

Tandem Copolymerization: An Effective Control of the Level of Branching and Molecular Weight Distribution

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Summary: The term “tandem catalysis” addresses the action of two or more different catalysts in a single reactor to yield a product that is otherwise inaccessible to the individual catalysts. Its application to the production of branched polyethylene from ethylene feedstock as well as of homopolymers or copolymers with controlled molecular weight distribution is a relatively recent and successful technique. A great variety of combinations of late and early metal precursors, in different experimental conditions, have been successfully employed in tandem processes to prepare polyolefins with improved properties and performance parameters. In this article, we report on two examples of tandem catalysis, where either cooperative or independent actions take place.

Keywords: EP copolymers; LLDPE; metallocene catalysts; MWD; Polyolefins

Introduction

A great deal of research has been recently focused on the development of homogeneous multi-catalyst systems aimed at producing in a single reactor different homopolymers or copolymers or even copolymers of ethylene exclusively from ethylene feedstock.^[1] This technique, also known as tandem catalysis, is expected to become increasingly important for the production of new materials, especially copolymers with tailored microstructure and rheology.^[1,2] Indeed, it is now apparent that the combination of two or more catalysts in the same reactor allows one to produce macromolecular materials with properties that each

single catalyst is unable to achieve. There are two ways of designing a multi-catalyst system:

1. Each catalyst in the mixture works independently of the partner(s), and the homopolymers or copolymers (if the feed contains two different monomers) produced differ from each other only for the molecular weight distribution (MWD) (type 1);
2. One catalyst produces α -olefins (if two oligomerization catalysts are employed, α -olefins with different Schulz-Flory distributions are generally obtained), while the second (or third) catalyst copolymerizes the generated α -olefins with the monomer. This method is denoted as *Concurrent Tandem Catalysis* (type 2).

While the use of a type 1 system allows to control the molecular weight and the MWD of homopolymers by an *in situ* blending of two or more polymers^[1b,3], the use of a type 2 system provides an effective control on the level and nature of branching in a single polymer.^[2,4] As a

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result, properties such as density, rigidity, permeability and environmental stress-crack resistance can be varied systematically.

This work is aimed at highlighting the great potential of metallocene catalysts, alone or in conjunction with late transition metal catalysts, to produce polyolefins featured with tailored MWD, level of branching and topology, by simply varying the components of the multi-catalyst system. To this purpose we have selected the following catalyst combinations: *rac*-[Me₂Si(2-Me-4-(1-Naph)Ind)₂]ZrCl₂ (**1**)/[Me₂Si-(Ind)(Flu)]ZrCl₂ (**2**)/MAO and [η⁵-C₅Me₄]SiMe₂(^tBuN)]TiCl₂ (**3**)/(organyl)-2-(imine)pyridyl)CoCl₂/MAO (organyl = phenyl (**4**), ethylthiophenyl (**5**), benzo[*b*]thiophenyl (**6**)) (Scheme 1).^[4]

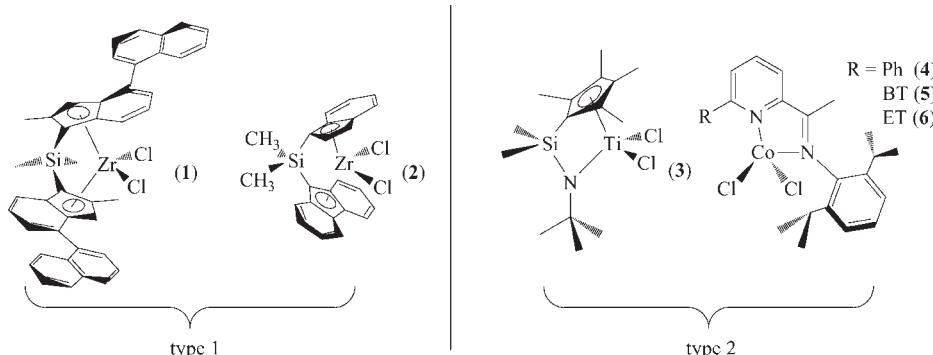
In the case of system **1**, ethylene-propylene copolymers were investigated using a 1:5 mixture of **1** and **2**. Independent reactions with the separate catalysts were also carried out for comparative purposes. Also, the activity and the reaction rate of the two single-site catalysts were employed to model the NMR data for the materials obtained with the dual-catalyst system as well as to interpret the DSC and SEC data.^[5]

In the case of early/late dual-catalyst system, the constrained geometry catalyst (CGC) (**3**) was used in conjunction with the oligomerization cobalt(II) catalysts **4**, **5** or **6**.

Experimental Part

Materials

All operations were performed under a dry Argon atmosphere using standard Schlenk glassware. Argon (Linde) was deoxygenated and dried with an oxisorb cartridge from Messer Griesheim prior to use. Ethylene (Messer Griesheim) and propylene (Linde) was deoxygenated and dried through two columns containing the BASF catalyst R3-11 and activated molecular sieves (4 Å), respectively, prior to use. Toluene (Merck) was dried over KOH overnight, filtered, degassed under vacuum, and purified under argon through two columns filled with the BASF catalyst R3-11 and activated molecular sieves (4 Å), respectively, prior to use. The catalytic precursor *rac*-[Me₂Si(2-Me-4-(1-Naph)Ind)₂]ZrCl₂ (**1**) was purchased from Boulder Scientific Inc. and [Me₂Si-(Ind)(Flu)]ZrCl₂ (**2**) and [η⁵-C₅Me₄]SiMe₂(^tBuN)]TiCl₂ (**3**) from MCAT GmbH. The complexes (phenyl)-2-(imine)pyridyl-CoCl₂ (**4**), (benzo[*b*]thiophenyl)-2-(imine)pyridyl)CoCl₂ (**5**) and (ethylthiophenyl)-2-(imine)pyridyl)CoCl₂ (**6**) were synthesized according to a published procedure. The cocatalyst MAO for polymerization was prepared by removing toluene and AlMe₃ from a commercially available MAO toluene solution (10 wt.-% aluminum, Crompton GmbH). The MAO solution



Scheme 1.

Sketches of the catalyst precursors employed in this study: *rac*-[Me₂Si(2-Me-4-(1-Naph)Ind)₂]ZrCl₂ (**1**)/[Me₂Si-(Ind)(Flu)]ZrCl₂ (**2**); [η⁵-C₅Me₄]SiMe₂(^tBuN)]TiCl₂ (**3**)/ (phenyl)-2-(imine)pyridyl)CoCl₂ (**4**) or (benzo[*b*]thiophenyl)-2-(imine)pyridyl)CoCl₂ (**5**) or (ethylthiophenyl)-2-(imine)pyridyl)CoCl₂ (**6**).

was filtered on a D4 funnel and evaporated at 50 °C under vacuum. The resulting white residue was heated further to 50 °C under vacuum overnight. A stock solution of MAO (100 mg·mL⁻¹) was prepared by dissolving solid MAO in toluene. The solution was used within three weeks to avoid self-condensation effects of the MAO.

Polymerizations

All polymerization reactions were performed in a double-walled Büchi AG glass reactor (1 L) equipped with magnetic driven mechanical stirrer and a temperature and pressure controller. The autoclave was dried under vacuum at 95 °C for 1 h and then cooled to room temperature under an argon atmosphere. Polymerizations were carried out at 30 °C. The propylene and ethylene pressure for every run were set, and the pressure was kept constant during the polymerization; ethylene was fed constantly (semibatch process). The monomer concentrations were calculated using literature data. The polymerizations were started by injection of the catalyst precursors in the reaction medium.

Type 1: $\text{rac-}[\text{Me}_2\text{Si}(\text{2-Me-4-(1-Naph)Ind})_2]\text{ZrCl}_2$ / $[\text{Me}_2\text{Si-(Ind)(Flu)}]\text{ZrCl}_2$ /MAO

The reactions were run in 400 mL toluene and 400 mg MAO. The amount of catalyst precursor for the single-site series was 5 × 10⁻⁸ mol (**1**) and 5 × 10⁻⁷ mol (**2**). For the dual-site catalyst reactions, a mixture of **1** and **2** was used with a 1:5 molar ratio and a total catalyst amount of 1.5 × 10⁻⁷ mol. Since the activities ratio of **1** and **2** for ethylene feeds of ca. 50 mol % is 5:1, a 1:5 ratio of the two precursors was used to obtain balanced bimodal copolymers.

After a short polymerization period (propylene conversion < 5%) the reaction was stopped by addition of 1 mL of ethanol. The polymer solution was stirred overnight in an ethanol/HCl/water solution, filtered and washed with plenty of ethanol and

drying of the polymer in vacuum at 60 °C overnight.

Type 2: $[\eta^5\text{-C}_5\text{Me}_4]\text{SiMe}_2(\text{tBuN})\text{TiCl}_2$ / $(\text{organyl})\text{-2-(imine)pyridyl}\text{CoCl}_2$ /MAO (type 2)

The reactions were run in 200 mL toluene with MAO (2 mL, 100 mg·mL⁻¹), and saturated under 3 bar of ethylene. After complete temperature and pressure equilibration, appropriate volumes of toluene stock solutions of the precatalysts (both 2.5 × 10⁻³ M, overall toluene volume 1 mL) were injected into the autoclave in rapid sequence (cobalt always first) to start the concurrent ethylene oligomerization and polymerization processes. The ethylene consumption was measured by a digital Mass Flow (Bronkhorst High-Tech). The catalyst (Ti + Co) concentration was 1.25 × 10⁻⁵ M for all polymerizations. After 1 h the reaction was quenched by injecting ethanol (1 mL). The reaction mixture was poured into a solution (200 mL) prepared by mixing ethanol/HCl/water solution and stirred overnight. When the precipitated polymer was a rigid solid, it was filtered off, washed with water, ethanol, and dried at 60 °C under vacuum to constant weight. When the polymer was a rubbery solid, it was separated along with the toluene phase from the water phase. The solid/liquid mixture was washed with a saturated water solution of NaHCO₃ and water and then evaporated to dryness at 60 °C under vacuum.

Polymer Analysis

¹³C{¹H}-NMR samples of 300–500 mg were prepared by the dissolution of the polymers (10 mass %) in a mixture of 1,2,4-trichlorobenzene and 1,1,2,2-tetrachloro-1,2-dideuteroethane and were measured at 100 °C, pulse angle 30°, delay time 5 s, 1024 scans on a Bruker 400-MHz NMR spectrometer using the waltz16 decoupling method and referenced against C₂D₂Cl₄. The experimental peak characterization in the copolymers was

determined using the Randall method.^[6] The thermal behavior of the polymers was measured using a Mettler-Toledo DSC 821e, in the temperature range from –100 to 200 °C with a heating rate of 20 K·min^{–1}. To determine the melting temperatures, the second heating run was used. SEC was carried out with a Waters GPCV 2000 Alliance system equipped with a refractive index detector, viscometric detector, and a set of three columns, Styragel type (HT6, HT5, HT3). 1,2,4-Trichlorobenzene was used as solvent. The analyses were performed at 140 °C and 1.0 mL·min^{–1} flow rate. The system was calibrated with narrow molar mass distribution polystyrene standards and their Mark-Houwink^[7] constants using the universal method. The sample concentration was 1 mg·mL^{–1}, and 2,6-di-*tert*-butyl-4-methylphenol was used as thermostabilizer. The molar masses were calculated using the refractive index signal and literature constants for polyethylene (K) 0.0406 mL·g^{–1}, α 0.725) and corrected for propylene content using the method by Scholte et al.^[8] Thermal gravimetric analyses (TGA) were obtained under nitrogen (60 mL·min^{–1}) with a TGA Mettler Toledo instrument at 10 °C min^{–1} from 50 to 700 °C. Density measurements were performed foll-

owing the ISO 1133 standard procedure in ethanol after hot-melting the samples in a Plastograph.

Result and Discussion

Type 1: rac-[Me₂Si(2-Me-4-(1-Naph)Ind)₂]ZrCl₂/[Me₂Si-(Ind)(Flu)]ZrCl₂/MAO

Figure 1 reports the productivity, expressed as $\text{kg}_{\text{polymer}} \cdot \text{mol}_{\text{Zr}}^{-1} \cdot \text{h}^{-1} \cdot (\text{mol}_{\text{monomer}}/\text{L})^{-1}$, for both homopolymerization and ethylene-propylene copolymerizations in the presence of **1**, **2** and **1+2** as catalyst precursors. The contribution of **2** to the bimodal polymers is also reported. Catalyst **1** was the most active for polyethylene homopolymerization yielding a maximum productivity of about $800 \text{ t}_{\text{polymer}} \cdot \text{mol}_{\text{Zr}}^{-1} \cdot \text{h}^{-1} \cdot (\text{mol}_{\text{monomer}}^{-1}/\text{L})$. Catalyst **2** was much less active than **1** for the copolymerizations carried out with a high ethylene content, but it was as active as **1** for both polypropylene polymerization and ethylene-propylene copolymerization with a high propylene content. In general, the productivities of the dual-site systems were half way between those of the single-site catalysts.

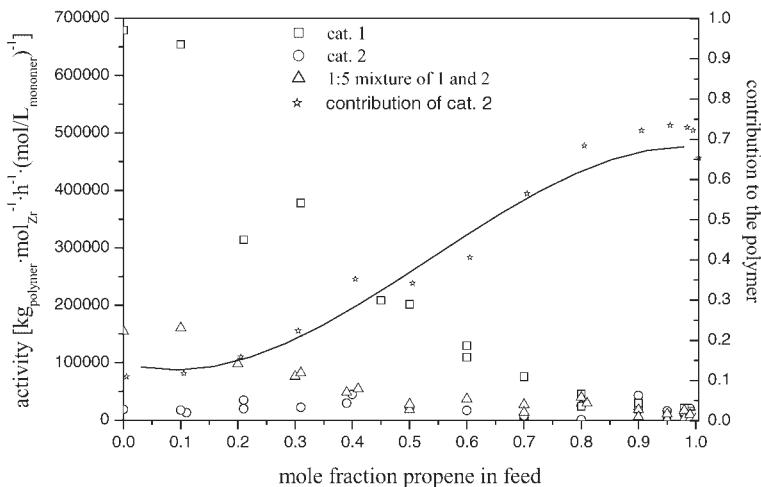


Figure 1.

Productivities of the single- and dual-site copolymerization systems. The contribution of **2** to the bimodal copolymers is also reported.

The contribution of **2** to the dual-site experiments was calculated from the single-site activity using a 1:5 molar ratio of the two catalysts. Due to the non-parallel course of the activities of the two catalysts, the contribution of **2** was not only dependent on the catalysts molar ratio but also on the mole fraction of propylene in the feed. In the feed range from 0 to 60 mol% the activity of **2** was more than 5 times lower than the activity of **1** and therefore the contribution of **2** to the dual-site experiments was smaller than 50%, the opposite occurred in the feed range from 70 to 100 mol%.

The propylene incorporation into the copolymers is reported in Figure 2. At high propylene concentration in the reactor, the difference between the two catalysts was very pronounced: **1** easily incorporated comonomer units while **2** hardly inserted more than 50 mol% of propylene even at very low ethylene-propylene ratios (99% propylene). It is worth mentioning at this stage that in a growing chain, the addition of new monomer and comonomer units is mainly determined by the reactivity ratios of the active site(s) of the catalyst. The present reactivity ratios, previously calculated, are reported in reference^[5]: **1** gave rather random copolymers and **2** alternat-

ing copolymers. The obtained propylene incorporation into the bimodal copolymers was an average value of both fractions.

The GPC results showed bimodal distributions of the products obtained with the dual-site systems. All separable signals had a polydispersity of 2, as expected for metallocene catalysis. No shoulders in the high or low molecular weight areas were observed and the NMR data proved as well that chain transfer reactions between the two active sites of the dual-site series are negligible.

Nevertheless the propylene molar fractions of the bimodal copolymers were average values obtained from the NMR spectra of the polymer mixtures. When these results were plotted against the DSC or GPC data, untypical results for EPMs were observed (see Figure 3). For one fraction, produced by **1**, the propylene rates were too low and for the other fraction they were too high, hence a correction was made by modelling the NMR spectra applying the Markov II statistics.^[5]

The arrows in Figure 3 indicate the expected molecular weights of the two polymer fractions in the bimodal copolymers and, after fitting by modelling, it was shown that the two active sites are actually working independently of each other.

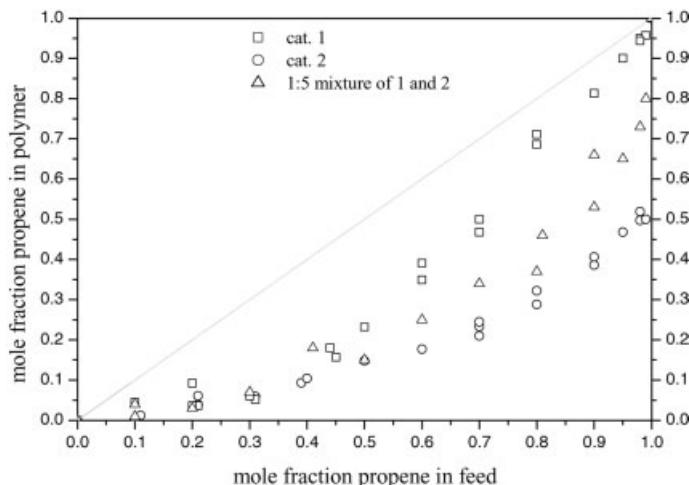
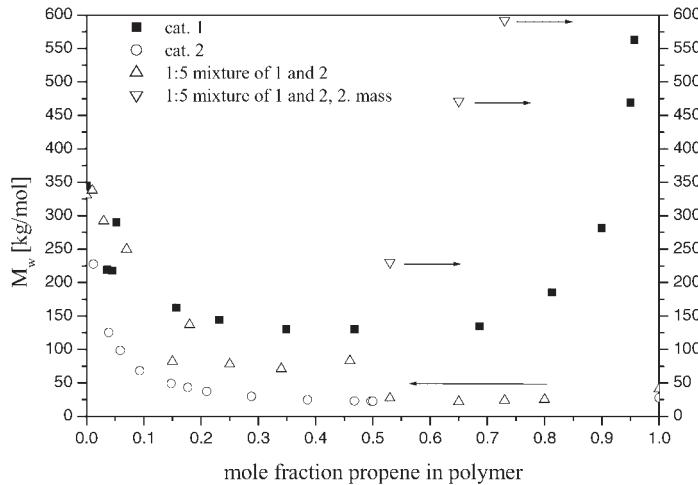


Figure 2.

Propylene incorporation into the monomodal and bimodal copolymers.

**Figure 3.**

Molecular weight of the EPMs from single- and dual-site series.

Type 2: $[\eta^5\text{C}_5\text{Me}_4]\text{SiMe}_2(\text{BuN})\text{TiCl}_2/\text{(organyl)-2-(imine)pyridyl}\text{CoCl}_2/\text{MAO}$

The molar fraction of cobalt (χ_{Co}) was varied from 0 to 1, while the overall metal concentration ($\text{Co} + \text{Ti}$) was fixed at $1.25 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$. Under comparable conditions, the cobalt catalysts were found to be more efficient than the titanium one, yet within the same order of magnitude ($10^5\text{--}10^6$). From the data reported in Table 1, one may readily realize that χ_{Co} is the key factor to control the amount of α -olefins produced^[9–13]. As previously mentioned, the χ_{Co} value greatly influences the material properties (Table 1). Indeed, copolymers prepared at lower χ_{Co} than 0.15 appeared as rigid white solids, while increasing χ_{Co} colorless rubbery materials were obtained. Indeed, both the extent of α -olefin incorporation and the number and type of branches are strictly related to χ_{Co} , as it determines the concentration of α -olefins in the reactor. The relationship between χ_{Co} and the level of branching for the catalyst system **3/6/MAO** is shown in Figure 4.

Increasing χ_{Co} from 0.05 to 0.75 has been found to increase the number of branches from 27 and 254 per 1000 carbon atoms for the system **3/6/MAO**, from 35 to 160 for **3/5/MAO** and from 24 to 119 for **3/4/MAO**,

which is consistent with the specific activity of the three oligomerization catalysts. Noteworthy, the distribution of the branches^[6] in the polymer backbone was in excellent accord with the molar distribution of the α -olefins produced Table 1. For instance, the system **3/4/MAO** produced only ethyl branching reflects the specific selectivity of **3** for butenes^[14]. In the case of the systems **3/5/MAO** and **3/6/MAO**, the distribution of the branches was in accord with the molar distribution of the α -olefins (**3/5/MAO** = ethyl 85 %, butyl 13 %, hexyl 2 %; **3/6/MAO** = ethyl 91 %, butyl 8 %, hexyl 1 %).

The DSC analysis of the copolymers showed that T_m varies from 136.9°C to 47°C for the semicrystalline materials, while T_g varies from -60 to -54°C for the amorphous materials (Figure 5).^[13,15,16]

The polydispersity of all copolymers was close to 2, which indicates that the effect of the cobalt catalyst is exclusively that of producing α -olefins, whereas the branched polyethylene is exclusively obtained by an insertion reaction at the CGC catalyst.

From a perusal of Table 1, one may readily infer that the present tandem systems provide a better control of the macromolecular topology as compared to

Table 1. Ethylene polymerization with the tandem catalytic system **3/4**/MAO, **3/5**/MAO, **3/6**/MAO

	Run ^{a)}	mol (Co)	Mol (Ti)	$\chi_{Co}^{b)}$	Al/Co	Al/Ti	$A^{c)}$	$M_w^{d)}$ (kg · mol $^{-1}$)	$M_w/M_n^{d)}$	$T_m^{e)}$ (°C)	$T_g^{f)}$ (°C)	total br. ^{g)}	C_2 br. ^{g)}	C_4 br. ^{g)}	$\geq C_6$ br. ^{g)}
3/MAO	1	0.00	2.50	0.00	27580	1420	960	570	1.99	136.9	—	0	0	0	0
	2	0.13	2.37	0.05	9190	1620	1090	625	530	1.92	97	24	100	0	0
	3	0.38	2.12	0.15	5520	1840	1250	567	534	1.93	52	56	100	0	0
	4	0.63	1.87	0.25	520	2760	1540	549	1.54	—	—	60.2	57	0	0
	5	1.25	1.25	0.50	1840	5520	1430	452	1.79	—	—	55.2	88	100	0
	6	1.88	0.62	0.75	1840	5520	1430	452	1.85	—	—	52.3	119	100	0
3/5/MAO	7	0.13	2.37	0.05	27580	1450	632	551	2.14	110.6	—	27	83	17	0
	8	0.38	2.12	0.15	9190	1620	1510	458	2.40	104.8	—	74	82	15	3
	9	0.63	1.87	0.25	5520	1840	2650	270	1.92	—	—	60.0	189	85	13
	10	1.25	1.25	0.50	2760	5520	1470	147	2.03	—	—	55.0	249	86	12
	11	1.88	0.62	0.75	1840	5520	4560	172	2.14	—	—	53.7	254	85	13
	12	0.13	2.37	0.05	27580	1620	640	532	1.97	98	—	35	90	10	1
3/6/MAO	13	0.38	2.12	0.15	9190	1840	1010	556	1.78	47	—	62.3	46	91	8
	14	0.63	1.87	0.25	5520	2760	1131	565	1.50	—	—	60.0	101	92	7
	15	1.25	1.25	0.50	2760	5520	1430	374	2.21	—	—	54.3	156	91	8
	16	1.88	0.62	0.75	1840	1450	670	332	2.8	—	—	52.0	161	93	6

^{a)} Reaction conditions: glass-reactor, 1 L (Co + Ti) precatalyst, 2.5 × 10^{−6} mol; MAO cocatalyst, 3.5 × 10^{−3} mol; toluene, 200 mL; polymerization time, 1 h; stirrer rate, 450 rpm; C₂H₄ pressure, 3 bar; temperature, 30 ± 2 °C.

^{b)} $\chi_{Co} = [Co]/([Co] + [Ti])$.

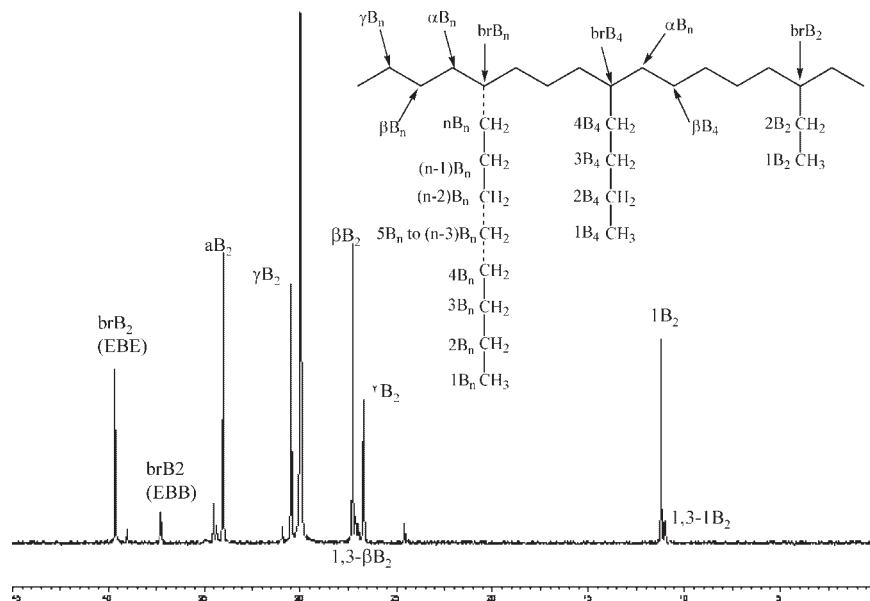
^{c)} Activity expressed as kg polymer (mol Ti × h)^{−1}.

^{d)} Determined by GPC.

^{e)} Determined by DSC.

^{f)} Number of branches per 1000 C atoms calculated from ¹³C{¹H}-NMR.

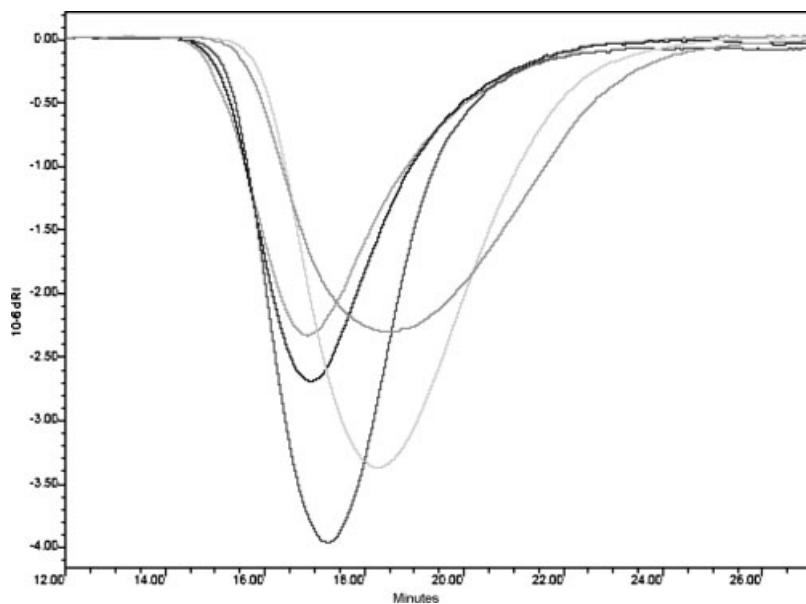
^{g)} α -Olefin incorporation calculated from ¹³C{¹H}-NMR.

**Figure 4.**

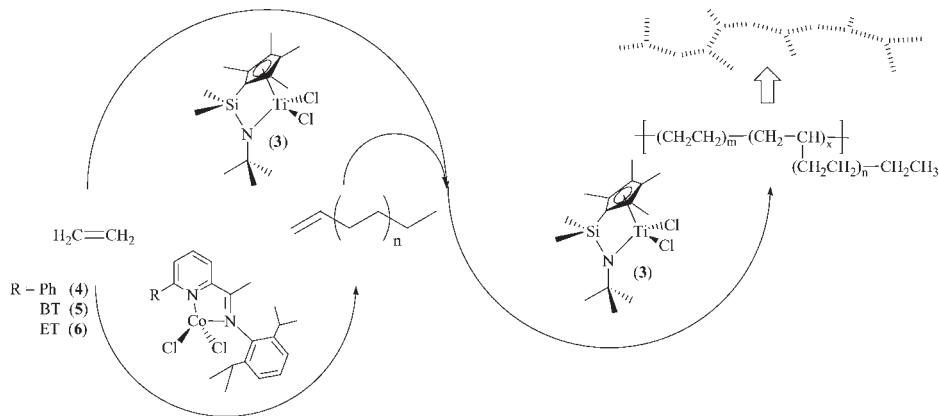
$^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of the polymers produced by the tandem **3/4**/MAO system at $\chi_{\text{Co}} = 0.15$.

the so called “chain walking” catalysts, which generally lead to the production of low density polyethylene with long branching and non-linear structure.^[17,18] Notably,

the polyethylene produced with the **3/5**/MAO catalytic system at $\chi_{\text{Co}} > 0.25$ has been found to have density values as low as 0.860 g cm^{-3} , which are typical of LDPE,

**Figure 5.**

GPC traces of the copolymers obtained with the **3/5**/MAO catalytic system at different χ_{Co} .

**Scheme 2.**

Tandem catalysis scheme with $[\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{(^tBuN)}]\text{TiCl}_2$ (3) in conjunction with (phenyl)-2-(imine)pyridyl-CoCl₂ (4) (benzo[b]thiophenyl)-2-(imine)pyridyl-CoCl₂ (5) or (ethylthiophenyl)-2-(imine)pyridyl-CoCl₂ (6).

and no precedent in tandem catalytic systems^[3].

concluded that binary systems can be a solution for the synthesis of new tailor made materials.

Conclusion

This account shows that by an appropriate choice of the catalysts and experimental conditions, it is now possible to fine tune the characteristics of the resulting polyolefins in a way that is hardly achievable by the use of only one single-site catalysts. Comparing the activities of the two metallocene catalysts used in the type 1 process, a series of single-site experiments in combination with dual-site copolymerizations can be used to calculate the contributions of the two active sites to the bimodal polymers. This provides a reliable method to split the overall propylene content of the bimodal polymers into the fractions produced by each catalyst. In the case of the type 2 tandem catalytic systems, it has been also shown that the combination in the same reactor of a late metal oligomerization catalysts with an early metal copolymerization catalyst allows for the conversion of a single ethylene feedstock into branched polyethylenes, spanning from semicrystalline LLDPE to amorphous, rubbery products, by simply varying the molar fraction of the oligomerization catalyst. It can be

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