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

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The selective and high-yielding synthesis of fully amorphous ultra-high molecular weight atactic polypropylene (UHMWaPP), with weight-average molecular weights (M_w) up to 2.0 MDa and narrow polydispersities is reported; permethylindenyl-phenoxy (PHENI*) titanium complexes immobilised on solid polymethylaluminoxane (sMAO) are remarkably efficient single-site catalysts for propylene polymerisation, with activities up to 12 000 $\text{kg}_{\text{PP}}\ \text{mol}_{\text{Ti}}^{-1}\ \text{h}^{-1}\ \text{bar}^{-1}$. UHMWaPP was found to be a high-performance thermoplastic elastomer, exhibiting an ultimate tensile strength of 1.08 MPa (at 184% strain), and remarkably high ductility, with a tensile strain at break of >1900%. Excellent elastic recovery is observed with a set value as low as 7% in stress–strain hysteresis experiments. The mechanical properties reported are compared with commercial olefinic thermoplastic elastomers, demonstrating the potential of this technology to compete with commercial copolymers and composites as an elastic homopolymer.

Introduction

Commercially, polypropylene (PP) is predominantly synthesised using conventional Ziegler–Natta (ZN) catalyst technologies.[1] The inherent chirality of the titanium centres on the $TiCl_3$ crystal surface results in highly crystalline isotactic polymers.[2] It is clear from detailed computational modelling of these mechanistically elusive systems that sterics play a key role in enforcing stereoselectivity, with the $-CH_3$ group of the propylene interacting with chlorides adjacent to the metal centre.[3] Tacticity and molecular weights (M_w) are highly coupled in these systems,[4] with low M_w partially crystalline atactic PP (aPP) obtained as a by-product.[5] The isotactic PP (*i*PP) produced in this manner has a non-uniform distribution of stereodefects, resembling a stereoblock microsctructure in contrast to the uniform polymers produced by single-site metallocene catalysts; it has been claimed that this is responsible for the difference in physical properties of these two classes of polymers.[6] Group four metallocene and post-metallocene catalysts are typically used where independent control over polymer tacticity and molecular weight are desired and have been shown to be particularly effective in the synthesis of elastomeric high molecular weight aPP which is inaccessible using Ziegler–Natta technology.[7,8] The relationship between the symmetry of single-site catalysts and resulting polypropylene tacticity is well understood,[9,10] with complexes in the C_{2v} and C_2 point groups typically producing atactic and isotactic PP respectively, while asymmetric C_1 complexes are reported to produce polymers with microstructures ranging from highly isotactic to atactic.[9] Stereoselectivity in prochiral monomer insertion results principally from enantiomorphic site control with steric constraints enforcing a preference for either the *re* or *si* configuration of the monomer. C_2-*ansa*-metallocenes are particularly effective, with the bridge requiring conformational rigidity of the ligand.[11,12]

Amorphous high molecular weight aPP (HMWaPP, M_w > 200 kDa) is a material of growing industrial interest; beneficial elastic and optical properties lead to broad applications as adhesives, compatibilisers and as additives in a range of polymeric materials.[5,7] There has been limited development of catalysts that are selective for the synthesis of such materials, with metallocene and post-metallocene complexes of titanium and zirconium receiving the most attention.[8,13] The synthesis of ultra-high molecular weight aPP (UHMWaPP, M_w > 1 MDa) has been reported, though typically only in relatively low-yielding processes.[13,14] Ultra-high molecular weight homopolymers of higher olefins from 1-butene to 1-octadecene have also been reported, typically in moderate yields or under forcing low-temperature conditions, with relatively limited specific catalyst development, exploration of polymer properties, and few proposed applications.[15–19]

Ultra-high molecular weight homopolypropylene elastomers, synthesised by Rieger *et al.* as stereodefective isotactic

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PP, were shown to have beneficial mechanical properties, including improved elastic recovery compared to lower M_w elastomeric PP.[20] Homopolymer olefinic thermoplastic elastomers would offer beneficial processability and recyclability when compared with more conventional cross-linked rubbers.[21,22] One such class of elastomer, ethylene propylene rubber (EPM), is commercially synthesised using highly active titanium cyclopentadienyl-amidinate complexes.[23]

Post-metallocene *ansa*-bridged complexes based on nitrogen and oxygen donors – such as the Constrained Geometry Complexes (CGCs),[24,25] Phenoxy-Induced Complexes of Sumitomo (PHENICS),[26–28] and our recently-reported permethylindenyl (C_9Me_6, Ind*, I*) analogue, PHENI*[29] – have been shown to be highly active catalysts for ethylene polymerisation, with the latter producing substantially disentangled UHMWPE and demonstrating a remarkable 22-fold increase in activity over the analogous PHENICS complex. In the polyethylene case, solid polymethylaluminoxane (sMAO) has proven to be a highly competent dual-function activating catalyst support, forming strongly immobilised metallocene catalysts for use in heterogeneous slurry-phase reactions. These systems can produce polyolefins with single-site catalysis characteristics.[30–32] Based on these results, we hypothesised that the PHENI* complexes would also be competent catalysts for UHMWPP.

In this work, we report the application of permethylindenyl-phenoxy (PHENI*) complexes in the homopolymerisation of propylene, both in solution-phase and sMAO-supported regimes. We demonstrate extremely high activities, excellent control, and the selective production of high and ultra-high molecular weight amorphous atactic polypropylene. The polypropylenes are shown to have excellent tensile and elastic properties, comparable to commercial engineering thermoplastic elastomers.

Results and discussion

Synthesis of complexes and pre-catalysts

Both CGCs and PHENICS complexes have been shown to have better catalytic activity than more traditional Kaminsky metallocenes utilising hydrocarbon ligands. Increased molecular weights are also observed in addition to more effective comonomer enchainment.[24,33,34] The PHENICS catalysts are particularly notable for their very high temperature stability, with high activities maintained even at elevated temperatures (>200 °C).[28] The permethylindenyl ligand has previously been shown to enhance the activity of Cp*-based ligands both in metallocene and CGC analogues.[25,35–42] This is attributed to facile η^5,η^3-haptotropic ring slip – which lowers the barrier to associative addition;[43–46] the steric kinetic stabilisation of the ligand;[47] and the positive inductive effect of polyalkylation resulting from σ–π hyperconjugation.[48] We have previously introduced the PHENI* ligand which is a development of PHENICS ligands, incorporating the many benefits of I*, and which shows higher activities both than the I* CGC analogues introduced by Williams *et al.* and the indenyl PHENICS analogue.[25,29,43]

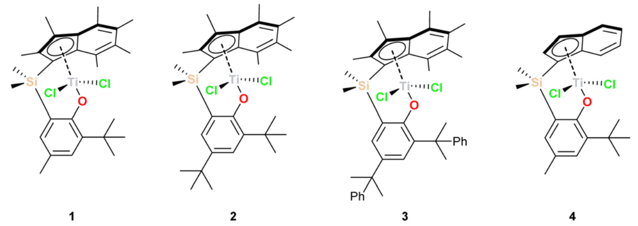

Chart 1 Complexes used in this study.

Titanium dichloride complexes **1–3**, utilising PHENI* ligands, $^{Me_2}SB(^{R_1R_2}ArO,I^*)TiCl_2$ ($\{(\eta^5\text{-}C_9Me_6)Me_2Si(2\text{-}R_1\text{-}4\text{-}R_2\text{-}C_6H_2O)\}TiCl_2$; R_1, R_2 = Me, ^{t}Bu, or CMe_2Ph), were synthesised as previously reported.[29] These complexes, and additionally the indenyl-PHENICS complex **4** ($^{Me_2}SB(^{tBu,Me}ArO,I)TiCl_2$; $\{(\eta^5\text{-}C_9H_6)Me_2Si(2\text{-}^t\text{Bu-4-Me-}C_6H_2O)\}TiCl_2$; I = C_9H_6), were then immobilised on sMAO following a standard procedure,[49] with $[Al_{sMAO}]/[Ti] = 200$, to afford $\mathbf{1_{sMAO}}$–$\mathbf{4_{sMAO}}$ (Chart 1).

Polymerisation of propylene to afford ultra-high molecular weight polypropylene

Initial polymerisation studies using sMAO-supported solid catalysts were performed in 150 mL ampoules using 10 mg $\mathbf{1_{sMAO}}$–$\mathbf{4_{sMAO}}$ with 2 bar propylene in 50 mL hexanes for 30 minutes with MAO ($[Al_{MAO}]/[Ti] = 1000$) acting as co-catalytic initiator and scavenger across a temperature of polymerisation (T_p) range of $60 \le T_p \le 80$ °C (Table 1). As was found previously for ethylene polymerisation using supported catalysts,[29] $\mathbf{2_{sMAO}}$ displays the highest activity, 3200 $kg_{PP}\ mol_{Ti}^{-1}\ h^{-1}\ bar^{-1}$ at 60 °C, with the trend $\mathbf{2_{sMAO}} > \mathbf{1_{sMAO}} > \mathbf{3_{sMAO}}$. Comparing the indenyl and permethylindenyl analogues ($\mathbf{1_{sMAO}}$ and $\mathbf{4_{sMAO}}$) – a larger increase in activity is seen even than for ethylene polymerisation, being 26-fold greater for the I* complex at T_p =

Table 1 Propylene polymerisation results with sMAO supported catalysts $\mathbf{1_{sMAO}}$–$\mathbf{4_{sMAO}}$. Polymerisation conditions: 10 mg catalyst, 2 bar propylene, 50 mL hexanes, 30 minutes, and MAO ($[Al_{MAO}]/[Ti] = 1000$). (a) $kg_{PP}\ mol_{Ti}^{-1}\ h^{-1}\ bar^{-1}$ (b) $kg_{pp}\ g_{cat}^{-1}\ h^{-1}\ bar^{-1}$ (c) Determined by GPC, PDI = M_w/M_n

Catalyst	T_p/°C	Activity[a]	Productivity[b]	M_w[c]/kDa	PDI[c]
$\mathbf{1_{sMAO}}$	60	2600	0.19	470	2.2
	70	1400	0.10	370	2.3
	80	1100	0.080	230	2.3
$\mathbf{2_{sMAO}}$	60	3200	0.17	630	2.2
	70	2200	0.16	430	2.2
	80	1600	0.11	350	2.1
$\mathbf{3_{sMAO}}$	60	1700	0.12	370	2.3
	70	620	0.044	290	2.3
	80	640	0.047	200	2.2
$\mathbf{4_{sMAO}}$	60	100	0.0075	96	4.5
	70	37	0.0026	63	3.2
	80	19	0.0013	75	3.5

[a] $kg_{PP}\ mol_{Ti}^{-1}\ h^{-1}\ bar^{-1}$. [b] $kg_{pp}\ g_{cat}^{-1}\ h^{-1}\ bar^{-1}$. [c] Determined by GPC, PDI = M_w/M_n.

60 °C. The weight-average molecular weight (M_w) of the resulting polypropylenes was determined by gel permeation chromatography (GPC) (Table 1 and Fig. 1, 2). The PHENI* sMAO supported catalyst $\mathbf{1_{sMAO}}$ produced aPP with a 5-fold higher M_w than the analogous PHENICS sMAO supported catalyst, $\mathbf{4_{sMAO}}$, as well as having reduced polydispersity (PDI, $Đ$). sMAO supported catalyst $\mathbf{2_{sMAO}}$ produced the highest molecular weight polymers of the three PHENI* supported catalysts studied, up to 630 kDa at T_p = 60 °C.

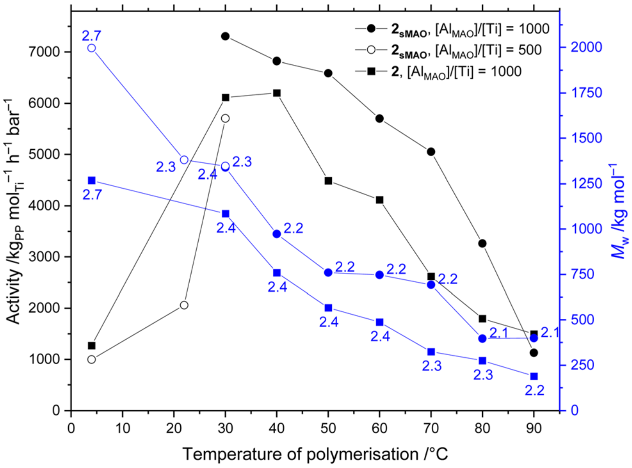

Fig. 1 Propylene polymerisation activity and polypropylene molecular weight (polydispersity values (PDI, $Đ = M_w/M_n$) annotated) as a function of the temperature of polymerisation using homogeneous and sMAO-supported $^{Me_2}SB(^{tBu_2}ArO, I^*)TiCl_2$ (**2**, and $\mathbf{2_{sMAO}}$ respectively). Polymerisation conditions: 0.714 μmol Ti (10 mg solid catalyst, or 414 μg complex), 2 bar propylene, 50 mL hexanes, 10 minutes, and MAO ($[Al_{MAO}]/[Ti]$ = 500 or 1000).

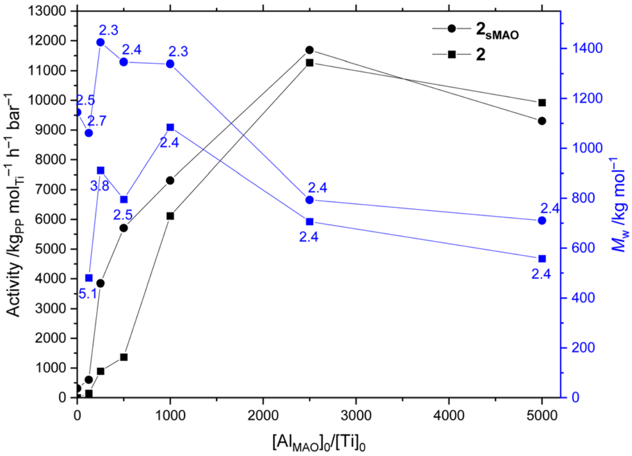

Fig. 2 Propylene polymerisation activity and polypropylene molecular weight (polydispersity values (PDI, $Đ = M_w/M_n$) annotated) as a function of $[Al_{MAO}]/[Ti]$ using homogeneous phase and sMAO-supported $^{Me_2}SB(^{tBu_2}ArO, I^*)TiCl_2$ (**2**, and $\mathbf{2_{sMAO}}$ respectively). Polymerisation conditions: 0.714 μmol Ti (10 mg solid catalyst, or 414 μg complex), 2 bar propylene, 50 mL hexanes, 10 minutes, and 30 °C.

The formation of hexanes-soluble aPP led to an increasingly viscous reaction mixture during the course of the polymerisation. Runs were attempted as before with $\mathbf{2_{sMAO}}$ at T_p < 60 °C but the increased viscosity resulting from a greater polymer yield inhibited stirring. Thus, the reaction time was reduced to 10 minutes to allow complete thermal profiling of $\mathbf{2_{sMAO}}$ over a range of $4 \leq T_p \leq 90$ °C (Fig. 1). As there was no advantage to be gained from a morphological templating effect of supported polymerisation, the homogeneous polymerisation activity of complex **2** was also investigated. Polymerisation conditions were as for runs using sMAO-supported solid catalysts, using 0.714 μmol **2** (414 μg, [Ti] = 14 μM, equal to the quantity supported on 10 mg $\mathbf{2_{sMAO}}$). As anticipated, the activities of $\mathbf{2_{sMAO}}$ and **2** are broadly consistent, with the moderate increase in sMAO-supported activities largely attributed to the 20% increase in [Al] (from $[Al_{MAO}]/[Ti]$ = 1000 in solution-phase, to $[Al_{(sMAO + MAO)}]/[Ti]$ = 1200 with $\mathbf{2_{sMAO}}$) which is shown *vide infra* to effect an increase in activity. While the per-mole$_{Ti}$ activities were consistent it should be noted that the per-mass$_{cat}$ productivities of the solution-phase system are far in excess of the supported catalysts.

A typical molecular weight temperature profile was observed using both $\mathbf{2_{sMAO}}$ and **2** (Fig. 1), with M_w increasing as polymerisation temperature decreases due to the increase in the rate of chain termination processes, including β-elimination and chain transfer, relative to propagation.[50,51] With $\mathbf{2_{sMAO}}$, M_w was found to be largely unaffected by the reduction in reaction time from 30 to 10 minutes, and continued to increase to 1.3 MDa at 30 °C. In solution-phase polymerisations with **2**, polymer molecular weights were found to be consistently lower than when the catalyst is supported on sMAO though still affording UHMWaPP, up to 1.1 MDa at 30 °C, and 1.3 MDa at 4 °C. Polydispersities are low across this temperature range, with $M_w/M_n \leq 2.7$, indicative of well-controlled single-site catalysis, which is maintained both in homogeneous phase and when supported on sMAO, showing that the supported system retains the benefits of homogeneous molecular catalysis. The production of UHMWaPP under ambient temperature conditions and moderate pressure is of potential industrial significance.

The effect of reaction scale

That polymerisation activity was found to be highest at 30 °C and decreases with increasing temperature – that is, with decreasing solubility of propylene in hexanes[52] – is evidence that the catalytic activity of complex **2** in both homogeneous and supported regimes is limited principally by the availability of propylene in the system, with monomer diffusion being rate limiting. Further studies at higher pressures of propylene would be required to find the performance ceiling. This is evidenced by a 34% increase in activity of $\mathbf{2_{sMAO}}$, to 9800 kg_{PP} mol_{Ti}^{-1} h^{-1} bar^{-1}, when the solvent volume was increased to 250 mL in a larger reaction vessel leading to a more dilute, lower viscosity solution; more efficient stirring; and a reduced mass-transport barrier for the dissolution of propylene. In this large-scale regime, the quantity of MAO added was also increased five-fold to $[Al_{MAO}]/[Ti]$ = 5000 in order to maintain a consistent initial concentration of aluminium, $[Al_{MAO}]$ = 14 mM.

To explore this further, the effects of reaction scale were investigated with **2**, with higher catalyst dilutions leading to an increase in per-mole activity (see Fig. S1 in the ESI†). Activity appears to be proportional to the reciprocal concentration of catalyst, increasing to a value of 12 000 kg_{PP} mol_{Ti}^{-1} h^{-1} bar^{-1} at one eighth relative dilution ([Ti] = 1.8 μM). The mass of MAO cocatalyst added was not changed, maintaining a concentration of $[Al_{MAO}]$ = 14 mM. The weight-average molecular weight of the resulting polypropylenes was found to increase from 1.1 to 1.5 MDa at one eighth dilution, showing a trend towards higher molecular weights at higher dilutions.

The effect of catalyst loading

The performance of both complex **2** and sMAO supported catalyst $\mathbf{2_{sMAO}}$ was investigated at T_p = 30 °C as a function of the ratio $[Al_{MAO}]/[Ti]$, ranging from 0 to 5000 (Fig. 2). In the absence of an aluminium cocatalyst, activity was found to be moderate with $\mathbf{2_{sMAO}}$ and no activity was recorded with **2**. This demonstrates the dual-function nature of solid polymethylaluminoxane as an activating support.[30] Increasing the MAO loading resulted in increased polymerisation activities up to a maximum value at 2500 equivalents of 12 000 and 11 000 kg_{PP} mol_{Ti}^{-1} h^{-1} bar^{-1} for $\mathbf{2_{sMAO}}$ and **2** respectively. This activity compares well with some of the most active polypropylene catalysts in literature: the $TiCl_4$–Al/Mg system reported by Rishina *et al.* and the fluorenyl zirconocene reported by Resconi *et al.* have activities of 22 000 and 29 000 kg_{PP} mol^{-1} h^{-1} respectively when used in liquid propylene,[7,53] a far greater concentration of monomer than the 2 bar pressure used in this work.[54] Runs were attempted using **2** and other alkyl aluminium cocatalysts – TMA, TEA, and TIBA – in place of MAO, but negligible activity was recorded in these cases. The catalyst system $\mathbf{2_{sMAO}}$/TIBA by contrast did show moderate polymerisation activity (279 kg_{PP} mol_{Ti}^{-1} h^{-1} bar^{-1} at 60 °C), further demonstrating the activating nature of the sMAO support.

As expected, M_w was found to decrease with increasing MAO loading (Fig. 2) as a result of increased chain transfer to aluminium, with $\mathbf{2_{sMAO}}$ and **2** having maxima at $[Al_{MAO}]/[Ti]$ = 250 and 1000 respectively (1.4 and 1.1 MDa respectively). Polymerisations at 4 and 22 °C were performed with $\mathbf{2_{sMAO}}$ at $[Al_{MAO}]/[Ti]$ = 500 as a balance between high M_w and high activities, and at 4 °C with **2** and $[Al_{MAO}]/[Ti]$ = 1000 (Fig. 1). Activities were comparatively much reduced in these lower temperature conditions, though still classed as "very high",[55] and molecular weight was found to increase still further reaching 2.0 MDa at T_p = 4 °C with $\mathbf{2_{sMAO}}$. In homogeneous polymerisation with **2**, the increase in M_w at low temperature was less dramatic, reaching 1.3 MDa at 4 °C. The titanium phenoxy-imine and 2,2′-thiobis(6-*tert*-butyl-4-methylphenoxy) (TBP) complexes reported by Saito *et al.* and Miyatake *et al.* respectively were able to produce aPP with M_w > 8 MDa but with activities of only 48 kg_{PP} mol_{Ti}^{-1} h^{-1} bar^{-1} (20 °C, 1 bar) and 8900 kg_{PP} mol_{Ti}^{-1} h^{-1} (25 °C, liquid propylene) respectively,[13,14] significantly lower than $\mathbf{2_{sMAO}}$, reported in this work with activities up to 12 000 kg_{PP} mol_{Ti}^{-1} h^{-1} bar^{-1} (30 °C, 2 bar).

Exploration of polymer properties; elastomeric UHMWaPP

Differential scanning calorimetry (DSC) confirmed the identity of the polymers as wholly amorphous aPP, with no melting endotherm observed. Glass transitions were observed between −12 and −3 °C, with $\Delta C_{p,Tg}$ values in the region 0.4–0.6 J $°C^{-1}$ g^{-1}, consistent with the values reported by Wilkinson *et al.* for aPP and the predictions of Hirai and Eyring that, for a perfectly amorphous polyolefin, $\Delta C_{p,Tg}$ should be 2.97 calories per degree per mole of chain atoms (corresponding to a value of 0.591 J $°C^{-1}$ g^{-1} for PP).[56–58] The PP synthesised by the indenyl complex $\mathbf{4_{sMAO}}$ has a T_g of −12 °C, in perfect agreement with literature values for aPP,[56] with the PHENI* complexes $\mathbf{1_{sMAO}}$–$\mathbf{3_{sMAO}}$ producing PP with slightly elevated T_g values, presumably due to the higher molecular weights in these cases.

$^{13}C\{^1H\}$ Nuclear Magnetic Resonance (NMR) spectra were recorded at 298 K in chloroform-*d* and assigned according to the analysis of Miyatake *et al.* and are characteristic for atactic polypropylene.[59–62] There was minimal evidence found for 2,1-insertion regioerrors in the $^{13}C\{^1H\}$ NMR spectra, particularly for aPP synthesised by $\mathbf{1_{sMAO}}$, $\mathbf{2_{sMAO}}$, and **2**.[63–65] This behaviour is typical for early transition metal post-metallocenes, where 2,1 regioerrors are usually rare <1 mol%.[66] The presence of resonances at $\delta^{13}{}_{C}$ = 14–18 and 30–44 ppm in the NMR spectra of aPP synthesised by $\mathbf{3_{sMAO}}$, and $\mathbf{4_{sMAO}}$ indicate an increased degree of 2,1-insertions, and thus poorer regiocontrol, in these cases.

The absence of Bragg reflections in the Wide-Angle X-ray Scattering (WAXS) pattern is also indicative of a fully amorphous material. The PHENI* complexes reported in this work are some of the highest activity catalysts in the literature, and to the authors' knowledge the only such catalysts efficiently able to produce ultra-high molecular weight amorphous polypropylene (aPP) with low poly dispersity.

To facilitate mechanical characterisation, a batch of 33 g UHMWaPP (M_w = 1.2 MDa, $Đ$ = 2.7) was cryogenically milled to a powder-like material and pressed at 180–200 °C to form an optically transparent plate. The bulk density was determined according to ISO1183, and was found to be 876 kg m^{-3}.[67] Optical transmissivity was found to be 85% across the visible light region (380–750 nm), approaching the values of more conventional transparent polyolefin block copolymers.[68] Optical haze (T_{diff}/T_{tot}) is calculated to be 50–60%, and total reflection measured at 7%, both quantities decreasing at longer wavelengths of incident light. The mechanical properties of the polymer were analysed according to ISO527.5A (Fig. 3) using type 5A test specimens.[69] The Youngs modulus was found to be 2.05 MPa. The ultimate tensile strength was 1.08 MPa, at a strain of 184%, where a zero-slope condition is achieved demonstrating "yield-like" behaviour comparable to EPM copolymers (Fig. 3b).[70]

Break characteristics could not be determined; the elongation at break was higher than could be tested, but is at least

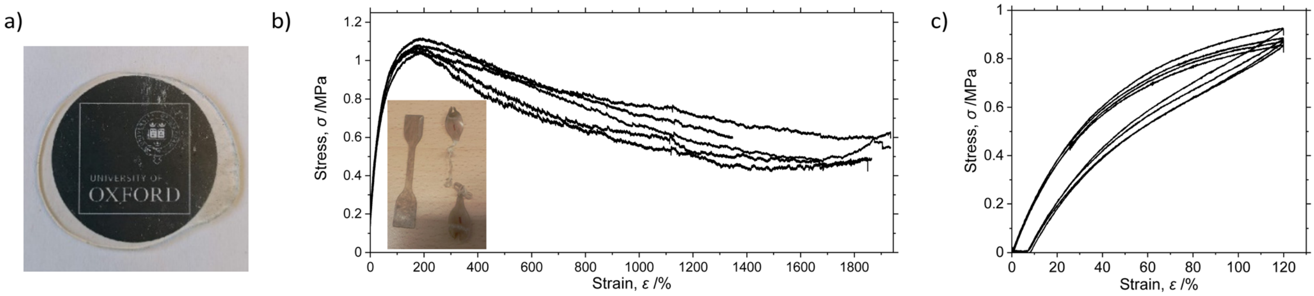

Fig. 3 (a) Image of pressed transparent disc of UHMWaPP; (b) engineering stress–strain curves (inset: image of dog-bone samples before and after tensile testing), and (c) stress–strain hysteresis curves obtained from UHMWaPP samples.

1900%, indicative of a tough, highly ductile material. Strain hardening was not observed. The "almost atactic" PP synthesised by Rishina *et al.* using $Ti(O^iPr)_4$ has M_w up to 98 kDa and exhibits an ultimate tensile strength of 2.3 MPa, and a strain at break of 550%; in this case, a yield point was not observed, with stress increasing nonlinearly to a limiting value.[71]

Elastic hysteresis curves were obtained by stress-relaxation from 120% strain (Fig. 3c) according to the ASTM D638 protocol used by Rieger *et al.*[20] Excellent elastic recovery is observed with a set value of 7–8%. This is much less than for lower molecular weight aPPs, which suffer from large set values resulting from irreversible deformation typical of low crystallinity thermoplastic polyolefins. Behaviour is comparable to that reported by Rieger *et al.*, who further noted the comparable performance with commercial thermoplastic elastomers such as the Kraton™ styrene–butadiene-styrene block copolymer.[20]

Ethylene–propylene copolymer rubbers are the most closely-related widely-studied materials, with the metallocene-catalysed materials produced by Faingol'd *et al.* having tensile strengths of 2.4–15.2 MPa and elongations at break up to 840% – slightly stronger but substantially less ductile than UHMWaPP.[72] Unlike UHMWaPP, these polymers have a degree of crystallinity and exhibit mechanical strain hardening.

The elastomeric mechanical properties of UHMWaPP are postulated to be, at least in part, due to physical crosslinking made possible by the ultra-high molecular weights, which limits irreversible deformation by reducing chain mobility.[73–75]

These data compare favourably with commercial thermoplastic elastomers, such as the olefin block copolymers from Dow (*e.g.* INFUSE™ 9817), with a density of 877 kg m^{-3}, a Youngs modulus of 2.31 MPa, an ultimate tensile strength of 7.00 MPa, an elongation at break of 1700%, and a compression set of 15%,[76] or the olefinic thermoplastic elastomers from DuPont (*e.g.* MULTIFLEX™ TPO 50 D 41 81171) with a density of 890 kg m^{-3}, and an elongation at break of 650%.[77] By comparison the UHMWaPP reported in this work shows a stiffness of 2.05 MPa, elongation of >1900%, and a tension set of 7%. The initial mechanical properties of this UHMWaPP show highly promising results, suggesting that they may have to ability to encroach on the properties of more conventional materials. Such polymers, in particular UHMWaPP, warrant further study to determine commercial applicability.

Conclusions

Selective synthesis of UHMWaPP by an industrially viable high-yielding process has been described.

ansa-Permethylindenyl-phenoxy (PHENI*) complexes have proven to be highly active catalysts for the polymerisation of propylene in both solution-phase and when supported on solid polymethylaluminoxane (sMAO). We observe activities up to 12 000 kg_{PP} mol_{Ti}^{-1} h^{-1} bar^{-1} at 2 bar propylene pressure, and this appears to be limited principally by reaction conditions. Furthermore, the product is a fully amorphous ultra-high molecular weight atactic polypropylene (UHMWaPP). Molecular weights were measured up to 2.0 MDa by GPC, among the highest values reported in the literature.

UHMWaPP demonstrates mechanical behaviour that is broadly comparable to EPM and other commercial thermoplastic elastomers, including remarkable ductility with a strain at break of >1900%, and a low elastic set of 7% in elastic recovery hysteresis experiments.

This work demonstrates the potential of PHENI* catalysts to synthesise efficiently homopolymeric UHMWaPP under mild conditions. The material properties of UHWMaPP are potentially competitive with commercial composite and copolymeric thermoplastic elastomers, with advantages in processability and recyclability, while offering optical transparency, comparable strength, and high ductility.

Data availability

Experimental details, polymerisation data and polymerisation characterisation data has been provided in the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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