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## Switchable Living Nickel(II) $\alpha$ -Diimine Catalyst for Ethylene Polymerisation<sup>†</sup>

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**Design and synthesis of a Ni(II) “sandwich”  $\alpha$ -diimine complex (1) resulted in a switchable catalyst for the living polymerisation of ethylene over a range of temperatures and pressures. Varying these conditions produced a well-defined tetrablock copolymer comprising branched and highly linear polyethylenes. This copolymer improved the toughness of a phase separated LDPE/HDPE blend by nonreactive interfacial compatibilisation.**

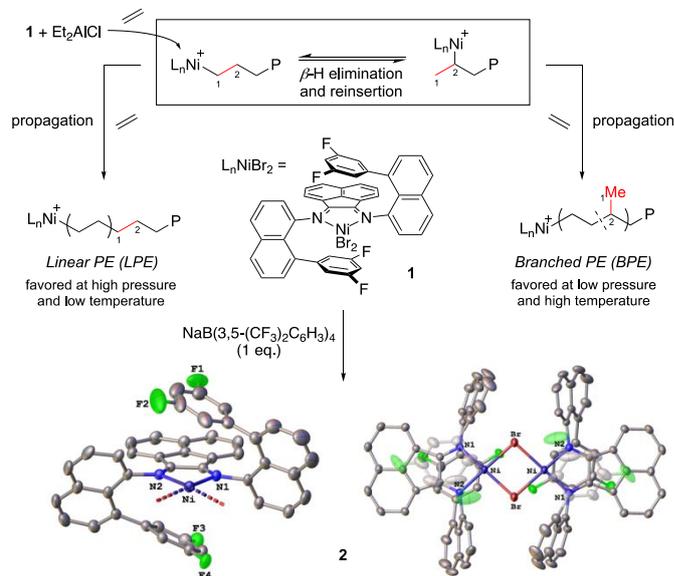
Polyethylene (PE) is the most abundant plastic worldwide, with more than 70 million tonnes produced annually.<sup>1</sup> Its versatile microstructure affords a range of physical properties, explaining the wide variety of PE applications. For example, high-density polyethylene (HDPE) contains few or no branches, making it a hard semicrystalline material with a melting temperature ( $T_m$ ) of 135 °C. With higher branching content, low-density polyethylene (LDPE) is a softer and more flexible material, with  $T_m$  values typically between 105–115 °C. PE is commonly used in the packaging sector: HDPE as containers and LDPE as lids and film wraps.

Although these lightweight materials have eased mass transport of goods, they are mostly single-use products, which contribute to plastic pollution. Moreover, separating HDPE and LDPE in recycling streams is challenging, and solid-state blend products suffer from reduced tensile performance.<sup>2</sup> Although these plastics are synthesized from the same monomer, differences in architecture lead to macrophase separated mixtures,<sup>3,4</sup> compromising their mechanical integrity. These factors contribute to low global recycling rates of plastic packaging materials.<sup>5</sup>

Our group has recently shown that well-defined olefin multiblock copolymers (BCPs) facilitate physical compatibilisation of phase separated PE and isotactic

polypropylene (*i*PP) blends.<sup>6,7</sup> In order to enhance the tensile properties of the otherwise brittle segregated PE/*i*PP polymer blend, BCPs were synthesized with precise control of block microstructure and molecular weight. We envisioned using a similar strategy for HDPE/LDPE compatibilisation.

There are several methods to synthesize HDPE-*b*-LDPE BCPs. Chain shuttling polymerisation produces olefin BCPs with alternating semicrystalline and amorphous segments.<sup>8</sup> However, precise control over block length and microstructure is not possible due to stochastic chain shuttling processes. A second strategy is the controlled copolymerisation of ethylene and higher  $\alpha$ -olefins. Well-defined BCPs can be achieved



**Scheme 1** Chain-walking mechanism of Ni(II)  $\alpha$ -diimine catalysed ethylene polymerisation and X-ray crystal structure of the dicationic complex **2**. Counterions, solvent, and hydrogen atoms have been omitted for clarity. Displacement ellipsoids shown at 50% probability. (left) View of half of the dimer (Br atoms omitted for clarity). (right) Top view of the dimer (ligand fluoroarenes faded for clarity).

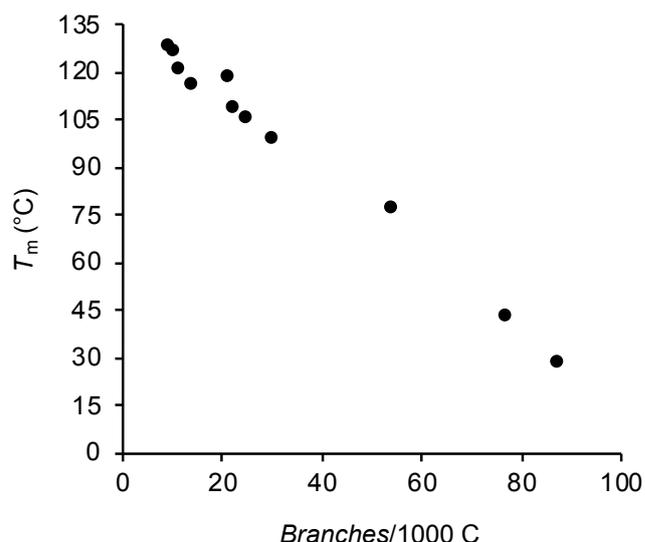
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through sequential monomer addition, but tapering of the microstructure between each consecutive block can occur.<sup>9–13</sup> These methods have been used to make polyolefin thermoplastic elastomers in one-pot polymerisations, but there are few reports of olefin compatibilisation additives.<sup>14–16</sup>

In this work, we developed a switchable Ni(II) sandwich  $\alpha$ -diimine catalyst (**1**) for the living homopolymerisation of ethylene to give both linear and highly branched polymers (Scheme 1). Attempts to obtain quality single crystals of **1** for X-ray analysis were unsuccessful. Instead, complex **2** (Scheme 1) was synthesized as a structural analogue of the active catalyst **1** and its structure was confirmed by single crystal X-ray diffraction. Screening complex **1** against other reported Brookhart-Daugulis-type systems<sup>17–19</sup> confirmed its high activity and ability to sustain living behaviour over a wide range of reaction conditions (Table 1 and Supporting Information, Table S6). The living nature of the **1**-mediated ethylene polymerisation permits precise control over block architecture and number average molecular weight ( $M_n$ ). A stimuli-responsive mechanism allows triggered synthesis of linear-enriched polyethylenes (LPEs) and branched polyethylenes (BPEs).

This class of Ni catalysts is uniquely able to install branches in the absence of a comonomer through chain-walking.<sup>9,20–22</sup> The propagating complex undergoes multiple events where  $\beta$ -hydride elimination is followed by reinsertion with the opposite regiochemistry (Scheme 1). Migration of the catalyst from position 1 to position 2 and further monomer enchainment produces a *methyl* branch; long chain branches are almost entirely absent in our system as determined by <sup>1</sup>H NMR spectroscopic analysis (see Supporting Information, Figure S14).

Changes in reaction conditions control chain-walking with catalyst **1** to produce either LPE or BPE. As with other Ni(II)  $\alpha$ -diimine systems,<sup>23–29</sup> branching decreases with an increase in ethylene pressure as well as a decrease in reaction temperature (Table 1). Changes in branching content produce polyethylenes with a range of melting temperatures (Figure 1). We observed that polymer  $T_m$  decreases linearly with increasing number of



**Figure 1** Polymer  $T_m$  as a function of *methyl* branch content per 1000 backbone carbons.

branches. At 6 atm and  $-35$  °C, highly linear PE is produced (Table 1, entry 4,  $T_m = 128$  °C). In contrast, at 1 atm and  $20$  °C, highly branched, amorphous polymer (112 B/1000 C) with no  $T_m$  is produced (Table 1, entry 9). Therefore, we can access PE materials with diverse branching content using solely ethylene and a single catalyst.<sup>30</sup>

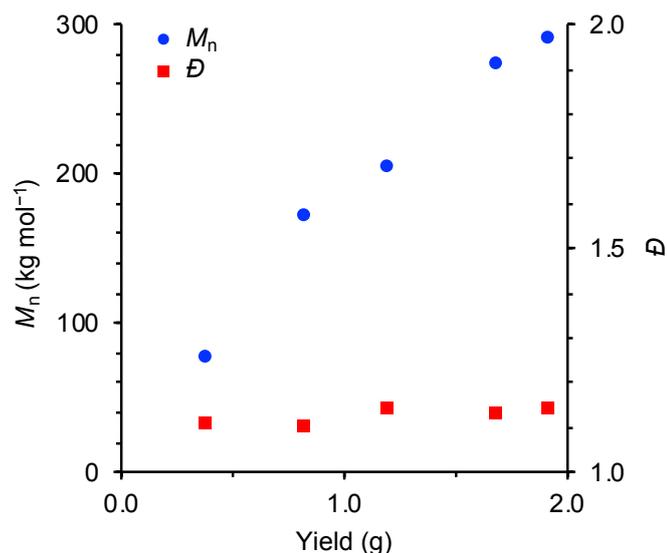
We next sought to demonstrate control over the switchable system in order to synthesize olefin BCPs in a single pot reaction. Activation of **1** with  $\text{Et}_2\text{AlCl}$  promotes the living polymerisation of ethylene;<sup>31</sup>  $M_n$  increases linearly with conversion, and dispersity ( $\mathcal{D}$ ) remains low (Figure 2). Living polymerisation behaviour is sustained over the working temperature range of  $-35$ – $20$  °C and the pressure range of 1–6 atm (Table 1). This controlled polymerisation enabled the synthesis of BCPs with distinct LPE and BPE blocks of tuneable size.

Alternating reaction conditions to moderate branching

**Table 1** Ethylene polymerisation using **1**: Effect of reaction temperature and ethylene pressure.<sup>a</sup>

Entry	$P$ (atm)	$T_{\text{rxn}}$ (°C)	Yield (g)	$M_n^{\text{theo.}}$ (kg mol <sup>-1</sup> ) <sup>b</sup>	$M_n$ (kg mol <sup>-1</sup> ) <sup>c</sup>	$\mathcal{D}$ <sup>c</sup>	$T_m$ (°C) <sup>d</sup>	$\Delta H$ (J g <sup>-1</sup> ) <sup>d</sup>	B/1000 C <sup>e</sup>
1	6	20	1.31	262	343	1.07	43	6	77
2	6	0	0.81	162	208	1.17	109	78	22
3	6	$-20$	0.30	60	68	1.22	121	112	11
4	6	$-35$	0.05	10	14	1.20	128	196	9
5	3	20	0.82	164	171	1.09	29	4	87
6	3	0	0.85	170	174	1.11	99	40	30
7	3	$-20$	0.24	48	62	1.24	116	101	14
8 <sup>f</sup>	3	$-35$	0.03	6	6	1.27	127	191	10
9	1	20	0.28	56	59	1.08	– <sup>g</sup>	– <sup>g</sup>	112
10	1	0	0.38	76	81	1.10	77	46	54
11	1	$-20$	0.18	36	47	1.23	106	80	25
12 <sup>f</sup>	1	$-35$	0.02	4	4	1.23	119	154	21

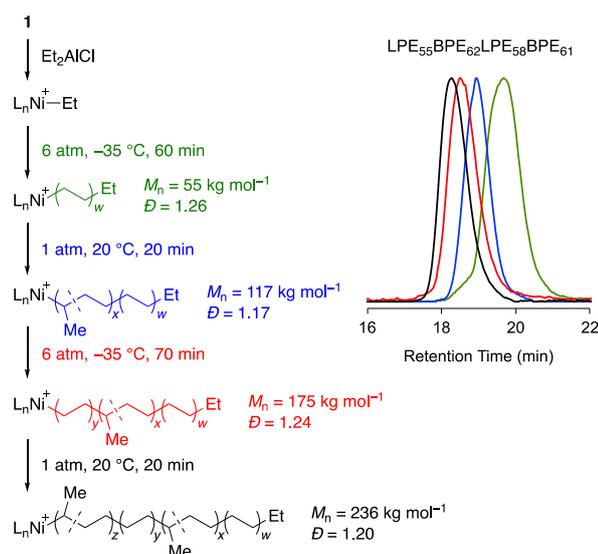
<sup>a</sup>Polymerisation conditions: **1** (5  $\mu\text{mol}$ ),  $\text{Et}_2\text{AlCl}$  (1.5 mmol), 100 mL toluene,  $t_{\text{rxn}} = 10$  min. <sup>b</sup>Theoretical molar mass = mass of polyethylene/mol Ni. <sup>c</sup>Determined using gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at  $150$  °C relative to polyethylene standards. <sup>d</sup>Melting point ( $T_m$ ) and heat of fusion ( $\Delta H$ ) determined using differential scanning calorimetry (DSC), melting endotherm of second heat. <sup>e</sup>*Methyl* branches per 1000 backbone carbons determined using <sup>1</sup>H NMR spectroscopy. <sup>f</sup>**1** (20  $\mu\text{mol}$ ). <sup>g</sup>No  $T_m$  observed.



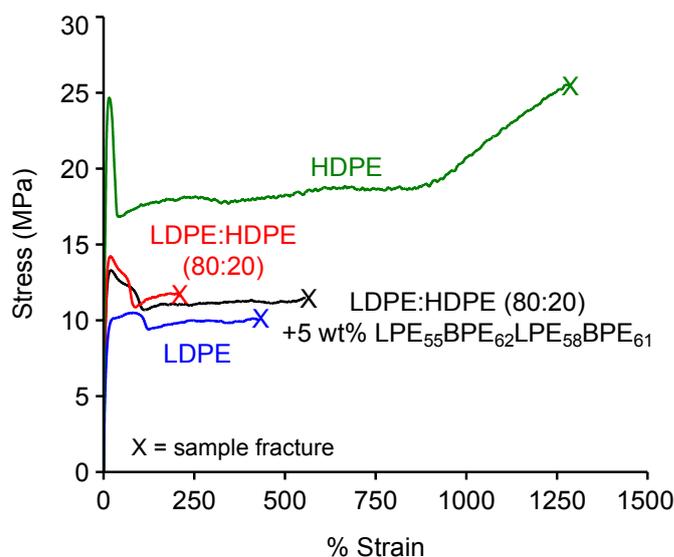
**Figure 2** Plot of  $M_n$  and  $D$  vs. yield for the polymerisation of ethylene by **1**/ $\text{Et}_2\text{AlCl}$  ( $20\text{ }^\circ\text{C}$ , 3 atm  $\text{C}_2\text{H}_4$ ).

content produced a LPE-*b*-BPE tetrablock copolymer (Figure 3). Starting at  $-35\text{ }^\circ\text{C}$  and 6 atm, a first LPE block was made with a  $T_m$  of  $130\text{ }^\circ\text{C}$ . After switching to  $20\text{ }^\circ\text{C}$  and 1 atm, a second amorphous BPE block was made. We noticed that the newly introduced amorphous segment decreased the overall  $T_m$  to  $124\text{ }^\circ\text{C}$ , which persisted following the addition of the third LPE block and the fourth BPE block. DSC analysis of this tetrablock copolymer showed only one melt peak, suggesting that the crystallinity of the LPE fragments was retained (Supporting Information, Figure S15). The final alternating LPE-*b*-BPE BCP consisted of four blocks of  $M_n \approx 60\text{ kg mol}^{-1}$  each and  $D \approx 1.2$ . We denoted this architecture as  $\text{LPE}_{55}\text{BPE}_{62}\text{LPE}_{58}\text{BPE}_{61}$  where the subscript specifies the  $M_n$  ( $\text{kg mol}^{-1}$ ) of each individual PE block.

By testing tensile properties, we evaluated the ability of the tetrablock copolymer to compatibilise an 80:20 LDPE/HDPE



**Figure 3** Synthesis and GPC characterization of LPE-*b*-BPE tetrablock copolymer.



**Figure 4** Representative stress-strain curves of HDPE, LDPE, blend, and compatibilised blend (subscript specifies block  $M_n$  in  $\text{kg mol}^{-1}$ ) strained at a rate of  $100\% \text{ min}^{-1}$ .

blend (normally phase separated at the melt).<sup>3,4</sup> Blends were prepared using a twin screw melt extruder at  $190\text{ }^\circ\text{C}$ , and test specimens for uniaxial tensile testing were made by melt compression using a stainless-steel mold at  $180\text{ }^\circ\text{C}$ . We recorded uniaxial stress-strain curves of commercial HDPE and LDPE as well as segregated and compatibilised 80:20 LDPE/HDPE blends (Figure 4). Without compatibiliser, the blend had poor mechanical integrity compared to its parent homopolymers. Although the blend yielded at slightly higher stress (14 MPa), it failed at 210% strain as opposed to the tougher LDPE, which broke at 426% strain. After addition of just 5 wt% of  $\text{LPE}_{55}\text{BPE}_{62}\text{LPE}_{58}\text{BPE}_{61}$ , the blend showed enhanced tensile properties with an increased strain at break (553%) and similar yield stress (13 MPa) relative to the uncompatibilised mixture. The enhancement of blend mechanical properties by  $\text{LPE}_{55}\text{BPE}_{62}\text{LPE}_{58}\text{BPE}_{61}$  is consistent with improvements achieved by other well-defined BCP compatibilisation additives.<sup>6,32</sup>

## Conclusion

In conclusion, we report a living catalyst system capable of preparing PEs with tuneable branching densities. This method enabled the synthesis of linear and branched multiblock copolymers from a single monomer. Specific temperature and pressure triggers afforded precise control over block length and microstructure. The synthesized tetrablock copolymer enhances the toughness of LDPE/HDPE blends at ratios where they are otherwise phase separated.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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