</sup>Bu)<sub>4</sub> 1 mol%, no solvent, 140 min melt time with temperature increase from 150 to 200 °C. <sup>b</sup> Degree of polymerization (DP) and number average molecular weight ( $M_n$ ) were calculated from <sup>1</sup>H NMR by end group analysis. <sup>c</sup> Determined by DSC. <sup>d</sup>  $T_d$  (decomposition temperature) and mass loss of the samples was determined by TGA. <sup>e</sup> Evident mass loss of 50% was observed at temperature 353 °C. n.d. – not determined due to polymer insolubility.

Scheme 3 Polycondensation reaction to obtain polyesters and polyamides from diester **3**.

Having monomer **3** in hand, we attempted the melt polycondensation reaction with different co-monomers (Scheme 3). Titanium (IV) *n*-butoxide was used as the catalyst for this reaction.<sup>20</sup> This resulted in a red-brown solid insoluble in all the most common solvents including trifluoroacetic acid. This stood in contradiction to the findings reported by Warwel *et al.*,<sup>20</sup> where authors claimed to characterize the same polyesters using gel permeation chromatography (GPC), although no experimental data was provided therein. To confirm the formation of macromolecules, the reaction was stopped at an earlier stage and the formed oligomers (soluble in conventional organic solvents) were characterized by NMR spectroscopy. The obtained oligomers and polymers were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The obtained polyesters have relatively low melting temperatures between 9 and 42 °C (Table 2, entries 1–7), which is characteristic of linear aliphatic polyesters. Significantly higher was the melting temperature for polyamide (152 °C, Table 2, entry 8), which is due to the formation of hydrogen bonds in comparison to polyesters. Heats of fusion varied from 25 to 73 J g<sup>-1</sup>. Aliphatic polyesters exhibited degradation

temperatures around 400 °C, however, the polyester containing 1,4-cyclohexanediol block unit showed an increased degradation temperature of 446 °C due to the higher rigidity of the polymer that such a monomer provides.

## Conclusions

In summary, a novel process of obtaining functional polymer materials from methyl oleate was developed. Self-cross metathesis of methyl oleate in the presence of substantial amounts of methyl linoleate was investigated and the reaction was optimized to obtain diester **2** with high selectivity and yield. Subsequent polycondensation with a co-monomer (diol or diamine) resulted in the formation of polymeric materials which were characterized using TGA and DSC.

## Data Availability Statement

Data for this paper, including gas chromatograms of catalytic reactions, NMR, TGA, and DSC characterization data, are available at the HAL repository at <https://hal.science>.



## Author contributions

Paweł Krzesiński: investigation, data curation, formal analysis, visualization, writing – original draft. Vincent César: funding acquisition, writing – review & editing. Karol Grela: funding acquisition, writing – review & editing. Sergio Santos: investigation, data curation, formal analysis, writing – original draft. Pablo Ortiz: conceptualization, supervision, writing – review & editing.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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