Calix[4]arene-derived nickel diphosphine complexes for LLDPE synthesis *via* orthogonal tandem and one-pot catalysis

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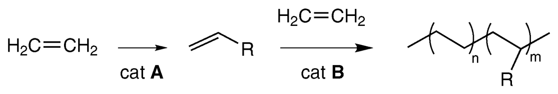
LLDPE with narrow polydispersity was produced from ethylene by orthogonal tandem catalysis using a mixture of *cis*-*P*,*P*′-dibromo{5,17-dibromo-11,23-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene}nickel (1) and $ZrCl_2Cp_2$ (3) in the presence of methylaluminoxane; the polymer produced has only ethyl branches as ramification.

Introduction

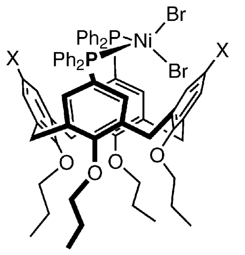
Linear low-density polyethylene (LLDPE) consists of a polyethylene backbone substituted by a significant number of short chain branches which confer to the polymer a higher tensile strength and puncture resistance than low-density polyethylene (LDPE). The presence of ramifications diminishes the melting temperature and the crystallinity of the polymer, making this material less brittle and also easier to process than high-density polyethylene (HDPE).

LLDPE is commonly produced by transition metal-catalysed copolymerisation of ethylene with an α-olefin, for example 1-butene or 1-hexene.[1] LLDPE can also be produced in the presence of two non-interfering catalysts, **A** and **B**, either *via* orthogonal tandem catalysis or according to a one-pot, two-step sequence.[2] In both methods, the catalyst **A** oligomerises ethylene, the oligomers thus produced being then co-polymerised with ethylene by the second catalyst **(B)** (Scheme 1).[3] Catalysts of type **A** include a variety of nickel,[3a,4] cobalt,[5] iron,[6] chromium[7] and metallocene[8] complexes, while a titanium or zirconium complex is usually employed as **B**-type catalyst. The *main drawback* of orthogonal tandem catalysis is that in almost all reported studies the oligomerisation catalyst **A** generates a statistical distribution of 1-alkenes, so that the copolymer produced by **B** contains a variety of branches. In this case, the precise polymer structure cannot be predicted, nor be determined by simple spectroscopic techniques. Thus, there is a lack of tandem catalysts producing well-defined LLDPE.

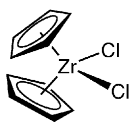


Scheme 1

Recently, we discovered the highly active and selective ethylene[9a] and propene[9b] dimerisation catalysts **1** and **2**, each based on an upper rim-, distally-diphosphinated calix[4]arene.



1 (X = Br); **2** (X = H)



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Both complexes are thermally very robust. Their high activity (TOFs up to 1.2 × 10^6 h^{-1} in ethylene dimerisation) was found to rely on a particular molecular motion, during which the P–Ni–P bite angle periodically increases, reaching its highest value when the metal crosses the calixarene axis (Fig. 1). While the angle between the two P–Ni bonds increases, that between the other two bonds shrinks. Thus, in catalytic intermediates of the type $[Ni(diphos)(alkyl)(ethylene)]^+$, which are likely to adopt a square planar geometry, the alkyl and the ethylene ligands are pushed together, incidentally facilitating the insertion step.

In this study we show that a mixture of **1** and **3** (**3** = $[Cp_2ZrCl_2]$) can, in combination with MAO, efficiently be employed for producing LLDPE either *via* orthogonal tandem catalysis or sequential two-step, one-pot catalysis. The present work provides a rare example of tandem copolymerization in which the copolymer produced contains only ethyl branches. It is noteworthy that to date very few metallocalixarenes have been used in olefin polymerisation.[10]

Results and discussion

For the preparation of LLDPE by orthogonal tandem catalysis, the nickel precatalyst **1** was employed as ethylene

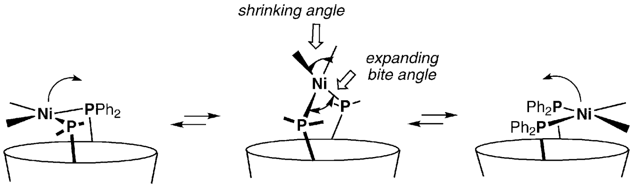

Fig. 1 Molecular fanning motion of $[NiLX_2]$ complexes (L = calix-diphosphine; X_2 = halide$_2$ or Cp).

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Table 1 Orthogonal tandem/one-pot copolymerisation of ethylene and butene[a]

Entry	$P(C_2H_4)$/bar	Ni/Zr	*m*(polymer)/g	Ethyl branches[b] (%)	M_w[c]/g mol^{-1}	PDI[c]	T_m[d]/°C	X_c[e] (%)
1[f]	10	0	1.271	0.0	348 000	2.7	140.4	58.9
2	10	2	1.065	Trace	307 400	2.9	139.1	61.0
3	10	20	0.330	0.4	346 700	2.1	131.8	48.4
4	10	50	0.237	0.6	265 000	2.0	131.3	39.5
5	10	100	0.138	1.0	212 800	2.0	128.0	39.6
6[g]	10	20	0.442	Trace	305 300	2.1	138.7	56.5
7	20	2	1.126	Trace	224 000	3.0	138.3	64.8
8	20	20	0.490	Trace	323 400	2.0	132.4	45.2
9	20	50	0.402	0.5	316 600	2.0	131.6	45.2
10	20	100	0.252	0.9	285 800	2.0	128.4	43.7
11[h]		4.5	0.616	2.7	139 400	6.1	120.1	48.8

[a] **1** 0.0060 g (4.5 μmol), toluene 22 cm^3, MAO 400 equiv./M, T_{inital} = 20 °C, 30 min. [b] Determined by ^{13}C NMR.[12] [c] Determined by HT SEC at 150 °C in 1,2,4-trichlorobenzene. [d] Crystalline melting temperature determined by DSC. [e] Crystallinity determined from X_c (%) = $(\Delta H_m/\Delta H_m^*) \times 100$ (ΔH_m^* = 293 J g^{-1} for HDPE). [f] Amount of complex **3**: 0.0003 g (0.112 μmol). [g] MAO 570 equiv./M. [h] One-pot catalysis with a two-step sequence: (i) **1** (0.0060 g, 4.5 μmol), toluene (22 cm^3), $P(C_2H_4)$ = 30 bar, MAO 400 equiv./Ni, T_{inital} = 20 °C, 1 h; (ii) **3** (0.0003 g, 1 μmol), toluene (6.3 cm^3), $P(C_2H_4)$ = 1 bar, MAO 1000 equiv./Zr, *T* = 40 °C, 22 h.

dimerisation catalyst (catalyst **A** in Scheme 1). It was associated with the zirconocene complex **3**, operating as copolymerisation catalyst (catalyst **B**). Both complexes were activated with methylaluminoxane (MAO). During catalysis, the temperature inside the autoclave was regulated and kept around 19–23 °C to prevent isomerisation of 1-butene into the less reactive 2-butenes.

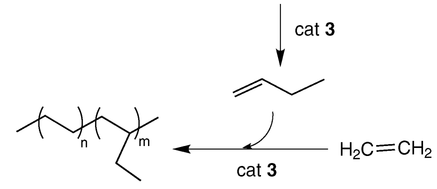
Two series of experiments were carried out, namely at ethylene pressures of 10 and 20 bar, respectively (Table 1, entries 2–6 and 7–10). Within each series the Ni/Zr ratio was varied from 2 to 100, the amount of Ni being the same in each run. The incorporation of 1-butene was found to increase with increasing Ni/Zr ratio, higher Ni/Zr ratios incidentally leading to higher butene/Zr ratios. The physical properties of the copolymers varied similarly within each series when changing the Ni/Zr ratio. Thus for example, by decreasing the relative amount of Zr, the melting point of the polymeric material decreased. Note that in the sole presence of the zirconocene complex (Table 1, entry 1) linear polyethylene was produced, the latter being characterized by a high melting point (140.4 °C) and a high degree of crystallinity (58.9%). As shown by ^{13}C NMR, there was no indication for the presence of branches in this particular case.

The major difference between the tests run at 10 and 20 bar concerns the molecular weights of the polymers, which were higher in the second case. Moreover, the observed activities were higher in the 20 bar series, hence reflecting the higher ethylene concentration under these conditions. The lower proportion of branches in the second series was deduced from the ^{13}C NMR spectra as well as from qualitative IR experiments (presence of CH_3 symmetrical bending bands at 1377 and at 770 cm^{-1} for CH_2 rocking vibrations of ethyl side branches). These findings were further confirmed by the physical properties of the copolymers, which showed higher melting temperatures and percentages of crystallinity (Table 1).

As stated above, whatever the pressure, the incorporation of 1-butene increased with an increasing Ni/Zr ratio. Ni/Zr ratios ≥ 20 led to polymers with a significantly lower melting temperature (T_m) and lower degree of crystallinity (Table 1, compare entries 2 and 5: Ni/Zr = 2, T_m = 139.1 °C, traces of ethyl branches *vs.* Ni/Zr = 100, T_m = 128.0 °C, 1.0% ethyl branches). Higher Ni/Zr ratios logically led to higher 1-butene concentrations inside the reactor during the copolymerisation, and therefore favoured coupling of butene with the growing polymer chain. In keeping with other studies, the increased butene/Zr ratio resulted in polymers with lower molecular weight as well as lower polydispersity (Table 1, entry 2 and 5: Ni/Zr = 2, M_w = 307 400 g mol^{-1}, PDI = 2.9 *vs.* Ni/Zr = 100, M_w = 212 800 g mol^{-1}, PDI = 2.0).[11]

We further noted that as the amount of MAO increased, the insertion of 1-butene *vs.* ethylene decreased leading to a lower branched copolymer (Table 1, entries 3 and 6: MAO 400 eq., 0.4% ethyl branches *vs.* MAO 570 eq., traces of ethyl branches), but we have no rational explanation for this phenomenon.

As shown by a previous study, ethylene dimerisation with complex **1**/MAO carried out under temperature non-controlled conditions leads to high amounts of 2-butenes (1-butene/2-butenes = 5/95), the catalyst itself becoming gradually inactive.[9a] We found that addition after 1 h reaction time of $ZrCl_2Cp_2$/ethylene to such a reaction mixture (Ni/Zr = 4.5), again led to LLDPE. The copolymerisation of ethylene/*trans*-2-butene has already been reported and is known to occur *via* a Zr-catalysed isomerisation of *trans*-2-butene into 1-butene, which, once formed, is incorporated in the growing polymer chain (Scheme 2).[13] The copolymer obtained under these "one-pot–two steps" conditions (Table 1, entry 11) had a lower molecular weight (139 400 g mol^{-1}) and displayed a lower melting temperature (120.1 °C) than the copolymers



Scheme 2 Formation of LLDPE under "one pot–two steps" catalysis (reaction temperature of step 1 not being regulated).

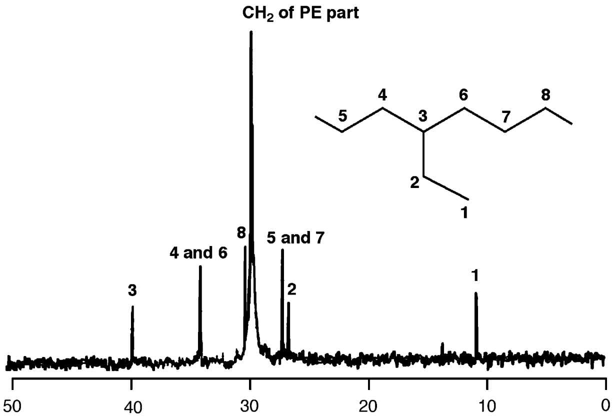


Fig. 2 ^{13}C NMR spectra of the copolymer containing 2.7% of ethyl branches produced by the one-pot **1**/**3**/MAO system (Table 1, entry 11).

obtained in the above tandem reactions. Analysis of the polymer revealed that these experiments led to 2.7% of butene incorporation (Fig. 2), no methyl side branches being detected. Thus, in view to the fact that in this sequence of reactions the Ni/Zr ratio was only 4.5 (*vs.*, *e.g.*, 100 in the tandem experiment 5 which led to 1% of ethyl branches) it is possible to conveniently produce LLDPE with a higher degree of branching without increasing the amount of Ni.

In this study, well defined LLDPE with narrow polydispersity was obtained by orthogonal tandem and one-pot, two-step catalysis. The high control of the polymers microstructure having only ethyl branches as ramification (up to 2.7%), relies on the ability of the diphosphinated calix[4]arene complex **1** to produce selectively 1-butene or *trans*-2-butene, depending upon the reaction conditions. The amount of butene incorporated can be controlled by simple variation of the Ni/Zr ratio or by changing the time at which the second catalyst was added.

Experimental

Materials

All reactions involving air- and moisture-sensitive materials were performed in Schlenk flasks under dry nitrogen. Toluene was distilled over Na under dry nitrogen. *cis*-*P*,*P*′-Dibromo{5,17-dibromo-11,23-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix[4]arene}nickel (**1**) was prepared according to a previously published method.[9a] Cp_2ZrCl_2 from Aldrich and ethylene (N35) from Air Liquide were used as received. MAO 10 wt% (Aldrich) was used as a white powder which was obtained from a commercial toluene solution after evaporation of the solvent under vacuum (60 °C, 3 h). This treatment reduces the amount of residual trimethylaluminium to about 3%.

Procedure for forming LLDPE by orthogonal tandem catalysis

The catalytic runs were carried out in a 100 cm^3 glass-lined stainless steel autoclave containing a magnetic stirring bar. In a typical run, solutions of complex **1** (0.006 g, 4.5 μmol) and complex **3** (the **3**/**1** ratio varied in the range 2–100) in toluene solution were introduced under nitrogen into the autoclave whereupon a solution of MAO (400 equiv./M) in toluene (5 cm^3) was added. The total volume of toluene was completed to 22 cm^3. After stirring for *ca.* 1 min, the autoclave was pressurised with ethylene and the pressure (10 or 20 bar) was maintained at a constant value. During the runs described in this work, the temperature was kept between 19 and 23 °C. After 30 min, the autoclave was cooled to 7 °C and then depressurised. The polymer was precipitated with 400 cm^3 of acidic methanol. It was washed several times with methanol and dried in vacuum until a constant weight.

Formation of LLDPE according to a "one pot–two steps" procedure

The catalytic runs were carried out in a 100 cm^3 glass-lined stainless steel autoclave containing a magnetic stirring bar. A solution of complex **1** (0.006 g, 4.5 μmol) in toluene (19 cm^3) was introduced under nitrogen into the autoclave whereupon a solution of MAO (0.090 g, 400 equiv./Ni) in toluene (3 cm^3) was added. After stirring for *ca.* 1 min, the autoclave was pressurised with 30 bar of ethylene and the pressure was maintained at a constant value. During the dimerisation, the temperature raised from 20 to 43 °C. After 1 h, the autoclave was cooled to 8 °C and then depressurised to 1 bar over a period of 30 min. Solutions of complex **3** (0.0003 g, 1 μmol) and MAO (0.050 g, 1000 equiv./Zr) were added, and volume of toluene was completed to 30 cm^3. The autoclave was heated at 40 °C and pressurised with 1 bar of ethylene. The pressure was maintained at a constant value during 22 h. At the end of the reaction, the autoclave was cooled to 6 °C, and the polymer was precipitated with 400 cm^3 of acidic methanol. It was washed several times with methanol and dried in vacuum until a constant weight.

Polymer characterisation

^{13}C NMR spectra of polyethylene were recorded on a Bruker Avance 400 MHz instrument (100.6 MHz) at 140 °C. Polymer samples of 0.050–0.100 g were dissolved in 1,1,2,2-tetrachlorethane-d_2/1,2,4-trichlorobenzene (v/v 1:9) in 5 mm NMR tubes; pulse 30°, pulse delay 5 s, acquisition time 0.65 s, 15000 scans. High-temperature size exclusion chromatography (HT SEC) measurements were performed at 150 °C with a "PL220" apparatus (Column set HT-MixedB-TCB01) in 1,2,4-trichlorobenzene (with 0.2% Irganox). Calibration was made with linear PS samples. Differential scanning calorimetric (DSC) analysis was performed on a Perkin Elmer DSC7 calorimeter equipped with a CCA7 for temperature control. The scanning rate was 10 °C min^{-1} and the temperature range investigated was -120 to $+180$ °C. The instrument was calibrated using indium (mp 156.60 °C) standard. Fourier transform infrared spectroscopy was performed on a Bruker Vertex 70. Samples for FTIR were measured as powders using an optical microscopic autoimage system AT-IR attachment.

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