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# Aliphatic-aromatic polyesters from naturally occurring sinapic acid through acyclic-diene metathesis polymerization in bulk and green solvent Cyrene™

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KEYWORDS. Sinapic acid, naphthoic acid, renewable  $\alpha,\omega$ -dienes, aliphatic-aromatic polyesters, biobased polymers, Cyrene™.

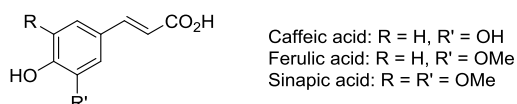
ABSTRACT. Green synthesis of renewable alternatives to fossil fuel-based (macro)molecules/polymers is more than ever a necessity. We recently developed a sustainable pathway to produce 6-hydroxy-5,7-dimethoxy-2-naphthoic acid (DMNA), which resembles the fossil-derived 6-hydroxy-2-naphthoic acid, from sinapic acid. To investigate the potential of DMNA as a building block for polymer syntheses, three novel DMNA-derived  $\alpha,\omega$ -dienes (M1-M3) were synthesized and engaged in acyclic-diene metathesis (ADMET) polymerization in a three-step study to prepare renewable aliphatic-aromatic polyesters (P1-P3). The first step aimed

to evaluate the activity of seven commercial metathesis catalysts for the solvent-free ADMET polymerization of M3. Although most of the studied catalysts exhibited good reactivity, 2<sup>nd</sup> generation Hoveyda-Grubbs catalyst (C4) proved the best. The second step was then started by varying the catalyst loading and testing M1 and M2 toward ADMET polymerization. Aliphatic-aromatic polyesters with number-average molecular weight ( $M_n$ ) up to 19.4 kDa ( $D = 1.88$ ) were obtained. Furthermore, the results showed that the properties can be finely tuned depending on the monomer and catalyst loading. Thermal analysis demonstrated that glass transition temperature ( $T_g$ ) and temperature at which 5% of the mass is lost ( $T_{d5\%}$ ) varied depending on the alkene chain length. A general thermal trend was established:  $T_g(P1) > T_g(P2) > T_g(P3)$  and  $T_{d5\%}(P1) < T_{d5\%}(P2) < T_{d5\%}(P3)$ . The third step of the ADMET study was to evaluate the tolerance of M1-M3 and C4 toward Cyrene<sup>TM</sup>, a green and high boiling point solvent derived from cellulose. The results revealed that Cyrene<sup>TM</sup> merits further investigation as a “general” non-toxic solvent for ADMET polymerization of other monomers, particularly those with high melting points.

## INTRODUCTION

The sustainability of polymer production can be primarily achieved on the basis of three items: (i) the renewability of raw materials, (ii) the greenness of polymerization processes, and (iii) the use of green solvents.<sup>1,2</sup> Regarding item (i), one of the current challenges to preserving nature while meeting our needs is the replacement of petroleum-based monomers such as phenol and its derivatives, which are used daily by the polymer industry, with new carbon-neutral alternatives.<sup>3</sup> Indeed, most of the wastes generated by the agri-food industries (*e.g.*, bunches, seeds, wood and bagasse) are rich in phenolic derivatives<sup>4</sup> such as *p*-hydroxycinnamic acids (*p*-HCA): caffeic,

ferulic and sinapic acids (Figure 1).<sup>5</sup> These three natural phenolic acids differ according to the nature of R and R' substituents on positions 3 and 5 of the aryl ring, as shown in Figure 1. To achieve item (ii), the green assessment of the production processes of monomers and polymers derived from ferulic, sinapic and caffeic acids (and more generally from lignin) has been studied recently.<sup>2</sup>

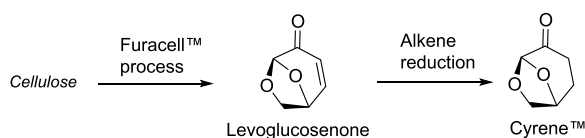


**Figure 1.** General structure of *p*-hydroxycinnamic acids

The transition to industrial production of renewable materials requires polymers that can compete with their fossil fuel-based counterparts in terms of properties. In this context, aliphatic-aromatic polyesters are polymers that are distinguished by their combination of excellent thermomechanical properties and biodegradability.<sup>6,7</sup> The presence of rigid rings in the main chains provides the polymer with thermal stability and strength, while the flexible linear units facilitate (bio)degradation.<sup>8</sup> Nevertheless, the significant presence of aromatic rings above a certain threshold can decrease or even prevent biodegradability.<sup>6</sup> Among the existing methods (*e.g.*, polycondensation<sup>9-12</sup> and ring-opening polymerization<sup>13-16</sup>) used to produce aliphatic-aromatic polyesters, acyclic-diene metathesis (ADMET) polymerization can be considered a unique strategy<sup>17</sup> as the monomer design can be finely-tuned, and the controlled ADMET polymerization of the designed monomers leads to polymers with precise control of the structures.<sup>17</sup> For example, straightforward synthesis of  $\alpha,\omega$ -diene monomer of ferulic acid followed by ADMET polymerization with diene monomers from oleic and erucic acid was reported by Meier *et al.*<sup>18</sup> The same research group used vanillin and fatty acids as renewable

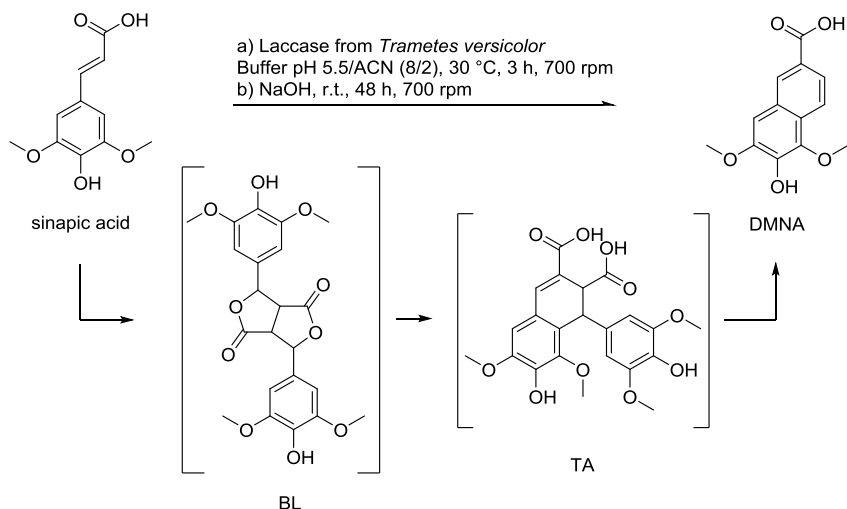
starting molecules to prepare monomers for ADMET polymerization.<sup>19</sup> Polymers with higher molecular weights (up to 50 kDa) – when compared to thiol-ene addition and polycondensation reactions of the same monomers – were isolated.<sup>19</sup> Using a chemo-enzymatic route, Allais *et al.* prepared six renewable  $\alpha,\omega$ -dienes dimers derived from ferulic acid that contain biobased diols (isosorbide<sup>20</sup> and butanediol) as linkers.<sup>21</sup> The glass transition temperature ( $T_g$ ) of the highly thermally stable polymers was tuned as a function of the diol and alkene chain length in the  $\alpha,\omega$ -diene monomers.<sup>21</sup> The same authors - also using a chemo-enzymatic pathway - synthesized  $\alpha,\omega$ -diene monomers based on syringaresinol in very good yields (71-78% depending on the targeted monomer) for ADMET polymerization.<sup>22</sup> Cramail *et al.* adopted an enzyme-catalyzed dimerization to obtain four bisphenols derived from vanillin or eugenol.<sup>23</sup> The ADMET polymerization was performed in a green solvent (polarclean) due to the high melting temperature of the monomers (over 80 °C) which can deteriorate the stability of the metathesis catalyst.<sup>23</sup> Indeed, the use of a solvent is sometimes unavoidable, which requires the selection of sustainable alternatives.<sup>1,2</sup> And here comes the aforementioned item (iii) which is the use of green solvents. Cyrene™ is a cellulose-derived compound that is readily prepared through the reduction of the  $\alpha,\beta$ -unsaturation of levoglucosenone (LGO) (Scheme 1), a rapidly emerging renewable platform molecule obtained from cellulose.<sup>24,25</sup> It is noteworthy to mention that Cyrene™ is REACH-compliant and thus recognized as a safe solvent. Since its first report in the literature, several published works have demonstrated the great potential of Cyrene™ as a sustainable alternative to toxic polar solvents, *e.g.* NMP, in many applications,<sup>26</sup> such as liquid/liquid and liquid/solid extractions,<sup>27,28</sup> multilayer graphene production,<sup>29</sup> metal-organic frameworks (MOF) synthesis,<sup>30</sup> amidification,<sup>31,32</sup> enzymatic reduction of  $\alpha$ -ketoesters,<sup>33</sup> biomimetic radical coupling,<sup>34</sup> polymerization,<sup>35,36</sup> or membrane synthesis.<sup>37</sup> We recently showed

the potential of Cyrene™ not only as a renewable solvent for ring-opening metathesis polymerization (ROMP) reactions, but also as a suitable medium to control the activity of highly active catalysts such as Hoveyda-Grubbs catalysts.<sup>35</sup> Nonetheless, to the best of our knowledge, no report has been published on the ability of Cyrene™ to conduct ADMET polymerization.



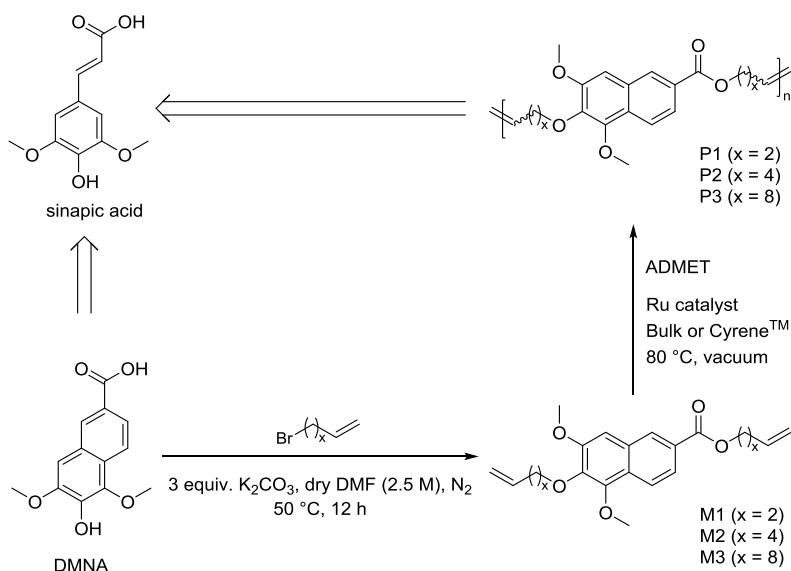
**Scheme 1.** Synthesis of Cyrene™ from cellulose

Considering the aforementioned three sustainability items (i, ii and iii), and our experience in the development and valorization of biobased phenols, we reported very recently a sustainable synthesis of 6-hydroxy-5,7-dimethoxy-2-naphthoic acid (DMNA) from sinapic acid at gram scale, through a one-pot two-step chemo-enzymatic process (Scheme 2).<sup>38</sup> Indeed, a green and preparative scale synthesis of DMNA was sought for the following two reasons. First, before our study, the synthesis of DMNA had only been performed on mg scale: 0.14 mg (64% yield) by Cai *et al.*<sup>39</sup> and 14 mg (27% yield) by Bunzel *et al.*<sup>40</sup> using multi-step reactions that employ hazardous reagents and generate a huge amount of waste. Second, DMNA resembles the fossil fuel-derived 6-hydroxy-2-naphthoic acid (NA) which is commonly used for the production of the high-value liquid crystal polymer Vectra®;<sup>41–43</sup> thus, we thought that DMNA could be a potential renewable building block for biobased materials. As shown in Scheme 3, the proposed process involves (a) a laccase-mediated dimerization of sinapic acid, and (b) a sodium hydroxide treatment at room temperature to produce DMNA *via* the intermediate formation of bislactone (BL) and thomasidioic acid (TA).<sup>33</sup> The transformation of BL to TA has been described previously under acidic or alkaline conditions.<sup>44–46</sup>



**Scheme 2.** Sustainable one-pot two-step synthesis of DMNA from sinapic acid

In the present work, new  $\alpha,\omega$ -diene monomers (M1-M3) with three different chain lengths were designed from DMNA as shown in Scheme 3. ADMET polymerization of M1-M3 was then performed in bulk and using the green solvent Cyrene<sup>TM</sup>. The structures and thermal properties of the new DMNA-based polymers were also investigated.



**Scheme 3.** Synthesis of the DMNA-derived monomers (M1-M3) and polymers (P1-P3)

described in this work

## EXPERIMENTAL

### Chemical and reagents

Cyrene was graciously provided by Circa group. Syringaldehyde, 10-bromodec-1-ene, proline, aniline, pyridine, malonic acid, Laccase from *Trametes versicolor* were purchased from Sigma Aldrich (Merck). 4-bromobut-1-ene was purchased from Acros Organics. 6-bromohex-1-ene and 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid (ABTS) were purchased from TCI. All catalysts were purchased from Sigma Aldrich (Merck) including: Grubbs Catalyst 1<sup>st</sup> generation (C1), Grubbs Catalyst 2<sup>nd</sup> generation (C2), dichloro[1,3-Bis(2-methylphenyl)-2-imidazolidinylidene](benzylidene)(tricyclohexylphosphine) ruthenium(II) (Grubbs Catalyst® M205) (C3), Hoveyda-Grubbs Catalyst 2<sup>nd</sup> generation (C4), dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene][[5-[(dimethylamino)sulfonyl]-2-(1-methylethoxy-O)phenyl]methylene-C] ruthenium(II) (Zhan Catalyst-1B) (C5), dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]{[2-(1-methylacetoxymethyl)phenyl]methylene} ruthenium(II) (Grubbs Catalyst® M510) (C6), Grubbs Catalyst 3<sup>rd</sup> Generation (C7). HPLC grade solvents were purchased from Thermofisher Scientific and used as received. NMR solvents including CDCl<sub>3</sub> and acetone-*d*<sub>6</sub> were purchased from Sigma and Eurisotop, respectively. Dimethylformamide (DMF) was dried in a MBRAUN-SPS-800. All chemicals were used directly without purification. Ultra-pure laboratory-grade water was obtained from MilliQ, 18.2 megaOhms. TLC analyses were performed on an aluminum strip coated with Silica Gel 60 F254 from Merck, revealed under UV-light (254 nm) then in presence of potassium permanganate staining solution. All manipulations with air-sensitive chemicals and reagents were performed using standard Schlenk techniques on a dual-manifold line, on a high-vacuum line.

## Characterization

*Nuclear Magnetic Resonance (NMR) spectroscopy.*  $^1\text{H}$  NMR spectra were recorded on a Bruker Fourier 300 (300 MHz) and were calibrated with residual acetone- $d_6$  signal at  $\delta$  2.05 and  $\text{CDCl}_3$  residual signal at 7.26 ppm. Data are reported as follows: chemical shift ( $\delta$  ppm), multiplicity, coupling constant (Hz), integration and assignment.  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Fourier 300 (75 MHz) and were calibrated with acetone- $d_6$  at  $\delta$  29.84 and  $\text{CDCl}_3$  at  $\delta$  77.16 ppm. All NMR assignments were also made using  $^1\text{H}$ - $^1\text{H}$  COSY,  $^1\text{H}$ - $^{13}\text{C}$  HMBC and  $^1\text{H}$ - $^{13}\text{C}$  HSQC spectra.

*Chromatographic purification* was accomplished by using a flash-prep LC system puriFlash® 4100 from Interchim with prepacked silica column (30  $\mu\text{m}$ , Interchim PF-Si30-HP), dual-wavelength collection ( $\lambda = 254$  and 320 nm) and a mixture of cyclohexane/ethyl acetate as eluant (sometimes acetic acid).

*Size exclusion chromatography (SEC)* was performed at 50  $^\circ\text{C}$  using an Agilent Technologies 1260 Infinity Series liquid chromatography system with an internal differential refractive index detector and two PLgel columns (5  $\mu\text{m}$  MIXED-D 300 x 7.5 mm) using HPLC grade THF as the mobile phase at a flow rate of 1.0 mL/min. Calibration was performed with polystyrene standards from Agilent Technologies.

*Thermogravimetric Analysis (TGA)* was measured with a TGA Q500 (TA Instruments). Typically,  $\sim 2$  mg of each sample was equilibrated at 50  $^\circ\text{C}$  for 30 min and was flushed with highly pure nitrogen gas. All the experiments were performed with a heating rate of 10  $^\circ\text{C}/\text{min}$  up to 600  $^\circ\text{C}$ . The reported values  $T_{d5\%}$  and  $T_{d50\%}$  represent the temperature at which 5% and 50% of the mass is lost, respectively.

*Differential Scanning Calorimetry (DSC)* was performed with a DSC Q20 (TA Instruments). Typically, ~8 mg sample was placed in a sealed pan, flushed with highly pure nitrogen gas and passed through a heat-cool-heat cycle at 10 °C/min in a temperature range of -80 °C to 100 °C. Three heat/cool cycles were done for each sample, where the last two cycles were dedicated to analyzing the heat flow of the sample after being cooled in controlled conditions. The  $T_g$  values recorded herein are those obtained from the third cycle. No melting temperature ( $T_m$ ) or any other thermal transitions were found above 100°C. For this reason, 100°C was set as the maximum temperature for all measurements

*Fourier-transform infrared spectroscopy (FTIR)* was recorded on a Cary 630 FTIR Spectrometer by Agilent.

*HPLC analysis* were carried out on a Dionex UltiMate 3000 equipped with a Accucore C18 AQ column (THERMOFISHER)(2.1 x 50 mm x 1.8 µm), a DAD at  $\lambda = 320, 254$  and 210 nm.

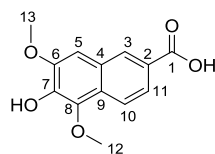
### **Laccase activity assay**

In a 12-well microplate, 1300 µL of tartaric buffer (pH 4.0) and 150 µL of laccase solution in water (0.5 mg.L<sup>-1</sup>) or 150 µL of water (for blank) were incubated at 30 °C, then 50 µL of ABTS solution in water (5 mmol.L<sup>-1</sup>) were introduced. Absorbance at 405 nm was recorded every 8 seconds for 5 min using an EPOCH2 microplate reader (Biotek). All measurements were performed in triplicate. Laccase activity was determined as 4.2 U.mg<sup>-1</sup> (µmol.min<sup>-1</sup>.mg<sup>-1</sup>) using Equation 1.

(1)  $a = \text{slope of ABTS concentration in function of time (}\mu\text{mol.L}^{-1}\text{)} / \text{Enzymatic concentration (mg.L}^{-1}\text{)}$

## Synthesis of 6-hydroxy-5,7-dimethoxy-2-napthoic acid (DMNA)

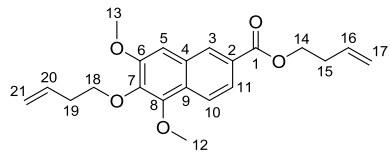
6.05 g of SA (27 mmol) were suspended in 30 mL of acetonitrile, then 110 mL of pH 5.5 buffer was added and the reaction was heated up at 30 °C and stirred at 700 rpm. 32 mg of laccase from *Trametes versicolor* (13.5 U) was dissolved in 10 mL of buffer and added to the medium. After 3 h, 45 mL of 3.5 M NaOH solution was added. After 50 h, reaction media was acidified with conc. sulfuric acid to pH 3, and a precipitate appeared. After 2 h, the precipitate was filtered, washed with deionized water and dried to afford DMNA as a pale-yellow solid (1.54 g, 6.2 mmol, 46%).



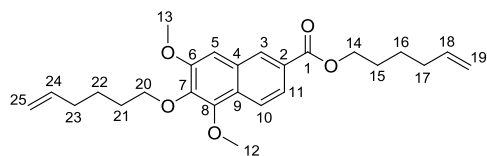
m.p. 228 °C.  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta_{\text{H}}$  (ppm): 8.48 (d,  $J = 1.7$  Hz, 1H, H<sub>3</sub>), 8.01 (d,  $J = 8.7$  Hz, 1H, H<sub>10</sub>), 7.91 (dd,  $J = 8.7$  and 1.7 Hz, 1H, H<sub>11</sub>), 7.32 (s, 1H, H<sub>5</sub>), 4.02 (s, 3H, H<sub>13</sub>), 3.99 (s, 3H, H<sub>12</sub>).  $^{13}\text{C}$  NMR (acetone- $d_6$ )  $\delta_{\text{C}}$  (ppm): 168.0 (C<sub>1</sub>), 150.9 (C<sub>6</sub>), 141.3 (C<sub>8</sub>), 141.1 (C<sub>9</sub>), 130.6 (C<sub>3</sub>), 128.2 (C<sub>4</sub>), 127.8 (C<sub>2</sub>), 126.7 (C<sub>7</sub>), 124.2 (C<sub>11</sub>), 121.6 (C<sub>10</sub>), 104.1 (C<sub>5</sub>), 60.9 (C<sub>12</sub>), 56.4 (C<sub>13</sub>).

## Monomers syntheses

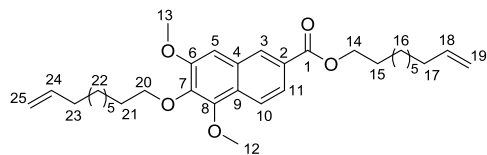
DMNA (1 equiv.) and K<sub>2</sub>CO<sub>3</sub> (3 equiv.) were dissolved in dry DMF (C = 2.5 M) under nitrogen. Bromo-alkene (2.1 equiv.) was then added, and the mixture was stirred and heated at 50 °C for 12 h. Reaction was quenched with water ( $v_{\text{water}} = v_{\text{DMF}}$ ) and the aqueous layer was extracted three times with ethyl acetate (3  $v_{\text{water}}$ ). Organic layers were combined, washed with brine, dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated. Crude product was purified by flash chromatography on silica gel (cyclohexane:AcOEt = 90:10).



A brown viscous oil was obtained (60%).  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta_{\text{H}}$  (ppm): 7.95 (s, 1H, H<sub>3</sub>), 7.53 (d,  $J = 8.7$  Hz, 1H, H<sub>10</sub>), 7.38 (dd,  $J = 8.8, 1.6$  Hz, 1H, H<sub>11</sub>), 6.78 (s, 1H, H<sub>5</sub>), 5.45 (m, 2H, H<sub>16</sub> and H<sub>20</sub>), 4.68 (m, 2H, H<sub>17</sub>), 4.57 (m, 2H, H<sub>21</sub>), 3.88 (t,  $J = 6.7$  Hz, 2H, H<sub>14</sub>), 3.63 (t,  $J = 6.7$  Hz, 2H, H<sub>18</sub>), 3.51 (s, 3H, H<sub>13</sub>), 3.47 (s, 3H, H<sub>12</sub>).  $^{13}\text{C}$  NMR (acetone- $d_6$ )  $\delta_{\text{C}}$  (ppm): 166.9 (C<sub>1</sub>), 156.5 (C<sub>6</sub>), 148.7 (C<sub>8</sub>), 143.8 (C<sub>7</sub>), 136.0 (C<sub>16</sub>), 135.4 (C<sub>20</sub>), 132.0 (C<sub>4</sub>), 130.0 (C<sub>3</sub>), 128.1 (C<sub>2</sub>), 127.4 (C<sub>9</sub>), 123.6 (C<sub>10</sub>), 122.6 (C<sub>11</sub>), 117.6 (C<sub>17</sub>), 116.9 (C<sub>21</sub>), 104.7 (C<sub>5</sub>), 73.5 (C<sub>18</sub>), 64.5 (C<sub>14</sub>), 61.8 (C<sub>12</sub>), 56.3 (C<sub>13</sub>), 35.4 (C<sub>19</sub>), 33.9 (C<sub>15</sub>).



A viscous oil was obtained (48%).  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta_{\text{H}}$  (ppm): 8.39 (s, 1H, H<sub>3</sub>), 7.98 (d,  $J = 8.7$  Hz, 1H, H<sub>10</sub>), 7.80 (d,  $J = 8.6$  Hz, 1H, H<sub>11</sub>), 7.22 (s, 1H, H<sub>5</sub>), 5.74 (m, 2H, H<sub>18</sub> and H<sub>24</sub>), 4.96 (m, 2H, H<sub>19</sub>), 4.86 (m, 2H, H<sub>25</sub>), 4.26 (t,  $J = 6.6$  Hz, 2H, H<sub>14</sub>), 4.02 (t,  $J = 6.3$  Hz, 2H, H<sub>20</sub>), 3.94 (s, 3H, H<sub>13</sub>), 3.90 (s, 3H, H<sub>12</sub>), 3.78 (m, 2H, H<sub>15</sub>), 1.82-1.39 (m, 10H, H<sub>17</sub>, H<sub>23</sub>, H<sub>21</sub>, H<sub>16</sub> and H<sub>22</sub>).  $^{13}\text{C}$  NMR (acetone- $d_6$ )  $\delta_{\text{C}}$  (ppm): 166.9 (C<sub>1</sub>), 155.0 (C<sub>6</sub>), 148.0 (C<sub>8</sub>), 143.0 (C<sub>7</sub>), 139.4 (C<sub>18</sub>), 139.0 (C<sub>24</sub>), 130.9 (C<sub>4</sub>), 130.0 (C<sub>3</sub>), 128.2 (C<sub>2</sub>), 127.4 (C<sub>9</sub>), 123.6 (C<sub>10</sub>), 122.6 (C<sub>11</sub>), 115.1 (C<sub>19</sub>), 114.2 (C<sub>25</sub>), 104.1 (C<sub>5</sub>), 73.9 (C<sub>20</sub>), 65.3 (C<sub>14</sub>), 61.8 (C<sub>12</sub>), 56.2 (C<sub>13</sub>), 34.1-33.9 (C<sub>21</sub>, C<sub>15</sub>, C<sub>16</sub> and C<sub>22</sub>), 26.0-25.9 (C<sub>17</sub> and C<sub>23</sub>).



A viscous oil was obtained (57%):  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta_{\text{H}}$  (ppm): 8.46 (s, 1H, H<sub>3</sub>), 7.99 (m, 1H, H<sub>10</sub>), 7.91 (d,  $J = 8.7$  Hz, 1H, H<sub>11</sub>), 7.31 (s, 1H, H<sub>5</sub>),

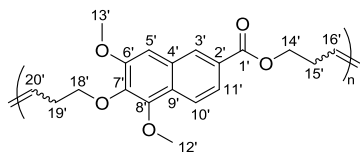
5.81 (m, 2H, H<sub>18</sub> and H<sub>24</sub>), 5.04 (m, 2H, H<sub>19</sub>), 4.82 (m, 2H, H<sub>25</sub>), 4.35 (m, 2H, H<sub>14</sub>), 4.18 (t,  $J = 6.4$  Hz, 1H, H<sub>20</sub>), 4.02 (s, 3H, H<sub>13</sub>), 3.99 (s, 3H, H<sub>12</sub>), 3.87 (s, 3H, H<sub>15</sub>), 1.80 (m, 4H, H<sub>17</sub> and H<sub>23</sub>), 1.36 (m, 26H, H<sub>21</sub>, H<sub>16</sub> and H<sub>22</sub>). <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>)  $\delta_C$  (ppm): 169.5 (C<sub>1</sub>), 154.4 (C<sub>6</sub>), 151.1 (C<sub>8</sub>), 141.5 (C<sub>7</sub>), 140.4 (C<sub>18</sub>), 140.1 (C<sub>24</sub>), 130.4 (C<sub>4</sub>), 128.4 (C<sub>3</sub>), 128.0 (C<sub>2</sub>), 126.9 (C<sub>9</sub>), 122.1 (C<sub>10</sub>), 121.8 (C<sub>11</sub>), 114.8 (C<sub>19</sub> and C<sub>25</sub>), 104.3 (C<sub>5</sub>), 74.4 (C<sub>20</sub>), 65.6 (C<sub>14</sub>), 61.1 (C<sub>12</sub>), 56.6 (C<sub>13</sub>), 34.7 (C<sub>21</sub>, C<sub>15</sub> and C<sub>16</sub>), 27.0 (C<sub>17</sub> and C<sub>23</sub>).

## Polymer Syntheses

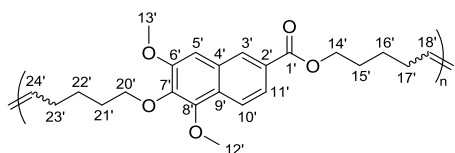
*Solvent-free polymerization:* Monomer (1 equiv.) and *p*-benzoquinone (3 equiv. relative to the catalyst) were stirred at 80 °C, under vacuum for 5 min. Catalyst (0.1-10 mol%) was added and the reaction was continued, under vacuum for a predetermined time. The reaction was quenched with a solution of THF/ethyl vinyl ether (9:1). The crude product was reprecipitated in cold methanol. Separation of the precipitated product was done based on the state of the polymer formed. For viscous-sticky P2 and P3, the product was clinging to the bottom of the Erlenmeyer flask. To remove the polymer, a minimum amount of low-boiling solvent (acetone or CH<sub>2</sub>Cl<sub>2</sub>) was used to recover the product. This was followed by evaporation of the recovery solvent and drying of the polymer product under vacuum for 24 h. In the case of the solid P1, after reprecipitation in cold methanol, the purified polymer was filtered, collected on the filter paper and dried under vacuum for 24 h.

*Solution polymerization:* Monomer (1 equiv.) and *p*-benzoquinone (3 equiv. relative to the catalyst) were dissolved in Cyrene™ (2 and 4 mol.L<sup>-1</sup>) at room temperature under N<sub>2</sub>. Catalyst (1 or 5 mol%) was added and the reaction was continued, under vacuum at 80 °C for a predetermined time. The reaction was quenched with a solution of THF/ethyl vinyl ether (9:1).

The crude product was reprecipitated in cold methanol. The purified polymer was isolated as described above for the solution-free polymerization.



A brown powder was obtained.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta_{\text{H}}$  (ppm): 8.41 (d,  $J = 11.8$  Hz, 1H,  $\text{H}_{10'}$ ), 8.03 (t,  $J = 8.9$  Hz, 1H,  $\text{H}_{3'}$ ), 7.91 (t,  $J = 9.0$  Hz,  $\text{H}_{11'}$ ), 7.01 (d,  $J = 7.5$  Hz, 1H,  $\text{H}_{5'}$ ), 5.71 (m, 2H,  $\text{H}_{16'}$  and  $\text{H}_{20'}$ ), 4.36 (m, 2H,  $\text{H}_{14'}$ ), 4.14 (t,  $J = 6.9$  Hz, 2H,  $\text{H}_{18'}$ ), 4.01 (s, 3H,  $\text{H}_{13'}$ ), 3.94 (s, 3H,  $\text{H}_{12'}$ ), 2.57 (m, 4H,  $\text{H}_{19'}$  and  $\text{H}_{15'}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta_{\text{C}}$  (ppm): 167.0 ( $\text{C}_{1'}$ ), 153.8 ( $\text{C}_{6'}$ ), 148.1 ( $\text{C}_{8'}$ ), 142.0 ( $\text{C}_{7'}$ ), 130.0 ( $\text{C}_{4'}$ ), 129.9 ( $\text{C}_{10'}$ ), 129.4 ( $\text{C}_{16'}$  and  $\text{C}_{20'}$ ), 127.3 ( $\text{C}_{2'}$ ), 123.3 ( $\text{C}_{11'}$ ), 122.0 ( $\text{C}_{3'}$ ), 103.7 ( $\text{C}_{5'}$ ), 73.5 ( $\text{C}_{18'}$ ), 64.5 ( $\text{C}_{14'}$ ), 61.6 ( $\text{C}_{13'}$ ), 56.0 ( $\text{C}_{12'}$ ), 33.7 ( $\text{C}_{19'}$ ), 32.3 ( $\text{C}_{15'}$ ).



A brown viscous oil was obtained.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta_{\text{H}}$  (ppm): 8.36 (s, 1H,  $\text{H}_{10'}$ ), 7.96 (d,  $J = 8.4$  Hz, 1H,  $\text{H}_{3'}$ ), 7.85 (d,  $J = 8.4$  Hz, 1H,  $\text{H}_{11'}$ ), 6.98 (s, 1H,  $\text{H}_{5'}$ ), 5.42 (m, 2H,  $\text{H}_{18'}$  and  $\text{H}_{24'}$ ), 4.28 (m, 2H,  $\text{H}_{14'}$ ), 4.03 (m, 2H,  $\text{H}_{20'}$ ), 3.94 (s, 3H,  $\text{H}_{13'}$ ), 3.89 (s, 3H,  $\text{H}_{12'}$ ), 3.78 (m, 2H,  $\text{H}_{15'}$ ), 3.22 (m, 10H,  $\text{H}_{17'}$ ,  $\text{H}_{23'}$ ,  $\text{H}_{21'}$ ,  $\text{H}_{16'}$  and  $\text{H}_{22'}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta_{\text{C}}$  (ppm): 167.1 ( $\text{C}_{1'}$ ), 153.7 ( $\text{C}_{6'}$ ), 147.9 ( $\text{C}_{8'}$ ), 142.0 ( $\text{C}_{7'}$ ), 131.5 ( $\text{C}_{24'}$ ), 129.8 ( $\text{C}_{18'}$ ), 129.8 ( $\text{C}_{4'}$ ), 129.3 ( $\text{C}_{3'}$ ), 127.9 ( $\text{C}_{2'}$ ), 123.1 ( $\text{C}_{9'}$ ), 121.8 ( $\text{C}_{10'}$ ), 106.6 ( $\text{C}_{11'}$ ), 103.6 ( $\text{C}_{5'}$ ), 73.80 ( $\text{C}_{20'}$ ), 65.1 ( $\text{C}_{14'}$ ), 61.5 ( $\text{C}_{12'}$ ), 55.8 ( $\text{C}_{13'}$ ), 32.2 ( $\text{C}_{17'}$  and  $\text{C}_{23'}$ ), 29.6 ( $\text{C}_{21'}$ ), 28.2 ( $\text{C}_{15'}$ ), 25.9 ( $\text{C}_{16'}$

and  $\text{C}_{22'}$ ).

A brown viscous oil was obtained.  $^1\text{H}$  NMR

(acetone- $d_6$ )  $\delta_H$  (ppm): 8.41 (s, 1H, H<sub>3'</sub>), 7.99 (m, 1H, H<sub>10'</sub>), 7.89 (d,  $J = 8.7$  Hz, 1H, H<sub>11'</sub>), 7.29 (s, 1H, H<sub>5'</sub>), 5.38 (m, 2H, H<sub>18'</sub> and H<sub>24'</sub>), 4.32 (m, 2H, H<sub>14'</sub>), 4.14 (m, 1H, H<sub>20'</sub>), 4.01 (s, 3H, H<sub>13'</sub>), 3.98 (s, 3H, H<sub>12'</sub>), 3.87 (s, 3H, H<sub>15'</sub>), 1.95 (m, 4H, H<sub>17'</sub> and H<sub>23</sub>), 1.76-1.32 (m, 23H, H<sub>21'</sub>, H<sub>16'</sub> and H<sub>22'</sub>). <sup>13</sup>C NMR (acetone- $d_6$ )  $\delta_C$  (ppm): 167.1 (C<sub>1'</sub>), 151.0 (C<sub>7'</sub>), 141.4 (C<sub>8'</sub>), 141.2 (C<sub>6'</sub>), 131.2 (C<sub>18'</sub> and C<sub>24'</sub>), 130.3 (C<sub>4'</sub>), 128.3 (C<sub>3'</sub>), 127.9 (C<sub>2'</sub>), 126.8 (C<sub>9'</sub>), 124.0 (C<sub>10'</sub>), 121.7 (C<sub>11'</sub>), 104.2 (C<sub>5'</sub>), 74.3 (C<sub>14'</sub>), 65.5 (C<sub>20'</sub>), 61.9 (C<sub>15'</sub>), 61.0 (C<sub>12'</sub>) 56.6 (C<sub>13'</sub>), 33.3 (C<sub>17'</sub> and C<sub>23'</sub>), 26.9 (C<sub>21'</sub>, C<sub>16'</sub> and C<sub>22'</sub>).

## RESULTS AND DISCUSSION

### Synthesis of sinapic acid-derived $\alpha,\omega$ -dienes

DMNA was first synthesized from sinapic acid using the chemo-enzymatic procedure described previously (Scheme 2). Three commercially available bromoalkenes (4-bromobut-1-ene, 6-bromohex-1-ene, and 10-bromodec-1-ene) were chosen to prepare  $\alpha,\omega$ -diene monomers (M1-M3 in Scheme 3) and to study the dependence of polymers' rigidity and thermal properties on the alkene chain length. M1-M3 were prepared in anhydrous dimethylformamide (DMF) in the presence of K<sub>2</sub>CO<sub>3</sub> at 50 °C according to the procedure reported by Allais *et al.*<sup>21</sup> After 12 h, the resulting products were purified by flash chromatography and characterized by NMR spectroscopy. The characteristic resonances of the terminal olefinic protons of M1, (H<sub>16</sub>, H<sub>20</sub>) and (H<sub>17</sub>, H<sub>21</sub>), appear at 5.45 and 4.62 ppm, respectively. The corresponding resonances of the carbon signals C<sub>16</sub>, C<sub>20</sub>, C<sub>17</sub> and C<sub>21</sub> are also observed at 136.0, 135.4, 117.6 and 116.9 ppm, respectively (ESI, Figure S1). Similarly, the NMR spectra of the purified products of the reactions involving 6-bromohex-1-ene and 10-bromodec-1-ene confirmed the successful

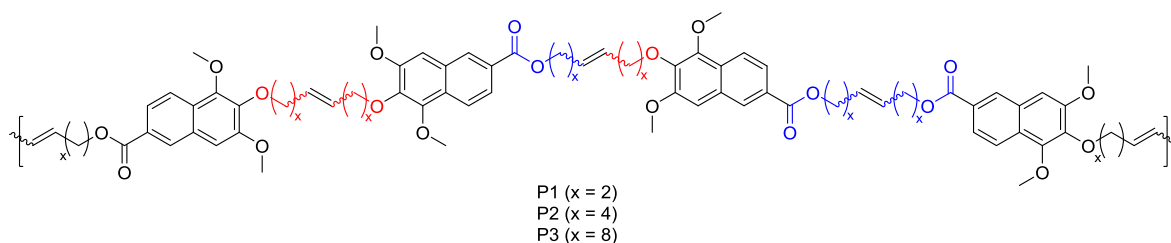
preparation of the corresponding monomers, M2 and M3 (for more information, see Figures S2 and S3 in the ESI).

### **ADMET polymerization: catalyst screening**

The reactivity of seven Ru-based metathesis catalysts (Figure 2) toward ADMET polymerization of M3 (Figure 3) was first studied. These catalysts were: 1<sup>st</sup> and 2<sup>nd</sup> generation of Grubbs catalysts (C1 and C2), a derivative of C2 with mono-*ortho*-substituted *N*-heterocyclic carbene (NHC) (C3), 2<sup>nd</sup> generation Hoveyda-Grubbs catalyst (C4), Zhan catalyst-1B (C5), another Grubbs type catalyst (C6), and 3<sup>rd</sup> generation of Grubbs catalysts (C7). These catalysts are the most commonly used Ru catalysts in metathesis transformations. In particular, C1, C2, C4 and C7 catalysts are more widely used due to their versatility and robustness. In addition, metathesis reactions using these catalysts can generally be carried out in the presence of various functional groups such as carbonyls, aromatic rings and alcohols.<sup>47</sup>

The experiments were conducted in bulk at 80 °C under vacuum using a Schlenk tube in the presence of 1 mol% Ru catalysts and 1,4-benzoquinone (3 equiv. based on the catalyst) (ESI, Table S1). A vacuum was applied to completely remove the formed ethylene and shift the equilibrium towards polymerization. Also, benzoquinones are additives used to suppress double bond isomerization,<sup>48</sup> a well-known side reaction that occurs on terminal alkene substrates in the presence of Ru-based olefin metathesis catalysts.<sup>49</sup> <sup>1</sup>H NMR of crude reaction samples was first measured to determine the conversion. The results revealed that having a less bulky NHC (coordinated by Ru, C3) had a detrimental effect on the conversion of M3. Indeed, except for C3 which only reached 50% conversion after 48 h (ESI, Table S1, run 3), full conversion (> 99%)

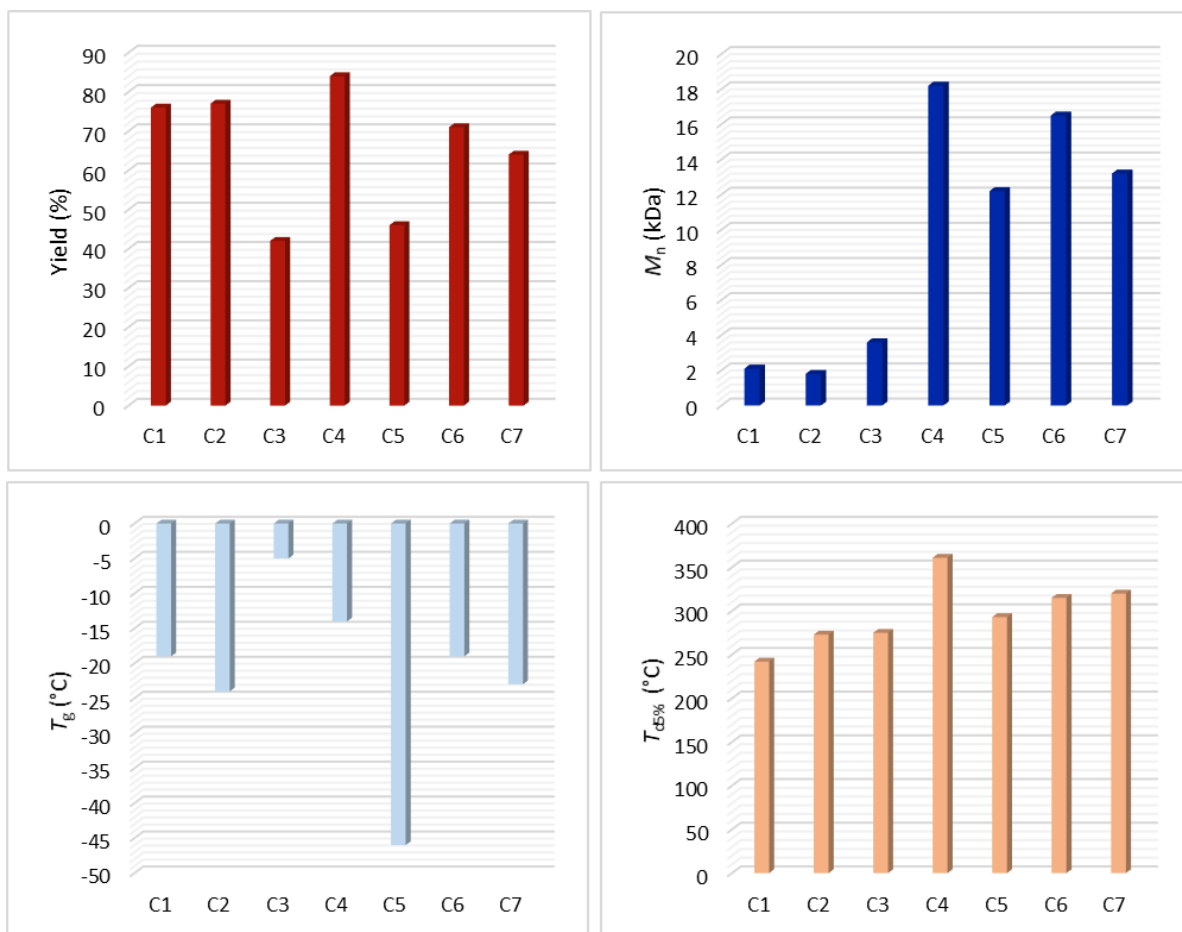
was observed in all cases after 4 h. Furthermore, no monomer isomerization and ring-closing metathesis (RCM) of the monomer and formed oligomers/polymers were detected by NMR analyses regardless of the catalyst used, even in the presence of C3 which is known to be an efficient catalyst for RCM. This is probably due to the higher tendency of the terminal olefins of the substituted decene to undergo polymerization rather than RCM. On the other hand, since the DMNA-derived monomers are all asymmetric, each end of the alkene has the potential to react with the same or different olefin chains of another molecule (see Scheme 4, red-red, blue-red, blue-blue). As expected, due to the relatively long distances between the olefinic bonds and functional groups on both sides of the DMNA molecule, no regioselectivity was observed. Such behaviour has already been observed in the literature.<sup>19,21,22</sup> The polymers were precipitated in cold methanol and recovered in good yields. It is important to note that the allyl vinyl ether added to stop/terminate the reaction has deactivated the metathesis catalyst and solubilized it in the liquid phase during purification/precipitation. Thus, the isolated polymers no longer show any trace of the metal catalysts used.



**Scheme 4.** Representation of the connection types of the irregular structure of P1-P3

As shown in Figure 3, although comparative yields were obtained, the highest yield (84%) was attained for the C4-mediated reaction. Furthermore, no more than 46% of the polymer could be recovered when C5 was employed due to the very sticky nature of the precipitated polymer. The formation of aliphatic-aromatic polyesters can be supported by both <sup>1</sup>H and <sup>13</sup>C NMR with the disappearance of resonances ascribed to terminal olefins and the appearance of

peaks assigned to the internal olefins (for more information, see Figures S3 and S6 in the ESI). Size exclusion chromatography (SEC) showed that only four catalysts (C4-C7) led to polymers with unimodal molecular weight distribution and a good number-average molecular weights ( $M_n$ ) up to 18.2 kDa ( $D = 2.03$ ) (Figure 3). On the other hand, when C1-, C2- and C3-catalyzed polymers were analyzed by SEC, results showed multimodal distribution chromatograms (ESI, Figures S7-S9) of short oligomers with  $M_n$  ranging from 1.8 to 3.6 kDa (Figure 3). Nevertheless, the low reactivity of C1 is interesting as it is much cheaper than the other metathesis catalysts. C1 has been reported as an inactive catalyst in ADMET polymerization of short alkene chains-containing monomers due to its tendency to isomerize the double bond followed by cleavage of its labile vinyl bond formed during polymer propagation.<sup>18,23</sup> Such behavior was muted for  $\alpha,\omega$ -dienes monomers having longer aliphatic chains.<sup>23,50</sup>



**Figure 3.** Results of the ADMET polymerizations of M3 performed using ruthenium-based catalysts C1-C7

The thermal properties of the polymers were investigated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). It is known that ADMET polymers formed from  $\alpha,\omega$ -dienes of decene arms lead to negative  $T_g$  (as low as  $-28.4$  °C) due to the flexibility of the long carbon chains.<sup>21</sup> In the present work, a similar trend was observed, while highlighting the effect of the catalyst nature on the  $T_g$  of the polyesters. The results presented in Figure 3 show that there is no obvious trend of the effect of molecular weight on the recorded value of  $T_g$ ; nevertheless, by changing the catalyst, a range of  $T_g$  from  $-46$  °C (C5) to  $-5$  °C (C3) was obtained. Such difference may be due to microstructural variations such as cis/trans ratios in

the polymer chains. On the other hand, TGA showed that long polymers obtained using C4, C6 and C7 have excellent stability. The  $T_{d5\%}$  of the corresponding polymers were 361 °C, 315 °C and 325 °C, respectively. However, a drop in thermal stability of shorter oligomers was observed, e.g.,  $T_{d5\%}$  was decreased to 242 °C for C1-mediated ADMET polymer. Since C4 gave the best results in terms of yield, molecular weights and thermal properties, we decided to fix this catalyst for the rest of the experiments described in this work.

### **ADMET polymerization: monomer and C4-loading screening**

Before testing the tendency of M1 and M2 to undergo ADMET polymerization in the presence of C4, we decided to polymerize M3 using different catalyst loading ranging from 0.1 mol% to 10 mol% for the following reasons. First, to reveal the effect of ruthenium up- and down-loading on the molecular weights and properties of the polymer. Second, to decrease the cost of the reaction by maximizing the ratio of monomer to the expensive C4 catalyst. The results are summarized in Table 1.

Keeping in mind a  $M_n$  of 18.2 kDa ( $\mathcal{D} = 2.03$ ) when 1 mol% of C4 was engaged, with a few exceptions, the first set of experiments (runs 8-12) reveals that  $M_n$  value was affected by the amount of C4 loading. A ruthenium up-loading from 1 mol% to 5 mol% increased  $M_n$  to 19.4 kDa ( $\mathcal{D} = 1.88$ ) (run 11), however, a down-loading to 0.1 mol% decreased  $M_n$  to 13.5 kDa ( $\mathcal{D} = 1.91$ ) (run 8). Nevertheless, looking at run 12 (as well as runs 15, 18) one can observe that, above an upper limit of catalyst loading, a drop of  $M_n$  was recorded. For example, 10 mol% of C4 decreased  $M_n$  to 10.4 kDa ( $\mathcal{D} = 1.87$ ). Interestingly, no significant influence of C4 loading on the thermal properties of P3 was detected as will be discussed later in this work (*vide infra*).

After having optimized the reaction conditions, M1 and M2 monomers were engaged in solvent-free ADMET polymerization (Table 1). Three loadings of C4 were chosen, 0.2 mol%, 1 mol%, and 5 mol%. <sup>1</sup>H NMR spectra of the resulting polymers (P1 and P2, Scheme 3) were recorded (ESI, Figures S4, S5) and confirmed the polymer structure/formation. Resonances ascribed to terminal olefins of the monomers at 5.45 and 4.70-4.55 ppm (M1) and 5.74 and 4.98-4.86 ppm (M2) disappeared. Moreover, the internal olefins of P1 and P2 appeared at 5.71 and 4.42 ppm, respectively. Regardless of the presence of smaller alkene chains in M1 and M2, no evidence of RCM of the monomers and oligomers/polymers was detected by NMR. This is probably due to the ring strain of DMNA aromatic rings which prevented intramolecular ring-closing metathesis. Similar behavior has been reported for ADMET polymers produced from syringaresinol.<sup>22</sup>

**Table 1.** Solvent-free ADMET polymerization of M1-M3 using C4

| Run <sup>a</sup> | Monomer <sup>b</sup> | Catalyst loading (mol%) | Time (h) <sup>c</sup> | Yield (%) <sup>d</sup> | $M_n$ (kDa) <sup>e</sup> | $\bar{D}$ <sup>e</sup> | $T_g$ (°C) <sup>f</sup> | $T_{d5\%}$ (°C) <sup>g</sup> |
|------------------|----------------------|-------------------------|-----------------------|------------------------|--------------------------|------------------------|-------------------------|------------------------------|
| 8                | M3                   | 0.1                     | 2                     | 70                     | 13.5                     | 1.91                   | -22                     | 275                          |
| 9                | M3                   | 0.2                     | 5                     | 69                     | 17.8                     | 1.72                   | -15                     | 348                          |
| 10               | M3                   | 2                       | 1                     | 87                     | 13.8                     | 1.85                   | -21                     | 317                          |
| 11               | M3                   | 5                       | 1                     | 88                     | 19.4                     | 1.88                   | -13                     | 363                          |
| 12               | M3                   | 10                      | 4                     | 80                     | 10.4                     | 1.87                   | -14                     | 344                          |
| 13               | M2                   | 0.2                     | 7                     | 80                     | 5.9                      | 1.83                   | -3                      | 274                          |
| 14               | M2                   | 1                       | 6                     | 73                     | 7.6                      | 2.10                   | -10                     | 274                          |

|    |    |     |   |    |     |      |     |     |
|----|----|-----|---|----|-----|------|-----|-----|
| 15 | M2 | 5   | 4 | 76 | 5.4 | 1.75 | -20 | 285 |
| 16 | M1 | 0.2 | 7 | 78 | 9.6 | 2.23 | 38  | 233 |
| 17 | M1 | 1   | 7 | 80 | 8.9 | 2.08 | 40  | 223 |
| 18 | M1 | 5   | 7 | 68 | 2.8 | 1.19 | 38  | 197 |

<sup>a</sup> Runs 1-7 are reported in Table S1 in ESI, C4 was used as the metathesis catalyst, in bulk (solvent-free), 1,4-benzoquinone (3 equiv. per C4), 80 °C, vacuum ( $10^{-3}$  bar). <sup>b</sup> M1-M3 shown in Scheme 3. <sup>c</sup> Duration required to attain full conversion as determined by <sup>1</sup>H NMR (except for runs 16-18). <sup>d</sup> Isolated yield after purification and drying, yield = (isolated mass/theoretical mass)  $\times$  100. <sup>e</sup> Determined by SEC in DMF (10 mM LiBr) at 50 °C,  $D$  = dispersity. <sup>f</sup> Glass transition temperature determined by DSC, temperature ramp 10 °C/min. <sup>g</sup> TGA degradation temperatures at which 5 % ( $T_{d5\%}$ ) mass loss was observed under nitrogen.

Table 2. Amount of biobased contents in P1-P3

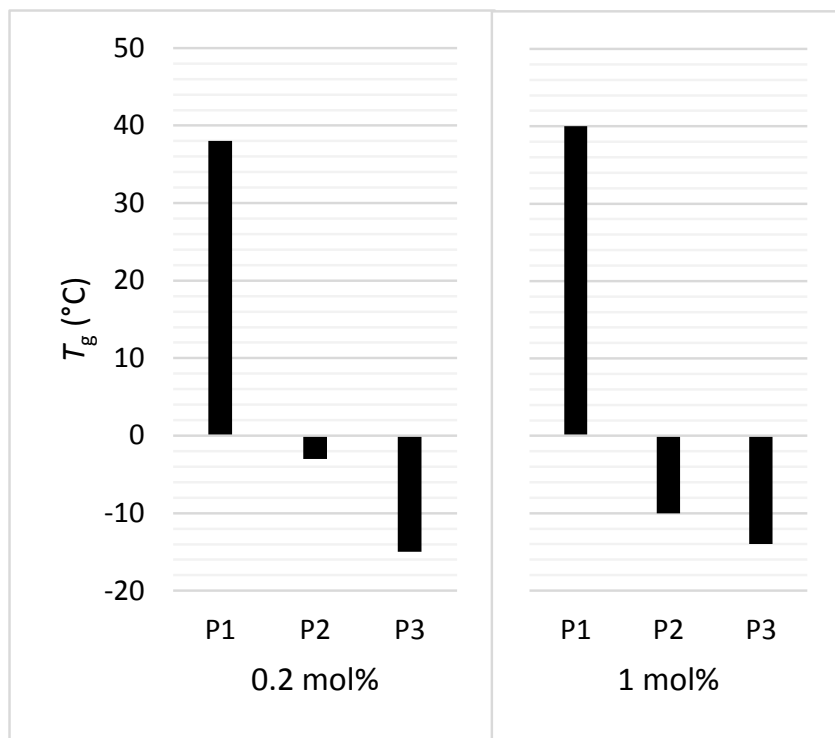
| Biobased content   | Definition   | Calculations <sup>a</sup>             | P1 (%) | P2 (%) | P3 (%) |
|--|--|---------------------------------------|--------|--------|--------|
| <b>Biobased carbon content to total organic carbon (TOC)</b> | Amount of carbon derived from biomass present in the product | $x^{TOC} = 100 \frac{M_A}{M_A + M_B}$ | 61.9   | 52.0   | 39.4   |
| <b>Biobased mass content</b>                                 | Amount of biobased polymer in the product                    | $m = 100 \frac{W_A}{W_A + W_B}$       | 60.1   | 51.09  | 40.8   |

<sup>a</sup>Constituents: A, biobased portion of the polymer; B, fossil-fuel-based portion of the polymer;  $M_A$ , mass of carbon in A constituent;  $M_B$ , mass of carbon in B constituent;  $W_A$ , mass of A constituent;  $W_B$ , mass of B constituent.

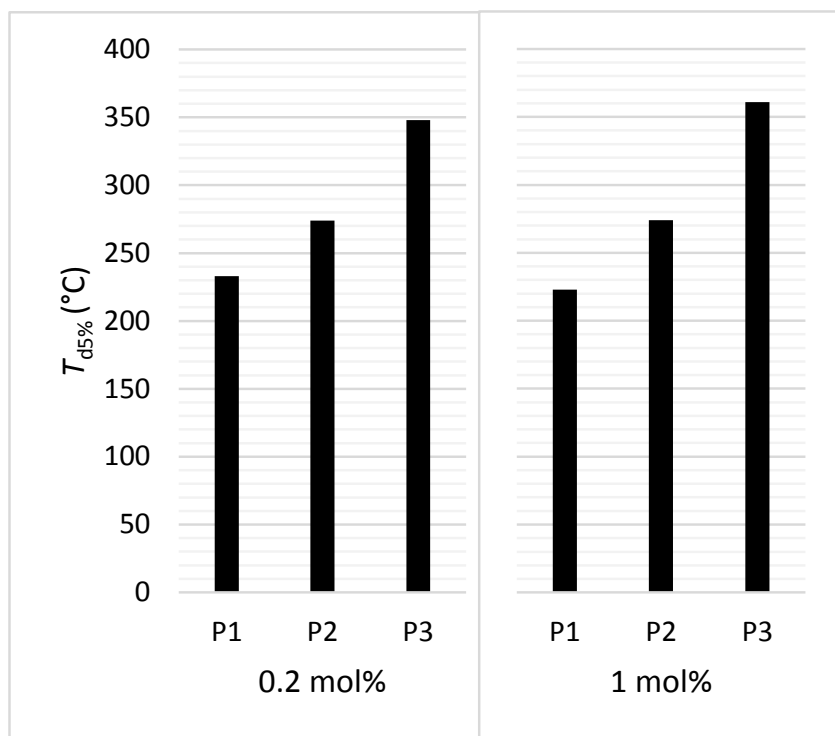
On the other hand, the results revealed that, in general, when switching from M3 (with decene arms) to M1 (with butene arms), the molecular weight was remarkably decreased as a function of monomer and catalyst ratio. For example, if 5 mol% of catalyst is taken as a criterion, a drop of  $M_n$  from 19.4 kDa ( $D = 1.88$ , run 11) to 5.4 kDa ( $D = 1.75$ , run 15) and 2.8 kDa ( $D = 1.19$ , run 18) for M3, M2 and M1, respectively, is observed. Thus, screening of three monomers revealed that longer alkyl lengths between olefins and functional groups improved the polymerization efficiency. This agrees with the work reported by DeBoer et al. on the negative effects of neighboring groups in ADMET polymerization.<sup>51</sup> Indeed, the reactivity of a ruthenium

metathesis catalyst is inversely proportional to the length of the alkene chain, especially when dealing with smaller chains such as allyl. More precisely, catalyst decomposition can occur using these substrates by 1-alkene-triggered decomposition or alcohol-induced degradation. The latter can happen due to the simultaneous coordination of the Ru center to the double bond and oxygens of DMNA-derived monomers. The mechanisms of these types of degradation are reviewed by Trzaskowski *et al.*<sup>52</sup> It is important to note that the biobased carbon content to total organic carbon and the biobased mass content of the polymers varied depending on the monomers used. As shown in Table 2,  $x^{\text{TOC}}$  and  $m$  decreased from 61.9 and 60.1 to 39.4 and 40.8% when moving from P1 to P3, respectively.

The thermal properties of P2 and P3 were studied by DSC and TGA. As in the case of P3, no melting temperature ( $T_m$ ) of P1 and P2 was seen on the DSC thermograms; however, a strong dependence of  $T_g$  on the alkene chain of the monomers was interestingly revealed (Figure 4). For example, in the case of 0.2 mol% catalyst loading,  $T_g$  was considerably increased from -15 °C to -3 °C and 38 °C when alkene arms were changed from more flexible decene to less flexible hexene and more rigid butene chains, respectively. Notably, a similar trend, *i.e.*,  $T_g(\text{P1}) > T_g(\text{P2}) > T_g(\text{P3})$ , was observed for higher ruthenium loading (1 mol%) - the results are overviewed in Figure 4. TGA analysis of P1-P3 showed a remarkable difference in thermal stability depending on the polymerized monomer (Figure 5). For example, when switching from P1 to P3, the thermal stability was increased from 233 °C to 348 °C ( $\Delta T_{\text{d5\%}} = 115$  °C) and from 223 °C to 361 °C ( $\Delta T_{\text{d5\%}} = 138$  °C) if 0.2 mol% and 1 mol% of C4 were employed, respectively. This can be attributed to the difference in molecular weights (*vide supra*) or/and the higher stability of longer aliphatic chains.



**Figure 4.** Overview of  $T_g$  of P1-P3 obtained using 0.2 mol% and 1 mol% of C4



**Figure 5.** Overview of  $T_{d5\%}$  of P1-P3 obtained using 0.2 mol% and 1 mol% of C4

### **Cyrene™ as a biobased solvent for ADMET polymerization**

Although ADMET polymerization is usually performed in bulk, the metathesis catalyst can withstand temperatures up to 80-100 °C; otherwise, it decomposes. Thus, the use of a solvent in the case of monomers with melting points above 80-100 °C is unavoidable. It is also preferable that the solvent has a boiling point above 200 °C in order to have a sufficiently low vapor pressure so that the reaction can be performed under vacuum which helps eliminating the ethylene formed. The selected solvent has also to be tolerant (non-reactive) towards the functional groups of the monomers and the metathesis of the olefins.  $\text{CH}_2\text{Cl}_2$  is commonly used as a solvent for ADMET; however, it is a highly toxic molecule that should be replaced by a green solvent. Furthermore, when  $\text{CH}_2\text{Cl}_2$  is used as a solvent, no vacuum can be applied due to its low boiling point, which affects the molecular weight as well as the conversion. To mimic this challenge, other reports have described the use of commercially available solvents such as diethyl phthalate, and dioctyl phthalate.<sup>53</sup> But once more these solvents are non-renewable and toxic which shows the importance of discovering green and high boiling point solvent that can be adopted in such polymerization experiments. Building on the valuable properties of Cyrene™, we decided to discover, the tolerance of C4 to perform ADMET polymerization of M1-M3 in Cyrene™ (Table 3). Cyrene™ is not only derived from cellulose but also has a high boiling point of 226 °C which allowed us to conduct the reactions at 80 °C under a dynamic vacuum.

**Table 3.** ADMET polymerization of M1-M3 in Cyrene™

| Run <sup>a</sup> | Monomer | Catalyst loading | Time | Yield | $M_n$ | $\bar{D}^c$ | $T_g$ | $T_{d5\%}$ |
|------------------|---------|------------------|------|-------|-------|-------------|-------|------------|
|------------------|---------|------------------|------|-------|-------|-------------|-------|------------|

|           | [mol.L <sup>-1</sup> ] <sup>b</sup> | (mol%) | (h) <sup>c</sup> | (%) <sup>d</sup> | (kDa) <sup>e</sup> | (°C) <sup>f</sup> | (°C) <sup>g</sup> |
|-----------|-------------------------------------|--------|------------------|------------------|--------------------|-------------------|-------------------|
| <b>19</b> | M3 [2]                              | 1      | 4                | 71               | 13.8               | 1.89 -15          | 367               |
| <b>20</b> | M3 [4]                              | 1      | 4                | 98               | 11.7               | 1.83 -20          | 351               |
| <b>21</b> | M3 [4]                              | 5      | 6                | 66               | 17.4               | 1.64 -22          | 317               |
| <b>22</b> | M2 [4]                              | 1      | 6                | 77               | 13.6               | 2.03 15           | 280               |
| <b>23</b> | M1 [4]                              | 1      | 7                | 86               | 4.9                | 1.60 13           | 242               |

<sup>a</sup> C4 was used as the metathesis catalyst, Cyrene<sup>TM</sup> was used as solvent, 1,4-benzoquinone (3 equiv. per C4), 80 °C, vacuum (10<sup>-3</sup> bar). <sup>b</sup> monomer concentration in g.mol<sup>-1</sup>. <sup>c</sup> Duration required to attain full conversion as determined by <sup>1</sup>H NMR. <sup>d</sup> Isolated yield after purification and drying, yield = (isolated mass/theoretical mass) x 100. <sup>e</sup> Determined by SEC in DMF (10 mM LiBr) at 50 °C,  $\mathcal{D}$  = dispersity. <sup>f</sup> Glass transition temperature determined by DSC, temperature ramp 10 °C/min. <sup>g</sup> TGA degradation temperatures at which 5 % ( $T_{d5\%}$ ) mass loss was observed under nitrogen.

M3 was first reacted with 1 mol% of C4 for 4 h at two different concentrations in Cyrene<sup>TM</sup> (2 and 4 mol.L<sup>-1</sup>) (runs 19 & 20, Table 3). The results were very similar to the reactions in bulk (Table S1 and Figure 3). However, a slight decrease in  $M_n$  from 13.8 kDa ( $\mathcal{D}$  = 1.89) to 11.7 kDa ( $\mathcal{D}$  = 1.83) was observed in more concentrated solution (2 vs. 4 mol.L<sup>-1</sup>, runs 19 vs. 20). As recycling Cyrene<sup>TM</sup> consumes energy (due to its high boiling point) and as the decrease in the quantity of waste generated is a necessity for a greener process, the concentration of 4 mol.L<sup>-1</sup> was set. Interestingly, increasing the catalyst loading to 5 mol% increased  $M_n$  to 17.4 ( $\mathcal{D}$  = 1.64, run 21); however, it took longer to reach full conversion and a decrease in yield to 66% and in  $T_{d5\%}$  to 317 °C were observed. ADMET polymerization of M2 and M1 was then attempted using 1 mol% of C4. Interestingly, despite the difference in  $T_g$  of P2 and P1 in bulk and Cyrene<sup>TM</sup> (runs 14, 17 vs. 22, 23), when switching from M2 to M1, the ADMET polymers (P2 and P1) showed a decrease in  $M_n$  from 13.6 kDa ( $\mathcal{D}$  = 2.03) to 4.9 kDa ( $\mathcal{D}$  = 1.60) and in  $T_{d5\%}$  from 280 °C to 242 °C.

## CONCLUSION

DMNA was first produced on a gram scale from sinapic acid through our in-house chemo-enzymatic pathway. Three  $\alpha,\omega$ -dienes (M1-M3) were then synthesized via etherification and esterification reactions using bromoalkenes with different chain lengths ( $C_4$ ,  $C_6$  and  $C_{10}$ ). ADMET polymerization of M3 was then performed in bulk using seven different metathesis catalysts. 2<sup>nd</sup> generation Hoveyda-Grubbs catalyst (C4) showed the best activity and led to P3 polymers with  $M_n$  of 19.4 kDa ( $D = 1.88$ ) and  $T_g$  and  $T_{d5\%}$  equal to  $-13\text{ }^\circ\text{C}$  and  $363\text{ }^\circ\text{C}$ , respectively. Interestingly, by switching to M2 and M1, a considerable increase in  $T_g$  and a drop in  $T_{d5\%}$  were observed. The potential of Cyrene<sup>TM</sup> to be used as a green solvent for ADMET of M1-M3, was also tested and found to be successful, warranting further attention to this compound as a "general" green solvent for ADMET polymerization. Nonetheless, it must be recognized that solvent cost is a very important aspect to consider when discussing the scalability and industrial relevance of a polymerization process. A drawback of Cyrene<sup>TM</sup> is its higher cost compared to common solvents such as  $\text{CH}_2\text{Cl}_2$ . However, it is worth mentioning that a BBI H2020 flagship project called Resolute, led by Circa Group and in which our lab (i.e. URD ABI) is a partner, aims to build a plant in our region for industrial scale production of Cyrene and thus significantly lower its price.

## ASSOCIATED CONTENT

**Supporting Information.** The following files are available free of charge. Table S1 of the ADMET polymerizations of M3 using different metathesis catalysts,  $^1\text{H}$  and  $^{13}\text{C}$  NMR of M1-M3 and P1-P3 (Figures S1-S6), SEC of runs 1-23 of all prepared polymers (Figures S7-29), DSC

of runs 1-23 of all prepared polymers (Figures S30-S52), TGA of runs 1-23 of all prepared polymers (S53-S73) and pictures of typical polymers P1, P2 and P3 (Figure S74).

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### Author Contributions

SF, AF and FA conceptualized this work. Experiments were designed by SF. Experiments were performed by NZ. SF and AF supervised NZ. Formal analysis and visualization were performed by SF and AF. SF wrote the article. AF and FA reviewed and approved the article. FA acquired funding.

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