Supporting Information

Palladium-Catalyzed synthesis of oil-based functionalized polyolefin

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1. Experimental

1.1 General

All manipulations of air- and water-sensitive compounds were carried out using standard Schlenk, high-vacuum, and glovebox techniques. Deuterated solvents used for NMR were dried and distilled prior to use. ¹H NMR spectra was recorded by a Bruker Ascend Tm 400 spectrometer at ambient temperature unless otherwise stated. The chemical shifts of the ¹H NMR spectra were referenced to the residual solvent; Coupling constants are in Hz. Molecular weight and molecular weight distribution of the polymer were determined by gel permeation chromatography (GPC) with a PL-220 equipped with two Agilent PLgel Olexis columns at 150 °C using o-dichlorobenzene as a solvent, and the calibration was made using polystyrene standard and are corrected for linear polyethylene by universal calibration using the Mark-Houwink parameters of Rudin: $K = 1.75 \times 10^{-2}$ cm³/g and R = 0.67 for polystyrene and $K = 5.90 \times 10^{-2}$ cm³/g and R = 0.69 for polyethylene. DSC measurements were performed on a TA Instruments DSC250. Samples (ca. 5 mg) were annealed by heating to 150 °C at 10 °C /min, cooled to -50 °C at 50 °C /min, and then analyzed while being heated to 150 °C at 10 °C /min.

Standard test method ASTM 638 was followed to measure the mechanical properties of the polyethylene sample. Polymers were melt-pressed at 30 to 35 °C above their melting point to obtain the test specimens. The test specimens had 25 mm gauge length, 2 mm width, and thickness of 0.5 mm. Stress/strain experiments were performed at 10 mm/min by means of a Universal Test Machine (UTM2502) at room temperature. At least three specimens of each copolymer were tested. Water contact angles on polymer films were measured with Contact Angle Meter SL200B (Solon Tech. Co., Ltd.) by the dynamic sessile drop method. Samples for water contact angle measurements were prepared by the evaporation of 3 to 5 % (w/w) solutions in toluene onto glass slides under ambient conditions. The solvent was evaporated on top of a hot plate for 30 minutes, and a second layer of the polymer solution was then applied in order to make the film thicker. The water contact angles of the polymer thin

films were measured using a contact angle goniometer at 25 °C with an accuracy of \pm 4°. The reported values are the average of at least six measurements made at different positions of the film.

1.2 Procedure for polymer sampleization and terpolymerization. In a typical experiment, a 350 mL glass thick-walled pressure vessel was charged with toluene, a desired amount of comonomer, and a magnetic stir bar in the glovebox. The pressure vessel was connected to a high-pressure line, and the solution was degassed. The vessel was warmed to the desired temperature using an oil bath and allowed to equilibrate for 5 min. The metal catalyst PO-Pd in CH₂Cl₂ was injected into the polymerization system via syringe. With rapid stirring, the reactor was pressurized, maintained at a desired ethylene pressure, and stirred continuously for a desired period. The pressure vessel was vented, the polymerization was quenched via the addition of MeOH (5 mL), and the polymer was precipitated using excess MeOH. After filtration, the polymer sample was obtained and dried at 80 °C for 24 h under vacuum. The polar monomer incorporation (mol%) was calculated from NMR analysis.

1.3 Preparation of sulfur vulcanized crosslinked polymer. A total amount of 2 g polymer sample was dissolved in 40 mL of TOL at 90 °C under nitrogen. After 30 min of reaction, add sulfuric acid (ie 20 mg ZnO, 6 mg stearic acid, 3 mg accelerator MBT, accelerator 4 mg TMTD, 5 mg sulfur), the solvent was drained and dried under vacuum at 60 °C for 12 hours. The rubber mixture was thermoformed using a hydraulic press at 10 MPa, 160 °C, and cured for 20 minutes to produce a 1 mm thick sheet for subsequent use.

1.4 Synthesis of plant oil-based monomers.



BEO was prepared via esterification using oleic acid. A typical procedure is given as follows: 4-bromo-1-butene (50 mmol, 6.75 g), oleic acid (50 mmol, 14.12 g), TMG (50 mmol, 5.76 g) and 30 ml DMF were loaded into a 200 mL round bottom flask, the reaction mixture was heated to 40 °C and the reaction was carried out for 12 h. The reaction was carried out at 40 °C. A pale yellow BEO liquid was obtained by extracting from water several times and drying under vacuum. Yield 90 % (16.38 g). HEO, DEO, and CEO are similarly prepared as BEO.

1.5 Synthesis of MIMIS.



In detail, 2-amino-4-hydroxy-6-methylpyrimidine (4.0 g, 32 mmol) and hexamethylene diisocyanate (HMDI) (31.0 mL, 192 mmol) were added into a 100 mL single-necked flask. After being purged with N₂ for 5 min, the reaction mixture was allowed to react at 100 °C for 20 h. Once completed, the product was filtered and washed with n-hexane three times. The purified monoisocyanato methylisocytosine (MIMIS) powder was further dried in a vacuum oven at 50 °C for 24 h. ¹H NMR (400 MHz, CDCl₃) δ = 13.1 (s, 1H, CH₃-C-N<u>H</u>), 11.9 (s, 1H, CH₂-NH-(C=O)-N<u>H</u>), 10.2 (s, 1H, CH₂-N<u>H</u>-(C=O)-NH), 5.8 (s, 1H, C=C<u>H</u>), 3.3 (m, 4H, C<u>H₂-NH-(C=O)-NH and C<u>H₂-NCO</u>), 2.2 (s, 3H, C<u>H₃-C=CH</u>), 1.6 (m, 4H, N-CH₂-C<u>H₂), 1.4 (m, 4H, N-CH₂-CH₂-C<u>H₂) ppm.</u></u></u>

1.6 Synthesis of P-CEO-UPy and P-CEO/NB-UPy.



A typical procedure is given as follows: MIMIS (0.08 g, 0.29 mmol) and P-CEO 1M (1 g, 0.32 mmol) were dissolved in TOL (30 mL). After stirring for 5 min under a N_2 atmosphere, two drops of DBTDL were added. The reaction mixture was reacted at 100 °C for 24 h. The turbid suspension was filtered, and the white product was washed with MeOH three times. The purified product was dried in a vacuum oven at 50 °C for 24 h.



2. ¹H NMR spectra of plant oil-based monomers

Figure S1. ¹H NMR spectrum of BEO.







Figure S3. ¹H NMR spectrum of DEO.





3. ¹H NMR spectra of the polymer samples



Figure S5. ¹H NMR spectrum of the polyethylene synthesized by PO-Pd from Table 1, Entry 1. ($C_2D_2Cl_4$, 120°C)









Figure S7. ¹H NMR spectrum of the polymer sample from Table 1, Entry 3. (C₂D₂Cl₄, 120°C)

Figure S8. ¹H NMR spectrum of the polymer sample from Table 1, Entry 4. (C₂D₂Cl₄, 120°C)

$$\frac{I(COOCH2)/2}{\text{Incorporation (\%)} = \frac{\overline{I(COOCH2)}}{2} + \frac{I(CH2) + I(CH3) - 29}{4} *100\% = 0.9\%$$







Figure S10. ¹H NMR spectrum of the polymer sample from Table 1, Entry 6. $(C_2D_2Cl_4, 120^{\circ}C)$



Figure S11. ¹H NMR spectrum of the polymer sample from Table 1, Entry 7. $(C_2D_2Cl_4, 120^{\circ}C)$

$$\frac{I_1/2}{\text{Incorporation (\%) of HEO} = \frac{I1}{2} + \frac{I2}{2} + \frac{I(CH3 + CH2) - 37 - 8 \times \frac{I2}{2}}{4} *100\% = 0.8\%$$





Figure S12. ¹H NMR spectrum of the polymer sample from Table 1, Entry 8. $(C_2D_2Cl_4, 120^{\circ}C)$

$$Incorporation (\%) \text{ of HEO} = \frac{I1}{2} + \frac{I2}{2} + \frac{I(CH3 + CH2) - 37 - 8 \times \frac{I2}{2}}{4} *100\% = 1.0\%$$

$$I_2/2$$

$$Incorporation (\%) \text{ of NB} = \frac{I1}{2} + \frac{I2}{2} + \frac{I(CH3 + CH2) - 37 - 8 \times \frac{I_2}{2}}{4} *100\% = 7.2\%$$



Figure S13. ¹H NMR spectrum of the polymer sample from Table 1, Entry 9. $(C_2D_2Cl_4, 120^{\circ}C)$

Incorporation (%) of HEO =
$$\frac{I_1/2}{I_1 + I_2 + I_2$$



Figure S14. ¹H NMR spectrum of the polymer sample from Table 1, Entry 10. $(C_2D_2Cl_4, 120^{\circ}C)$

Incorporation (%) of HEO =
$$\frac{I_1/2}{I_1 + I_2 + I_2$$



Figure S15. ¹H NMR spectrum of the polymer sample from Table 1, Entry 11. $(C_2D_2Cl_4, 120^{\circ}C)$

$$Incorporation (\%) \text{ of CEO} = \frac{I1}{2} + \frac{I2}{2} + \frac{I(CH3 + CH2) - 37 - 8 \times \frac{I2}{2}}{4} *100\% = 2.0\%$$

$$I_2/2$$

$$Incorporation (\%) \text{ of NB} = \frac{I1}{2} + \frac{I2}{2} + \frac{I(CH3 + CH2) - 37 - 8 \times \frac{I2}{2}}{4} *100\% = 5.0\%$$

4. Mechanical properties



Figure S16. Stress-strain curves for selected copolymer samples (PE: entry 1).



Figure S17. Stress-strain curves (a)-(i) for selected copolymer samples (P-BEO 1M: entry 2, P-HEO 1M: entry 3, P-DEO 1M: entry 4, P-HEO/NB: entry 6, 7 and 8, P-HEO/DCPD: entry 9 and 10) (In the polymer nomenclature, the number after the comonomer represents its concentration during copolymerization).



Figure S18. Stress-strain curves of HDPE/CO composites: (a) HDPE/CO 80/20, (b) P-HEO-1M/CO 80/20, (c) HDPE/CO/P-HEO-1M 75/20/5, (d) P-CEO-1M/CO 80/20, (e) HDPE/CO/P-CEO-1M 75/20/5.



Figure S19. Curves of stress and strain for HDPE blends with different plant oils: (a) HDPE/ESO 80/20, (b) HDPE/RO 80/20, (c) HDPE/TO 80/20, (d) HDPE/ESO/P-HEO-1M 75/20/5, (e) HDPE/RO/P-HEO-1M 75/20/5, (f) HDPE/TO/P-HEO-1M 75/20/5.



Figure S20. Mechanical properties for the polymer samples before and after vulcanization.



Figure S21. Effect of UPy on the mechanical properties of (a) P-CEO 1M and (b) P-CEO/NB 1M/0.5M. (In the polymer nomenclature, the number after the comonomer

represents its concentration during copolymerization).



5. SEM micrographs of fracture surface for composites

Figure S22. SEM image of the liquid nitrogen quenching surfaces for HDPE blends with different plant oils: (a) HDPE/ESO 80/20, (b) HDPE/ESO/P-HEO-1M 75/20/5, (c) HDPE/RO 80/20, (d) HDPE/RO/P-HEO-1M 75/20/5, (e) HDPE/TO 80/20, (f) HDPE/TO/P-HEO-1M 75/20/5. The scale bar of 20 μ m in SEM micrograph of HDPE/ESO (80/20) blend is applicable to all other micrographs.

6. DSC of polymers



Figure S23. DSC of the polymer sample from Table 1, Entry 1.



Figure S24. DSC of the polymer sample from Table 1, Entry 2.



Figure S25. DSC of the polymer sample from Table 1, Entry 3.



Figure S26. DSC of the polymer sample from Table 1, Entry 4.



Figure S27. DSC of the polymer sample from Table 1, Entry 5.



Figure S28. DSC of the polymer sample from Table 1, Entry 6.



Figure S29. DSC of the polymer sample from Table 1, Entry 7.



Figure S30. DSC of the polymer sample from Table 1, Entry 8.



Figure S31. DSC of the polymer sample from Table 1, Entry 9.







Figure S33. DSC of the polymer sample from Table 1, Entry 11.



7. GPC of polymers





Figure S35. GPC of the polymer sample from Table 1, Entry 2.



Figure S36. GPC of the polymer sample from Table 1, Entry 3.



Figure S37. GPC of the polymer sample from Table 1, Entry 4.



Figure S38. GPC of the polymer sample from Table 1, Entry 5.



Figure S39. GPC of the polymer sample from Table 1, Entry 6.



Figure S40. GPC of the polymer sample from Table 1, Entry 7.



Figure S41. GPC of the polymer sample from Table 1, Entry 8.



Figure S42. GPC of the polymer sample from Table 1, Entry 9.



Figure S43. GPC of the polymer sample from Table 1, Entry 10.



Figure S44. GPC of the polymer sample from Table 1, Entry 11.