Supplementary Information

Synthesis of Functional Polyolefins via Ring-Opening Metathesis Polymerization of Ester-functionalized Cyclopentene and Its Copolymerization with Cyclic Comonomers

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1. General experimental and materials

1.1 Materials

3-Cyclopentene-1-carboxylic acid and methanol, isopropanol, and tert-butanol were purchased from Tokyo Chemical Industry Co., Ltd. unless otherwise mentioned. And they were used as received at the highest purity available. N,N'-dicyclohexylcarbodimide (DCC) and 4-dimethylaminopyridine (DMAP) were of analytical grade and utilized as received from Energy Chemicals. Grubbs’ 3rd generation catalyst (G3) was purchased from Sigma-Aldrich Corporation. Solvents were distilled from drying agents under nitrogen before use: dichloromethane (DCM, CH₂Cl₂), diethyl ether and toluene from sodium/potassium. Other chemicals and solvents (petroleum ether, ethyl acetate, etc) were used without further purification. All reactions were carried out under nitrogen or vacuum using standard Schlenk techniques.

1.2 Instruments and analysis

¹H NMR (400MHz) and ¹³C NMR (100MHz) spectra were acquired with the Bruker Avance III 400 spectrophotometer utilizing the deuterated solvent as the lock and the residual reagent and TMS as an internal reference. Chemical shifts for ¹H and ¹³C NMR were referenced to residual signals from CDCl₃ (¹H: δ = 7.26 ppm and ¹³C: δ = 77.23 ppm).

Fourier Translation Infrared (FT-IR) spectra were recorded on a Bruker Vector 33 FT-IR spectrometer.

High-resolution mass spectrometry (HRMS) was carried out by an AB SCIEX 5600 + TOF-MS mass spectrometer.

Gel permeation chromatography (GPC) was employed to determine MWs and PDI via Water-150C apparatus equipped with Waters Styragel HR3 and HR4 columns and a Water 2414 refractive index detector. THF was used as the eluent with a flow rate of 1.0 mL/min at 40 °C. Injections were made at 0.3% w/v sample concentration using a 50 μL injection volume. As for universal calibration, the retention time was calibrated against narrow MWD polystyrene (PS) standards to give number average molecular weight (Mₙ) and weight average molecular weight (Mₘ) values.

Thermal properties of the polymers were analyzed using a TA Q20 DSC equipped with a
controlled cooling accessory at a heating rate of 10 °C/min unless otherwise noted. The samples were scanned for multiple cycles to eliminate the effect from the previous synthetic processing or annealing history of the samples and the results reported were the third scan in the cycle.

1.3 General procedures for the synthesis of monomers

Methyl cyclopent-3-enecarboxylate (CPM)

![Chemical structure of Methyl cyclopent-3-enecarboxylate (CPM)]

Synthesis of the cyclic monomers was accomplished based on the literature procedures.[1] Into a 150 mL three-neck round bottomed flask equipped with a stir bar, DCM (80 mL) and 3-cyclopentene-1-carboxylic acid (2 g, 18 mmol) were added and cooled to 0 °C under nitrogen. Methanol (1 g, 31.2 mmol) was added and then DMAP (0.35 g, 2.8 mmol) was added. The mixture was stirred to dissolve them. DCC (11.7 g, 56.5 mmol) was dissolved into another 30 mL DCM and then slowly transferred into the solution above. The reaction was allowed to process for 4 h at 0 °C and subsequently to warm to RT for another 2 h. Then it was quenched by pouring into diethyl ether (100 mL) and deionized water (50 mL), the organic phase was extracted three times with diethyl ether. And the combined organic solution was washed with brine and dried over anhydrous MgSO₃. The solvents were evaporated and the crude product was further purified by silica column chromatography using petroleum ether/ethyl acetate as eluent. After purification, methyl cyclopent-3-enecarboxylate (2 g) was obtained as colourless liquid (Yield 84%). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 5.73 – 5.55 (m, 2H), 3.68 (s, 3H), 3.22-3.03 (m, 1H), 2.66 (t, J = 7.0 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃, ppm): δ = 176.55 (s), 128.89 (s), 51.69 (s), 41.35 (s), 36.22 (s). HRMS: [M+H]⁺ calcd for C₇H₁₀O₂: 127.1532, found: 127.1556.

 iso-Propyl cyclopent-3-enecarboxylate (CPIP)
The same procedure described above for the synthesis of monomer of CPM as followed, iso-propyl cyclopent-3-enecarboxylate (2.2 g) was obtained as colourless liquid (Yield 87%). $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta = 5.67 - 5.48$ (m, 2H), $5.05 - 4.82$ (m, 1H), $3.08 - 2.91$ (m, 1H), $2.65 - 2.45$ (m, 4H), $1.19 - 1.09$ (m, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$, ppm): $\delta = 175.66$ (s), $128.92$ (s), $67.48$ (s), $55.69$ (s), $41.69$ (s), $36.25$ (s), $34.88$ (s), $25.52$ (dd, $J = 137.9, 98.2$ Hz), $21.75$ (s). HRMS: [M+H]$^+$ calcd for C$_9$H$_{14}$O$_2$: 155.1957, found: 155.2060.

**tert-Butyl cyclopent-3-enecarboxylate (CPtB)**

The same procedure described above for the synthesis of monomer of CPM as followed, tert-butyl cyclopent-3-enecarboxylate (3.2 g) was obtained as colourless liquid (Yield 84%). $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta = 5.70 - 5.56$ (m, 2H), $3.10 - 2.90$ (m, 1H), $2.61$ (t, $J = 7.0$ Hz, 4H), $1.45$ (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$, ppm): $\delta = 175.54$ (s), $128.99$ (s), $79.95$ (s), $42.53$ (s), $36.31$ (s), $28.10$ (s). HRMS: [M+H]$^+$ calcd for C$_{10}$H$_{16}$O$_2$: 169.1162, found: 169.1302.

**1.4 General procedures for the synthesis of polymers**

**PCPM**

Methyl cyclopent-3-enecarboxylate (2 g, 15.9 mmol) was dissolved into DCM (4 mL, 4 M) in a 25 mL flame dried Schlenk flask under N$_2$ at 0 °C. Then G3 catalyst (51.6 mg, 0.23% mol) was added into the mixture quickly. After 2 h, 5 mL of ethyl vinyl ether was added to quench the reaction for 30 min. The solution was poured into 200 mL methanol to precipitate the product. The brown solid product was washed twice with another 200 mL methanol, and then filtered to drying in vacuo to constant weight. Yield: 1.6
g (80%). $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta = 5.34$ (d, $J = 18.5$ Hz, 2H), 3.63 (s, 3H), 2.38 (dd, $J = 17.7, 11.5$ Hz, 1H), 2.33 – 2.04 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$, ppm): $\delta = 175.35$ (s), 129.28 (s), 128.28 (s), 51.41 (s), 45.62 (s), 34.58 (s). GPC data (THF vs polystyrene standards): $M_n = 20.8$ kDa, $M_w = 34.6$ kDa (PDI = 1.66). DSC: $T_g$ -23 °C.

**PCPiP**

The same procedure described above for the synthesis of CPM as followed, polymer PCPiP (1.7 g) was obtained as white solid (Yield 79%). $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta = 5.33$ (d, $J = 18.9$ Hz, 2H), 5.08 – 4.86 (m, 1H), 2.31 (d, $J = 6.4$ Hz, 1H), 2.19 – 2.02 (m, 4H), 2.02 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$, ppm): $\delta = 174.28$ (d, $J = 27.4$ Hz), 128.97 (d, $J = 53.7$ Hz), 127.83 (d, $J = 79.6$ Hz), 69.67 – 64.26 (m), 45.52 (d, $J = 37.8$ Hz), 36.21 – 33.13 (m), 21.93 (s). GPC data (THF vs polystyrene standards): $M_n = 21.6$ kDa, $M_w = 35.2$ kDa (PDI = 1.63). DSC: $T_g$ -28 °C.

**PCPtB**

The same procedure described above for the synthesis of CPtB as followed, polymer PCPtB (1.7 g) was obtained as white solid (Yield 84%). $^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta = 5.37$ (s, 2H), 2.25 (d, $J = 7.8$ Hz, 1H), 2.16 (d, $J = 40.1$ Hz, 4H), 1.41 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$, ppm): $\delta = 173.90$ (d, $J = 86.7$ Hz), 130.17 – 128.02 (m), 79.89 (d, $J = 39.0$ Hz), 45.95 (d, $J = 83.5$ Hz), 34.69 (t, $J = 25.6$ Hz), 28.18 (s). GPC data (THF vs polystyrene standards): $M_n = 25.5$ kDa, $M_w = 45.9$ kDa (PDI = 1.7). DSC: $T_g$ -7.5 °C.

**1.5 General procedures for copolymerization of CPM with cyclopentene**

**CPM-co-CP**

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The same method generally described above for the CPM polymerization above was followed. The chosen comonomer concentrations overall were 4 M, and the feed ratio was set at 1:1, 1:5, and 1:10 with increasing proportion of cyclopentene, respectively. Other polymerization conditions: G3 catalyst, 0.23% mol; DCM as solvent; temperature, 0 °C; time, 1 h.

1.6 General procedures for copolymerization of CPM with norbornene

CPM-co-NB

The same method generally described above for the CPM polymerization above was followed. The chosen comonomer concentrations overall were 4 M, and the feed ratio was set at 1:1, 1:5, and 1:10 with increasing proportion of norbornene, respectively. Other polymerization conditions: G3 catalyst, 0.23% mol; DCM as solvent; temperature, 0 °C; time, 1 h.

1.7 General procedures for copolymerization of CPM with cyclohexene

CPM-co-CH

The same method generally described above for the CPM polymerization above was followed. Two polymerization runs have total comonomer concentrations of 4 M, and one polymerization run was conducted at 10 M total comonomer concentration. The feed ratio was set at 1:1, 1:5, and 1:10 with increasing proportion of cyclohexene, respectively. Other polymerization conditions: G3 catalyst, 0.23% mol; DCM as solvent; temperature, 0 °C;
1.8 General procedures for copolymerization of CPM with cyclooctadiene

CPM-co-COD

The same method generally described above for the CPM polymerization above was followed. The chosen total comonomer concentrations were 4 M, and the feed ratio was set at 1:1, 1:5, and 1:10 with increasing proportion of cyclooctadiene, respectively. Other polymerization conditions: G3 catalyst, 0.23% mol; DCM as solvent; temperature, 0 °C; time, 1 h.

2. Supporting Figures

2.1 NMR spectra of synthetic products

Fig. S1 ¹H NMR spectra of CPM and its polymer.
Fig. S2 $^{13}$C NMR spectra of CPM and its polymer.

Fig. S3 $^1$H NMR spectra of CPiP and its polymer.

Fig. S4 $^{13}$C NMR spectra of CPiP and its polymer.
Fig. S5 $^1$H NMR spectra of CPtB and its polymer.

Fig. S6 $^{13}$C NMR spectra of CPtB and its polymer.
Fig. S7 ¹H NMR spectra of CPM-co-CP.

Fig. S8 ¹³C NMR of copolymers of methoxycarbonyl functionalized cyclopentene with norbornene and norbornene homopolymer.
Fig. S9 $^1$H NMR spectra of CPM-co-CH.

Fig. S10 $^{13}$C NMR spectra of CPM-co-CH.
Fig. S11 $^1$H NMR of copolymers of methoxycarbonyl functionalized cyclopentene with cyclooctadiene and cyclooctadiene homopolymer.

As exhibited in the spectrum, two new peaks appeared at 127.7 and 132.5 ppm in

Fig. S12 $^{13}$C NMR of copolymers of methoxycarbonyl functionalized cyclopentene with cyclooctadiene and cyclooctadiene homopolymer.

As exhibited in the spectrum, two new peaks appeared at 127.7 and 132.5 ppm in
addition to the CPM-CPM (\textit{cis} 129.4 and \textit{trans} 130.1 ppm) and COD-COD (\textit{cis} 129.6 and \textit{trans} 130.0 ppm) dyads, which can be assigned to the alternating CPM-COD dyad. According to the quantitative $^{13}$C NMR investigation, the copolymers are composed of approximately 4.6% alternating dyads in CPM11COD, 6.6% alternating dyads in CPM15COD, and 3.2% alternating dyads in CPM110COD respectively.

![Fig. S13 $^1$H NMR spectra of PCP-A (a), and $^{13}$C NMR spectra of PCP-A (b). The deuterated solvent CDCl$_3$ ($^1$H: $\delta = 7.26$ ppm and $^{13}$C: $\delta = 77.23$ ppm) as the lock and the residual reagent and TMS as an internal reference.](image-url)
2.2 GPC profiles

**Fig. S14** GPC traces of methoxycarbonyl functionalized cyclopentene/cyclooctadiene copolymer.

**Fig. S15** GPC traces of methoxycarbonyl functionalized cyclopentene/cyclohexene copolymer.
2.3 DSC curves

Fig. S17 DSC curves of copolymers of methoxycarbonyl functionalized cyclopentene and cyclopentene, and polycyclopentene (PCP) produced via ROMP.
**Fig. S18** DSC curves of copolymers of methoxycarbonyl functionalized cyclopentene and cyclooctadiene, and polycyclooctadiene (PCOD) produced by ROMP.

**Fig. S19** DSC curves of copolymers of methoxycarbonyl functionalized cyclopentene and cyclohexene.
References