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## ADMET polymerization of bio-based biphenyl compounds

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Four biphenyl monomers derived from vanillin or eugenol were synthesized and polymerized by ADMET methodology. The biphenyl compounds were produced by enzymatic dimerization of 2-methoxy-4-methylphenol, methyl vanillate, vanillin and eugenol. Further chemical modifications of the obtained dimers such as transesterification, Wittig reaction or allylation led to  $\alpha,\omega$ -dienes. The reactivity of these bio-based monomers towards ADMET polymerization employing several catalysts was investigated. Only oligomers were obtained when the diallylated compound was employed. The polymers based on dieugenol and the bis-unsaturated diester exhibit good thermal stability and Tg at 17 and 54 °C, respectively. Polymerization of the divinyl compound obtained by Wittig reaction of divanillin showed reasonably molar mass of 30 000 g/mol, a high Tg at around 160 °C and a thermostability with a 5% weight loss occurring at 380 °C.

### Introduction

Due to important environmental concerns and petrol depletion, the chemical industry is currently considering the use of renewable building blocks for the synthesis of polymers.<sup>1-9</sup> Especially, the substitution of fossil aromatic compounds derived from benzene is a topic of current interest.<sup>10-12</sup> Lignin, the second most abundant renewable biopolymer after cellulose and source of phenolic compounds after depolymerisation, is considered as the most interesting substitute.<sup>13-19</sup>

Acyclic diene metathesis (ADMET) polymerization is a step-growth polymerisation driven by the release of a condensate, usually ethylene. ADMET is typically performed on  $\alpha,\omega$ -dienes to produce well-defined polymers with unsaturated backbones. This methodology revealed to be an efficient polymerization method.<sup>20, 21</sup> Indeed, due to the tolerance of the catalysts towards a wide range of substrates, a multitude of bio-based (bis)unsaturated molecules were polymerized by ADMET methodology in the recent years.<sup>22-26</sup>

In particular, the polymerization and copolymerization of lignin derivatives by ADMET have been reported. Meier and coworkers prepared and polymerized bis-unsaturated esters from ferulic acid<sup>27</sup> and vanillin.<sup>27, 28</sup> The  $\alpha,\omega$ -diene derived from ferulic acid was obtained by reaction with allyl bromide, which led simultaneously to the formation of the allyl ester from the carboxylic acid and allyl ether on the phenol moiety.<sup>27</sup> On the other hand, vanillyl phenol moiety was etherified by

reaction with allyl bromide and subsequently esterified with methyl undecenoate, in a 1:1 molar ratio or with dimethyl adipate, a bio-based compound, in a 2:1 molar ratio, leading to  $\alpha,\omega$ -dienes, respectively.<sup>28</sup> Allais and coworkers produced bisphenols by enzymatic transesterification of ethyl dihydroferulate with isosorbide, 1,3-propanediol and 1,4-butanediol.<sup>29</sup> Etherification of the bisphenols with bromoalkene led to  $\alpha,\omega$ -dienes.<sup>30</sup>

Eugenol, a naturally occurring unsaturated compound extracted from clove oil was also polymerized by ADMET methodology.<sup>31</sup> The  $\alpha,\omega$ -dienes were prepared by linking two molecules of eugenol with an alkyl chain, a carbonate or a diethylene glycol moiety.

All these  $\alpha,\omega$ -dienes were polymerized by ADMET leading to polymers exhibiting Tg between -31 and 18 °C depending on the monomer and comonomer employed.

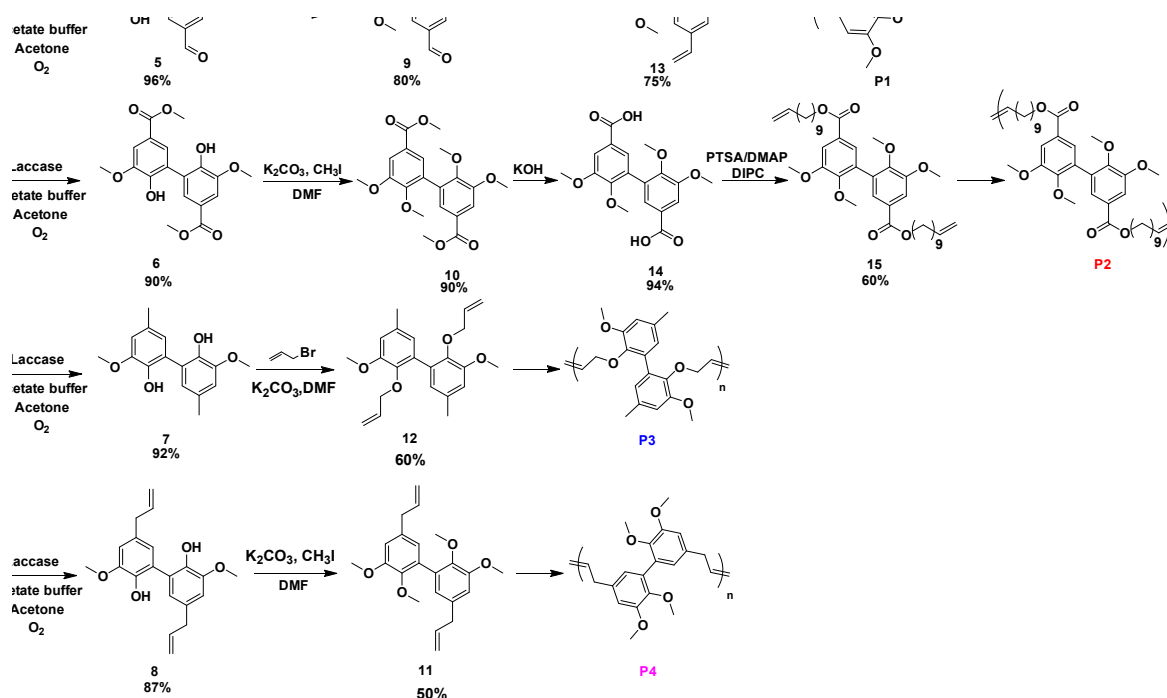
Symmetrical biphenyl monomers can also be obtained by oxidative phenolic coupling catalyzed by an enzyme such as horseradish peroxidase or laccase.<sup>32-36</sup> In a previous work, we have investigated the enzymatic coupling of several phenolic compounds potentially derived from lignin. Employing a laccase from *Trametes Versicolor*, we developed a process to selectively synthesize vanillin-based biphenyl compounds in large quantity and high yield.<sup>37</sup> Semi-aromatic polyesters based on this biphenyl platform were also prepared.<sup>37, 38</sup>

In this paper, we report the synthesis and ADMET polymerization of bis-unsaturated bio-based biphenyl compounds. First, phenolic compounds, derived from vanillin and eugenol, were dimerized *via* oxidative phenolic coupling catalyzed by laccase. The obtained biphenyl compounds were then chemically modified to yield  $\alpha,\omega$ -dienes. ADMET polymerization of these unsaturated monomers was performed employing several catalysts. The structures and thermo-mechanical properties of the resulting polymers were investigated.

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† Electronic Supplementary Information (ESI) available: [<sup>1</sup>H, <sup>13</sup>C NMR of the monomers, SEC, DSC and TGA analyses of the polymers].



**Scheme 1** Synthesis and polymerization of  $\alpha,\omega$ -dienes from vanillin **1**, methyl vanillate **2**, 2-methoxy-4-methylphenol **3** and eugenol **4**.

## Results and discussion

### Monomer synthesis

Vanillin **1**, methyl vanillate **2**, 2-methoxy-4-methylphenol **3** and eugenol **4** were used as starting material for the synthesis of building blocks (Scheme 1). Phenol **2** and **3** can be obtained respectively by oxidative esterification and by hydrogenation of a lignin derivative, vanillin.<sup>39, 40</sup> The four bio-based phenols were dimerized using a green process, employing a laccase from *Trametes versicolor* as catalyst, yielding the bisphenyl compounds **5**, **6**, **7** and **8**.<sup>37</sup>

The phenols of the dimers **5**, **6** and **8** were then methylated yielding methylated divanillin **9**, methylated diester **10** and methylated dieugenol **11**. The phenols of **7** were allylated, yielding the bis-unsaturated monomer **12**. A Wittig reaction was performed on methylated divanillin **9**, employing methyltriphosponiumiodide as Wittig reagent, yielding the divinyl compound **13**. The last bis-unsaturated compound was prepared from methylated diester **10**. Diester **10** was hydrolyzed into the diacid **14** and subsequently esterified with

undecenol, a bio-based compound, yielding the  $\alpha,\omega$ -dienes **15**. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of all the molecules are displayed in the supporting information (see Figures SI 1–26).

### Polymer synthesis

The  $\alpha,\omega$ -dienes **15**, **13**, **12** and **11** were polymerized by acyclic diene metathesis (ADMET) polymerization resulting in **P1**, **P2**, **P3** and **P4**, respectively (Scheme 1). Due to the incompatibility between the high melting temperature of the monomers (over 80 °C) and the thermal stability of the catalyst, the polymerizations were performed in solvent. *Polarclean* was selected as solvent for its high boiling point, its compatibility with Grubbs catalyst and its sustainability.<sup>23, 26</sup> Thus, the polymerizations were performed employing Grubbs catalyst (2 mol%) in *Polarclean* solvent at a concentration of 0.22 mol/L, under vacuum, at 80 °C, for 18 h.

The first step of this study focuses on the reactivity of the  $\alpha,\omega$ -diene to ruthenium-based olefin metathesis catalysts. The catalyst efficiency depends on the functional groups of the diene to be polymerized and other factors like the melting point or solubility of the monomers.<sup>20</sup> In order to select the catalyst which leads to the polymer with the highest molar mass, each monomer was polymerized employing 2 mol% of Grubbs 1st (G1), Grubbs 2nd (G2), Hoveyda-Grubbs 1st (HG1) and Hoveyda-Grubbs 2nd (HG2) generation catalysts (Figure S 27) at 80 °C under dynamic vacuum. It has been reported in literature that olefin isomerization (double bond migration) can be observed in ADMET polymerization when employing G2 and HG2 catalysts. However, such an isomerization can be limited by using quinone-type compounds.<sup>41, 42</sup> Thus, when G2 and HG2 were used, 5 mol% of 1,4-benzoquinone was added to limit isomerization in the cases of monomers **11**, **12** and **15**. The polymers were purified by reprecipitation in cold methanol, yielding a white solid. The polymer molar masses with respect to the catalyst used are summarized in Table 1. The SEC profiles of the highest molar masses of **P1**, **P2**, **P3** and **P4** employing HG2, G1, HG1 and HG2 respectively, are shown in the supporting information (Figure S28). **P1** and **P4** synthesized from divinyl, **13**, and methylated dieugenol, **11**, respectively, exhibited the highest molar mass whereas the polymerization of **12** leads to oligomers (**P3**). More details about the polymer structures were extracted from <sup>1</sup>H NMR analyses (Figures 1-4).

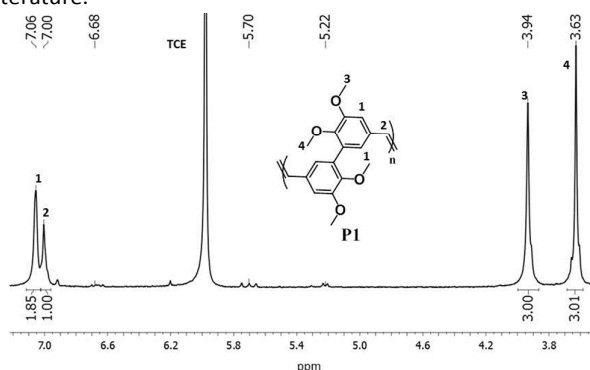
**Table 1:** Properties of polymers P1, P2, P3 and P4 synthesized by ADMET of biphenyl compounds.

Monomers	Polymer	Catalyst	$\bar{M}_n^a$ (g/mol)	$\bar{D}^a$
<b>13</b>	P1	G1	/	/
		HG1	/	/
		G2	16 000	1.4
		HG2	29 000	1.7
<b>15</b>	P2	G1	11 000	1.6
		HG1	7 000	1.6
		HG2	10 000	1.6
<b>12</b>	P3	G1	/	/
		HG1	7 000	1.1
		HG2	/	/
<b>11</b>	P4	G1	/	/
		HG1	6 000	1.3
		HG2	40 000	1.7

<sup>a</sup>Determined by SEC in DMF, PS calibration, / no precipitation

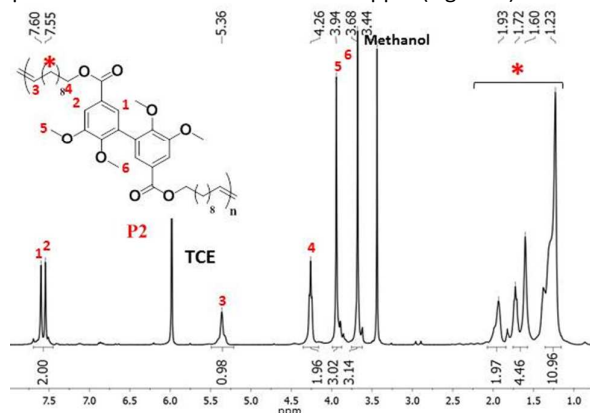
**13** exhibits a conjugation between the double bond and the aromatic ring. The synthesis of low molar masses poly(*p*-phenylenevinylene)s-type polymers by ADMET in presence of molybdenumcarbene complex has already been reported.<sup>43, 44</sup> High molar mass, defect-free, all-*trans* poly(*p*-phenylenevinylene)s can be prepared employing Ruthenium-based catalysts, G2 and HG2.<sup>45, 46</sup> In the present study, only G2

and HG2 catalysts led to polymers and the highest molar mass, 29 000 g/mol, was achieved employing HG2 catalyst. The <sup>1</sup>H NMR spectrum of the polymer synthesized employing HG2 catalyst is displayed in Figure 1. The decrease of the signals at 6.68, 5.701 and 5.22 ppm attributed to the terminal double bonds on the <sup>1</sup>H NMR spectrum of **P1** also indicates the successful polymerization. The integration of these signals characteristic of the chain-end moieties enables the calculation of a molar mass of 33 000 g/mol, in agreement with the SEC analyses. The spectrum also shows signals of the methoxy protons at 3.94 and 3.63 ppm, signals of the aromatic protons at 7.06 ppm and signal of the methylene protons at 7.00 ppm. Such analysis proves the all-*trans* configuration of the vinylic bonds. Indeed, no signal is detected at 6.65 ppm, which is the value of *cis*-vinylic bonding signals reported in literature.<sup>44</sup>



**Figure 1:** <sup>1</sup>H NMR spectrum of **P1** in TCE, at room temperature.

Dimer **15** possesses an aliphatic chain of 10 carbons between the aromatic ring and the terminal double bond. Polymers prepared from **15** employing G1, HG1 and HG2 catalysts were recovered as precipitates in cold methanol (Table 1). The highest molar masses of 11 000 g/mol, were achieved employing G1 and HG2 catalysts. The <sup>1</sup>H NMR spectrum of **P2** shows signal of the methoxy protons at 3.92 and 3.66 ppm, signal of the aromatic protons at 7.53 ppm and signals of the aliphatic chain between 1.00 and 2.00 ppm (Figure 2).



**Figure 2:** <sup>1</sup>H NMR spectrum of **P2** in TCE, at room temperature.

The disappearance of the signals at 5.00 and 4.35 ppm attributed to the terminal double bonds and the appearance of

a signal at 5.34 ppm assigned to internal double bonds, indicate the success of the polymerization.

Dimer **12** contains a heteroatom in  $\beta$ -position of the terminal double bond. It is well-known that heteroatoms can be included in ADMET polymerization if sufficient "spacing" separates the active olefin site and the functional group containing the heteroatom itself.<sup>47</sup> The polymer prepared from **12** employing HG1 catalyst was recovered as precipitate in cold methanol (Table 1). **P3** exhibited the lowest molar mass of the study, 7 000 g/mol. The <sup>1</sup>H NMR spectrum of **P3** shows the signal characteristic of aromatic, methoxy and methyl protons, respectively at 6.60, 3.75, and 2.21 ppm (Figure 3).

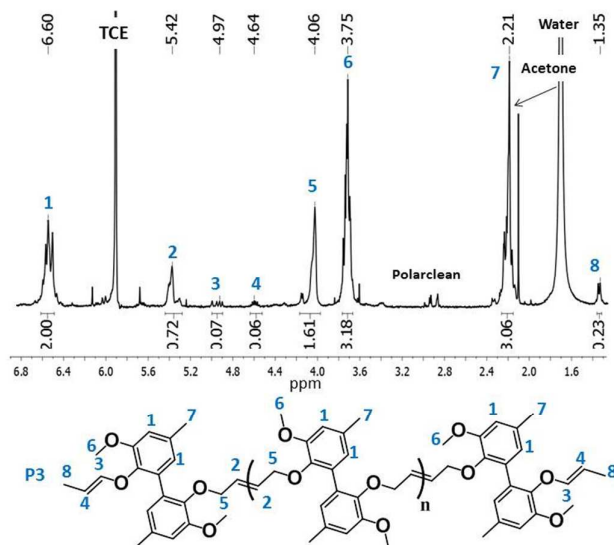


Figure 3: <sup>1</sup>H NMR spectrum of **P3** in TCE, at room temperature.

The signals at 5.42 and 4.06 ppm are assigned to internal double bonds and methylene in  $\alpha$ -position of the ether moiety. The integration of the signal at 4.06 ppm, lower than 2.00, indicates the occurrence of isomerization. In addition, a doublet at 1.35 ppm can be attributed to the methyl group in  $\gamma$ -position of the ether moiety. These vinyl ether moieties are not reactive towards ADMET polymerization and can act as chain stoppers.<sup>47</sup> These chain ends allowed us to calculate a degree of polymerization of 13. This value is a little lower than the value of 20 determined by SEC analyses. Thus, only oligomers were synthesized by ADMET polymerization of **13**, probably due to the complexation of the non-bonded electrons of the heteroatom with the metal center.

The ADMET polymerization of dieugenol **8** employing G1, HG1, G2 and HG2 catalysts did not lead to the formation of polymers. The phenolic moieties might deactivate the Grubbs catalysts. Thus, the polymerization was performed on methylated dieugenol, **11**. The polymers prepared from **11** employing HG1, G2, HG2 catalysts were recovered as precipitates in cold methanol (Table 1). The highest molar mass of 40 000 g/mol was achieved in presence of HG2 catalyst. The <sup>1</sup>H NMR spectrum of **11** showed 3 broad signals between 6.40 and 7.20 ppm. The signal at 7.02 ppm and 6.29 ppm were attributed to the aromatic ring and to the internal double bonds in  $\beta$ -position of the aromatic ring

(Figure 4).<sup>31</sup> However, the signal at 6.73 ppm is characteristic of the *trans* configuration of the vinylene bonds into stilbenes. The integration of the signal at 2.54 ppm, commonly assigned to benzyl protons was 0.66 instead of 2. These two observations suggested the isomerization of eugenol into isoeugenol. This isomerization commonly occurs in eugenol metathesis due to the thermodynamical stability of the resulting styrene derivative and the kinetically faster subsequent metathesis to stilbene oligomers. In our case, 60% of the units were stilbene derivatives. The duplication of the methoxy signals could be attributed to the presence of both kinds of units.<sup>48</sup>

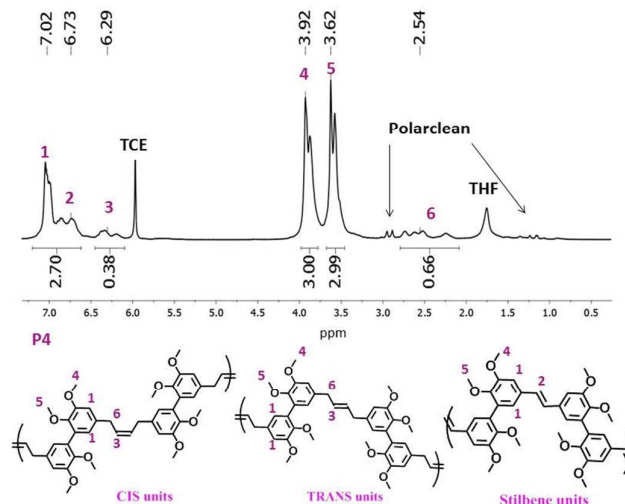


Figure 4: <sup>1</sup>H NMR spectrum of **P4** in TCE, at room temperature.

#### Thermal and thermo-mechanical characterizations

The thermo-mechanical properties of the ADMET-based polymers were analyzed by DSC, TGA, and DMA (Table 2). DSC analyses revealed the amorphous character of the polymers (Figure S32). Depending on their structures, the polymers present a glass transition temperature ranging from 4 to 157 °C. As expected, the reduction of the number of atoms between the aromatic ring and the terminal double bond of the monomer resulted in a Tg increase. Indeed, **P2** exhibits the lowest Tg due to its C12 aliphatic chain. The presence of oxygen atoms into **P3** backbone leads to a lower Tg (17 °C) in comparison to **P4** (54 °C). Tg of **P1** seems to be at 157 °C but is difficult to detect by DSC due to the rigidity of the conjugated polymer. In order to confirm this value and to investigate the thermo-mechanical properties of **P1**, DMA analyses were performed (Figure 5). The end of the glassy state was revealed by the decrease of the storage modulus E' at 140 °C. The rubbery state was reached when E' stops decreasing at 250 °C. The transition between the two states was spread on 110 °C due to its rigid conjugated structure. The maximum of tan $\delta$  was measured at 208 °C. Tg of **P1** was 100 °C higher than the Tg of **P4** although the structures of **13** and **11** differ by only one carbon between the aromatic ring and the double bond. The high Tg of **P1** may be explained by its conjugated backbone and its all-*trans* structure, whereas the Tg of **P4** is

lower due to its ill-defined structure (isomerizations) and *cis-trans* configurations.

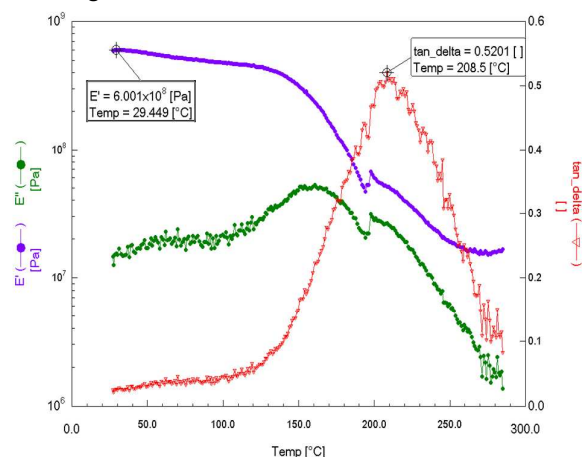


Figure 5: DMA analysis of divinyl ADMET Polymer, **P1**, using 3-point bending test at 1 Hz from 20 to 300 °C at 10 K/min.

The thermal stability of the polymers was evaluated by TGA under air (Figure S33). 5 wt% loss of **P3** appeared at 250 °C, due to its oligomeric structure. The thermal robustness of **P1**, **P2** and **P4** is high; the latter exhibit 5 wt% loss at temperatures between 310 and 380 °C.

Table 2: Thermo-mechanical properties of polymers, P11, P12, P13 and P14 synthesized by ADMET.

Monomer	Polymer	Catalyst	T <sub>g</sub> (°C) <sup>a</sup>	Td5% (°C) <sup>b</sup>
<b>13</b>	P1	HG2	156	380
<b>15</b>	P2	HG2	4	310
<b>12</b>	P3	HG1	17	250
<b>11</b>	P4	HG2	54	330

<sup>a</sup>Determined by DSC second heating cycle, <sup>b</sup>Determined by TGA under air; Temperature of 5% degradation.

## Conclusions

Four  $\alpha,\omega$ -dienes were synthesized from biobased biphenyl compounds deriving from vanillin and eugenol. Their reactivity towards ADMET polymerization was investigated. A screening of Grubbs catalysts allowed us to synthesize three families of polymers with reasonable molar masses between 11 000 and 40 000 g/mol. Only oligomers were obtained when the diallylated compound was employed probably because the heteroatom close to the terminal double bond reduces the activity of Grubbs catalyst. Methylated dieugenol and the bis-unsaturated diesters deriving from methyl vanillate and undecenol exhibit good thermal stability and T<sub>g</sub> at 17 and 54 °C, respectively. The polymerization of divinyl compounds obtained by Wittig reaction of divanillin led to a polymer with a high T<sub>g</sub> at around 160 °C and a thermostability with a 5% weight loss occurring at 380 °C.

## Experimental

### Material

Laccase from *Trametes versicolor*, iodomethane (99%) eugenol (99%), sodium acetate (99%), acetic acid (99.7%), %, N,N'-Diisopropylcarbodiimide (DIPC 99%), *p*-toluenesulfonic acid monohydrate (PTSA 99%), 4-(Dimethylamino)pyridine (DMAP 99%) allyl bromide (99%), potassium *tert*-butoxide (98%) benzylidene-bis(tricyclohexylphosphine)dichlororuthenium (Grubbs 1st generation metathesis catalyst (97%)), **Dichloro(o-isopropoxyphenylmethylene)(tricyclohexylphosphine)ruthenium(I I)** (Hoveyda Grubbs 1st generation metathesis catalyst), **Benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(tricyclohexylphosphine)ruthenium** (Grubbs 2nd generation metathesis catalyst), **(1,3-Bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(o-isopropoxyphenylmethylene)ruthenium** (Hoveyda Grubbs 2nd generation metathesis catalyst (97%)) were purchased from Sigma Aldrich. Potassium carbonate (99%) was supplied by Prolabo. Vanillin (99%), methyl vanillate (99%) and 2-methoxy-4-methylphenol (98%) were purchased from Alfa Aesar *Polarclean* (methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate) was supplied by Solvay. All products and solvents (reagent grade) were used as received, unless mentioned explicitly.

### Instrumentations

All NMR experiments were performed at 298 K on a Bruker Avance 400 spectrometer operating at 400 MHz, in deuterated solvent (DMSO or tetrachloroethylene-TCE). Size exclusion chromatography (SEC) analyses were performed in DMF (80 °C) on a PL-GPC 50 plus Integrated SEC from Polymer laboratories-Varian with a series of three columns from PLgel (PLgel 5  $\mu$ m Guard (guard column 7.5 mm ID x 5,0 cm L); PLgel 5  $\mu$ m MIXED-D (7.5mm ID x 30,0 cm L) and PLgel 5 $\mu$ m MIXED-D (7,5 mm ID x 30,0 cm L)). The elution of the filtered samples was monitored using simultaneous refractive index and UV detection. The elution times were converted to molar mass using a calibration curve based on low dispersity (M<sub>w</sub>/M<sub>n</sub>) polystyrene (PS) standards. Differential Scanning Calorimetry (DSC) measurements were performed on DSC Q100 (TA Instruments). The sample was heated from 0 °C to 220 °C at a rate of 10 °C.min<sup>-1</sup>. Consecutive cooling and second heating run were also performed at 10 °C.min<sup>-1</sup>. The glass transition temperatures and melting points were calculated from the second heating run. Thermogravimetric analyses (TGA) were performed on TGA-Q50 system from TA instruments at a heating rate of 10 °C.min<sup>-1</sup> under nitrogen or air atmosphere as mentioned in the manuscript. DMA RSA 3 (TA instrument). The sample temperature was modulated from -80 °C to 250 °C, depending on the sample at a heating rate of 5 °C/min. The measurements were performed in a 3-point bending mode at a frequency of 1 Hz, an initial static force varying between 0.1 and 0.5 N and a strain sweep of 0.1%.

### Experimental procedure

#### General procedure for dimerization: synthesis of dimers 5 to 8

A solution of phenol substrate (**5-8**) (1.5 g) in acetone (20 mL) was added to NaOAc buffer (180 mL, 0.1 M, pH 5.0). The

solution was saturated in O<sub>2</sub> for 5 min. Laccase from *Trametes versicolor* (20 U, 12.4 mg) was added and the reaction was stirred at room temperature for 24 h. The precipitate was filtered off the solution and the product dried overnight at 80 °C under vacuum.

*Divanillin 5*: yield: 96%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ (ppm)): δ 9.85 (s, CHO), 7.50 (s, 2H Ar), 4.00 (s, OCH<sub>3</sub>).

<sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>, δ (ppm)): δ 191.04 (CHO), 150.70 (Ar-C), 147.95 (Ar-C), 128.30 (Ar-C), 127.69 (Ar-C), 124.52 (Ar-C), 109.10 (Ar-C), 55.88 (OCH<sub>3</sub>).

*Dimethyl divanillate 6*: yield: 90%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ (ppm)): δ 9.60 (s, 2H, HO), 7.46 (s, 4H, Ar), 3.90 (s, 6H, OCH<sub>3</sub>), 3.80 (s, 6H, OCH<sub>3</sub> ester).

<sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>, δ (ppm)): δ 166.04 (OCH<sub>3</sub> ester), 148.60 (Ar-C), 147.27 (Ar-C), 125.25 (Ar-C), 123.93(Ar-C), 119.21 (Ar-C), 110.89 (Ar-C), 55.97 (OCH<sub>3</sub>), 51.75(OCH<sub>3</sub> ester).

*2-Methoxy-4-methyl phenol dimer 7*: yield: 92%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ (ppm)): δ 6.73 (s, 2H, Ar) , 6.53 (s, 2H, Ar), 3.79 (s, 6H, OCH<sub>3</sub>), 2.23 (s, 6H, CH<sub>3</sub>).

<sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>, δ (ppm)): 147.52 (Ar-C), 140.99 (Ar-C), 126.92 (Ar-C), 125.68 (Ar-C), 123.04 (Ar-C), 111.61 (Ar-C), 55.85 (OCH<sub>3</sub>), 20.65 (CH<sub>3</sub>).

*Dieugenol 8*: yield: 87%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ (ppm)): δ 6.74 (s, 2H Ar), 6.52 (s, 2H Ar), 5.94 (q, 2H CH-CH<sub>2</sub>), 5.03 (d, 4H CH-CH<sub>2</sub>), 3.79 (s, OCH<sub>3</sub>), 3.27 (d, 2H CH<sub>2</sub>).

<sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>, δ (ppm)): δ 147.80 (Ar-C), 141.62 (Ar-C), 138.38 (CH-CH<sub>2</sub>), 129.57 (Ar-C), 125.67 (Ar-C), 122.62 (Ar-C), 115.28 (CH-CH<sub>2</sub>), 105.56 (Ar-C), 55.64 (OCH<sub>3</sub>), 39.19 (CH<sub>2</sub>).

#### General procedure for phenol methylation of **5**, **6** and **8**: synthesis of methylated divanillin **9** and methylated dimethyl vanillate **10** and methylated dieugenol **11**

Bisphenol **5**, **6** or **8** (26 mmol) was dissolved in DMF (120 mL). Potassium carbonate (15.2 g, 110 mmol) was added before a slow addition of iodomethane (9.6 mL, 158 mmol). After 15 h of stirring at 80 °C, the mixture was filtered and the resulting solution poured into cold water. The methylated compound, which precipitated was filtered off and dried under vacuum.

*Methylated divanillin 9*: yield: 80%

<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>, δ (ppm)): δ 9.94 (s, CHO), 7.58 (s, 2H Ar), 7.55 (s, 2H Ar), 3.95 (s, OCH<sub>3</sub>), 3.68 (s, OCH<sub>3</sub>)

<sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>, δ (ppm)): δ191.83 (CHO), 152.80 (Ar-C), 151.21 (Ar-C), 131.90 (Ar-C), 131.58 (Ar-C), 125.96 (Ar-C), 111.14 (Ar-C), 60.47 (OCH<sub>3</sub>), 55.93 (OCH<sub>3</sub>)

*Methylated dimethyl divanillate 10*: yield: 80%

<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>, δ (ppm)): δ 7.59 (s, 2H Ar), 7.41 (s, 2H Ar), 3.92 (s, OCH<sub>3</sub>), 3.84 (s, OCH<sub>3</sub>), 3.62 (s, OCH<sub>3</sub>)

<sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>, δ (ppm)): δ 165.63 (OCH<sub>3</sub> ester), 152.16 (Ar-C), 149.95 (Ar-C), 131.19 (Ar-C),124.44(Ar-C), 123.81 (Ar-C), 112.43 (Ar-C), 60.38 (OCH<sub>3</sub>), 55.7

*Methylated dieugenol 11*: yield: 50%

<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>, δ (ppm)): δ 6.93 (s, 2H Ar), 6.61 (s, 2H Ar), 6.03 (q, 2H CH-CH<sub>2</sub>), 5.13 (d, 4H CH-CH<sub>2</sub>), 3.89 (s, OCH<sub>3</sub>), 3.56 (s, OCH<sub>3</sub>), 3.42 (d, 2H CH<sub>2</sub>)

<sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>, δ (ppm)): δ 152.02 (Ar-C), 144.15 (Ar-C), 137.53 (CH-CH<sub>2</sub>), 134.73 (Ar-C), 132.29 (Ar-C), 122.19 (Ar-C), 115.77 (CH-CH<sub>2</sub>), 112.15(Ar-C), 59.80 (OCH<sub>3</sub>), 55.44 (OCH<sub>3</sub>), 39.29 (CH<sub>2</sub>)

#### Allylation of 2-methoxy-4-methylphenol dimer **7**: synthesis of **12**

Bisphenol compound **7** (8 g, 26 mmol) was dissolved in acetone (120 mL). Potassium carbonate (15.2 g, 110 mmol) was added before a slow addition of allyl bromide (13.5 mL, 158 mmol). After 15 h of stirring at 80 °C, the mixture was filtered, the solvent evaporated and the resulting solid dried under vacuum. Yield: 60%

<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>, δ (ppm)): δ 6.84 (s, 2H, Ar) , 6.55(s, 2H, Ar), 5.70 (m, 2H, CH-CH<sub>2</sub>), 4.99 (dd, 4H, CH-CH<sub>2</sub>), 4.21 (d, 4H, OCH<sub>2</sub>), 3.80(s, 6H, OCH<sub>3</sub>), 2.26(s, 6H, CH<sub>3</sub>)

<sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>, δ (ppm)): 151.98(Ar-C), 142.92(Ar-C), 134.95 (CH-CH<sub>2</sub>), 132.30(Ar-C), 132.17 (Ar-C), 123.03 (Ar-C), 116.43(CH-CH<sub>2</sub>), 112.67(Ar-C), 73.21(CH<sub>2</sub>), 55.36 (OCH<sub>3</sub>), 20.78 (CH<sub>3</sub>)

#### Wittig reaction on methylated divanillin **9**: synthesis of divinyl compound **13**

Triphenylphosphine (3 g, 11.4 mmol) was dissolved in toluene (30 mL). Iodomethane (0.7 mL, 11.4 mmol) was added dropwise. The mixture is stirred to reflux at 120 °C under nitrogen flow. Methyltriposponiumiodide precipitated and was filtered off and dried under vacuum.

To a solution of methyltriposponiumiodide (8.8 g, 22 mmol) in dry THF (36 mL), potassium tert-butoxide (2.7 g, 24 mmol) were added at 0 °C. After 1 h of stirring at room temperature under nitrogen, methylated divanillin **9** (3.2 g, 10 mmol) was added. The mixture is stirred at 35 °C for 24h. The solution was diluted with dichloromethane (75 mL), washed with water and 2 times with brine. The solvent of the organic phase is evaporated. The remaining reactants were eliminated by silica column purification using dichloromethane/cyclohexane 50/50. Yield: 75%

<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>, δ (ppm)): δ 7.17 (s, 2H Ar), 6.83 (s, 2H Ar), 6.70 (q, 2H CH-CH<sub>2</sub>), 5.77 (d, 2H CH-CH<sub>2</sub>), 5.19 (d, 2H CH-CH<sub>2</sub>) 3.87 (s, OCH<sub>3</sub>), 3.53 (s, OCH<sub>3</sub>)

<sup>13</sup>C NMR (400MHz, CDCl<sub>3</sub>, δ (ppm)): δ 152.34 (Ar-C), 145.84 (Ar-C), 136.25 (CH-CH<sub>2</sub>), 132.66 (Ar-C), 132.01 (Ar-C), 120.82(CH-CH<sub>2</sub>), 113.30 (Ar-C), 109.25 (Ar-C), 59.94 (OCH<sub>3</sub>), 55.53 (OCH<sub>3</sub>)

#### Hydrolysis of diester **10**: synthesis of diacid **14**

Diester **10** (7 mmol, 2.7 g) was dissolved in methanol (10 mL). Potassium hydroxide (45 mmol, 2.5 g) was added and the solution was warmed to reflux for 9h. The reaction was stopped with water (2.5 mL). The remaining diester was extracted with diethylether. The aqueous phase was acidified with HCl and the diacid precipitated. Yield: 94%

$^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ,  $\delta$  (ppm)):  $\delta$  7.63 (s, 2H Ar), 7.42 (s, 2H Ar), 3.96 (s,  $\text{OCH}_3$ ), 3.64 (s,  $\text{OCH}_3$ )

$^{13}\text{C}$  NMR (400MHz,  $\text{CDCl}_3$ ,  $\delta$  (ppm)):  $\delta$  166.72 (COOH), 152.21 (Ar-C), 149.91 (Ar-C), 131.06 (Ar-C), 123.86 (Ar-C), 112.88 (Ar-C), 59.89 (Ar-C), 55.84 ( $\text{OCH}_3$ ), 55.86 ( $\text{OCH}_3$ )

#### Esterification of diacid 14 with undecenol: synthesis of bisunsaturated diester 15

Diacid 15 (8 mmol, 3 g,) was dissolved in  $\text{CH}_2\text{Cl}_2$  (80 ml) under stirring. Subsequently *p*-toluene sulfonic acid/4-dimethylaminopyridine catalyst in a molar ratio 1/1.2 was added. The flask was placed in an ice bath and subsequently an excess of undecenol (4.8 mL, 24 mmol) was added to the solution. Finally, *N,N'*-diisopropyl carbodiimide (DIPC, 7.2 ml 46 mol) was added dropwise under stirring. The reaction was left under stirring for 72 hours at room temperature. Afterwards the solution was washed three times with water, dried and the solvent was removed under reduced pressure. The product was a yellow brown viscous liquid. The acylurea formed was eliminated by filtration after dissolution of the product in toluene. The remaining reactants were eliminated by silica column purification using dichloromethane. Yield: 60%

$^1\text{H}$  NMR (400MHz,  $\text{CDCl}_3$ ,  $\delta$  (ppm)):  $\delta$  7.37 (s, 2H Ar), 7.58 (s, 2H Ar), 4.92 (m, 3H CH- $\text{CH}_2$ ), 4.25 (t, 2H  $\text{CH}_2$ -COO), 3.92 (s,  $\text{OCH}_3$ ), 3.62 (s,  $\text{OCH}_3$ ), 1.97 (m, 3H - $\text{CH}_2$ -), 1.67 (m, 2H - $\text{CH}_2$ -), 1.23 (m, 13H - $\text{CH}_2$ -)

$^{13}\text{C}$  NMR (400MHz,  $\text{CDCl}_3$ ,  $\delta$  (ppm)):  $\delta$  164.84 (COO), 152.12 (Ar-C), 150.30 (Ar-C), 138.56 (C=C), 131.26 (Ar-C), 125.08 (Ar-C), 123.50 (Ar-C), 114.34 (C=C), 112.55 (Ar-C), 64.59 ( $\text{OCH}_2$ ), 60.23 ( $\text{OCH}_3$ ), 56.06 ( $\text{OCH}_3$ ), 25.40-32.99 ( $\text{CH}_2$ )

#### ADMET polymerization: synthesis of P1, P2, P3 and P4

$\alpha,\omega$ -dienes (0.22 mmol) was dissolved in Polarclean (1 mL). Grubbs catalyst (2 mol%) was added to the flask. When needed, 1,4-benzoquinone (5 mol%) was added to limit isomerization. The flask was heated at 80 °C under vacuum for 18 h. Then 1 mL of ethyl vinyl ether was introduced to the flask to quench the reaction. The final polymer was dissolved into 1 mL of THF and reprecipitated in cold methanol.

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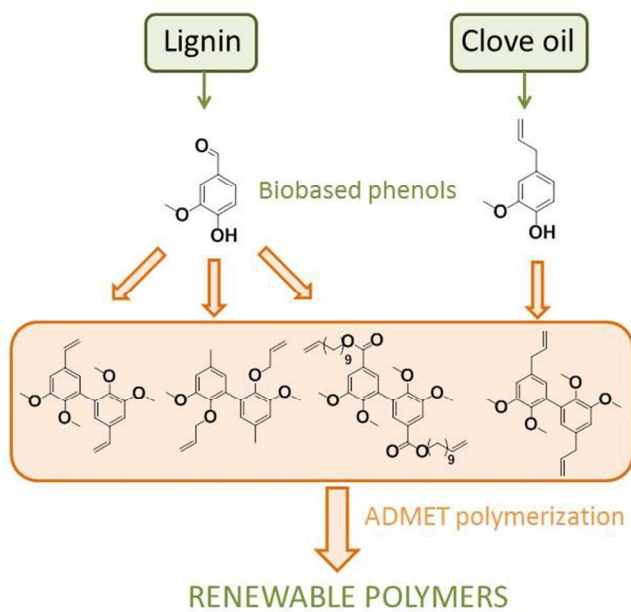
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Bio-based phenols were dimerized and involved as monomers in ADMET polymerization  
254x190mm (96 x 96 DPI)