

Efficient synthesis of thermoplastic elastomeric amorphous ultra-high molecular weight atactic polypropylene (UHMW_aPP)

Clement G. Collins Rice, Jean-Charles Buffet, Zoë R. Turner, and Dermot O'Hare

Chemistry Research Laboratory, University of Oxford, 12 Mansfield Road, Oxford, OX1 3TA, U.K.

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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.

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 Jenssen (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*-buty-4-hydroxytoluene (BHT) at 160 °C for 90 minutes and then filtered with a 10 μ m 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 μ L aluminium crucibles. An empty crucible was used as a reference, and the DSC was calibrated using indium and zinc. Low temperature runs were performed on a TA Instruments DSC 25, with a Refrigerated Cooling System 90 within a temperature range of –80–200 °C at a rate of 10 K min⁻¹. Samples were sealed in TA Instrument TZero pans, and an empty pan was used as a reference.

Thermogravimetry. Thermogravimetric analysis was performed by Mr Alexander Evans (University of Oxford) on a Perkin Elmer TGA 8000 thermogravimetric analyser within a temperature range of 50–800 °C. Polymer samples were loaded into pre-weighed ceramic pans, and heated at a rate of 20 K min⁻¹. A purge gas of either dry nitrogen or synthetic air (20% O₂ in N₂) was used.

Wide-angle X-ray scattering. X-ray diffraction was performed by Dr. Philip Kenyon (University of Oxford) on a PANalytical X'Pert Pro diffractometer in reflection mode, using copper K α radiation ($\lambda_{\alpha_1} = 1.540598 \text{ \AA}$, $\lambda_{\alpha_2} = 1.544426 \text{ \AA}$, $\alpha_1/\alpha_2 = 0.5$) at 40 kV and 40 mA. Samples were mounted on stainless steel sample holders, and scans were recorded from $2^\circ \leq 2\theta \leq 70^\circ$.

Mechanical analysis. Mechanical testing was performed by Ms Thea Høibjerg Glittum, and Ms Heidi Nornes Bryntesen (Norner AS, Norway). The UHMWPP sample was cut up and milled to a powder-like material using a cooling unit (liquid nitrogen). A thermal stabiliser (BHT) was added and the sample was pressed into plates (80 x 60 x 1 mm) at either 200 or 180 °C. Samples pressed at 200 and 180 °C gave the same results. Density was measured at room temperature (23 °C) according to ISO1183-1 (2012) on a Mettler Toledo XS204 instrument. Measurement was repeated three times. Tensile properties were determined at room temperature (23 °C) according to ISO527-1/2 using type 5A test specimens, on a Zwick Z010 instrument with a 5 kN load cell. The gauge length was $L_0 = 20 \text{ mm}$, and the gripping distance was $L = 50 \text{ mm}$. Testing speed was 50 mm min⁻¹. Samples were stopped at 1900%. Measurements were repeated 5 times.

Optical measurements. Polypropylene samples were pressed into discs, under a flow of dry N₂, at elevated temperature under a force of ca. 50 N using a TA Instruments HR-2 Discovery Hybrid Rheometer. Optical characterisation was performed using a PerkinElmer LAMBDA 1050+ UV/Vis/NIR Spectrophotometer with a 150 mm InGaAs Integrating Sphere using tungsten-halogen and deuterium-arc sources within a wavelength range of 250–1400 nm.

Literature preparations and commercially supplied materials. 2,3,4,5,6,7-hexamethylindene (SCG Chemicals Co., Ltd.), ⁿBuLi (1.6 M in hexanes, Sigma Aldrich), 4-methyl-2-*tert*-butylphenol (Sigma Aldrich), 6-bromo-2,4-di-*tert*-butylphenol (Alfa Aesar), and bromine (Sigma Aldrich) were all used as received. TiCl₄·2THF was prepared according to a literature procedure.² Et₃N was dried over KOH, distilled under static vacuum and freeze-pump-thaw degassed before use. 2,4-bis(α , α -dimethylbenzyl)phenol (Sigma Aldrich) was recrystallised from hot ethanol before use. Me₂SiCl₂ (Sigma Aldrich) was dried over pre-activated 3 Å molecular sieves before use. Allyl bromide was washed with NaHCO₃ followed by distilled water and dried over MgSO₄. PHENI* complexes **1–3** were synthesised according to a literature procedure,³ and the indenyl-PHENICS complex Me₂SB(^tBu,MeArO,Ind)TiCl₂ (**4**) was synthesised according to a modified literature procedure.⁴ Propylene (N2.5) was supplied by BOC Ltd. or Buse Gases Ltd. and used as received. Solid polymethylaluminumoxane (sMAO) was supplied by SGC Chemicals Co., Ltd. (Thailand) 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. Solid catalysts **1**_{sMAO}–**4**_{sMAO} were prepared according to a literature procedure.³

2. Experimental details

Propylene polymerisation studies using supported catalysts. A typical laboratory polymerisation run was performed as follows. 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 a propylene purge while the reaction

was brought to temperature in an oil bath or water/ice bath with the stirring set at 1000 rpm. The stopcock was opened to propylene at a pressure of 2 bar and the timer was started. On completion of the run, the vessel was closed to propylene and degassed. The mixture was decanted and the polymer precipitated from solution by the addition of dilute aqueous hydrochloric acid, and one of methanol, isopropanol, or acetone. The organic solvents were removed by rotary evaporation. The polymer was manually separated and dried in a vacuum oven until constant weight. All polymerisation runs were carried out at least in duplicate to ensure reproducibility.

Homogeneous propylene polymerisation studies. A typical homogeneous polymerisation run was performed as follows. 1000 equivalents methylaluminoxane (MAO) was introduced to a 150 mL Rotaflo ampoule containing a stirrer bar, and washed in with 49 mL hexanes. To this was added 1 mL of a pre-prepared stock solution of complex in toluene ($0.714 \mu\text{mol mL}^{-1}$). The polymerisation was then continued as for the polymerisations using supported catalysts described above.

3. Polymerisation studies

Catalyst /mg	T_p /°C	Time /mins	[Al _{MAO}]/[Ti]	V _{hexanes} /mL	Activity /kg mol _{Ti} ⁻¹ h ⁻¹ bar ⁻¹	Productivity /kg _{PP} g _{cat} ⁻¹ h ⁻¹ bar ⁻¹	M _w /kDa	PDI	
1_{sMAO}	10	60	30	1000	50	2610 ± 94	0.19	471.3	2.2
	10	70	30	1000	50	1440 ± 378	0.10	368.9	2.3
	10	80	30	1000	50	1121	0.080	234.2	2.3
2_{sMAO}	10	60	30	1000	50	3213 ± 595	0.17	633.9	2.2
	10	70	30	1000	50	2176 ± 23	0.16	426.9	2.2
	10	80	30	1000	50	1609 ± 22	0.11	353.6	2.1
3_{sMAO}	10	60	30	1000	50	1733 ± 326	0.12	374.9	2.3
	10	70	30	1000	50	623.9 ± 268	0.044	286.4	2.3
	10	80	30	1000	50	636.9 ± 34	0.047	196.6	2.2
4_{sMAO}	10	60	30	1000	50	104.5 ± 119	0.0075	95.9	4.5
	10	70	30	1000	50	36.94 ± 1	0.0026	63.2	3.2
	10	80	30	1000	50	18.74 ± 5	0.0013	75.2	3.5

Catalyst /mg	T_p /°C	Time /mins	[Al _{MAO}]/[Ti]	V _{hexanes} /mL	Activity /kg mol _{Ti} ⁻¹ h ⁻¹ bar ⁻¹	Productivity /kg _{PP} g _{cat} ⁻¹ h ⁻¹ bar ⁻¹	M _w /kDa	PDI	
2_{sMAO}	10	30	10	1000	50	7309 ± 291	0.52	1338.4	2.3
	10	40	10	1000	50	6825 ± 887	0.49	972.9	2.2
	10	50	10	1000	50	6591 ± 1119	0.47	760.0	2.2
	10	60	10	1000	50	5703 ± 28	0.41	746.7	2.2
	10	70	10	1000	50	5053 ± 1023	0.36	692.4	2.2
	10	80	10	1000	50	3262 ± 9	0.23	396.4	2.1
	10	90	10	1000	50	1129 ± 935	0.081	399.2	2.1
2_{sMAO}	10	30	10	5000	250	9761	0.26	1176.7	2.5
	10	30	103	5000	250	3596	0.70	1409.8	1.9

Catalyst /mg	T_p /°C	Time /mins	[Al _{MAO}]/[Ti]	V _{hexanes} /mL	Activity /kg mol _{Ti} ⁻¹ h ⁻¹ bar ⁻¹	Productivity /kg _{PP} g _{cat} ⁻¹ h ⁻¹ bar ⁻¹	M _w /kDa	PDI	
2_sMAO	10	30	10	0	50	312.8 ± 343	0.022	1144.4	2.5
	10	30	10	125	50	602.4 ± 105	0.043	1061.1	2.7
	10	30	10	250	50	3847 ± 868	0.27	1424.5	2.3
	10	30	10	500	50	5705 ± 1046	0.41	1346.2	2.4
	10	30	10	1000	50	7309 ± 291	0.52	1338.4	2.3
	10	30	10	2500	50	11685 ± 731	0.83	793.4	2.4
	10	30	10	5000	50	9304 ± 2681	0.66	710.8	2.4
2_sMAO	10	4	10	500	50	997.7 ± 237	0.071	1996.5	2.7
	10	23	10	500	50	2062 ± 171	0.15	1380.6	2.3
2/MAO	0.414	4	10	1000	50	1270 ± 98	2.2	1268.4	2.7
	0.414	30	10	1000	50	6117 ± 371	4.6	1085.0	2.4
	0.414	40	10	1000	50	6205 ± 187	9.2	759.0	2.4
	0.414	50	10	1000	50	4491 ± 941	6.6	567.2	2.4
	0.414	60	10	1000	50	4118 ± 478	6.1	487.4	2.4
	0.414	70	10	1000	50	2618 ± 621	3.9	324.5	2.3
	0.414	80	10	1000	50	1800 ± 650	2.7	275.3	2.3
	0.414	90	10	1000	50	1495 ± 333	2.2	189.1	2.2
2/MAO	0.414	30	10	1000	50	6117 ± 371	4.6	1085.0	2.4
	0.207	30	10	2000	50	6301 ± 1650	11	1407.0	2.5
	0.104	30	10	4000	50	8097 ± 2109	14	1346.6	2.3
	0.052	30	10	8000	50	11790 ± 570	20	1512.8	2.6
2/TMA	0.414	30	10	1000	50	-	-	-	-
2/TEA	0.414	30	10	1000	50	-	-	-	-
2/TIBA	0.414	30	10	1000	50	-	-	-	-
2_sMAO/TIBA	10	60	30	1000	50	279 ± 2	0.019		

Catalyst /mg	T_p /°C	Time /mins	[Al _{MAO}]/[Ti]	V _{hexanes} /mL	Activity /kg mol _{Ti} ⁻¹ h ⁻¹ bar ⁻¹	Productivity /kg _{PP} g _{cat} ⁻¹ h ⁻¹ bar ⁻¹	M _w /kDa	PDI	
2/MAO	0.414	30	10	0	50	-	-	-	
	0.414	30	10	125	50	147.7 ± 19	0.25	480.6	2.4
	0.414	30	10	250	50	892.4 ± 276	1.5	912.0	3.7
	0.414	30	10	500	50	1367 ± 187	2.4	795.7	2.5
	0.414	30	10	1000	50	6117 ± 371	11	1085.0	2.4
	0.414	30	10	2000	50	11270 ± 416	19	706.8	2.4
	0.414	30	10	5000	50	9924 ± 830	17	557.6	2.4
2/MAO	0.414	30	120	5000	250	2668 ± 60	4.6	1210.6	2.7
2/MAO	0.414	30	139	5000	250	6244	11		

Table S1. Polymerisation conditions: [Al_{support}]/[Ti] = 200, MAO, 2 bar propylene, 10 mg catalyst, and hexanes.

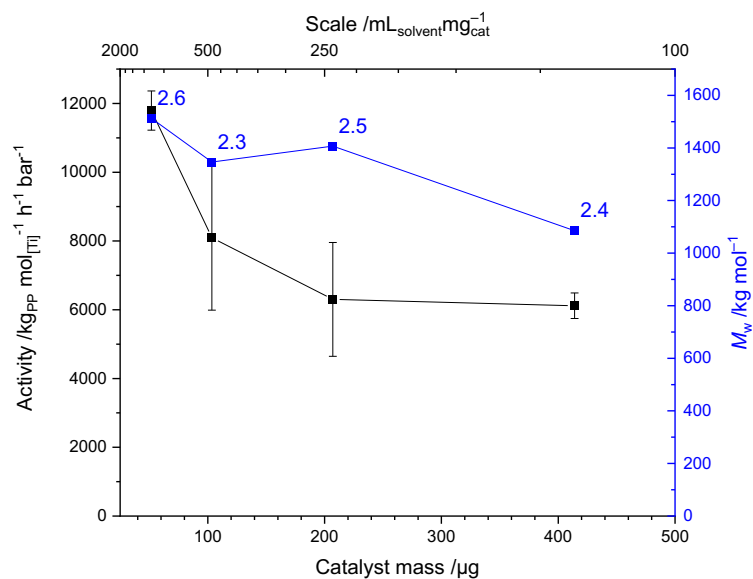


Fig. S1. Propylene polymerisation activity and polypropylene molecular weight (PDIs (M_w/M_n) annotated) as a function of mass of complex $\text{Me}_2\text{SB}(\text{tBu}_2\text{ArO}, \text{I}^*)\text{TiCl}_2$ (**2**). Polymerisation conditions: 2 bar propylene, 50 mL hexanes, 10 minutes, 30 °C, and 41.4 mg MAO.

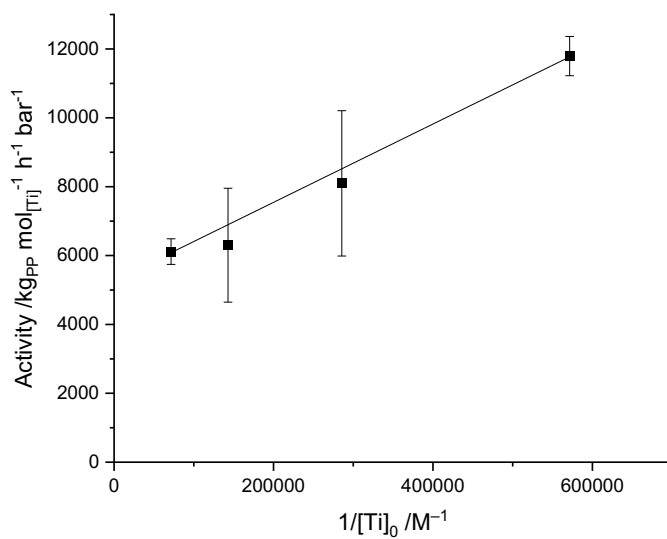


Fig. S2. Polymerisation activity as a function of initial catalyst concentration. activity ($\text{kg}_{\text{PP}} \text{h}^{-1} \text{bar}^{-1}$) = $0.011 \frac{1}{[\text{Ti}]_0} + 5300 \text{ mol}_{\text{Ti}}^{-1}$, $R^2 = 0.997$.

4. Gel permeation chromatography

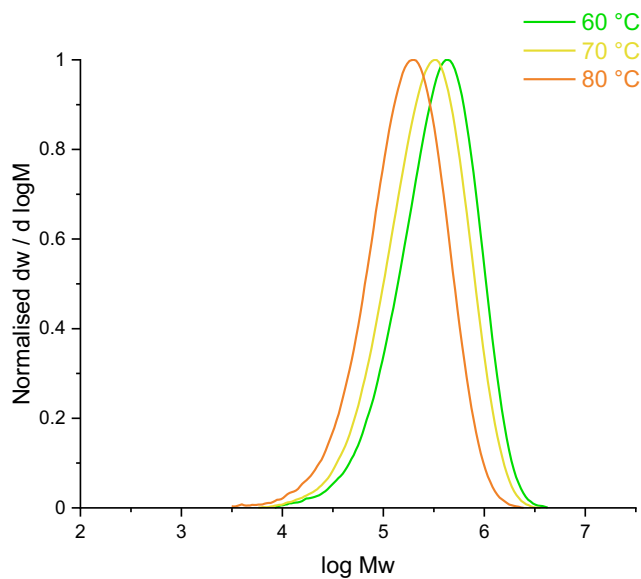


Fig. S3. Gel permeation chromatograms of PP synthesised by **1_sMAO** as a function of temperature. Polymerisation conditions: 10 mg catalyst, $[Al_{MAO}]/[Ti] = 1000$, 2 bar propylene, 50 mL hexanes, and 30 minutes.

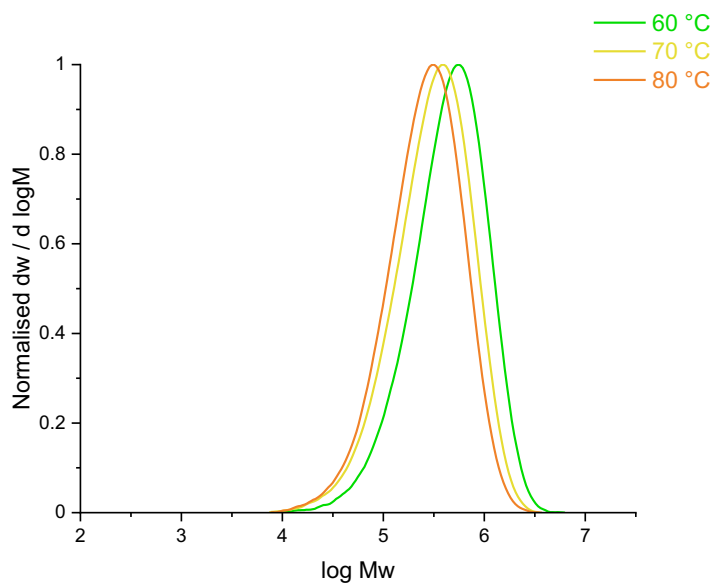


Fig. S4. Gel permeation chromatograms of PP synthesised by **2_sMAO** as a function of temperature. Polymerisation conditions: 10 mg catalyst, $[Al_{MAO}]/[Ti] = 1000$, 2 bar propylene, 50 mL hexanes, and 30 minutes.

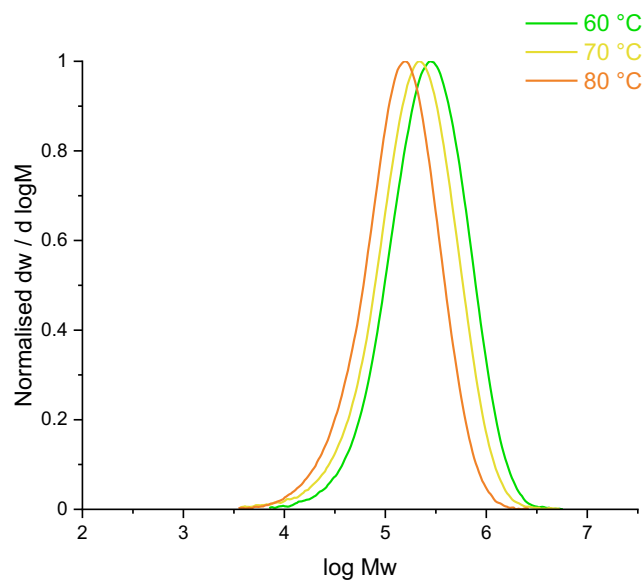


Fig. S5. Gel permeation chromatograms of PP synthesised by 3_{sMAO} as a function of temperature. Polymerisation conditions: 10 mg catalyst, $[Al_{MAO}]/[Ti] = 1000$, 2 bar propylene, 50 mL hexanes, and 30 minutes.

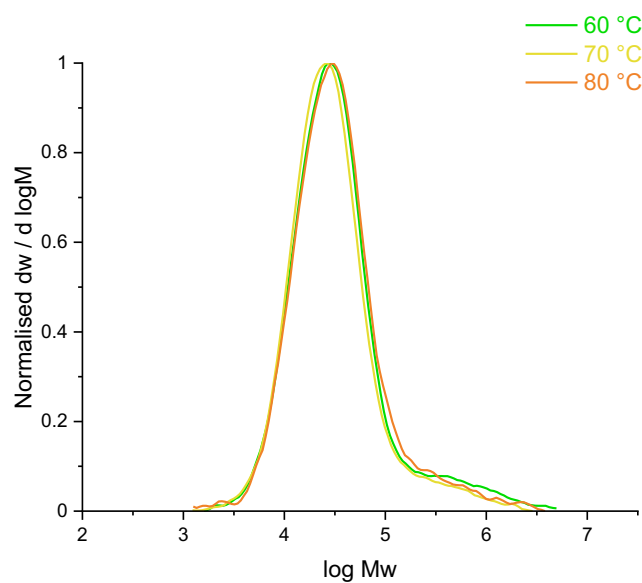


Fig. S6. Gel permeation chromatograms of PP synthesised by 4_{sMAO} as a function of temperature. Polymerisation conditions: 10 mg catalyst, $[Al_{MAO}]/[Ti] = 1000$, 2 bar propylene, 50 mL hexanes, and 30 minutes.

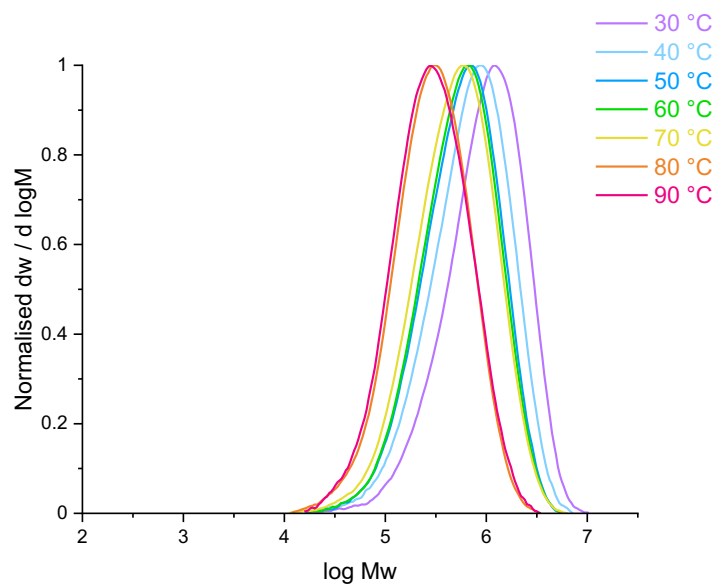


Fig. S7. Gel permeation chromatograms of PP synthesised by 2_{sMAO} as a function of temperature. Polymerisation conditions: 10 mg catalyst, $[Al_{MAO}]/[Ti] = 1000$, 2 bar propylene, 50 mL hexanes, and 10 minutes.

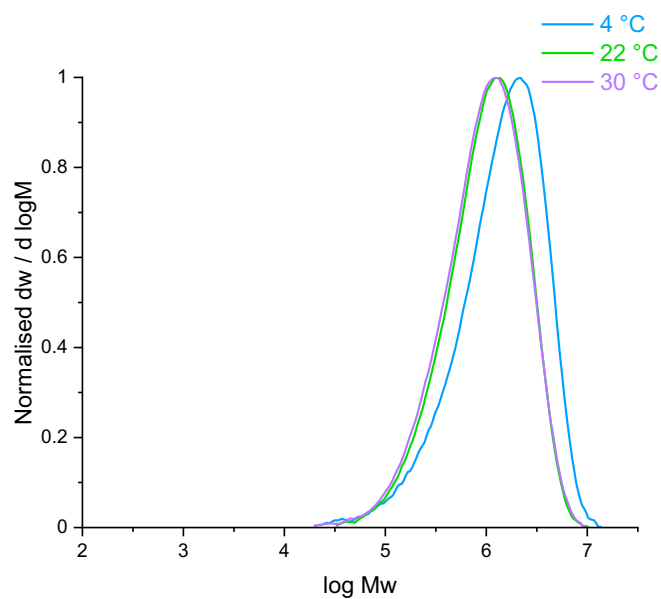


Fig. S8. Gel permeation chromatograms of PP synthesised by 2_{sMAO} as a function of temperature. Polymerisation conditions: 10 mg catalyst, $[Al_{MAO}]/[Ti] = 500$, 2 bar propylene, 50 mL hexanes, and 10 minutes.

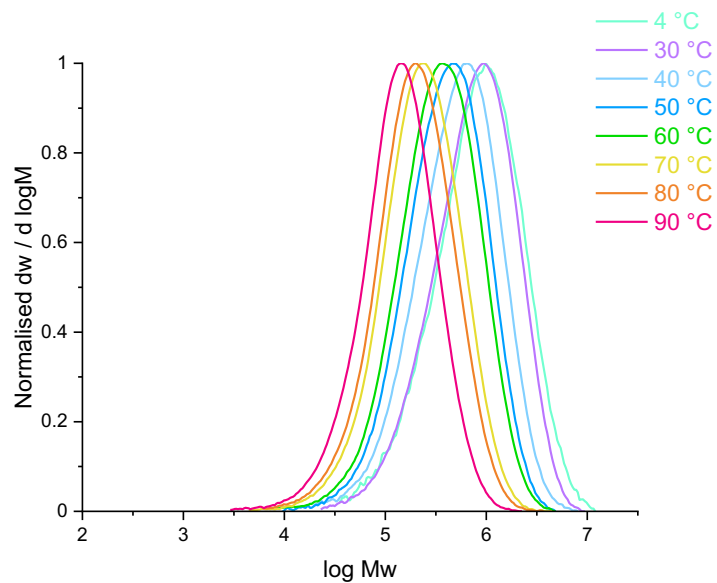


Fig. S9. Gel permeation chromatograms of PP synthesised by **2** as a function of temperature. Polymerisation conditions: 414 μg catalyst, $[\text{Al}_{\text{MAO}}]/[\text{Ti}] = 1000$, 2 bar propylene, 50 mL hexanes, and 10 minutes.

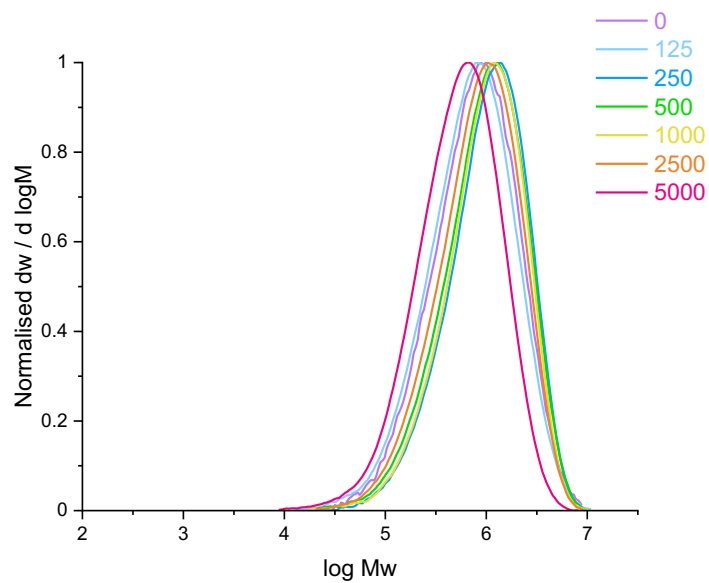


Fig. S10. Gel permeation chromatograms of PP synthesised by **2_{SMAO}** as a function of $[\text{Al}_{\text{MAO}}]/[\text{Ti}]$. Polymerisation conditions: 10 mg catalyst, 2 bar propylene, 50 mL hexanes, 30 °C, and 10 minutes.

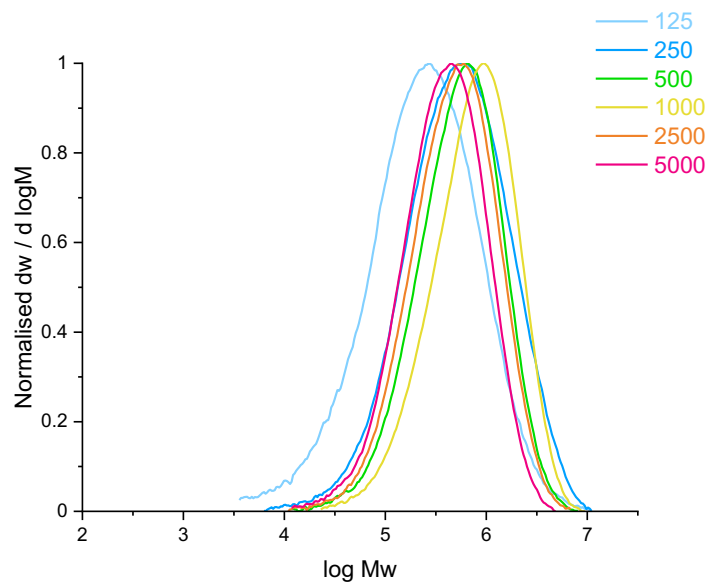


Fig. S11. Gel permeation chromatograms of PP synthesised by **2** as a function of $[Al_{MAO}]/[Ti]$. Polymerisation conditions: 414 μ g catalyst, 2 bar propylene, 50 mL hexanes, 30 $^{\circ}$ C, and 10 minutes.

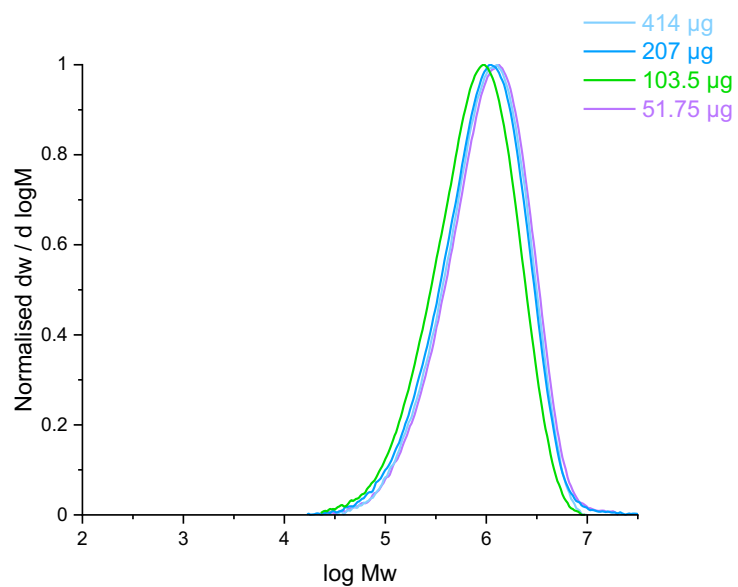


Fig. S12. Gel permeation chromatograms of PP synthesised by **2** as a function of catalyst mass. Polymerisation conditions: $[Al_{MAO}] = 14$ mM, 2 bar propylene, 50 mL hexanes, 30 $^{\circ}$ C, and 10 minutes.

5. Differential Scanning Calorimetry

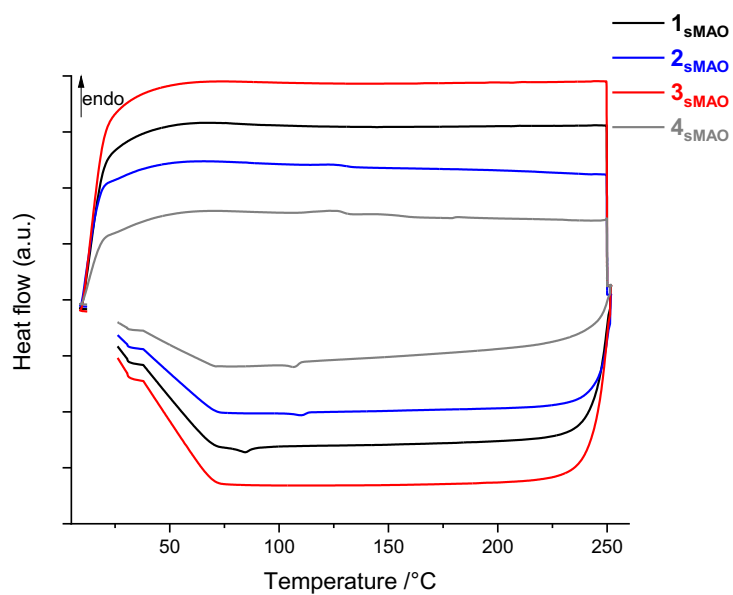


Fig. S13. Differential scanning calorimetry plots (at 20 K min^{-1} , second heating and cooling shown), of PP produced by the sMAO-supported catalysts 1_{sMAO} – 4_{sMAO} . Polymerisation conditions: 10 mg catalyst, 2 bar propylene, 50 mL hexanes, $[\text{Al}_{\text{MAO}}]/[\text{Ti}] = 1000$, 30 minutes, and $60 \text{ }^\circ\text{C}$.

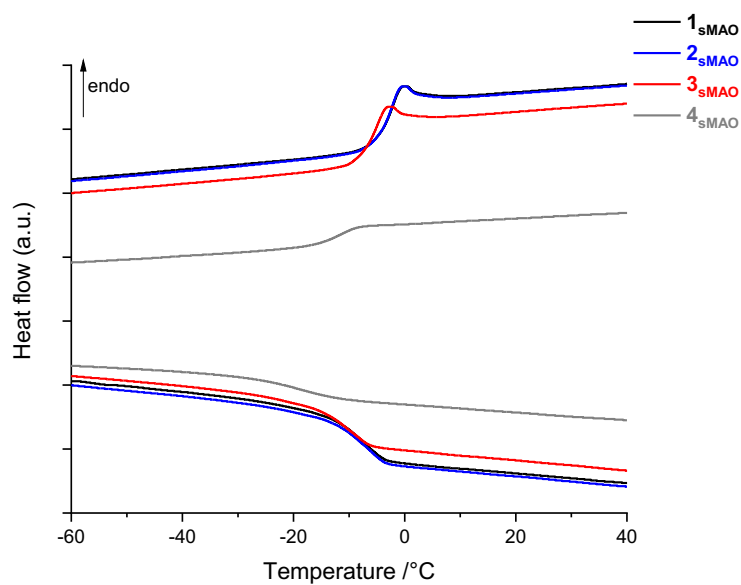


Fig. S14. Differential scanning calorimetry plots (at 10 K min^{-1} , second heating and cooling shown), of PP produced by the sMAO-supported catalysts 1_{sMAO} – 4_{sMAO} . Polymerisation conditions: 10 mg catalyst, 2 bar propylene, 50 mL hexanes, $[\text{Al}_{\text{MAO}}]/[\text{Ti}] = 1000$, 30 minutes, and $60 \text{ }^\circ\text{C}$.

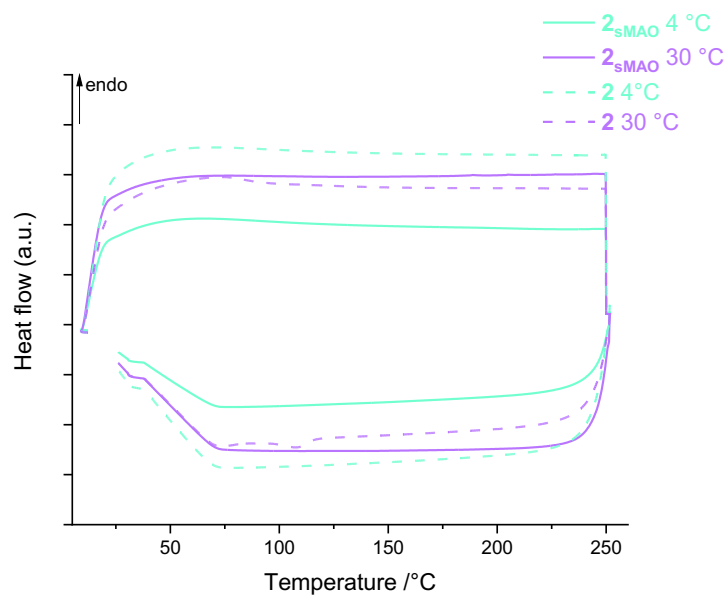


Fig. S15. Differential scanning calorimetry plots (at 20 K min⁻¹, second heating and cooling shown), of PP produced by the **2_{SMAO}** and **2**. Polymerisation conditions: 10 mg **2_{SMAO}** or 414 μg **2**, 2 bar propylene, 50 mL hexanes, [Al_{MAO}]/[Ti] = 1000, 30 minutes, and 60 °C.

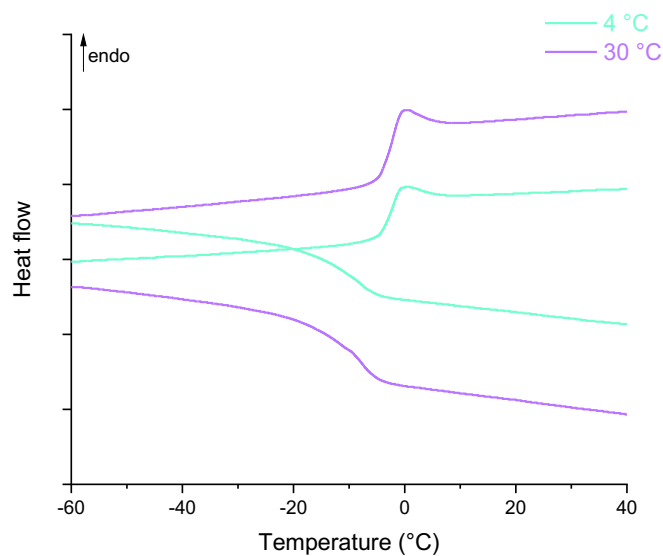


Fig. S16. Differential scanning calorimetry plots (at 10 K min⁻¹, second heating and cooling shown), of PP produced by **2_{SMAO}**. Polymerisation conditions: 10 mg catalyst, 2 bar propylene, 50 mL hexanes, [Al_{MAO}]/[Ti] = 1000, 10 minutes, and 4 or 30 °C.

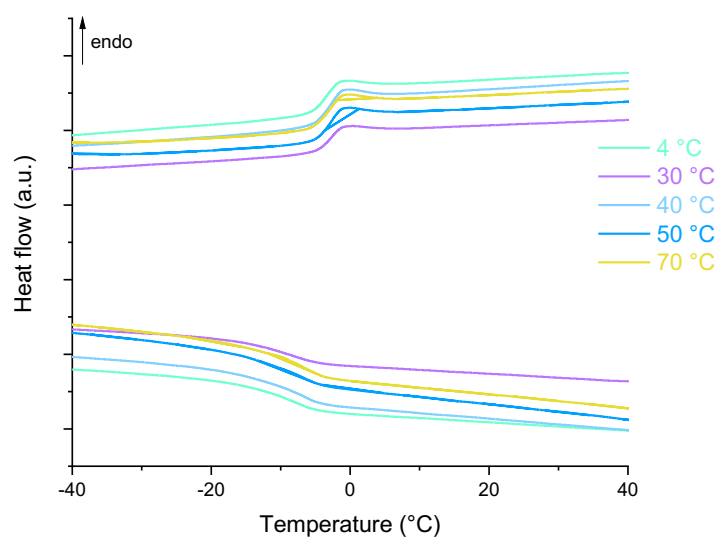


Fig. S17. Differential scanning calorimetry plots (at 10 K min^{-1} , second heating and cooling shown), of PP produced by **2**. Polymerisation conditions: $414 \mu\text{g}$ catalyst, 2 bar propylene, 50 mL hexanes, $[\text{Al}_{\text{MAO}}]/[\text{Ti}] = 1000$, 10 minutes, and 4 or $30 \text{ }^\circ\text{C}$.

Table S2. Thermal data for polypropylene synthesised by PHENI* complexes.

Sample	$T_g / ^\circ\text{C}$	$\Delta C_{p,Tg} / \text{J } ^\circ\text{C}^{-1} \text{ g}^{-1}$
1 _{sMAO} , $T_p = 60 \text{ }^\circ\text{C}$	-3.20	0.527
2 _{sMAO} , $T_p = 60 \text{ }^\circ\text{C}$	-3.63	0.513
3 _{sMAO} , $T_p = 60 \text{ }^\circ\text{C}$	-6.46	0.452
4 _{sMAO} , $T_p = 60 \text{ }^\circ\text{C}$	-12.01	0.179
2 _{sMAO} , $T_p = 4 \text{ }^\circ\text{C}$	-2.86	0.391
2 _{sMAO} , $T_p = 30 \text{ }^\circ\text{C}$	-2.85	0.480
2 , $T_p = 4 \text{ }^\circ\text{C}$	-3.61	0.520
2 , $T_p = 30 \text{ }^\circ\text{C}$	-3.03	0.418
2 , $T_p = 40 \text{ }^\circ\text{C}$	-3.31	0.542
2 , $T_p = 50 \text{ }^\circ\text{C}$	-3.33	0.482
2 , $T_p = 70 \text{ }^\circ\text{C}$	-3.34	0.547

5.1. Annealing

Crystallisation was not attained either by ageing at room temperature for a long time, or by annealing above the glass transition for 200 minutes.⁵

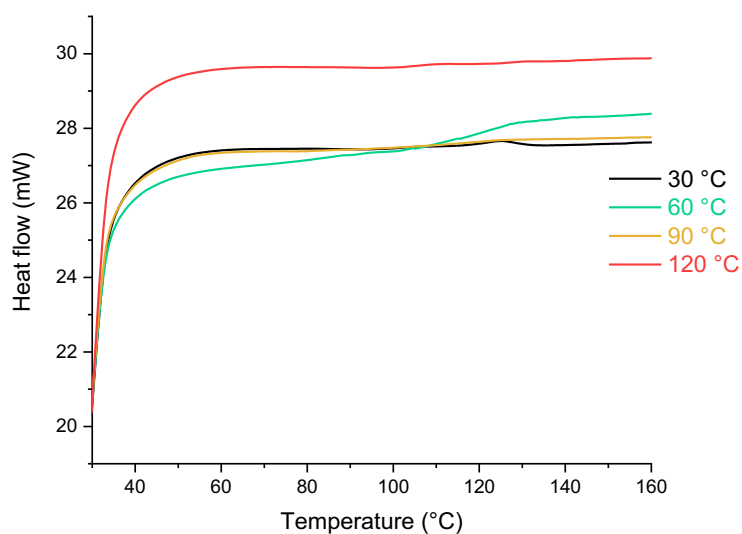


Fig. S18. Differential scanning calorimetry plots (at 10 K min^{-1} , second heating shown), of PP produced by **2**, after annealing for 200 minutes at different temperatures. Polymerisation conditions: $414 \mu\text{g}$ catalyst, 2 bar propylene, 250 mL hexanes, $[\text{Al}_{\text{MAO}}]/[\text{Ti}] = 5000$, 120 minutes, and $30 \text{ }^\circ\text{C}$.

6. Thermogravimetry

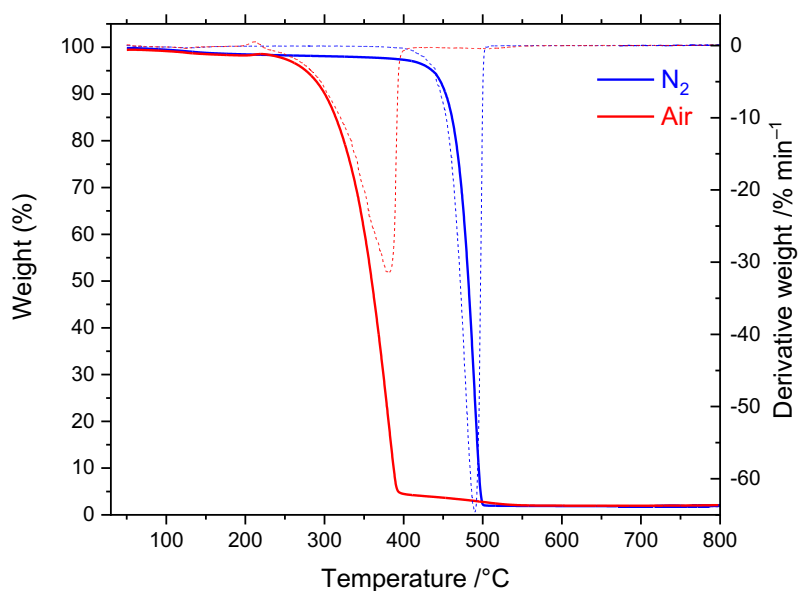


Fig. S19. Thermogravimetry plots of UHMWPP, at a heating rate of 20 K min^{-1} under an atmosphere of dry nitrogen and of synthetic air (20% O₂ in N₂). Polymerisation conditions: $414 \mu\text{g}$ catalyst, 2 bar propylene, 250 mL hexanes, $[\text{Al}_{\text{MAO}}]/[\text{Ti}] = 5000$, 139 minutes, and $30 \text{ }^\circ\text{C}$.

7. NMR spectroscopy

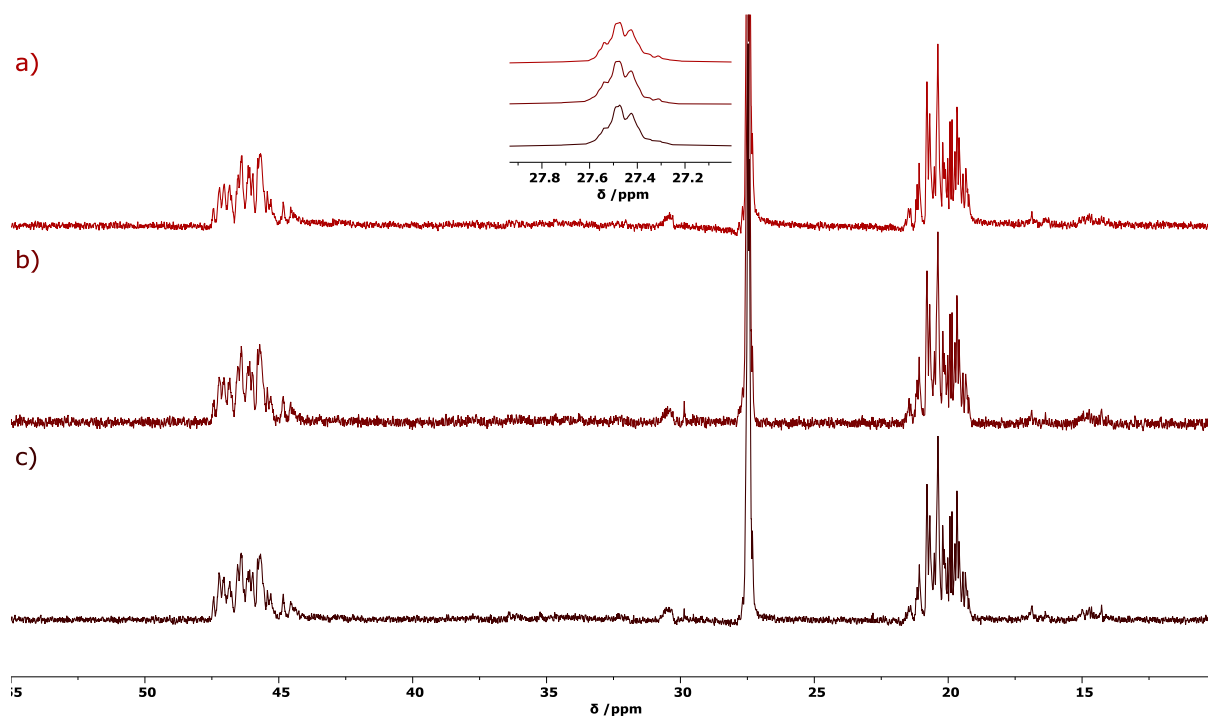


Fig. S20. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (151 MHz, chloroform-*d*, 298 K, $55 \leq \delta \leq 10$) of polypropylene synthesised by 1_{sMAO} at a) 60 °C, b) 70 °C, and c) 80 °C. Polymerisation conditions: 10 mg catalyst, $[\text{Al}_{\text{MAO}}]/[\text{Ti}] = 1000$, 2 bar propylene, 50 mL hexanes, 30 minutes, and 60–80 °C.

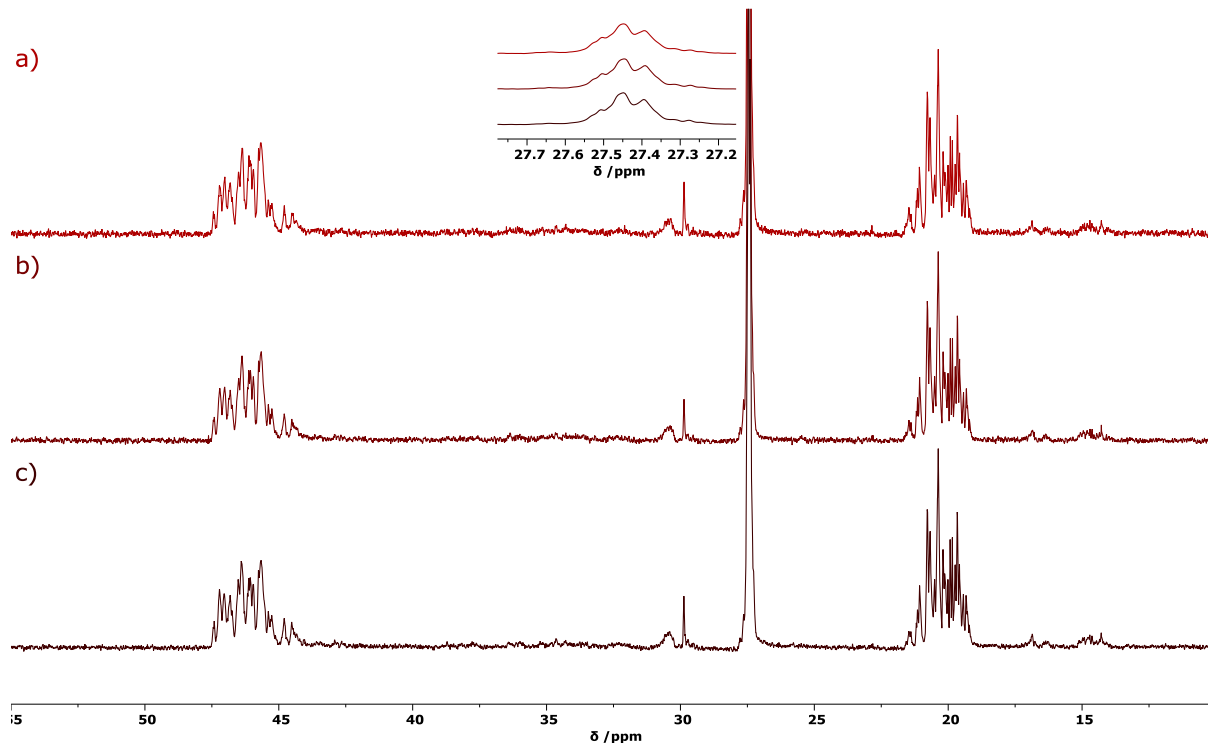


Fig. S21. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (126 MHz, chloroform-*d*, 298 K, $55 \leq \delta \leq 10$) of polypropylene synthesised by 2_{sMAO} at a) 60 °C, b) 70 °C, and c) 80 °C. Polymerisation conditions: 10 mg catalyst, $[\text{Al}_{\text{MAO}}]/[\text{Ti}] = 1000$, 2 bar propylene, 50 mL hexanes, 30 minutes, and 60–80 °C.

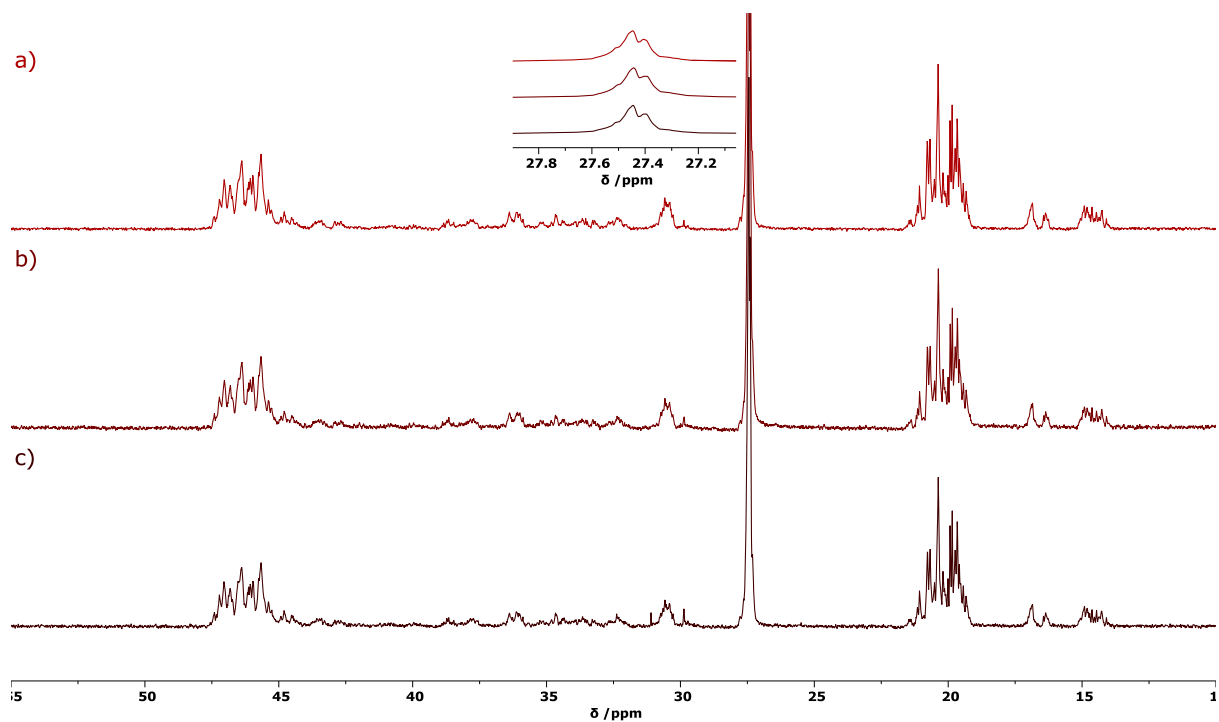


Fig. S22. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (126 MHz, chloroform-*d*, 298 K, $55 \leq \delta \leq 10$) of polypropylene synthesised by 3_{sMAO} at a) 60 °C, b) 70 °C, and c) 80 °C. Polymerisation conditions: 10 mg catalyst, $[\text{Al}_{\text{MAO}}]/[\text{Ti}] = 1000$, 2 bar propylene, 50 mL hexanes, 30 minutes, and 60–80 °C.

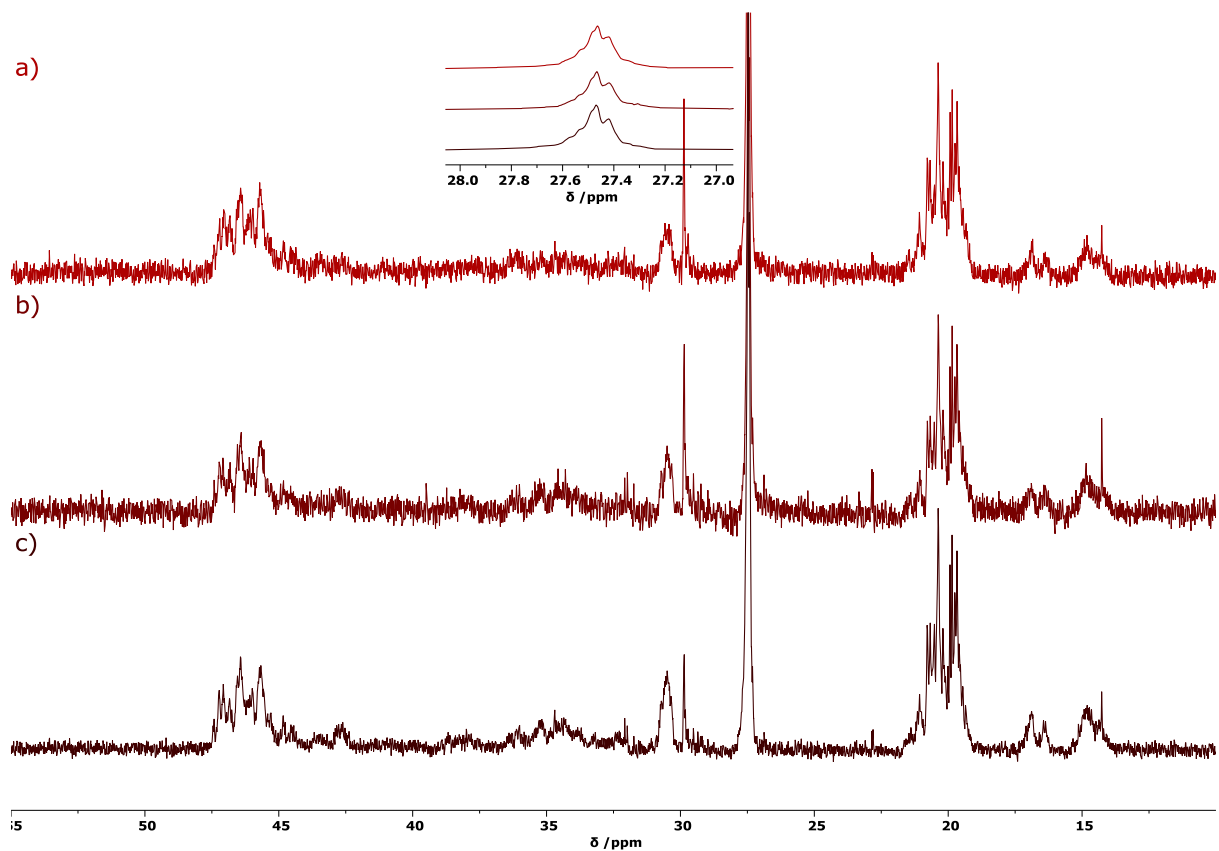


Fig. S23. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (151 MHz, chloroform-*d*, 298 K, $55 \leq \delta \leq 10$) of polypropylene synthesised by 4_{sMAO} at a) 60 °C, b) 70 °C, and c) 80 °C. Polymerisation conditions: 10 mg catalyst, $[\text{Al}_{\text{MAO}}]/[\text{Ti}] = 1000$, 2 bar propylene, 50 mL hexanes, 30 minutes, and 60–80 °C.

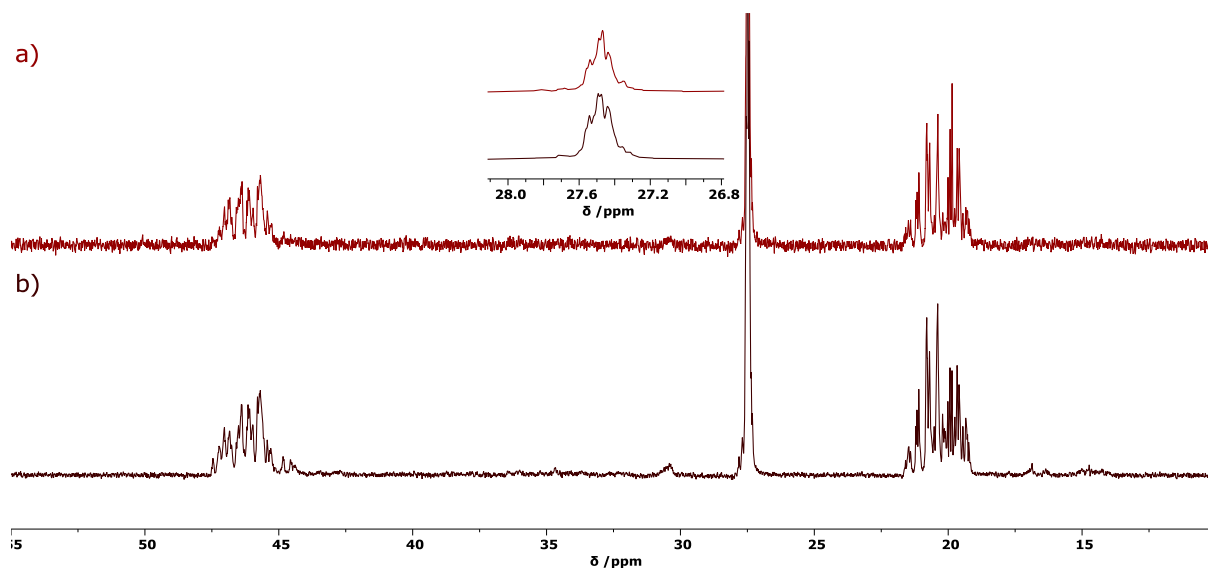


Fig. S24. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (151 MHz, chloroform- d , 298 K, $55 \leq \delta \leq 10$) of polypropylene synthesised by **2**_{SMAO} at a) 4 °C, $[\text{Al}_{\text{MAO}}]/[\text{Ti}] = 500$, and b) 30 °C, $[\text{Al}_{\text{MAO}}]/[\text{Ti}] = 1000$. Polymerisation conditions: 10 mg catalyst, 2 bar propylene, 50 mL hexanes, 10 minutes, and 4–30 °C.

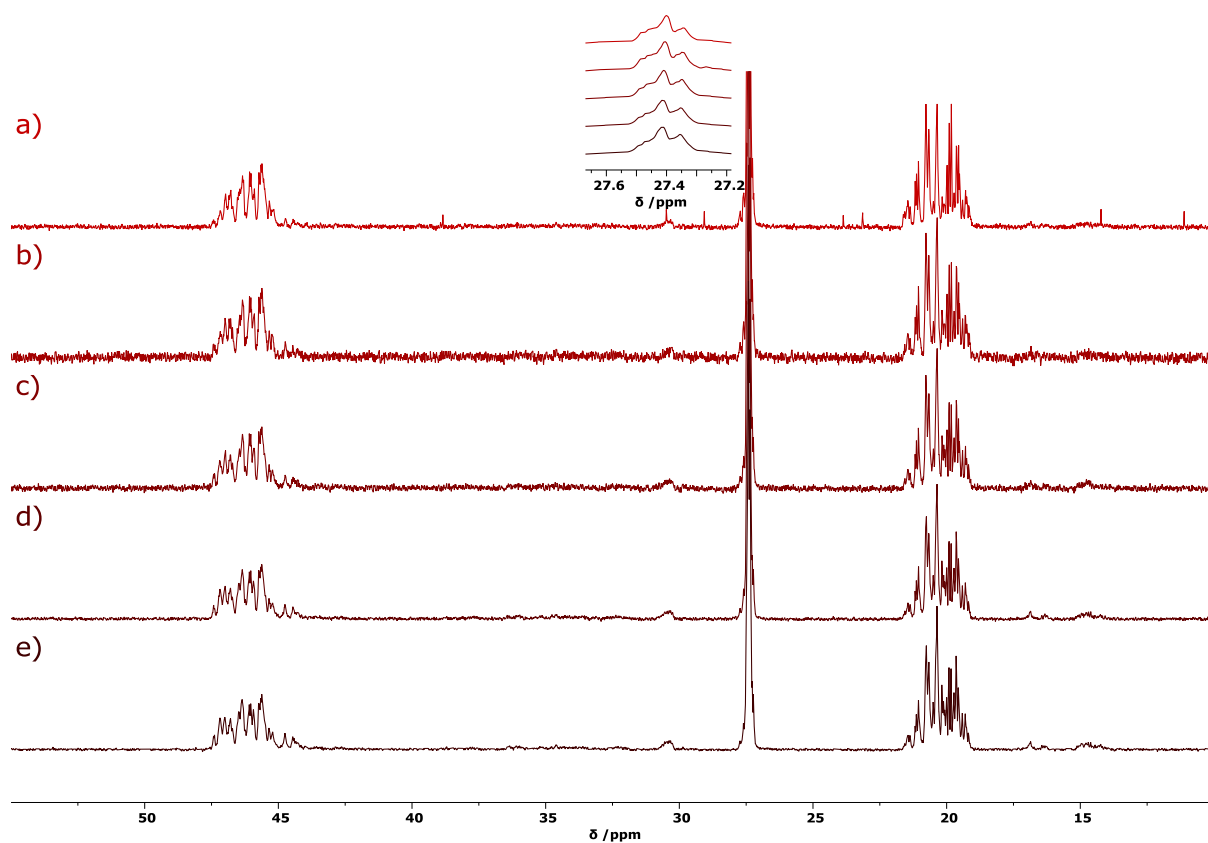


Fig. S25. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (151 MHz, chloroform- d , 298 K, $55 \leq \delta \leq 10$) of polypropylene synthesised by **2** at a) 4 °C, b) 30 °C, c) 50 °C, d) 70 °C, and e) 90 °C. Polymerisation conditions: 414 μg catalyst, 2 bar propylene, 50 mL hexanes, $[\text{Al}_{\text{MAO}}]/[\text{Ti}] = 1000$, and 10 minutes.

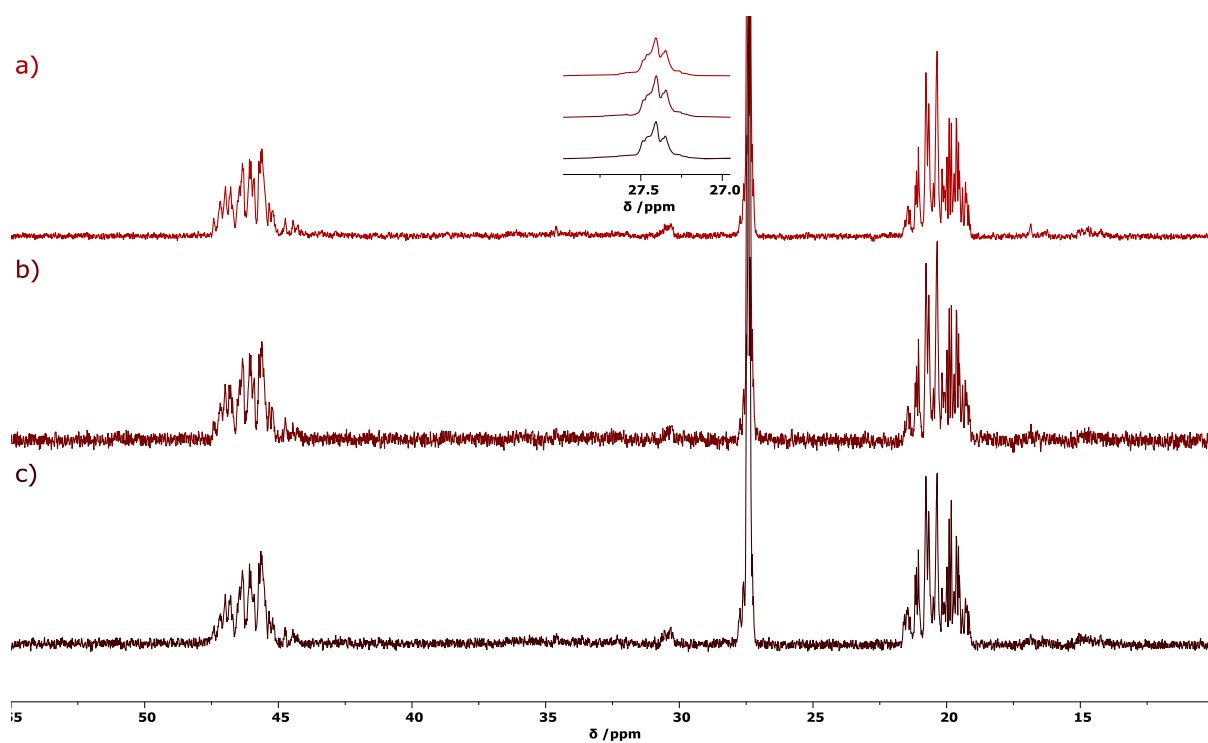


Fig. S26. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (151 MHz, chloroform-*d*, 298 K, $55 \leq \delta \leq 10$) of polypropylene synthesised by **2** using a) 2500, b) 1000, and c) 250 equivalents of MAO. Polymerisation conditions: 414 μg catalyst, 2 bar propylene, 50 mL hexanes, $[\text{Al}_{\text{MAO}}]/[\text{Ti}] = 250\text{--}2500$, 30 $^{\circ}\text{C}$, and 10 minutes.

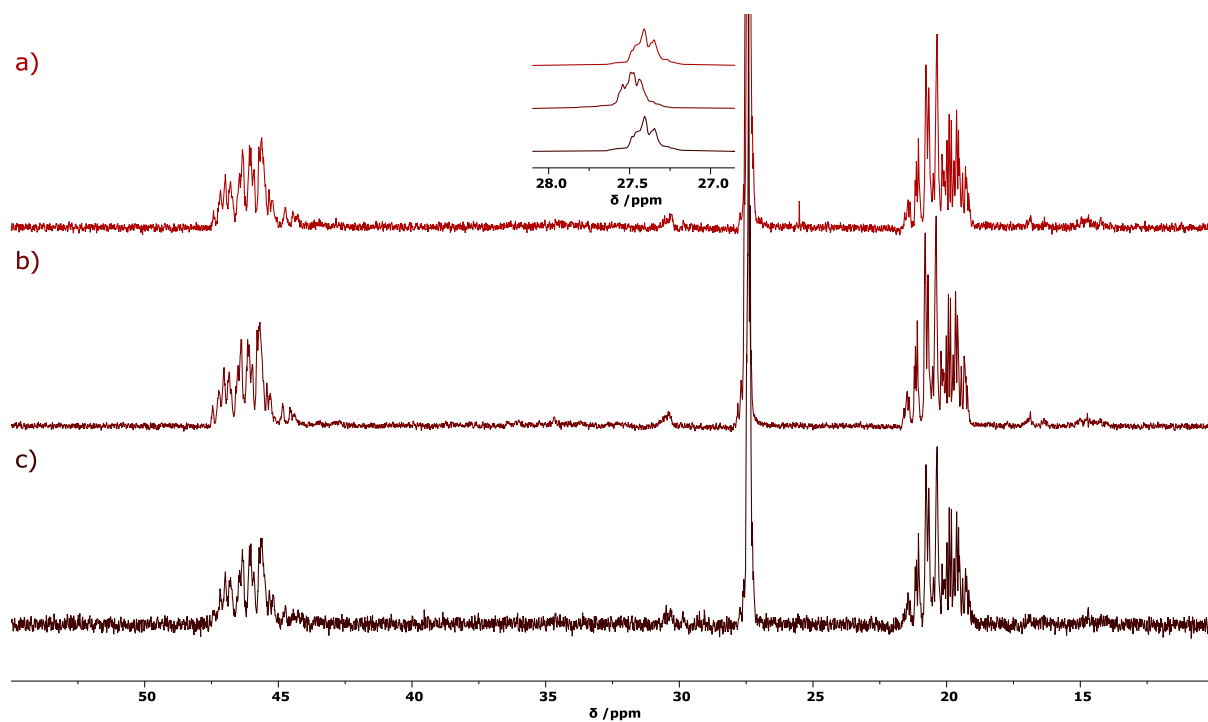


Fig. S27. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (151 MHz, chloroform-*d*, 298 K, $55 \leq \delta \leq 10$) of polypropylene synthesised by **2_{SMAO}** using a) 2500, b) 1000, and c) 250 equivalents of MAO. Polymerisation conditions: 10 mg catalyst, 2 bar propylene, 50 mL hexanes, $[\text{Al}_{\text{MAO}}]/[\text{Ti}] = 250\text{--}2500$, 30 $^{\circ}\text{C}$, and 10 minutes.

8. Infrared (FTIR) spectroscopy

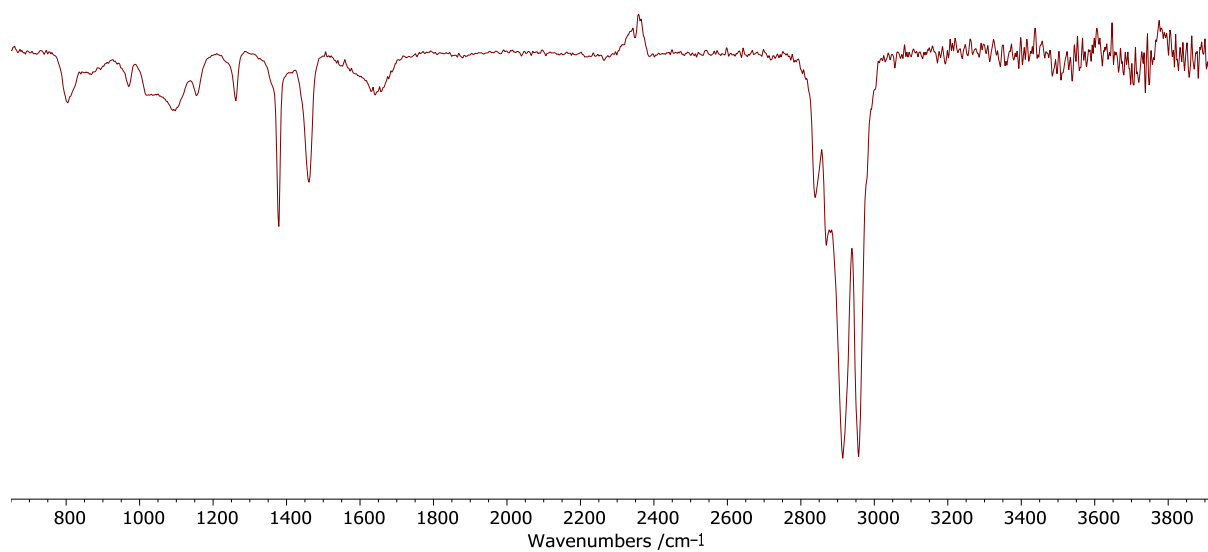


Fig. S28. FTIR spectrum of polypropylene synthesised using **2**_{SMAO}. Polymerisation conditions: 10 mg catalyst, 2 bar propylene, 50 mL hexanes, [Al_{MAO}]/[Ti] = 1000, 10 minutes, and 30 °C.

9. Wide-angle X-ray scattering

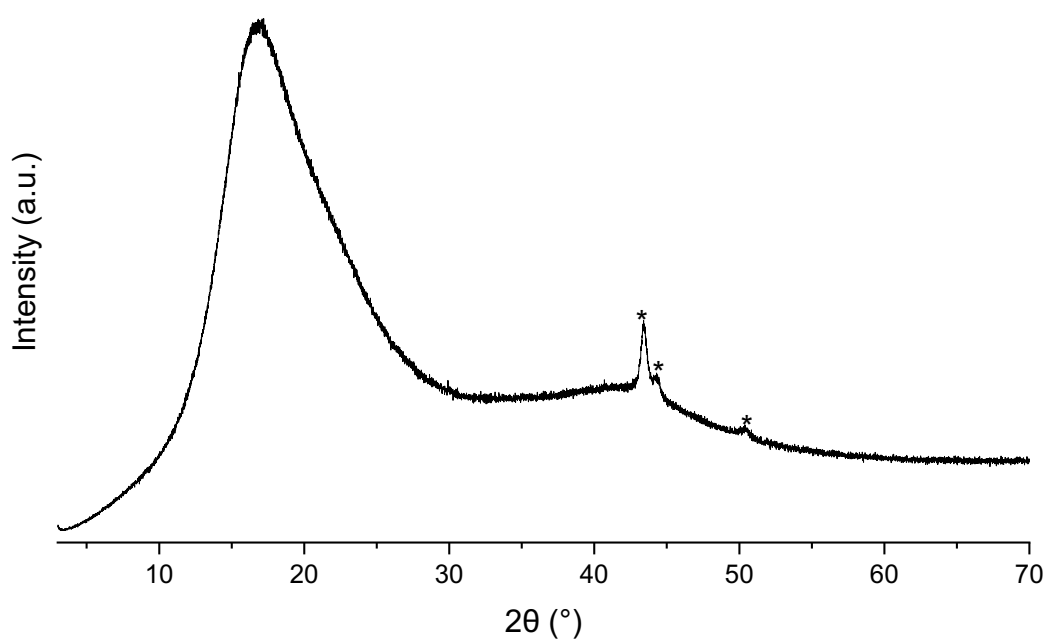


Fig. S29. X-ray diffraction pattern of a sample of UHMWPP. Reflections from the sample holder are denoted by an asterisk (*).

10. Mechanical measurements

Table S3. Aggregated tensile data data for UHMWAPP, with ESDs in parentheses.

Tensile modulus /MPa	Tensile strength /MPa	Tensile strain at strength /%	Tensile stress at break /MPa	Tensile strain at break /%
2.05 ± 0.15	1.08 ± 0.03	184 ± 8	–	>1900 %

Table S4. Tensile data from individual specimens of UHMWAPP.

No.	E_t /MPa	σ_Y /MPa	ϵ_Y /%	σ_M /MPa	ϵ_M /%	σ_B /MPa	ϵ_B /%	h /mm	b /mm	A_0 /mm ²
1	2.04	–	–	1.08	180.3	0.547	1934.5	0.87	4.3	3.74
2	1.90	–	–	1.05	182.2	0.596	1934.6	0.72	4.2	3.02
3	2.30	–	–	1.12	193.2	0.548	1918.6	0.82	4.2	3.44
4	2.02	–	–	1.07	189.8	0.424	1849.9	0.63	4.1	2.58
5	1.97	0.549	20.1	1.06	172.7	0.491	1864.1	0.63	3.7	2.33
Statistics, n = 5										
\bar{x}	2.05	0.549	20.1	1.08	183.6	0.521	1900.3	0.734	4.1	3.02
s	0.153	–	–	0.0269	8.1	0.0661	40.4	0.1092	0.2345	0.58
v [%]	7.46	–	–	2.50	4.41	12.68	2.13	14.88	5.72	19.32

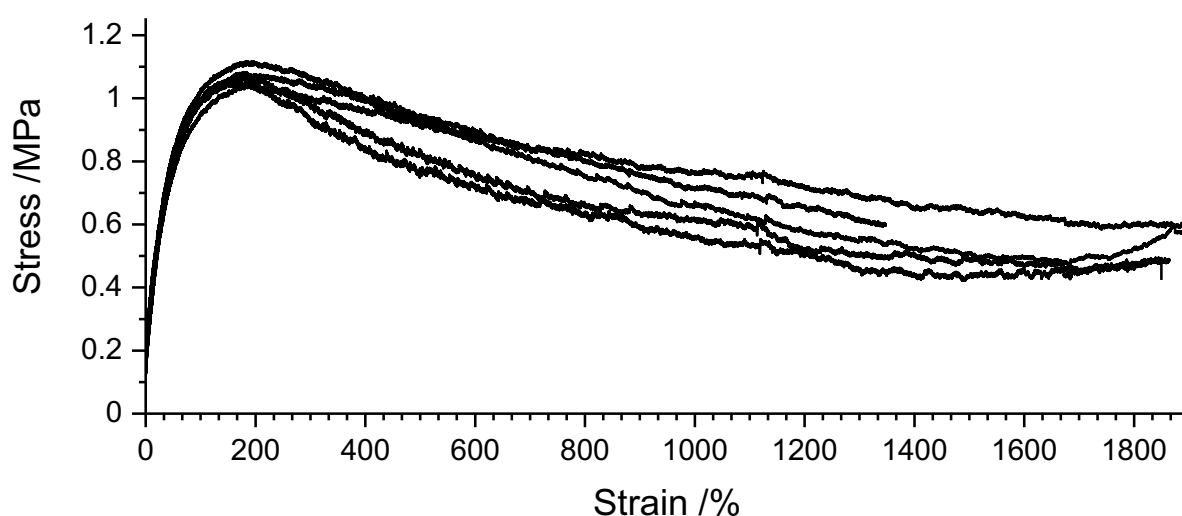


Fig. S30. Stress-strain curves for UHMWAPP.

Table S5. Stress relaxation data from UHMWAPP.

No.	F_{max} /N	$dL(F_{max})$ /mm	$dL(F_{max})$ /%	a_0 /mm	b_0 /mm
1	3.084	59.77	119.5	0.90	3.92
2	3.411	59.78	119.6	0.90	4.09
3	3.010	59.91	119.8	0.82	4.16
4	3.031	59.93	119.9	0.85	4.16
Statistics, n = 4					
\bar{x}	3.134	59.85	119.7	0.868	4.08

s	0.188	0.085	0.1709	0.0395	0.113
v [%]	5.985	0.143	0.1428	4.55	2.77

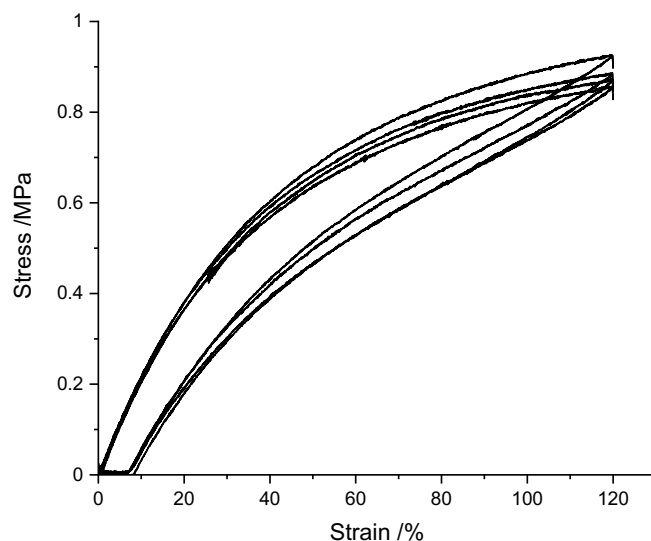


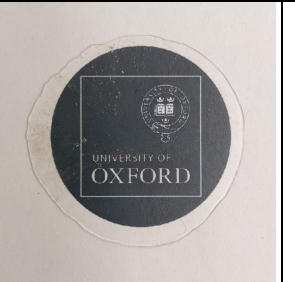
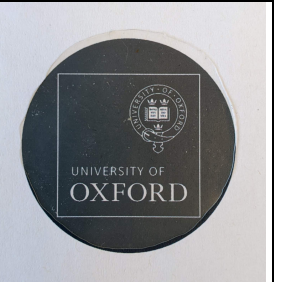


Fig. S31. Stress-strain hysteresis curves of UHMWPP.⁶

11. Optical measurements

Table S6. Optical characterisation data for UHMWPP samples at selected visible wavelengths. λ /nm, total transmittance (T_{tot} , %), diffuse transmittance (T_{diff} , %), and total reflectance (R_{tot} , %).

	a) Pressed at 160 °C Thickness 900 μm			b) Pressed at 80 °C Thickness 620 μm			c) Pressed at 180 °C Thickness 340 μm			d) Pressed at 160 °C Thickness 130 μm		
												
λ /nm	T_{tot}	T_{diff}	R_{tot}	T_{tot}	T_{diff}	R_{tot}	T_{tot}	T_{diff}	R_{tot}	T_{tot}	T_{diff}	R_{tot}
400	82.1	51.6	7.26	85.9	49.1	7.50	82.4	53.3	7.59	83.7	55.3	8.09
450	83.5	50.7	7.23	86.9	47.6	7.42	84.1	52.5	7.53	85.2	54.4	8.09
500	84.2	49.7	7.24	87.4	46.2	7.38	85.2	51.6	7.51	86.2	53.4	8.10
550	84.8	48.2	7.14	87.8	44.2	7.24	86.1	50.2	7.36	86.9	51.9	7.95
600	85.2	47.0	7.12	88.1	42.9	7.20	86.7	49.0	7.31	87.3	50.8	7.90
650	85.5	45.9	7.11	88.4	41.6	7.18	87.2	47.9	7.27	87.8	49.5	7.89
700	85.8	45.2	7.11	88.7	40.7	7.16	87.5	47.1	7.24	88.2	48.6	7.85
Average (380–750)	84.6	48.1	7.16	87.7	44.3	7.28	85.8	49.9	7.38	86.6	51.7	7.96

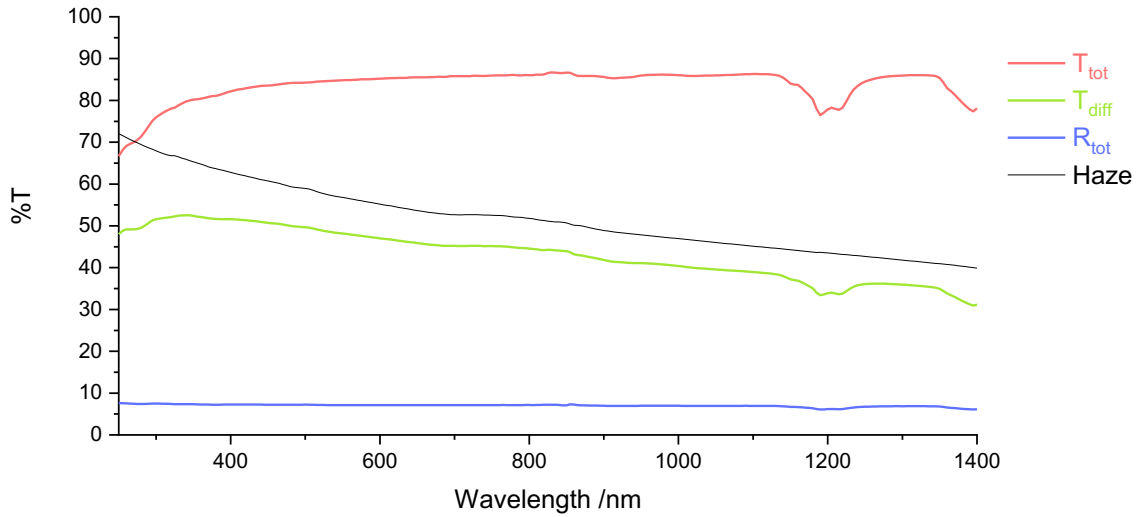


Fig. S32. Optical characteristics as a function of wavelength of sample a) (pressed at 160 °C, 900 μm) – total transmission (T_{tot} , %), diffuse transmission (T_{diff} , %), total reflectance (R_{tot} , %), and haze = T_{diff}/T_{tot} .

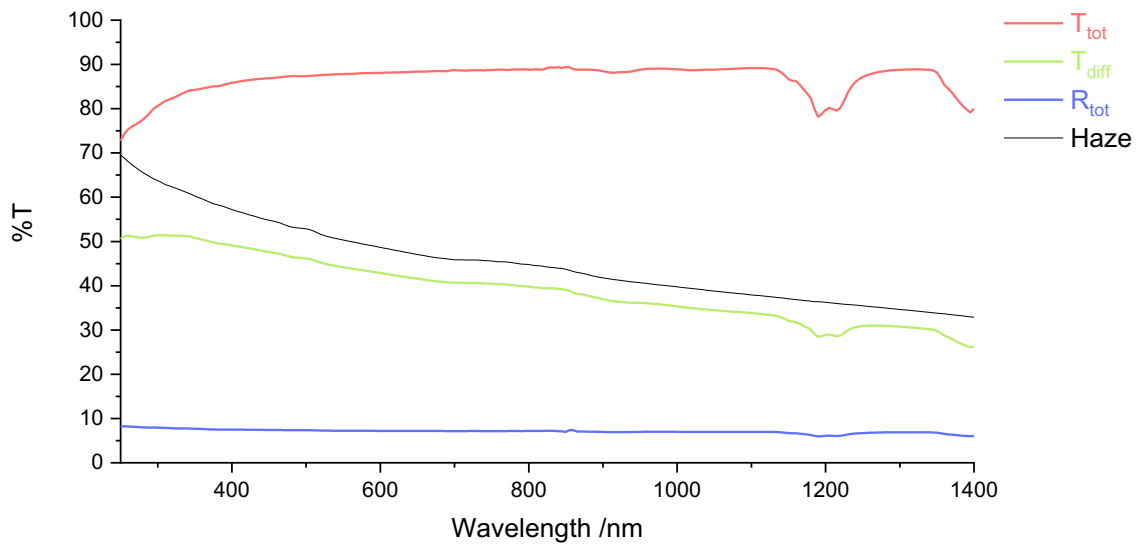


Fig. S33. Optical characteristics as a function of wavelength of sample b) (pressed at 80 °C, 620 μm) – total transmission (T_{tot}), diffuse transmission (T_{diff}), total reflectance (R_{tot}), and haze = T_{diff}/T_{tot} .

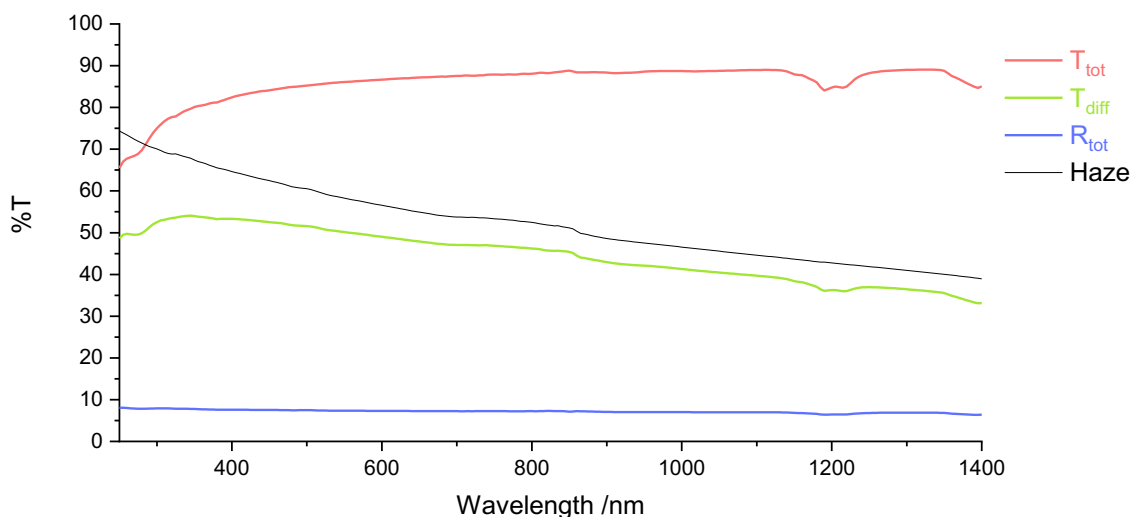


Fig. S34. Optical characteristics as a function of wavelength of sample c) (pressed at 180 °C, 340 μ m) – total transmission (T_{tot}), diffuse transmission (T_{diff}), total reflectance (R_{tot}), and haze = T_{diff}/T_{tot} .

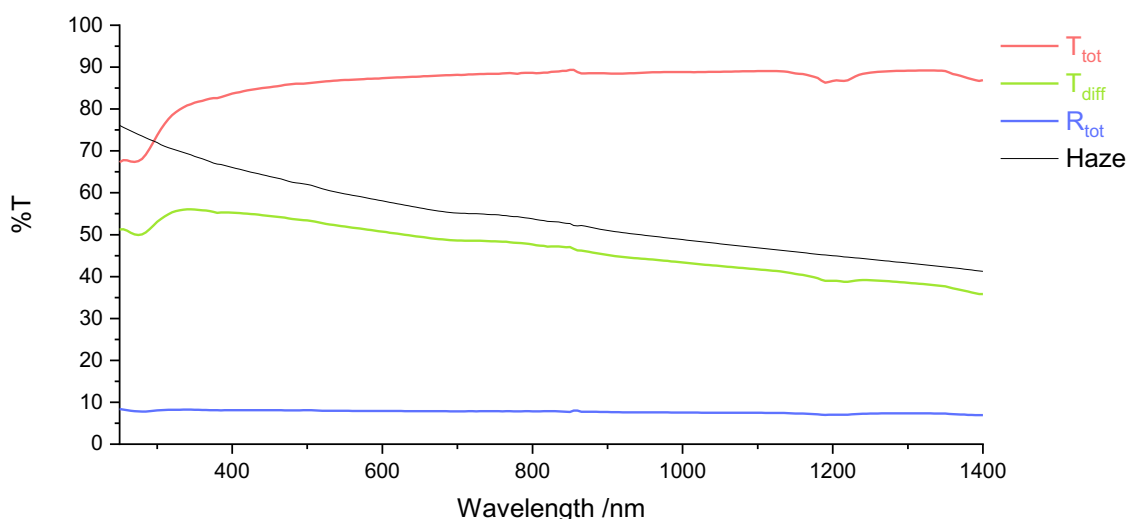


Fig. S35. Optical characteristics as a function of wavelength of sample d) (pressed at 160 °C, 130 μ m) – total transmission (T_{tot}), diffuse transmission (T_{diff}), total reflectance (R_{tot}), and haze = T_{diff}/T_{tot} .

12. References

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