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Electronic Supplementary Information (ESI)

Synthesis of New Polyesters by Acyclic Diene Metathesis Polymerization of Bio-Based α,ω-
Dienes Prepared from Eugenol and Castor Oil (Undecenoate)

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(i) $^1$H and $^{13}$C NMR spectra for monomers, crosslinker and polymers synthesized by ADMET polymerization

**4-Allyl-2-methoxyphenyl 10-undecenoate (M1)**

$^1$H NMR (CDCl$_3$): $\delta$ 1.33 (s, 10H, 5CH$_2$) 1.75-1.79 (quint, $J$=7.5 Hz, 2H, CH$_2$), 2.03-2.07 (quart, $J$=7.5 Hz, 2H, CH$_2$CH=CH$_2$), 2.55-2.58 (t, $J$=7.5 Hz, 2H, -CH$_2$COO-), 3.37-3.38 (d, $J$=6.8 Hz, 2H, Ar-CH$_2$), 3.81 (s, 3H, OCH$_3$), 4.92-5.02 (m, 2H, Ar-CH$_2$CH=CH$_2$), 5.08-5.13 (2H, -CH=CH$_2$), 5.78-5.86 (m, $J$=6.68, 6.68 and 6.77 Hz, 1H, -CH=CH$_2$), 5.92-6.0 (m, $J$=6.75, 6.75 and 6.79 Hz, 1H, Ar-CH$_2$CH=CH$_2$), 6.75-6.79 (m, 1HAr, CH), 6.93-6.94 ppm (m, 2HAr, 2CH). $^{13}$C NMR (CDCl$_3$): $\delta$ 25.1 (CH$_2$), 29.0 (CH$_2$), 29.1 (CH$_2$), 29.3 (CH$_2$), 29.4 (CH$_2$), 33.9 (CH$_2$COO-), 34.1 (CH$_2$), 40.2 (Ar-CH$_2$), 55.9 (OCH$_3$), 112.8 (CH), 114.3 (CH=CH$_2$), 116.2 (Ar-CH$_2$CH=CH$_2$), 120.7 (CH), 122.6 CH), 137.2 (Ar-CH$_2$CH=CH$_2$), 138.2 (C), 138.9 (C), 139.3 (CH=CH$_2$), 151.0 (C), 172.1 ppm (-COO-).

**Figure S1.** $^1$H NMR spectrum of 4-allyl-2-methoxyphenyl 10-undecenoate (M1)

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S-2
Figure S2. $^{13}$C NMR spectrum of 4-allyl-2-methoxyphenyl 10-undecenoate (M1)

5-Hexen-1-yl 10-undecenoate (M2)

$^1$H NMR (500 MHz, CDCl$_3$, ppm): $\delta$ 1.28-1.36 (s, 10H, 5CH$_2$), 1.44 (m, 2H, CH$_2$), 1.61-1.64 (m, 4H, 2CH$_2$), 2.02-2.08 (m, $J$=15.2 and 16.9 Hz, 4H, 2CH$_2$CH=CH$_2$), 2.26-2.29 (t, $J$=7.4 Hz, 2H, -CH$_2$COO-), 4.06 (t, $J$=6.5 Hz, 2H, -COOCH$_2$-), 4.91-5.02 (m, $J$=8.8 and 14.0 Hz, 4H, 2CH$_2$=CH-), 5.77-5.80 ppm (m, $J$=1.4 and 11.6 Hz, 2H, 2CH$_2$=CH-). $^{13}$C NMR (125 MHz, CDCl$_3$, ppm): $\delta$ 25.1 (CH$_2$), 25.3 (CH$_2$), 28.2 (CH$_2$), 29.0 (CH$_2$), 29.2 (CH$_2$), 29.3 (CH$_2$), 29.4 (CH$_2$), 33.4 (CH$_2$), 33.9 (CH$_2$), 34.5 (CH$_2$), 64.2 (-COOCH$_2$-), 114.3 (CH=CH$_2$), 139.3 (CH=CH$_2$), 174.1 ppm (-COO-).
Figure S3. $^1$H NMR spectrum of 5-hexen-1-yl 10-undecenoate (M2)

Figure S4. $^{13}$C NMR spectrum of 5-hexen-1-yl 10-undecenoate (M2)
10-Undecen-1-yl 10-undecenoate (M3)

$^1$H NMR (500 MHz, CDCl$_3$, ppm): $\delta$ 1.27-1.36 (s, 22H, 11CH$_2$), 1.60 (s, 4H, 2CH$_2$), 2.02-2.03 (d, $J$=6.4 Hz, 4H, 2CH$_2$CH=CH$_2$), 2.26-2.29 (t, $J$=7.4 Hz, 2H, -CH$_2$COO-), 4.03-4.05 (t, $J$=6.6 Hz, 2H, -COOCH$_2$-), 4.90-4.99 (m, $J$=9.3 and 17.1 Hz, 4H, 2CH$_2$=CH-), 5.76-5.81 ppm (d, $J$=6.8 Hz, 2H, 2CH$_2$=CH-). $^{13}$C NMR (125 MHz, CDCl$_3$, ppm): $\delta$ 26.0 (CH$_2$), 28.8 (CH$_2$), 29.0 (CH$_2$), 29.1 (CH$_2$), 29.2 (CH$_2$), 29.3 (CH$_2$), 29.4 (CH$_2$), 29.5 (CH$_2$), 29.6 (CH$_2$), 33.9 (CH$_2$), 34.5 (CH$_2$), 64.5 (-COOCH$_2$-), 114.2 (CH=CH$_2$), 139.2 (CH=CH$_2$), 174.0 ppm (-COO-).

Figure S5. $^1$H NMR spectrum of 10-undecen-1-yl 10-undecenoate (M3)
**Figure S6.** $^{13}$C NMR spectrum of 10-undecen-1-yl 10-undecenoate (M3)

5-Formylbenzene-1,2,3-triyl tris(undec-10-enoate) (CL)

$^1$H NMR (500 MHz, CDCl$_3$, ppm): δ 1.32-1.40 (s, 30H, 15CH$_2$) 1.70-1.76 (quint, $J$=7.5 Hz, 6H, 3CH$_2$), 2.02-2.06 (quart, $J$=7.0 Hz, 6H, 3CH$_2$:CH=CH$_2$), 2.53-2.56 (t, $J$=7.5 Hz, 6H, 3CH$_2$:COO$^-$), 4.92-5.01 (m, $J$=10.2 and 17.1 Hz, 6H, 3CH=CH$_2$), 5.77-5.85 (m, $J$=16.7, 16.8 and 17.0 Hz, 3H, 3CH=CH$_2$), 7.64 (s, 2HAr, 2CH), 9.92 ppm (s, 1H, -COH). $^{13}$C NMR (125 MHz, CDCl$_3$, ppm): δ 24.9 (CH$_2$), 29.0 (CH$_2$), 29.1 (CH$_2$), 29.2 (CH$_2$), 29.3 (CH$_2$), 29.4 (CH$_2$), 33.8 (CH$_2$), 114.3 (CH=CH$_2$), 121.7 (CH), 134.0 (Ar), 139.2 (CH=CH$_2$), 139.9 (Ar), 144.5 (Ar), 170.5 (-COO$^-$), 189.5 ppm (-CHO).
Figure S7. $^1$H NMR spectrum of 5-formylbenzene-1,2,3-triyl tris(undec-10-enoate) (CL)

Figure S8. $^{13}$C NMR spectrum of 5-formylbenzene-1,2,3-triyl tris(undec-10-enoate) (CL)
**Polymer (P1)**

P1 (sample run 8). $^1$H NMR (500 MHz, CDCl$_3$, ppm): $\delta$ 1.33 (CH$_2$) 1.75-1.79 (CH$_2$), 2.03-2.07 (CH$_2$CH=CH-), 2.55-2.58 (-CH$_2$COO-), 3.37-3.38 (Ar-CH$_2$), 3.81 (OCH$_3$), 5.39-5.67 (-CH=CH-), 6.15-6.44 (Ar-CH$_2$CH=CH-), 6.75-6.79 (CH), 6.93-6.94 ppm (CH). $^{13}$C NMR (125 MHz, CDCl$_3$, ppm): $\delta$ 25.1 (CH$_2$), 26.8 (CH$_2$), 29.0 (CH$_2$), 29.1 (CH$_2$), 29.3 (CH$_2$), 29.4 (CH$_2$), 32.6 (CH$_2$), 33.9 (CH$_2$), 34.1 (CH$_2$), 39.1 (CH$_2$), 55.9 (OCH$_3$), 112.8 (CH), 120.7 (CH), 122.6 (CH), 128.6 (Ar-CH$_2$CH=CH-), 132.5 (Ar-CH$_2$CH=CH-), 138.2 (C), 138.9 (-CO-), 151.0 (C), 172.1 ppm (-COO-).

**Figure S9.** $^1$H NMR spectrum (in CDCl$_3$ at 25 ºC) for (a) monomer (M1) and (b) polymer (P1)
Figure S10. $^{13}$C NMR spectrum (in CDCl$_3$ at 25 ºC) for (a) monomer (M1) and (b) polymer (P1)
Polymer PL1

PL1 (sample run 24). $^1$H NMR (500 MHz, CDCl$_3$, ppm): δ 1.32 (CH$_2$) 1.75 (CH$_2$), 1.97-2.03 (CH$_2$CH=CH-), 2.56 (COOCH$_2$-), 3.31-3.35 (Ar-CH$_2$-), 3.80 (OCH$_3$), 5.36- 5.68 (-CH=CH-), 6.18-6.44 (Ar-CH$_2$CH=CH-), 6.77 (CH), 6.92 (CH), 7.64 (CH), 9.92 ppm (-COH). $^{13}$C NMR (125 MHz, CDCl$_3$, ppm): δ 25.2 (CH$_2$), 26.8 (CH$_2$), 29.0 (CH$_2$), 29.1 (CH$_2$), 29.3 (CH$_2$), 29.4 (CH$_2$), 32.6 (CH$_2$), 33.9 (CH$_2$), 34.1 (CH$_2$), 39.1 (CH$_2$), 55.9 (OCH$_3$), 112.8 (CH), 120.7 (CH), 122.6 (CH), 128.6 (Ar-CH$_2$CH=CH-), 132.5 (Ar-CH$_2$CH=CH-), 138.2 (C), 138.9 (C), 144.5 (C), 151.2 (C), 170.5 (-COO-crosslinker), 172.2 (-COO-), 189.5 ppm (-COH).

Figure S11. $^1$H NMR spectrum (in CDCl$_3$ at 25 ºC) for (a) crosslinker (CL), (b) the resultant polymer (P1) prepared by ADMET polymerization of M1 (run 8), and (c) resultant polymer (PL1) prepared by the polymerization of M1 in the presence of CL (5.0 mol%, sample run 24)
Figure S12. $^{13}$C NMR spectrum (in CDCl$_3$ at 25 °C) for (a) crosslinker (CL), (b) the resultant polymer (P1) prepared by ADMET polymerization of M1 (run 8), and (c) resultant polymer (PL1) prepared by the polymerization of M1 in the presence of CL (5.0 mol%, sample run 24)
Polymer (P2)

**P2** (sample run 14). $^1$H NMR (500 MHz, CDCl$_3$, ppm): $\delta$ 1.27-1.28 (CH$_2$), 1.38-1.41 (CH$_2$), 1.60-1.63 (CH$_2$), 1.95-2.04 (CH$_2$CH=CH-), 2.26-2.29 (-CH$_2$COO-), 4.06 (-COOCH$_2$-), 5.33-5.42 ppm (-CH=CH-). $^{13}$C NMR (125 MHz, CDCl$_3$, ppm): $\delta$ 25.2 (CH$_2$), 25.9 (CH$_2$), 28.3 (CH$_2$), 29.2 (CH$_2$), 29.3 (CH$_2$), 29.4 (CH$_2$), 29.5 (CH$_2$), 32.3 (CH$_2$), 32.7 (CH$_2$), 32.8 (CH$_2$), 34.5 (CH$_2$), 64.3 (-COOCH$_2$-), 130.4 (-CH=CH-), 174.1 ppm (-COO-).

**Figure S13.** $^1$H NMR spectrum (in CDCl$_3$ in 25 ºC) for (a) monomer (M2) and (b) polymer (P2)
Figure S14. $^{13}$C NMR spectrum (in CDCl$_3$ in 25 °C) for (a) monomer (M2) and (b) polymer (P2)
Polymer P3

P3 (sample run 19). $^1$H NMR (500 MHz, CDCl$_3$, ppm): $\delta$ 1.29 (CH$_2$), 1.61 (CH$_2$), 1.96 (CH$_2$-CH=CH), 2.28 (-CH$_2$COO-), 4.05 (-COOCH$_2$-), 5.38 ppm (-CH=CH-). $^{13}$C NMR (125 MHz, CDCl$_3$, ppm): $\delta$ 25.2 (CH$_2$), 26.1 (CH$_2$), 28.8 (CH$_2$), 29.3 (CH$_2$), 29.4 (CH$_2$), 29.5 (CH$_2$), 29.6 (CH$_2$), 29.7 (CH$_2$), 29.8 (CH$_2$), 29.9 (CH$_2$), 32.7 (CH$_2$), 34.5 (CH$_2$), 64.5 (-COOCH$_2$-), 130.5 (-CH=CH-), 174.1 ppm (-COO-).

Figure S15. $^1$H NMR spectrum (in CDCl$_3$ in 25 ºC) for (a) monomer (M3) and (b) polymer (P3)
Figure S16. $^{13}$C NMR spectrum (in CDCl$_3$ in 25 °C) for (a) monomer (M3) and (b) polymer (P3)
(ii) Atmospheric pressure chemical ionization (APCI) mass spectra of monomers and crosslinker

**Figure S17.** APCI mass spectrum of 4-allyl-2-methoxyphenyl 10-undecenoate (M1)

**Figure S18.** APCI mass spectrum of 5-hexen-1-yl 10-undecenoate (M2)
Figure S19. APCI mass spectrum of 10-undecen-1-yl 10-undecenoate (M3)

Figure S20. APCI mass spectrum of 5-formylbenzene-1,2,3-triyl tris(undec-10-enoate) (CL)
(iii) Selected GPC traces and DSC thermograms of polymers

**Figure S21.** GPC traces of polymers P2 in ADMET polymerization under effect of different G2 loading

**Figure S22.** GPC traces of polymers P3 in ADMET polymerization under effect of different G2 loading
Figure S23. DSC thermograms (exo down) for (a) polymers P1 (sample run 8), PL1 (sample run 24) and (b) polymers P2 (sample run 14), P3 (sample run 19), second heating cycle at a heating/cooling rate of 10 °C min⁻¹