

Supplementary Material

Fully tuneable ethylene-propylene elastomers using a supported permethylindenyl-phenoxy (PHENI*) catalyst

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1. General details and instrumentation

General procedures. Air- and moisture-sensitive compounds were manipulated under an inert atmosphere of nitrogen, using standard Schlenk line techniques¹ on a dual manifold vacuum/nitrogen line or in an MBraun Labmaster 100 glovebox.

Pentane, hexanes, toluene and benzene were dried using an MBraun SPS 800 solvent purification system, stored over a potassium mirror, and degassed under partial vacuum before use. Anhydrous dichloromethane was dried using an MBraun SPS 800 system, stored over pre-activated 3 Å molecular sieves and degassed under partial vacuum before use. Tetrahydrofuran was distilled from sodium/benzophenone, stored over pre-activated 3 Å molecular sieves and degassed under partial vacuum before use.

Deuterated solvents were dried over potassium metal (benzene-*d*₆, and toluene-*d*₈) or CaH₂ (chloroform-*d*, pyridine-*d*₅, and tetrahydrofuran-*d*₈) and refluxed under reduced pressure, distilled under static vacuum, freeze-pump-thaw degassed three times and stored over pre-activated 3 or 4 Å molecular sieves. Chloroform-*d* was used as supplied for samples which were not air- and moisture-sensitive.

Solution NMR spectroscopy. NMR spectra were recorded on either a Bruker Avance III HD NanoBay NMR (9.4 T, 400.2 MHz), a Bruker Avance III NMR (11.75 T, 499.9 MHz), a Bruker NEO 600 (14.1 T, 600.4 MHz) with a broadband helium cryoprobe, or a Bruker Avance NMR (11.75 T, 500.3 MHz) with a ¹³C-detect cryoprobe. Spectra were recorded at 298 K unless otherwise stated and referenced internally to the residual *protio* solvent resonance. Chemical shifts, δ , are reported in parts per million (ppm) relative to tetramethylsilane ($\delta = 0$ ppm). Air-sensitive samples were prepared in a glovebox under an inert atmosphere of nitrogen, using dried deuterated solvents and sealed in 5 mm Young's tap NMR tubes. Quantitative ¹³C NMR spectroscopy was performed using an inverse-gated ¹H decoupling pulse sequence, a relaxation delay of 60 s, and 2.8 mg mL⁻¹ Cr(acac)₃ as a *T*₁ relaxation agent.

Solid-state NMR spectroscopy. Solid-state NMR spectra were recorded by Dr Nicholas Rees (University of Oxford) on a Bruker Avance III HD NanoBay solid-state NMR spectrometer (9.4 T, 399.9 MHz). Samples were spun at the magic angle at a spin rate of 10 kHz. ¹³C NMR spectra were referenced to adamantane.

Infrared spectroscopy. Fourier-transform infrared (FTIR) spectra were measured using a ThermoScientific Nicolet iS 5 FTIR spectrometer, using a germanium iD3 Attenuated Total Reflection accessory. A background spectrum was run prior to the samples and subtracted from the sample spectra.

Gel permeation chromatography. Gel permeation chromatography (GPC) was performed by Ms Liv Thobru, Ms Sara Rund Herum, and Ms Rita Jessen (Norner AS, Norway) on a high temperature gel permeation chromatograph with an IR5 infrared detector (GPC-IR5). Samples were prepared by dissolution in 1,2,4-trichlorobenzene (TCB) containing 300 ppm of 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT) at 160 °C for 90 minutes and then filtered with a 10 μm SS filter before being passed through the GPC column. The samples were run under a flow rate of 0.5 mL min⁻¹ using TCB containing 300 ppm of BHT as mobile phase with 1 mg mL⁻¹ BHT added as a flow rate marker. The GPC column and detector temperature were set at 145 and 160 °C respectively.

Differential scanning calorimetry. Differential scanning calorimetry was performed on a Perkin Elmer DSC 4000 System within a temperature range of 10–250 °C at a rate of 20 K min⁻¹. Polymer samples

were sealed in 100 μL aluminium crucibles. An empty crucible was used as a reference, and the DSC was calibrated using indium and zinc.

Rheology. Rheology was performed on a TA Instruments Discovery HR-2 hybrid rheometer using a temperature controlled stainless steel Peltier plate and a flat parallel plate geometry (20 mm diameter) with a working gap of 1000 μm . Approximately 200 mg of material was first vacuum compression moulded into a disc (10 mm diameter) at 180 $^{\circ}\text{C}$. Measurements were performed at 160 $^{\circ}\text{C}$ under a flow of dry nitrogen in continuous oscillation (direct strain) mode at a strain of 0.1% (within the LVE region) and a logarithmic frequency sweep was performed from 0.01–100 rad s^{-1} .

Mechanical analysis. Mechanical testing was performed on a TA Instruments Discovery DR-2 hybrid rheometer using the DMA mode (film tension) accessory. Approximately 100–150 mg of material was vacuum compression moulded into an ISO 37 Type 3 dogbone (width $b_1 = 4$ mm, length $L_0 = 10$ mm, thickness *ca.* 1 mm) at 150–180 $^{\circ}\text{C}$. Tensile properties were determined at ambient temperature at a constant strain rate of 500 $\mu\text{m s}^{-1}$ and repeated in triplicate.

Literature preparations and commercially supplied materials. 2,3,4,5,6,7-hexamethylindene (SCG Chemicals PLC), $n\text{BuLi}$ (1.6 M in hexanes, Sigma Aldrich), sulphur (Sigma Aldrich), 2-mercaptobenzothiazole (Sigma Aldrich), and 6-bromo-2,4-di-*tert*-butylphenol (Alfa Aesar) were all used as received. $\text{TiCl}_4 \cdot 2\text{THF}$ was prepared according to a literature procedure.² Et_3N was dried over KOH, distilled under static vacuum and freeze-pump-thaw degassed before use. Me_2SiCl_2 (Sigma Aldrich) was dried over pre-activated 3 \AA molecular sieves before use. Allyl bromide (Sigma Aldrich) was washed with NaHCO_3 followed by distilled water and dried over MgSO_4 . 1-Hexene, 1-dodecene, and 5-ethylidene-2-norbornene (Sigma Aldrich), and 1-octene (Alfa Aesar) were dried of CaH_2 , distilled under static vacuum, freeze-pump-thaw degassed three times and stored over pre-activated 3 or 4 \AA molecular sieves.

PHENI* catalyst **1** was synthesised according to a literature procedure.³ Ethylene, propylene (N2.5), and ethylene/propylene were supplied by BOC Ltd., CK Special Gases Ltd., CK Isotopes Ltd., or Buse Gasses Ltd. and used as received. Ethylene was passed through pre-activated molecular sieves before use. Solid polymethylaluminumoxane (sMAO) was supplied by SGC Chemicals PLC as a slurry in toluene which was dried under vacuum before use. MAO was supplied by Chemtura Corporation as a slurry in toluene which was dried under vacuum before use. HDPE was supplied by SCG Chemicals PLC.

2. Experimental details

Copolymerisation of ethylene and propylene. 1000 equivalents methylaluminumoxane (MAO) was introduced into a 150 mL Rotaflo[®] ampoule containing a stirrer bar. 10 mg supported catalyst was added to the ampoule and washed in with 50 mL hexanes. The vessel was sealed and was pumped onto a vacuum line and degassed under reduced pressure. It was cycled once more using an ethylene/propylene purge while the reaction was brought to temperature in an oil bath with the stirring set at 1000 rpm. The stopcock was opened to a mixed ethylene/propylene at a given monomer ratio (25:75, 50:50, or 75:25) and a total pressure of 2 bar, and the timer was started. On completion of the run, the vessel was closed to monomer and degassed. The mixture was rinsed out with fresh hexane and decanted into a 500 mL round-bottomed flask containing dilute aqueous hydrochloric acid. The organic solvents were removed by rotary evaporation. The polymer was manually separated from the aqueous phase and dried in a vacuum oven until constant weight. All polymerisation runs were carried out at least in duplicate to ensure reproducibility.

¹H NMR (600 MHz, 1,1,2,2-tetrachloroethane- d_2 , 403 K): δ 1.51, 1.42, 1.31, 1.14, 0.89, and 0.88 ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, 1,1,2,2-tetrachloroethane- d_2 , 403 K): δ 45.85, 45.63, 38.40, 37.94, 37.56, 33.26, 30.94, 30.74, 30.35, 29.96, 27.42, 24.86, 20.78, and 20.08 ppm.

Terpolymerisation of ethylene, propylene, and ethylenenorbornene. 1000 equivalents methylaluminoxane (MAO) was introduced into a 150 mL Rotaflo[®] ampoule containing a stirrer bar. 10 mg supported catalyst was added to the ampoule and washed in with 45 mL hexanes. In a sidearm, the desired amount of 5-ethylidene-2-norbornene (ENB) was added and washed in with 5 mL hexanes. The vessel was sealed and was pumped onto a vacuum line and degassed under reduced pressure. It was cycled once more using an ethylene/propylene purge while the reaction was brought to temperature in an oil bath with the stirring set at 1000 rpm. The stopcock was opened to a mixed ethylene/propylene (50:50) at a total pressure of 2 bar, and the timer was started. On completion of the run, the vessel was closed to monomer and degassed. The mixture was rinsed out with fresh hexane and decanted into a 500 mL round-bottomed flask containing dilute aqueous hydrochloric acid. The organic solvents were removed by rotary evaporation. The polymer was manually separated from the aqueous phase and dried in a vacuum oven until constant weight. All polymerisation runs were carried out at least in duplicate to ensure reproducibility.

^1H NMR (400 MHz, chloroform- d , 298 K): δ 7.26, 5.24, 5.01, 2.73, 2.69, 2.39, 2.35, 2.14, 2.10, 2.06, 1.83, 1.79, 1.75, 1.61, 1.56, 1.51, 1.49, 1.47, 1.41, 1.35, 1.26, 1.09, 0.85, and 0.83 ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, chloroform- d , 298 K): δ 147.42, 146.56, 111.23, 110.64, 49.90, 46.41, 45.91, 45.73, 45.42, 45.17, 45.11, 41.23, 39.45, 38.50, 38.37, 38.20, 38.03, 37.63, 37.59, 37.37, 37.30, 37.08, 36.30, 33.62, 33.31, 32.95, 30.57, 30.24, 29.94, 29.90, 27.63, 27.55, 27.50, 27.29, 27.12, 24.66, 24.47, 20.49, 19.93, 19.90, 19.87, 19.77, 19.72, 19.69, 14.53, and 14.01 ppm.

IR: 2955, 2922, 2852, 1461, 1377, 1260, 1153, 1018, 806, and 718 cm^{-1} .

Vulcanisation of EPDM. To a vial containing a magnetic stirrer bar was added 160 mg EPDM (synthesised using [ENB] = 58 mM; 5 mol% incorporation), 16 mg (10 phr; parts per hundred rubber) elemental sulphur (S_8), and 8 mg (5 phr) 2-mercaptobenzothiazole (MBT). The components were dissolved in toluene or xylene to ensure thorough mixing. The toluene was then removed in a vacuum oven overnight.

For the DSC experiments: to a 50 μL aluminium DSC pan, approximately 6–8 mg of EPDM/S/MBT was added, and the pan was subjected to a DSC heating protocol. Under the Dynamic Vulcanisation protocol, the reaction is heated to 300 $^\circ\text{C}$ at a rate of 2.5–20 $^\circ\text{C min}^{-1}$. Under the Isothermal Vulcanisation protocol, the reaction is heated to 180–200 $^\circ\text{C}$, held for 3 hours, then heated to 300 $^\circ\text{C}$. In both cases the protocol is repeated to obtain a baseline which is subtracted from the first heating cycle.

For the rheometry experiments: approximately 180 mg EPDM/S/MBT were pressed using a pellet press under 10 tons of pressure which was then placed on the rheometer plate at 25 $^\circ\text{C}$. Under continuous oscillation ($\omega = 1 \text{ rad s}^{-1}$; 0.2% strain), the temperature was raised to 200 $^\circ\text{C}$ at a heating rate of 20 $^\circ\text{C min}^{-1}$ and held for 6 hours.

^{13}C CPMAS ssNMR (101 MHz, 10 kHz, 298 K): δ 129.44 (br), 44.79, 36.83, 32.27, 29.47, 26.59, 23.78, and 19.39 ppm.

IR: 3112, 3079, 3039, 2955, 2922, 2849, 2365, 2329, 1695 (br), 1596, 1494, 1461, 1424, 1477, 1322, 1282, 1249, 1080, 1033, 1011, 864 (br), 751, 670, and 604 cm^{-1} .

Copolymerisation of propylene with 1-hexene. 1000 equivalents methylaluminoxane (MAO) was introduced into a 150 mL Rotaflo® ampoule containing a stirrer bar. 10 mg supported catalyst was added to the ampoule and washed in with 45 mL hexanes. In a sidearm, the desired amount of 1-hexene was added and washed in with 5 mL hexanes. The vessel was sealed and was pumped onto a vacuum line and degassed under reduced pressure. It was cycled once more using a propylene purge while the reaction was brought to temperature in an oil bath with the stirring set at 1000 rpm. The stopcock was opened to propylene (2 bar) and the timer was started. On completion of the run, the vessel was closed to monomer and degassed. The mixture was rinsed out with fresh hexane and decanted into a 500 mL round-bottomed flask containing dilute aqueous hydrochloric acid. The organic solvents were removed by rotary evaporation. The polymer was manually separated from the aqueous phase and dried in a vacuum oven until constant weight. All polymerisation runs were carried out at least in duplicate to ensure reproducibility.

¹H NMR (600 MHz, chloroform-*d*, 298 K): δ 5.8, 1.45, 1.28, 1.21, 1.16, 1.10, 1.06, 1.03, 1.01, 1.00, 0.95, 0.91, 0.90, 0.88, 0.82, 0.81, 0.76, and 0.74 ppm.

¹³C{¹H} NMR (151 MHz, chloroform-*d*, 298 K): δ 47.46, 47.23, 47.07, 46.85, 46.41, 46.10, 45.70, 45.42, 44.84, 44.56, 43.76, 43.45, 42.99, 42.75, 32.16, 30.48, 28.76, 27.49, 23.44, 23.37, 23.31, 21.48, 21.09, 20.80, 20.69, 20.39, 20.17, 20.02, 19.94, 19.86, 19.76, 19.67, 19.59, 19.46, 19.33, and 14.36 ppm.

3. Copolymerisation data tables

3.1. Ethylene-propylene copolymerisation data

Table S1 Polymerisation data using **1**. Polymerisation conditions: 10 mg catalyst, [Al]/[Ti] = 1000, 30 minutes, 50 mL hexanes.

$p(E)$ /bar	$p(P)$ /bar	Temperature /°C	Cocatalyst	Activity / $\text{kg}_{\text{EPM}} \text{mol}^{-1} \text{h}^{-1} \text{bar}^{-1}$	M_w /kDa	PDI	x_p (wt%)
2	0	60	MAO	1684 ± 476	2631.3	5.5	0.0
1	1	60	MAO	547 ± 289	290.4	3.1	54.0
0	2	60	MAO	3156 ± 677	633.9	2.2	100.0
2	0	60	TIBA	3719 ± 106	2087.5	5.2	0.0
1.5	0.5	60	TIBA	3107 ± 214	158.7	2.6	20.0
1	1	60	TIBA	3313 ± 64	149.7	2.3	42.5
0.5	1.5	60	TIBA	2803 ± 109	162.5	2.4	70.2
0	2	60	TIBA	279 ± 2	256.5	2.4	100.0
1	1	30	TIBA	2885 ± 229	275.2	2.6	41.0
1	1	40	TIBA	2674 ± 46	234.4	2.3	41.2
1	1	50	TIBA	3726 ± 168	168.8	2.4	40.1
1	1	60	TIBA	3313 ± 64	149.7	2.3	42.5
1	1	70	TIBA	3464 ± 97	147.1	2.6	43.2
1	1	80	TIBA	2157 ± 501	127.1	2.4	47.1
1	1	90	TIBA	1623 ± 476	97.6	2.6	47.3

3.2. Ethylene-propylene-diene terpolymerisation data

Table S2 Polymerisation data using 1. Polymerisation conditions: 10 mg catalyst, 30 minutes, 50 mL hexanes.

$p(E)$ /bar	$p(P)$ /bar	ENB / μ L	[ENB] /mM	Temperature /°C	Activity / $\text{kg}_{\text{EPM}} \text{mol}^{-1} \text{h}^{-1} \text{bar}^{-1}$	M_w /kDa	PDI	x_E (mol%)	x_P (mol%)	x_{ENB} (mol%)
1	1	0	0.0	60	3313 ± 64	149.7	2.3	43.6	56.4	0.0
0.6	0.6	78	11.6	60	5155 ± 254	165.4	2.4	55.9	42.2	1.8
1	1	156	23.2	60	2903 ± 155	199.9	2.5	56.1	39.8	4.1
1	1	312	46.4	60	1622 ± 281	185.1	2.7	58.3	37.0	4.7
0.6	0.6	625	92.9	60	1065 ± 38	203.9	3.2	51.0	35.6	13.4

3.3. Propylene-hexene copolymerisation data

Table S3 Polymerisation data using 1. Polymerisation conditions: 10 mg catalyst, 2 bar propylene, [MAO]/[Ti] = 1000, 30 minutes, 50 mL hexanes.

C6 / μ L	[C6] /mM	Temperature /°C	Activity / $\text{kg}_{\text{EPM}} \text{mol}^{-1} \text{h}^{-1} \text{bar}^{-1}$	M_w /kDa	PDI	x_{C6} (mol%)
0	0.0	60	3213 ± 595	633.9	2.2	0.0 ± 0.0
156	24.9	60	1812 ± 42	477.3	2.3	1.8 ± 0.6
312	49.9	60	1426 ± 136	493.3	2.4	2.7 ± 0.5
625	100.0	60	1875 ± 446	434.9	2.3	6.6 ± 0.3
937	149.9	60	1645 ± 107	448.1	2.3	5.7 ± 1.1
1250	199.9	60	860 ± 280	466.6	2.3	8.4 ± 0.2

4. Fineman-Ross analysis

$$f = F \frac{r_1 F + 1}{r_2 + F} \Rightarrow \frac{F}{f}(f - 1) = r_1 \frac{F^2}{f} - r_2$$

$$r_1 = \frac{k_{11}}{k_{12}}; r_2 = \frac{k_{22}}{k_{21}}$$

where $F = [E]/[P]$ in feed, $f = [E]/[P]$ in copolymer, and k_{nm} is the rate constant for the insertion of monomer m after monomer n .⁴

Table S4 Reactivity ratios for E/P copolymerisations at $T_p = 60$ °C.

Copolymerisation	r_E	r_P	$r_E^* r_P$
E/P	8.9 ± 1.8	0.12 ± 0.01	1.05 ± 0.08

Table S5 Fineman-Ross data for E/P copolymerisation at $T_p = 60$ °C. $F = [E]/[P]$ in feed, $f = [E]/[P]$ ($= x_P^{\frac{1}{f} - 1}$) in copolymer. $[E] \approx p \cdot 0.00175 \cdot \exp\left(\frac{2569}{1.98 \cdot T}\right)$, $[P] \approx p \cdot 0.00272 \cdot \exp\left(\frac{3260}{1.98 \cdot T}\right)$ for partial pressure, p , in bar and absolute temperature T .⁵ Incorporation determined from GPC-IR.

[E] /mM	[P] /mM	x_P (mol%)	F	f
129	190	14.3	0.68	6.00
86	381	33.0	0.23	2.03
43	571	61.1	0.08	0.64

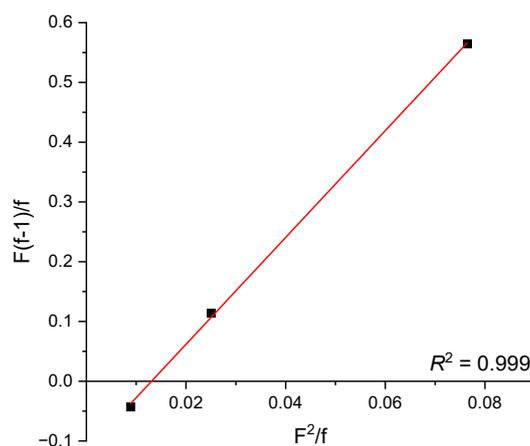


Figure S1 Fineman-Ross plot for ethylene/propylene copolymerisation at $T_p = 60$ °C.

5. Propylene/hexene copolymerisation

Propylene/LAO copolymers are much less studied than their E/LAO counterparts, though *i*PP/LAO, *s*PP/LAO, and *a*PP/LAO copolymers have been reported and the comonomer shown to modify the physical properties of the polymers.^{6,7} Following the synthesis of elastomeric UHMW α PP using **1**/MAO,⁸ the copolymerisation of propylene with 1-hexene was investigated.

In P/C6 copolymerisation, **1**/MAO displayed a seven-fold greater activity than **1**/TIBA. No positive comonomer effect was observed, and activities broadly decrease with increasing [C6] (Figure S2). Similarly, a positive comonomer effect was not found with the (ArMe₄Cp)TiCl₂ODipp complexes reported by Wu *et al.*,⁷ and of the complexes studied by Quijada *et al.*, only the isoselective SBIZrCl₂ catalyst showed a positive comonomer effect.⁶

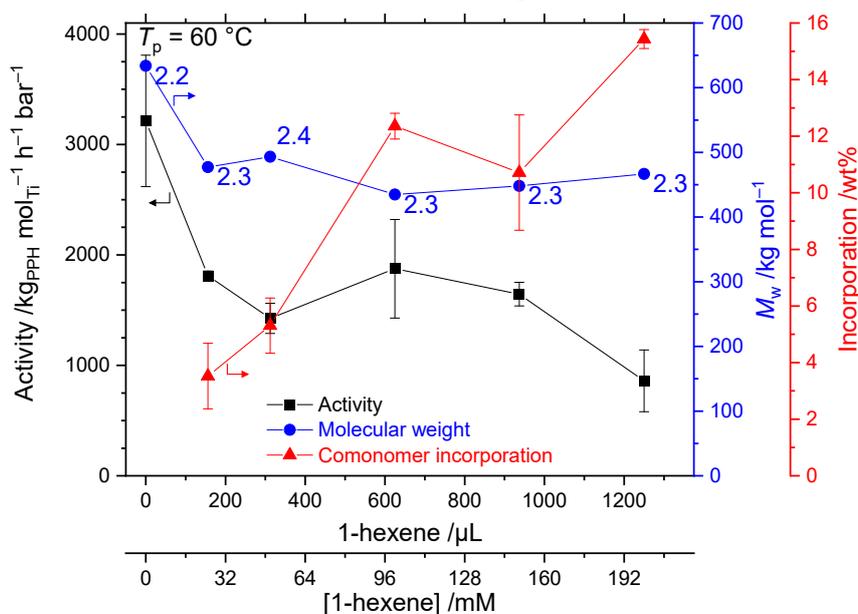


Figure S2 Mean copolymerisation activity of **1**/MAO and the molecular weight (M_w , PDIs annotated) and mean C6 incorporation of poly(propylene-*co*-hexene) (PPH) as a function of 1-hexene loading ($0 \leq V \leq 1250 \mu\text{L}$; $0 \leq c \leq 200 \text{ mM}$). Polymerisation conditions: 10 mg catalyst, 2 bar propylene, 50 mL hexanes, 40 mg MAO ($[Al]_{MAO}/[Ti]_0 = 1000$), 60 °C, and 30 minutes. Error bars shown at one standard deviation.

Molecular weight was found to be 25% decreased in the copolymer compared to the propylene homopolymer but remained approximately constant with increasing [C6] at $460 \pm 20 \text{ kDa}$. By contrast the *a*PP/C6 reported by Wu *et al.* showed lower molecular weights ($<200 \text{ kDa}$) which decreased with increasing incorporation.⁷ Quijada *et al.* demonstrated that isoselective catalysts produced polymers whose M_w did not depend on comonomer concentration, while syndioselective complexes produced polymers where M_w decreased with increasing comonomer concentration.⁶ Dispersities remained narrow, between 2.2 and 2.4. 1-Hexene incorporation was determined from quantitative ¹³C NMR spectroscopy and was found to increase approximately proportionally to [C6] up to 15.4 mol% at 1250 μL (200 mM). Incorporations up to 10.1 mol% are reported by Wu *et al.* at [C6] of 500 mM,⁷ and Arnold *et al.* used the complex EBHfCl₂ to synthesise *i*PP/LAO copolymers over the complete composition range.⁹ Uozumi *et al.* found that 1-hexene incorporation followed the trend aspecific < isospecific < syndiospecific.¹⁰ Despite the PHENI* system being aspecific, **1**/MAO is able to incorporate C6 more efficiently than these systems, with greater incorporations produced at lower comonomer concentrations. This may have implications in expanding the scope of applications for elastomeric UHMW α PP.⁸

6. Copolymerisation graphical results

Incorporation in the EPM copolymers was found to depend linearly on monomer feed composition with unit gradient.

Linear regression:

$$\begin{aligned} \text{TIBA: } x_{C_3} &= (1.008 \pm 0.049) (\%P) + (1.504 \pm 2.786); & R^2 &= 0.9906 \\ \text{MAO: } x_{C_3} &= (1.000 \pm 0.046) (\%P) + (-3.667 \pm 3.164); & R^2 &= 0.9957 \end{aligned}$$

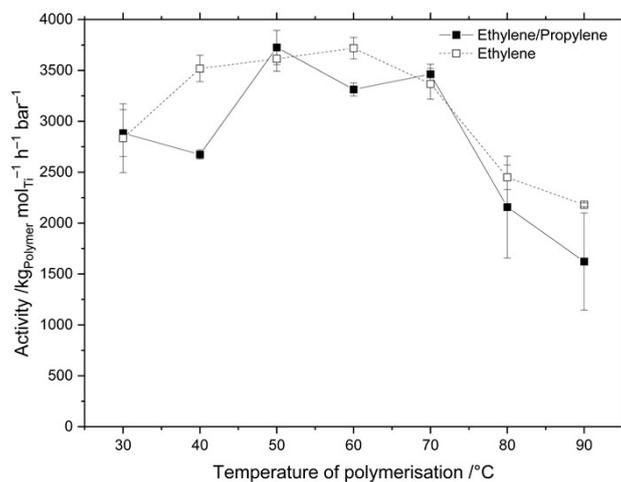


Figure S3 Mean polymerisation activity as a function of temperature of polymerisation using **1**/TIBA. Polymerisation conditions: 10 mg catalyst, 2 bar total pressure (either ethylene or 50:50 ethylene/propylene), 50 mL hexanes, 150 mg TIBA, and 30 minutes. Error bars shown at one standard deviation. Ethylene homopolymerisation data reproduced from *Chem. Commun.*, 2021, **57**, 8600.³

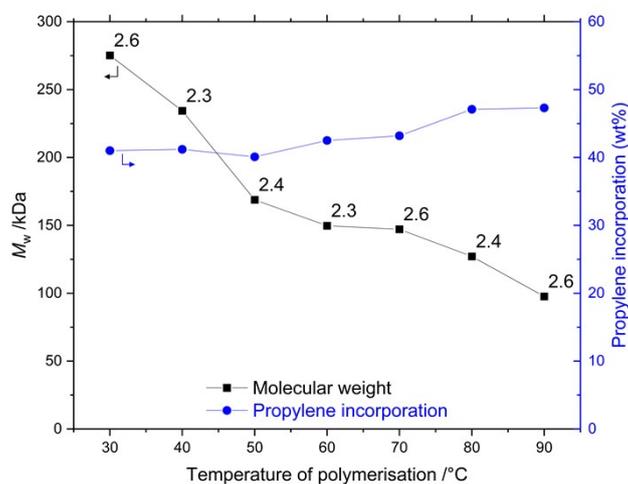


Figure S4 Weight-average molecular weight, with PDIs annotated, and propylene incorporation as a function of temperature of EPM synthesised using **1**/TIBA using 50:50 E/P and a temperature of polymerisation of 30–90 °C.

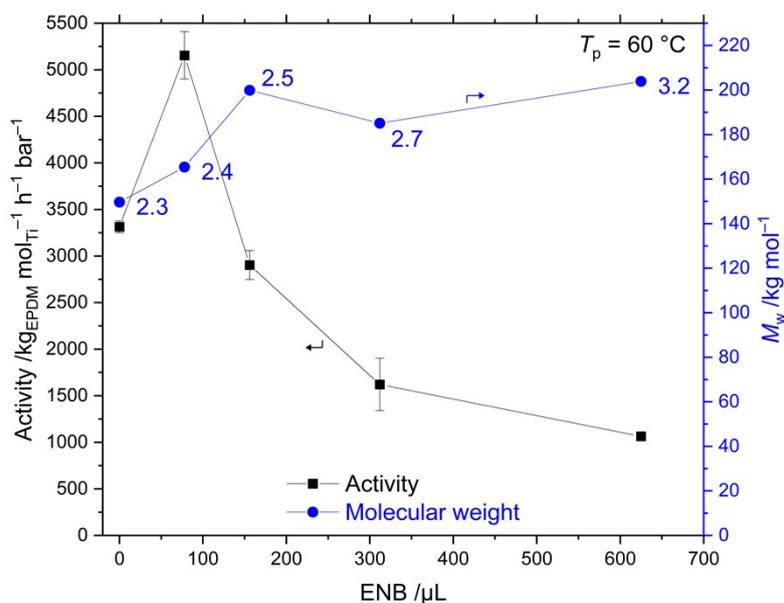


Figure S5 Mean terpolymerisation activity of **1**/TIBA and EPDM molecular weight (M_w , with PDIs annotated) as a function of ENB loading ($0 \leq V \leq 625 \mu\text{L}$; $0 \leq c \leq 93 \text{ mM}$). Polymerisation conditions: 10 mg catalyst, 2 bar ethylene/propylene (50:50), 50 mL hexanes, 150 mg TIBA, 60 °C, and 30 minutes. Error bars shown at one standard deviation.

7. EPDM vulcanisation

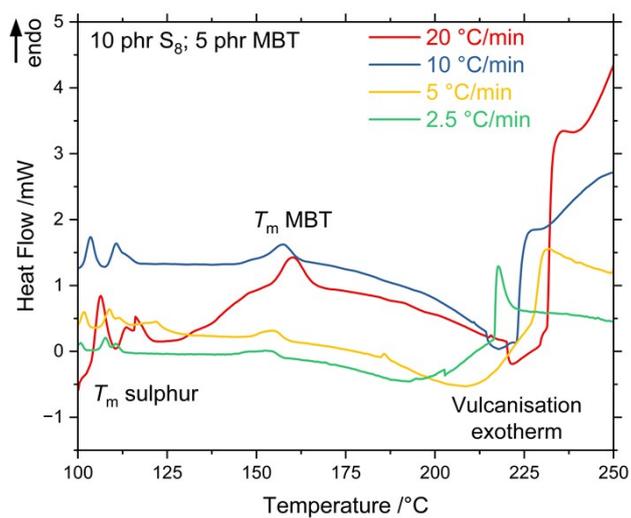


Figure S6 Differential scanning calorimetry thermograms for EPDM/S/MBT vulcanisation at heating rates of 2.5–20 °C min⁻¹.

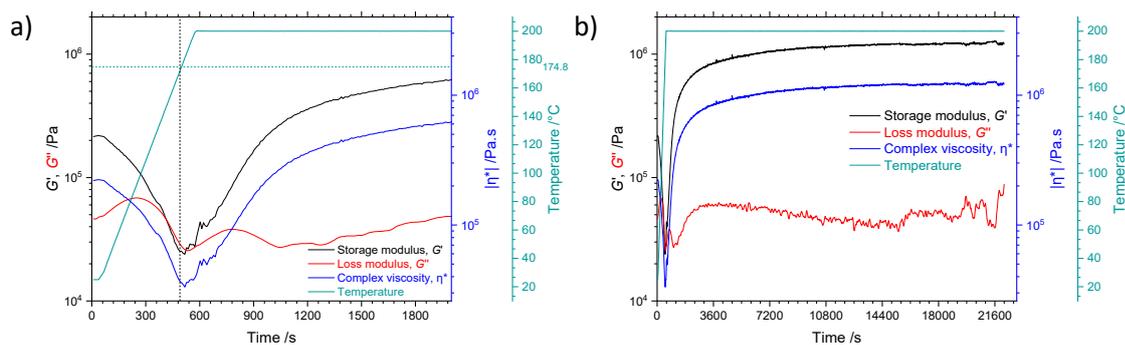


Figure S7 Rheometry ($\omega = 1 \text{ rad s}^{-1}$, 0.2% strain; temperature ramp 25–200 °C at 20 °C min^{-1}) as a function of time for EPDM/S/MBT vulcanisation. a) Initial phase ($t \leq 2000 \text{ s}$) showing onset of vulcanisation at 175 °C, and b) the whole experiment with 6 h cure time at 200 °C. Dynamic crosslinking shown by increase in storage modulus, G' , over time. Storage modulus, G' ; loss modulus, G'' ; complex viscosity, η^* .

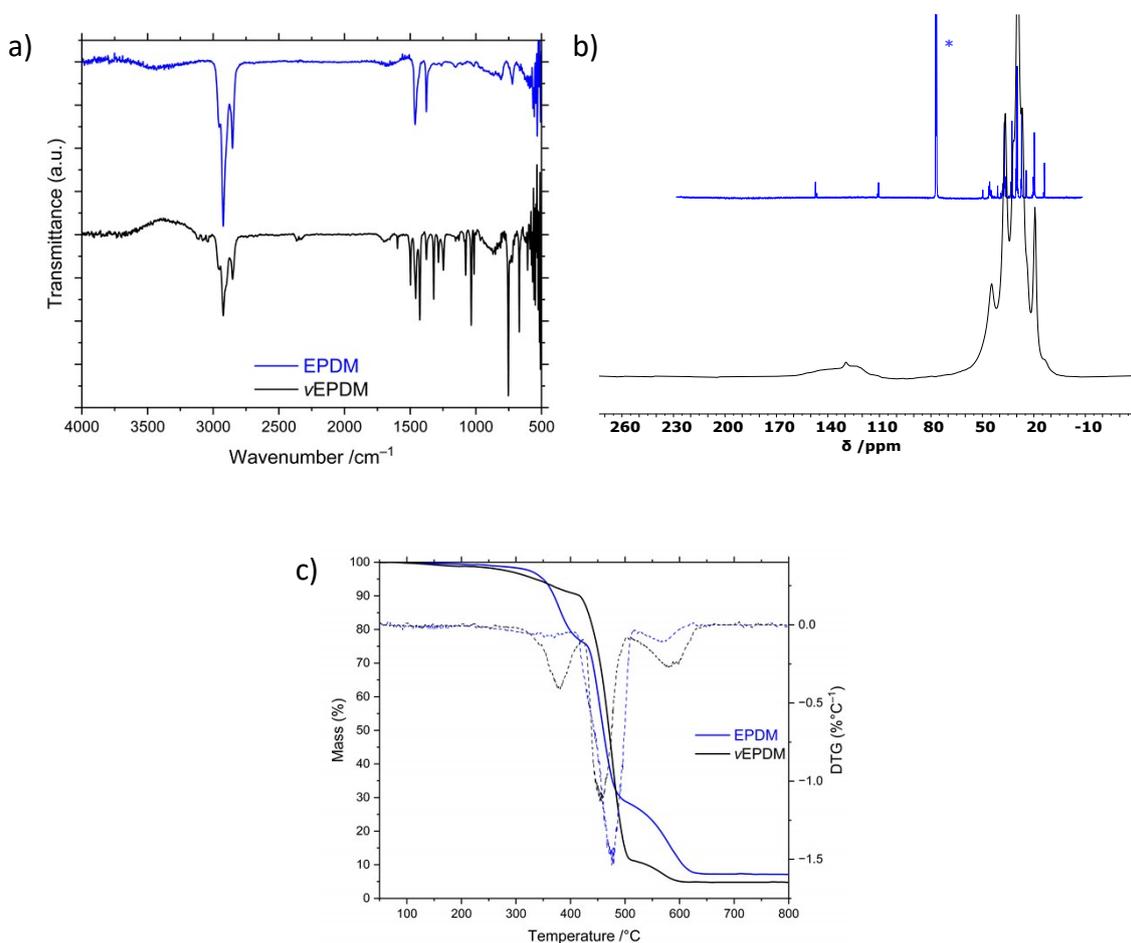


Figure S8 Characterisation of EPDM (blue) and vEPDM (black): a) IR spectroscopy, b) solution-phase (151 MHz, chloroform- d , 298 K, asterisk (*) denotes CDCl_3) and solid state (101 MHz, 10 kHz, 298 K) $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, and c) thermogravimetry.

8. Gel-permeation chromatography

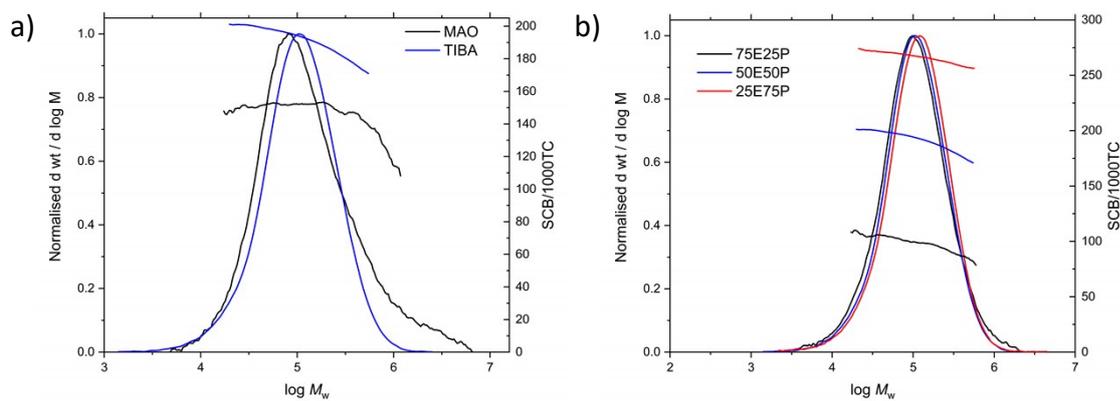


Figure S9 Gel permeation chromatograms of EPM synthesised by **1** as a function of a) cocatalyst, or b) monomer feed composition. Polymerisation conditions: 10 mg catalyst, [Al]/[Ti] = 1000, 2 bar ethylene/propylene, 50 mL hexanes, and 30 minutes.

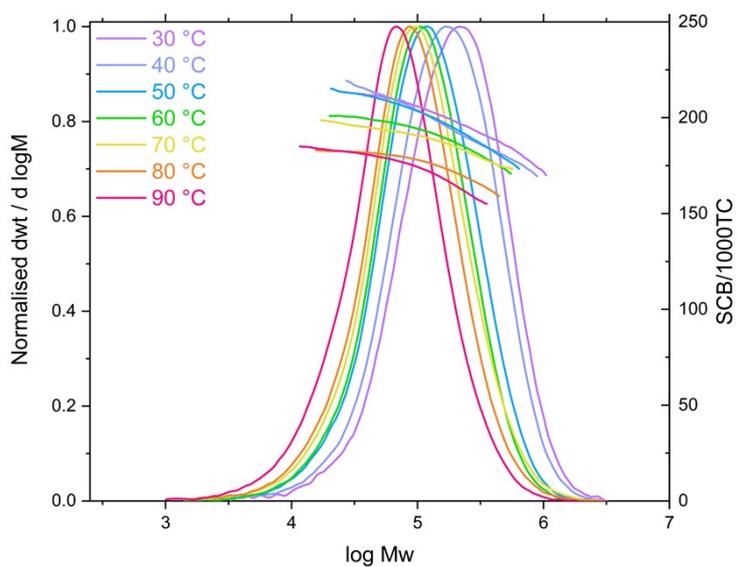


Figure S10 Gel permeation chromatogram of EPM synthesised by **1** as a function of polymerisation temperature. Polymerisation conditions: 10 mg catalyst, 150 mg TIBA, 2 bar ethylene/propylene (50:50), 50 mL hexanes, and 30 minutes.

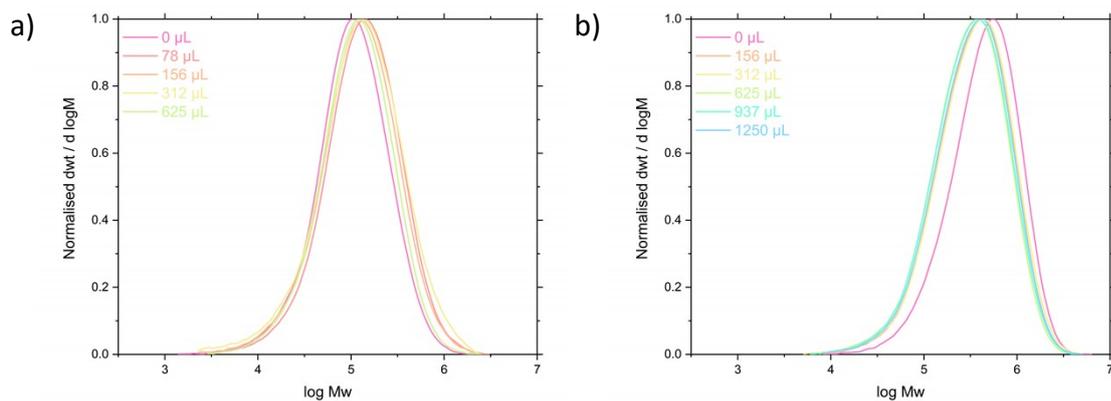


Figure S11 Gel permeation chromatograms of a) EPDM or b) PPH synthesised by **1** as a function of comonomer loading. Polymerisation conditions: a) 10 mg catalyst, 150 mg TIBA, 2 bar ethylene/propylene (50:50), 50 mL hexanes, and 30 minutes; b) 10 mg catalyst, $[Al_{MAO}]/[Ti] = 1000$, 2 bar propylene, 50 mL hexanes, and 30 minutes.

9. Rheology

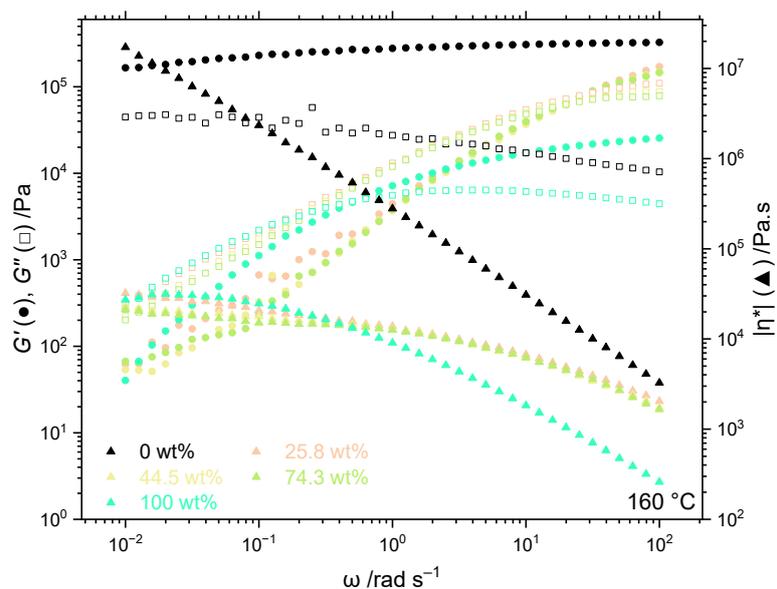


Figure S12 Frequency sweep rheometric curves measured at 160 °C for EPM synthesised by **1**/TIBA or **1**/MAO. Storage modulus, G' ; loss modulus, G'' ; complex viscosity, $|\eta^*|$; angular frequency, ω . Polymerisation conditions: 10 mg catalyst, 150 mg TIBA, 2 bar ethylene/propylene, 50 mL hexanes, 30 minutes, and 60 °C.

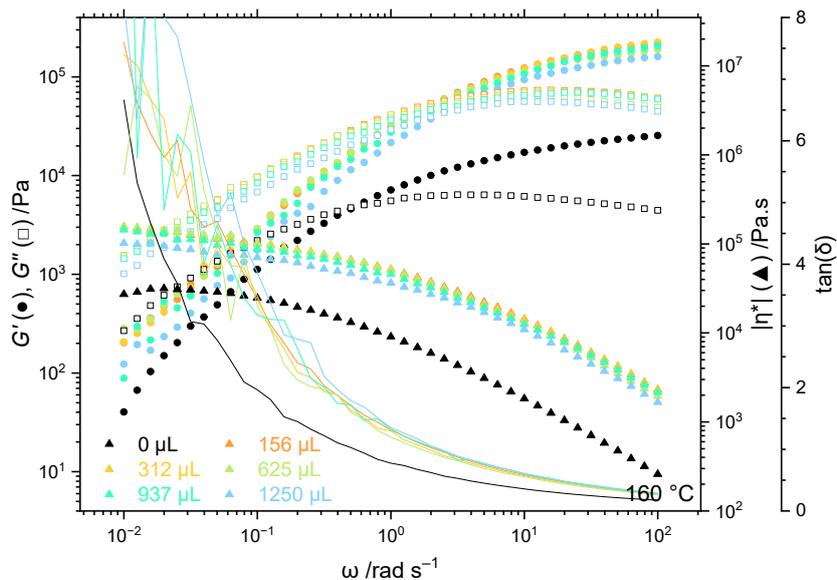


Figure S13 Frequency sweep rheometric curves measured at 160 °C for PPH synthesised by **1**/MAO. Storage modulus, G' ; loss modulus, G'' ; complex viscosity, $|\eta^*|$; phase angle, δ ; angular frequency, ω . Polymerisation conditions: 10 mg catalyst, $[Al_{MAO}]/[Ti] = 1000$, 2 bar propylene, 0–1.250 mL 1-hexene, 50 mL hexanes, 30 minutes, and 60 °C.

10. Differential scanning calorimetry

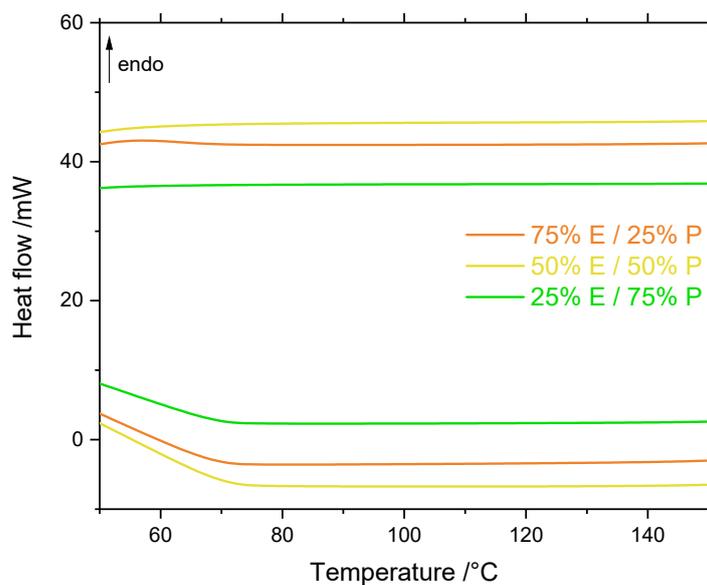


Figure S14 Differential scanning calorimetry plots (20 K min⁻¹; 2nd heating cycle shown) for EPM synthesised by **1**/TIBA. Polymerisation conditions: 10 mg catalyst, 150 mg TIBA, 2 bar ethylene/propylene, 50 mL hexanes, 30 minutes, and 60 °C.

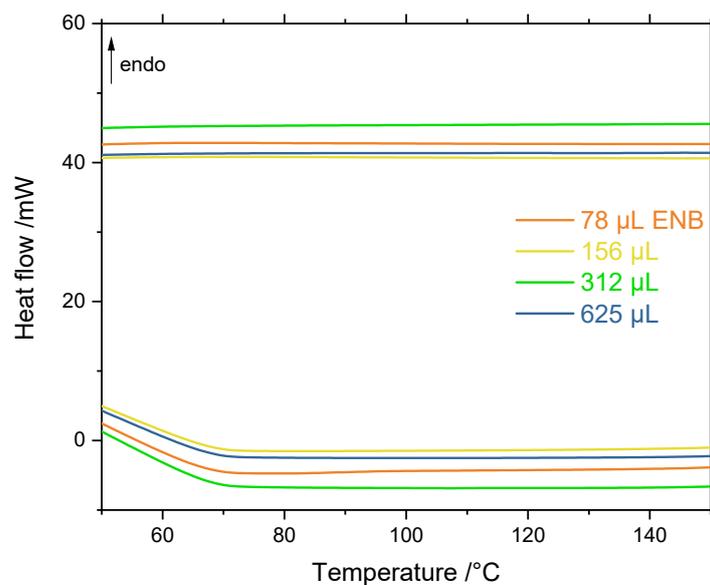


Figure S15 Differential scanning calorimetry plots (20 K min^{-1} ; 2nd heating cycle shown) for EPDM synthesised by **1**/TIBA. Polymerisation conditions: 10 mg catalyst, 150 mg TIBA, 78–625 μL ENB, 2 bar ethylene/propylene (50:50), 50 mL hexanes, 30 minutes, and 60 °C.

11. NMR spectroscopy

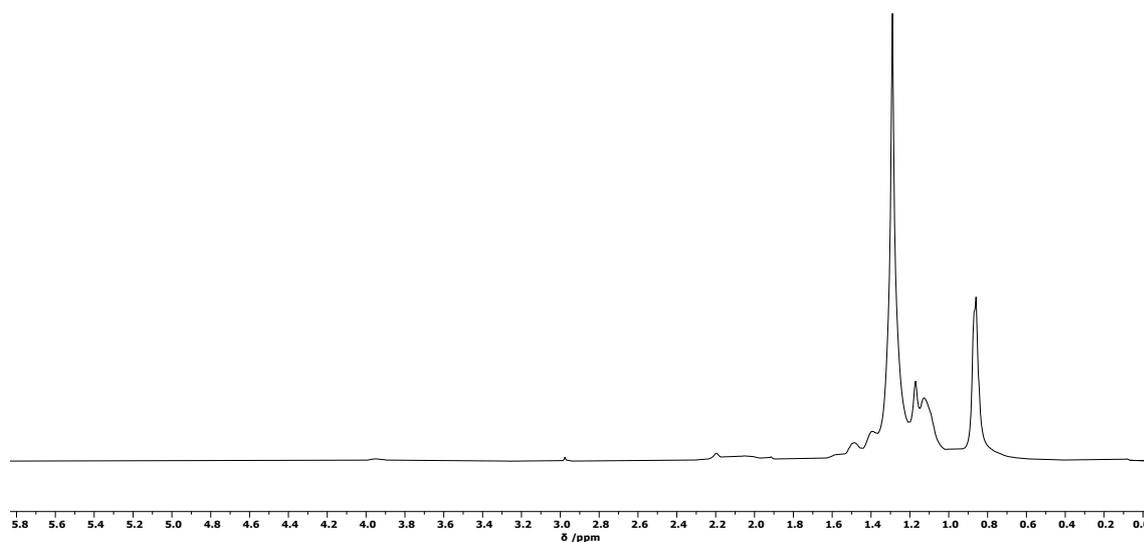


Figure S16 ¹H NMR spectrum (500 MHz, 1,1,2,2-tetrachloroethane-*d*₂, Cr(acac)₃, 403 K) of EPM. Polymerisation conditions: 10 mg **1**, 2 bar ethylene/propylene (50:50), [MAO]/[Ti] = 1000, 50 mL hexanes, 60 °C, and 30 minutes.

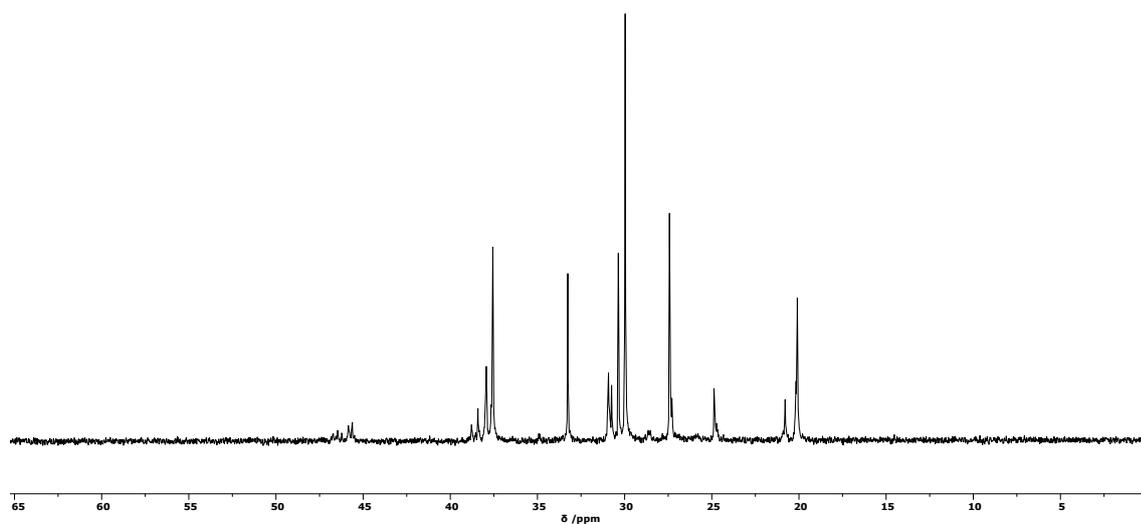


Figure S17 Quantitative $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz, 1,1,2,2-tetrachloroethane- d_2 , $\text{Cr}(\text{acac})_3$, 403 K) of EPM produced by **1**/MAO. Polymerisation conditions: 10 mg **1**, 2 bar ethylene/propylene (50:50), $[\text{MAO}]/[\text{Ti}] = 1000$, 50 mL hexanes, 60 °C, and 30 minutes.

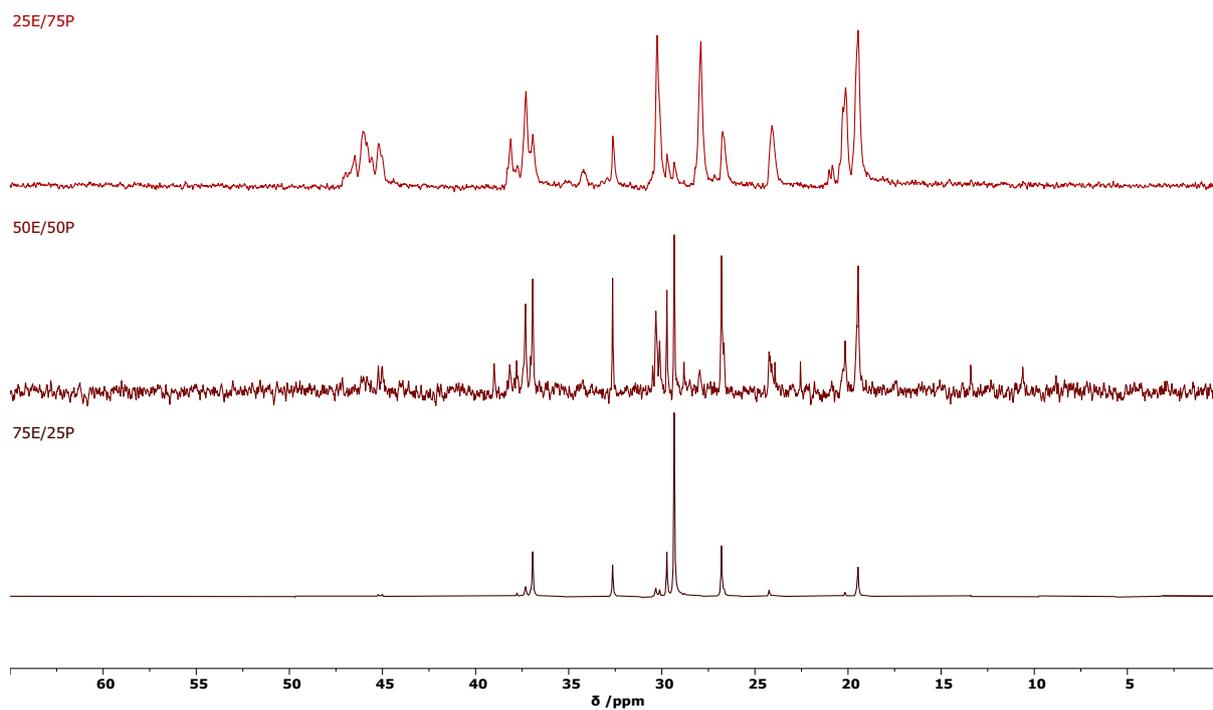


Figure S18 Quantitative $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (151 MHz, 1,1,2,2-tetrachloroethane- d_2 , $\text{Cr}(\text{acac})_3$, 403 K) of EPM produced by **1**/TIBA. Polymerisation conditions: 10 mg **1**, 2 bar ethylene/propylene, 150 mg TIBA, 50 mL hexanes, 60 °C, and 30 minutes.

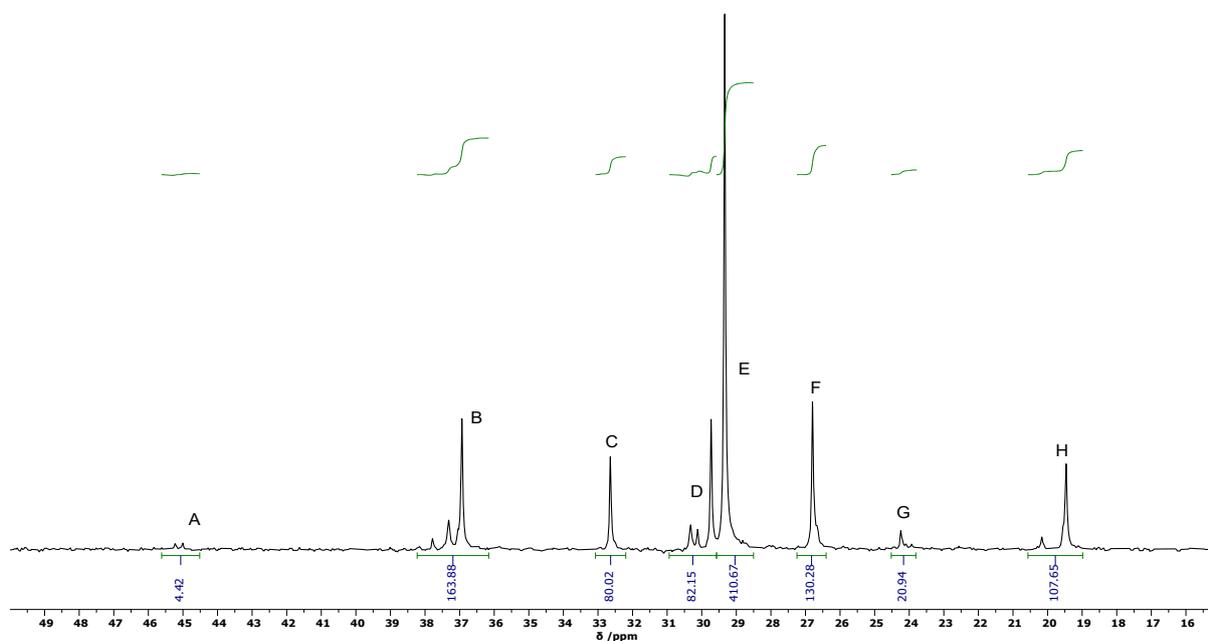


Figure S19 Quantitative $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz, 1,1,2,2-tetrachloroethane- d_2 , 403 K, $50 \geq \delta \geq 15$ ppm) of EPM, 16 mol% P incorporation. Integration according to Singh *et al.*¹¹

$$\text{EEE} = \text{A} - \text{B} + \text{C} + \text{D} + \text{E} + \text{F} + 3\text{G} - 2\text{H}$$

$$\text{EPE} = \text{C}$$

$$\text{PEE} + \text{EEP} = -\text{A} + \frac{1}{2}\text{B} - 2\text{G} + \text{H}$$

$$\text{EPP} + \text{PPE} = -2\text{A} + \text{B} - 4\text{C} + 2\text{H}$$

$$\text{PEP} = \text{G}$$

$$\text{PPP} = 3\text{A} - \frac{1}{2}\text{B} + 2\text{C} - \text{H}$$

Table S6 Triad distributions of EPM, synthesised at $T_p = 60$ °C, obtained from ^{13}C NMR spectroscopy. Analysis according to Singh *et al.*¹¹

Sample	mole fraction		triad distribution					
	[E]	[P]	[EEE]	[PEE]+[EEP]	[PEP]	[EPE]	[EPP]+[PPE]	[PPP]
50/50 MAO	0.59	0.41	0.26	0.25	0.06	0.14	0.17	0.13
25/75 TIBA	0.25	0.75	0.10	0.04	0.10	0.08	0.13	0.56
50/50 TIBA	0.50	0.50	0.37	-0.04	0.14	0.06	0.25	0.23
75/25 TIBA	0.84	0.16	0.58	0.21	0.03	0.12	0.08	-0.02

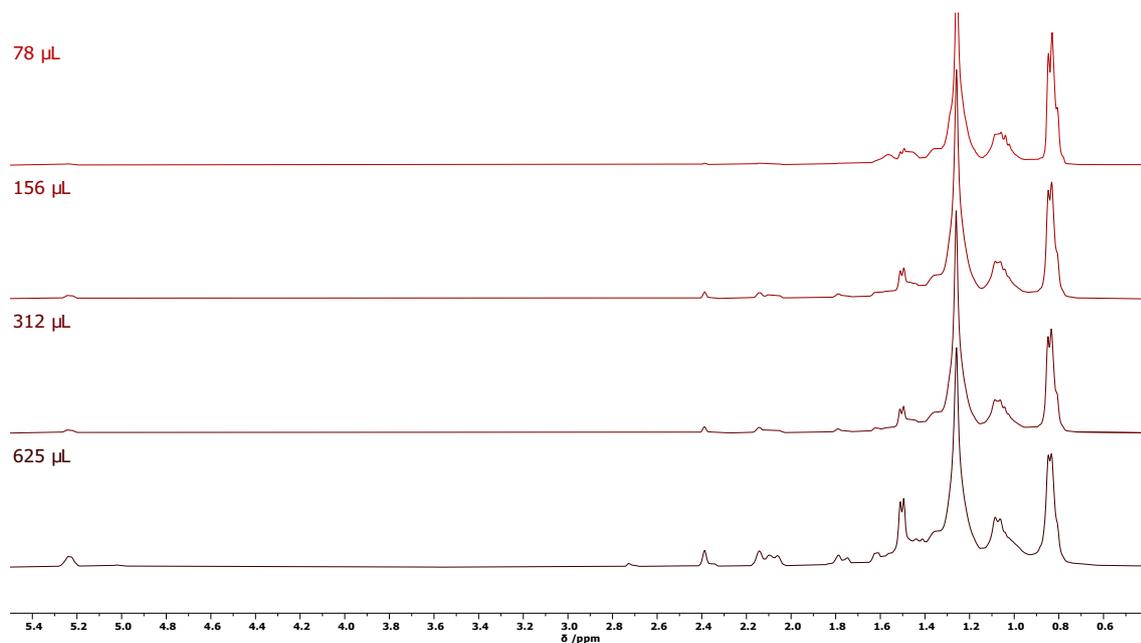


Figure S20 ^1H NMR spectra (400 MHz, chloroform- d , 297 K) of EPDM as a function of ENB loading. Polymerisation conditions: 10 mg **1**, 2 bar ethylene/propylene (50:50), 150 mg TIBA, 78–625 μL ENB, 50 mL hexanes, 60 $^\circ\text{C}$, and 30 minutes.

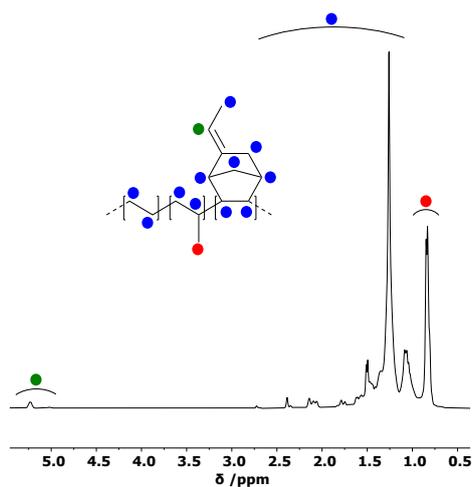


Figure S21 ^1H NMR spectrum (400 MHz, chloroform- d , 298 K) of EPDM, with assignments according to Leone et al.¹²

$$ENB_{mol\%} = \frac{H_{ENB}}{H_E + H_P + H_{ENB}}$$

$$H_{ENB} = \int \bullet$$

$$P_{mol\%} = \frac{H_P}{H_E + H_P + H_{ENB}}$$

$$H_P = \frac{1}{3} \int \bullet$$

$$E_{mol\%} = \frac{H_E}{H_E + H_P + H_{ENB}}$$

$$H_E = \frac{1}{4} \left[\int \bullet - \int \bullet - 11 \int \bullet \right]$$

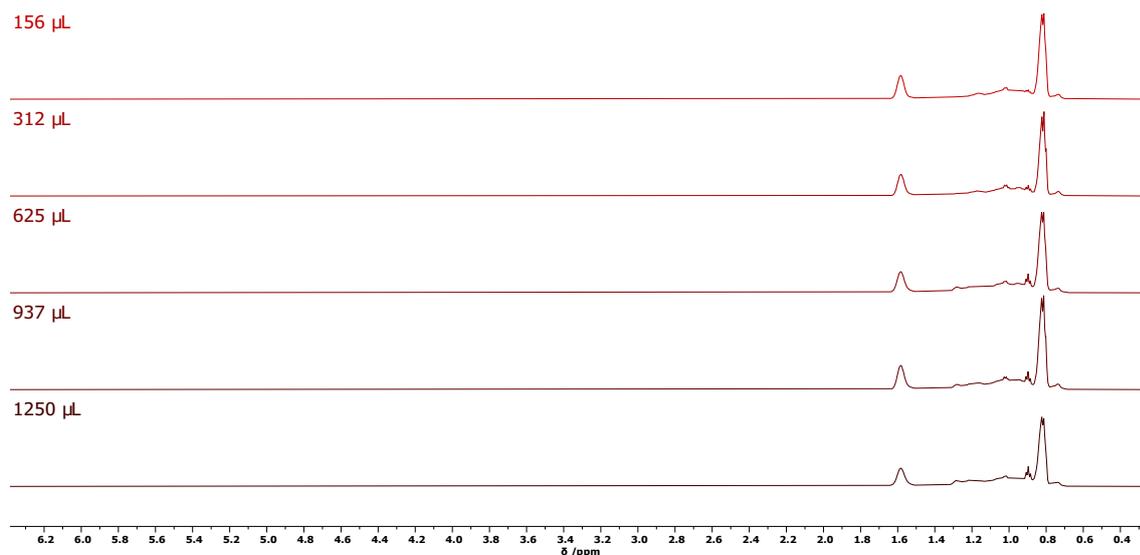


Figure S22 ^1H NMR spectra (600 MHz, chloroform-*d*, 298 K) of PPH as a function of C6 loading. Polymerisation conditions: 10 mg **1**, 2 bar propylene, 150 mg TIBA, 156–1250 μL 1-hexene, 50 mL hexanes, 60 $^\circ\text{C}$, and 30 minutes.

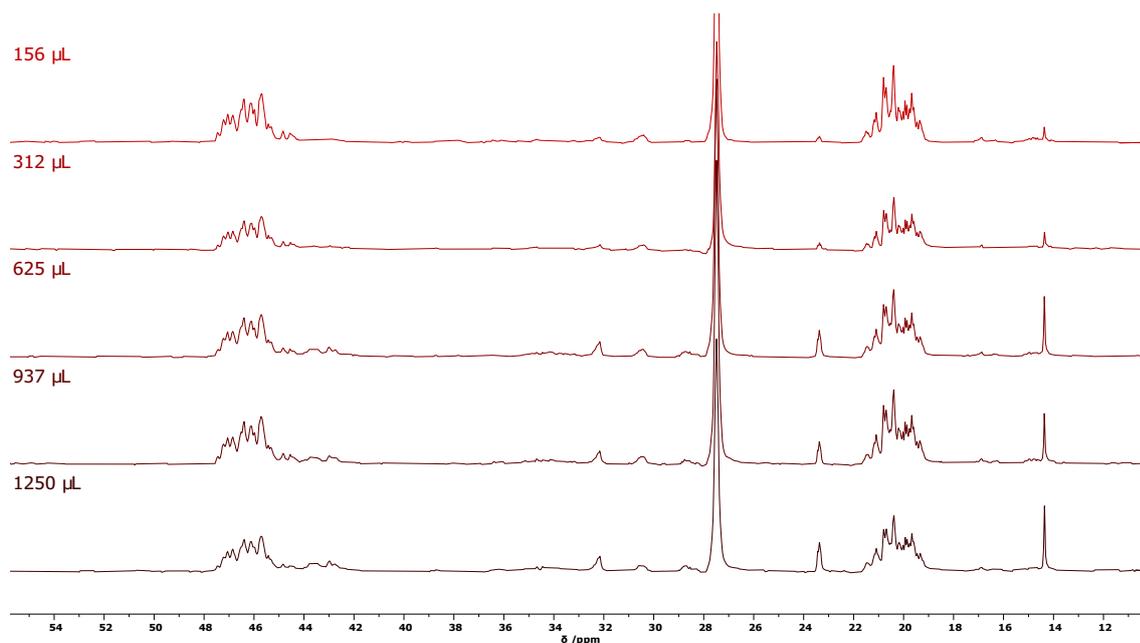


Figure S23 Quantitative $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (151 MHz, chloroform-*d*, 298 K) of PPH as a function of C6 loading. Polymerisation conditions: 10 mg **1**, 2 bar propylene, 150 mg TIBA, 156–1250 μL 1-hexene, 50 mL hexanes, 60 $^\circ\text{C}$, and 30 minutes.

12. References

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