ISSN 0023-1584, Kinetics and Catalysis, 2006, Vol. 47, No. 2, pp. 207–212. © MAIK “Nauka/Interperiodica” (Russia), 2006.

# Low Density Polyethylene by Tandem Catalysis with Single Site Ti(IV)/Co(II) Catalysts[1]

**M. Frediani**[a], **C. Bianchini**[b], **and W. Kaminsky**[c]
[a] Department of Organic Chemistry, University of Florence, Polo Scientifico,
via della Lastruccia 13, 50019 Sesto Fiorentino, Italy
[b] ICCOM-CNR, Area della Ricerca CNR di Firenze, via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy
[c] Institute of Technical and Macromolecular Chemistry, University of Hamburg, Bundesstrasse 45, 20146 Hamburg, Germany
e-mail: marco.frediani@unifi.it

Received July 11, 2005

**Abstract**—A variety of branched polyethylenes (PE), ranging from semicrystalline linear low density polyethylene to completely amorphous low density polyethylene and rubbery PE, can be produced from ethylene alone by tandem catalysis using as oligomerization catalysts the (imino)pyridyl Co(II) complexes $N^{BT}CoCl_2$ (**1**) ({6-(benzo[b]thiophen-2-yl)-2-(imine)pyridyl}$CoCl_2$), $N^{ET}CoCl_2$ (**2**) ({6-(4-ethylthiophen-2-yl)-2-(imine)pyridyl}$CoCl_2$), or $N^{Ph}CoCl_2$ (**3**) ({6-(phenyl)-2-(imine)pyridyl}$CoCl_2$) and as a copolymerization catalyst [$\eta^5$-$C_5Me_4$)$SiMe_2$(*t*-BuN)]$TiCl_2$ (**4**). The catalytic activity of the systems **1**/**4**/MAO, **2**/**4**/MAO, and **3**/**4**/MAO has been evaluated under comparable experimental conditions ($T = 30$°C, [ethylene] = 0.35 mol/l), varying the molar fraction of the cobalt precursors. A positive comonomer effect was observed for all the systems investigated. The maximum productivity (4570 kg PE (mol Ti)$^{-1}$ h$^{-1}$) was obtained for the benzothiophenyl-substituted cobalt complex. An effective control of the branching in the polymer backbone was achieved by varying either the oligomerization catalyst or its molar fraction. Completely amorphous materials with $T_g$ as low as –60°C could be obtained.

**DOI:** 10.1134/S002315840602008X

Over the past two decades, research has increasingly been directed towards the development of single-site catalytic systems, as they can produce polyethylenes (PE) with a tailored microstructure [1, 2], especially in terms of branching control. Branching affects many properties of PE, such as density, rigidity, permeability, and environmental stress-crack resistance [3–5].

In addition to radical processes at an elevated temperature and pressure [4], branched PE can be prepared either by the insertion polymerization of ethylene with α-diimine Pd(II) and Ni(II) catalysts [5] or by the copolymerization of ethylene with α-olefins by metallocenes and related catalysts [2, 3–5]. A third, innovative approach to branched PE is provided by the combination in the same reactor of oligomerization and copolymerization catalysts. This method is known as Concurrent Tandem Catalysis (CTC) [6].

In this paper, we describe three new CTC systems for the effective conversion of ethylene into a variety of materials, ranging from linear low density polyethylene (LLDPE) to rubbery PE. These systems comprise the (imino)pyridyl Co(II) oligomerization catalysts $N^{BT}CoCl_2$ (**1**) ({6-(benzo[b]thiophen-2-yl)-2-(imine)pyridyl}$CoCl_2$), $N^{ET}CoCl_2$ (**2**) ({6-(4-ethylthiophen-2-yl)-2-(imine)pyridyl}$CoCl_2$), $N^{Ph}CoCl_2$ (**3**) ({6-(phenyl)-2-(imine)pyridyl}$CoCl_2$) and the constrained geometry copolymerization catalyst [$\eta^5$-$C_5Me_4$)$SiMe_2$(*t*-BuN)]$TiCl_2$ (**4**) (CGC) (Scheme). The latter complex represents a milestone in ethylene homopolymerization [7] and copolymerization with α-olefins [8–10] and has already been employed in successful CTC processes in conjunction with both early and late metal catalysts [11–15]. The cobalt complexes are a recent discovery: upon activation with methyaluminoxane (MAO) they catalyze the oligomerization of ethylene to α-olefins. In the case of **1** and **2**, the reactions give α-olefins with Schulz-Flory distribution (essentially, butenes 82.0%, hexenes 14.8%, and octenes 2.7%) and turnover frequencies (TOF) as high as $10^6$ (mol of $C_2H_4$ (converted) (mol Co)$^{-1}$ h$^{-1}$), while **3** is selective for butene production with a TOF of ca $10^5$ [10].

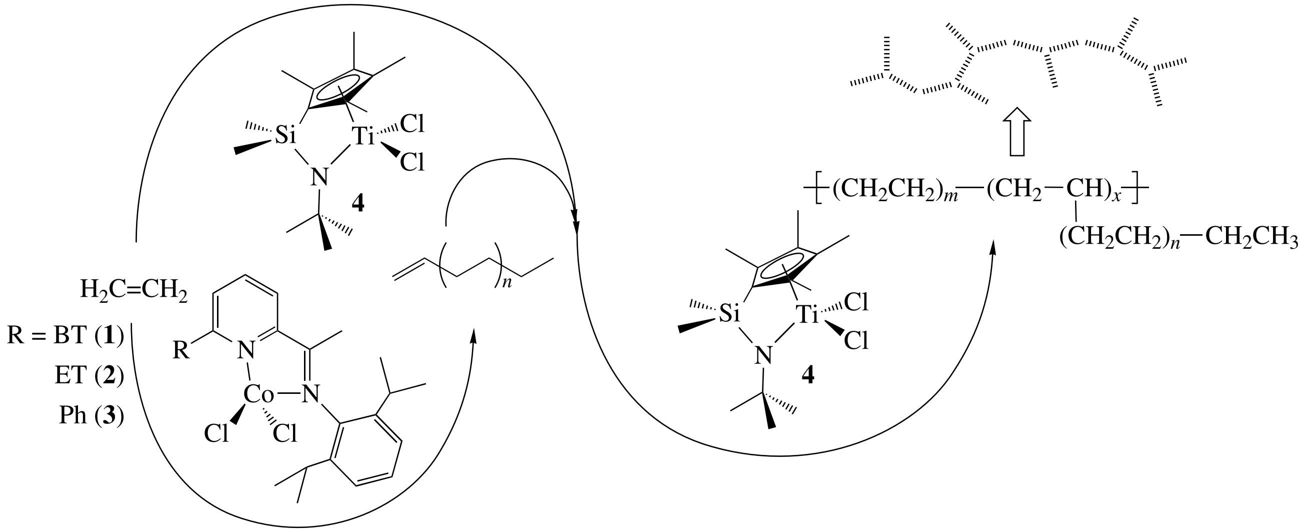
## EXPERIMENTAL

### Materials

Argon (≥99.996% from Linde) was deoxygenated and dried with an oxysorb cartridge from Messer Griesheim prior to use. Ethylene (Messer Greisheim ≥99.95%) was deoxygenated and dried through two

---

[1] The text was submitted by the authors in English.



**Scheme.**

columns containing the BASF catalyst R3-11 and activated molecular sieves (10 Å), respectively, prior to use. Toluene (≥99.5% from 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 (10 Å), respectively, prior to use. The imino(pyridine) cobalt complexes **1**, **2**, and **3** were synthesized according to a published procedure [10]. The catalyst precursor **4** was purchased from Boulder Scientific and used as received. The cocatalyst MAO for polymerization was prepared by removing toluene and $AlMe_3$ from a commercially available MAO toluene solution (10 wt % aluminum, Crompton). The MAO solution was filtered on a D4 funnel and evaporated to dryness 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) was prepared by dissolving solid MAO in toluene. The solution was used within 3 weeks to avoid self-condensation effects of the MAO. All manipulations of the air- and/or moisture-sensitive materials were carried out under a dry argon atmosphere in a glove box or using standard Schlenk-type techniques.

### *Ethylene Polymerization with **1/4**/MAO, **2/4**/MAO, **3/4**/MAO*

All polymerizations were performed in a double-walled Büchi AG glass reactor (1 l) equipped with a 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. Toluene (197 ml) was transferred into the autoclave under argon. Afterward, 2 ml of a stock toluene solution of MAO (100 mg/ml) was syringed into the autoclave, which was thermostated to 30°C and saturated under 3 bar of ethylene. After complete temperature and pressure equilibration, appropriate volumes of toluene stock solutions of the precatalysts (both $2.5 \times 10^{-3}$ 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. Generally, the exothermic heat of the reactions led to a temperature increase of the reaction mixtures of 1–2°C. The catalyst (Ti + Co) concentration was $1.25 \times 10^{-5}$ M for all polymerizations. After 1 h, the reaction was quenched by injecting 5 ml of ethanol into the autoclave, which was disconnected from the gas reservoir and vented. The reaction mixture was washed with 200 ml of a solution containing hydrochloric acid (200 ml), ethanol (425 ml), and water (1450 ml) and stirred overnight and dried at 60°C under vacuum. 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 $NaHCO_3$ and water and then evaporated to dryness at 60°C under vacuum.

### *Polymer Characterization*

$^{13}C\{^1H\}$ NMR spectra of polymer materials were recorded on a Bruker Advance 400 MHz instrument (100.6 MHz) at 100°C. Polymer samples of 300–500 mg were dissolved in a mixture of 1,2,4-trichlorobenzene and 1,1,2,2-tetrachloroethane-$d_2$ ($\delta = 74.24$ ppm) in 10-mm NMR tubes. Pulse width: 30°; pulse delay: 5 s; acquisition time: 0.65 s; scansion number: 1024. The spectra were elaborated by using the ACD/SpecViewer program. Glass-transition ($T_g$) and melting ($T_m$) temperatures of the polymer materials were determined by differential scanning calorimetry (DSC) with a Mettler Toledo DSC 821$^e$ instrument equipped with an intracooler and calibrated with the melting transition of indium (156.1°C). The polymer sample mass was

Ethylene polymerization with the tandem catalytic system **1**/**4**/MAO, **2**/**4**/MAO, **3**/**4**/MAO

| Catalytic system | Run[a] | Co, mol | Ti, mol | $\chi_{Co}$[b] | Al/Co | Al/Ti | $A$[c] | $M_w$[d], kg/mol | $M_w/M_n$[d] | $T_m$[e], °C | $T_g$[f], °C | Total br.[g] | $C_2$ br., %[g] | $C_4$ br., %[g] | ≥$C_6$ br., %[g] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **4**/MAO | 1 | 0.00 | 2.50 | 0.00 | | 1380 | 960 | 570 | 1.99 | 136.9 | – | 0 | 0 | 0 | 0 |
| **1**/**4**/MAO | 2 | 0.13 | 2.37 | 0.05 | 27580 | 1450 | 632 | 551 | 2.14 | 110.6 | – | 27 | 83 | 17 | 0 |
| | 3 | 0.38 | 2.12 | 0.15 | 9190 | 1620 | 1510 | 458 | 2.40 | 104.8 | – | 74 | 82 | 15 | 3 |
| | 4 | 0.63 | 1.87 | 0.25 | 5520 | 1840 | 2650 | 270 | 1.92 | – | –60.0 | 189 | 85 | 13 | 2 |
| | 5 | 1.25 | 1.25 | 0.50 | 2760 | 2760 | 4570 | 147 | 2.03 | – | –55.0 | 249 | 86 | 12 | 2 |
| | 6 | 1.88 | 0.62 | 0.75 | 1840 | 5520 | 4560 | 172 | 2.14 | – | –53.7 | 254 | 85 | 13 | 2 |
| **2**/**4**/MAO | 7 | 0.13 | 2.37 | 0.05 | 27580 | 1450 | 640 | 532 | 1.97 | 98 | – | 35 | 90 | 10 | 1 |
| | 8 | 0.38 | 2.12 | 0.15 | 9190 | 1620 | 1010 | 556 | 1.78 | 47 | –62.3 | 46 | 91 | 8 | 1 |
| | 9 | 0.63 | 1.87 | 0.25 | 5520 | 1840 | 1131 | 565 | 1.50 | – | –60.0 | 101 | 92 | 7 | 1 |
| | 10 | 1.25 | 1.25 | 0.50 | 2760 | 2760 | 1430 | 374 | 2.21 | – | –54.3 | 156 | 91 | 8 | 1 |
| | 11 | 1.88 | 0.62 | 0.75 | 1840 | 5520 | 670 | 332 | 2.8 | | –52.0 | 161 | 93 | 6 | 1 |
| **3**/**4**/MAO | 12 | 0.13 | 2.37 | 0.05 | 27580 | 1620 | 625 | 530 | 1.92 | 97 | – | 24 | 100 | 0 | 0 |
| | 13 | 0.38 | 2.12 | 0.15 | 9190 | 1840 | 1090 | 534 | 1.93 | 52 | –61.8 | 56 | 100 | 0 | 0 |
| | 14 | 0.63 | 1.87 | 0.25 | 5520 | 2760 | 1250 | 567 | 1.54 | – | –60.2 | 57 | 100 | 0 | 0 |
| | 15 | 1.25 | 1.25 | 0.50 | 2760 | 5520 | 1540 | 549 | 1.79 | – | –55.2 | 88 | 100 | 0 | 0 |
| | 16 | 1.88 | 0.62 | 0.75 | 1840 | 1450 | 1430 | 452 | 1.85 | – | –52.3 | 119 | 100 | 0 | 0 |

[a] Reaction conditions: glass-reactor, 1 l; (Co + Ti) precatalyst, $2.5 \times 10^{-6}$ mol; MAO cocatalyst, $3.5 \times 10^{-3}$ mol; toluene, 200 ml, polymerization time 1 h; stirrer rate 450 rpm; $C_2H_4$ pressure 3 bar, temperature 30 ± 2°C.

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

[c] Activity expressed as kg polymer (mol Ti)$^{-1}$ h$^{-1}$.

[d] Determined by GPC.

[e] Determined by DSC.

[f] Number of branches per 1000 C atoms calculated from $^{13}C\{^1H\}$ NMR.

[g] α-Olefin incorporation calculated from $^{13}C\{^1H\}$ NMR.

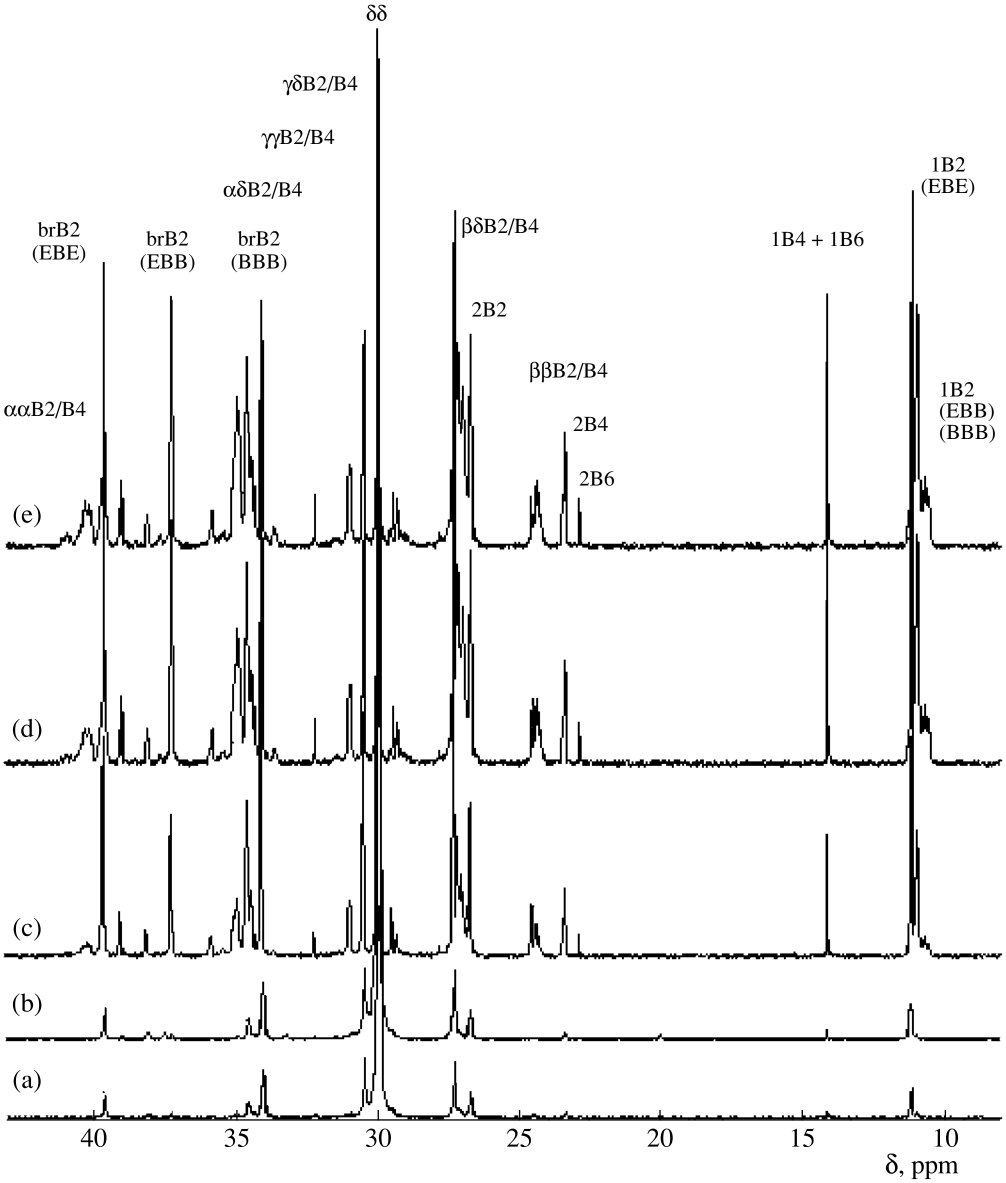
10 mg and aluminum pans were used. Any thermal history in the polymers was eliminated by first heating the specimen at a heating rate of 20 K/min to 200°C, cooling at 20 K/min to –100°C, and then recording the second scan from –100 to 200°C. The molecular weight ($M_w$) and molecular weight distribution ($M_w/M_n$) of the polymers were evaluated by gel permeation chromatography (GPC) with a Waters GPC 2000 system equipped with a set of three columns Styragel HT6, HT5, and HT3, and refractive index detector. The analyses were performed at 140°C using 1,2,4-trichlorobenzene as a solvent with an elution time of 1 ml/min and standard polystyrene as the reference.

## RESULTS AND DISCUSSION

The catalytic activity of **1**, **2**, and **3** towards ethylene was separately investigated to check the compatibility of each precursor with the CGT catalyst **4**. For an effective tandem system two components are, in fact, required, exhibiting a catalytic activity of the same order of magnitude.

Under the experimental conditions adopted in this work, the oligomerization catalysts were more active than the CGC **4** that gave an essentially linear high-density product (HDPE) with a melting temperature of 136.9°C (table). Under comparable conditions, the cobalt catalysts were more efficient than the titanium one, yet they were within the same order of magnitude ($10^5$–$10^6$). All oligomerization catalysts reached the maximum activity within the first five minutes. Therefore, 1 h was chosen as the reference time for the tandem reactions.

The table summarizes the results obtained. The molar fraction of cobalt ($\chi_{Co}$) was varied from 0 to 1, while the overall metal concentration (Co + Ti) was fixed at $1.25 \times 10^{-5}$ mol/l. The amount of MAO was 200 mg for each reaction. From a perusal of the data reported in the table, one can readily discern that $\chi_{Co}$ is the key factor controlling the amount of α-olefins produced, hence the productivity in copolymer and the material properties. For $\chi_{Co} \geq 0.15$, the productivity increased as compared to the homopolymer produced by **4** under the same conditions. In the case of **1**/**4**/MAO a maximum of 4570 kg (mol Ti)$^{-1}$ h$^{-1}$ was achieved for $\chi_{Co} = 0.50$. Beyond this value, a slight decrease in productivity was observed. A positive "comonomer effect" features many copolymerization reactions of ethylene with α-olefins by early transition metal catalysts [16–20] as well as tandem catalytic processes [1, 2, 8, 9].



$^{13}C\{^{1}H\}$ NMR spectra of the polymers produced by the tandem **1**/**2**/MAO system at $\chi_{Co}$ values of 0.05 (a), 0.15 (b), 0.25 (c), 0.50 (d), and 0.75 (e).

It is generally agreed that the comonomer effect is originated by an improved diffusion of the monomers, in consequence of an improved solubility of both the polymer and propagating metal alkyl, due to the reduced crystallinity resulting from α-olefin incorporation. The higher solubility apparently compensates for the negative effect on chain propagation caused by the disfavored insertion of α-olefins as compared to ethylene. Within this context, the "negative comonomer effect" observed at $\chi_{Co} < 0.15$ may be accounted for by the too low incorporation of α-olefins in the macromolecule chain, which would not improve the solubility while chain propagation decreases.

As previously mentioned, the $\chi_{Co}$ value greatly influences the material properties (table). Indeed, copolymers prepared at a lower $\chi_{Co}$ than 0.15 appeared as rigid white solids, while with increasing $\chi_{Co}$ colorless rubbery materials were obtained. Hence, both the extent of α-olefin incorporation and the number and type of branches are strictly related to $\chi_{Co}$, as it determines the concentration of α-olefins in the reactor. The relationship between $\chi_{Co}$ and the level of branching for the catalyst system **1**/**4**/MAO is clearly shown in the figure [14, 21], which also shows the assignment of the $^{13}C\{^{1}H\}$ NMR chemical shifts. The nomenclature adopted for the polymer backbone and branching carbons is that defined by Randall [24]. Methylene carbons are identified by a pair of greek letters to indicate the distance to branches in either direction, whereas the methyne carbons are identified by "br." Carbons in the side chains are identified by "$xB_n$," where the subscript "*n*" indicates the length of the branch in terms of the number of carbon atoms and "*x*" denotes the carbon number starting with the methyl carbon in position **1** [24].

Increasing $\chi_{Co}$ from 0.05 to 0.75 increases the number of branches from 27 and 254 per 1000 carbon atoms for the system **1**/**4**/MAO, from 35 to 160 for **2**/**4**/MAO, and from 24 to 119 for **3**/**4**/MAO, which is consistent with the specific activity of the three oligomerization catalysts [10]. It is noteworthy that the distribution of the branches in the polymer backbone is in excellent accord with the molar distribution of the α-olefins produced [10]. For instance, the system **3**/**4**/MAO produces only ethyl branching and reflects the specific selectivity of **3** for butenes, while in the case of the systems **1**/**4**/MAO and **2**/**4**/MAO, the distribution of the branches is in accord with the molar distribution of the α-olefins (**1**/**4**/MAO = ethyl 85%, butyl 13%, hexyl 2%; **2**/**4**/MAO = ethyl 91%, butyl 8%, hexyl 1%). The DSC analysis of the copolymers showed that $T_m$ varies from 136.9 to 47°C for the semicrystalline materials, while $T_g$ varies from –60 to –54°C for the amorphous materials [20, 22–24, 25].

Unlike α-olefin incorporation and branching, the molecular weight of the copolymers decreased with increasing $\chi_{Co}$. In the case of **1**/**4**/MAO, the value decreased from 570 kg/mol for the homopolymer produced by **4** to 147 kg/mol for $\chi_{Co} = 0.50$ (table). This trend is typical for ethylene-α-olefin copolymerization and has been rationalized by considering that the insertion of an α-olefin into the propagating alkyl chain gives rise to the formation of ethyl, butyl, or hexyl side chains depending on whether the inserted α-olefin is 1-butene, 1-hexene, or 1-octene. If the next α-olefin approaches the metal center immediately after an α-olefin insertion, its coordination will be disfavored for steric reasons, thus favoring the chain transfer. In this picture, the higher the number of α-olefins available for each titanium center, the higher the probability that low-molecular weight macromolecules will be produced. An analogous effect was found for the systems **2**/**4**/MAO and **3**/**4**/MAO.

It is worth observing that the polydispersity ($M_w/M_n$) was close to 2 for all copolymers (table). This indicates that, despite the presence of a dual catalytic system, the effect of the cobalt catalyst is exclusively that of producing α-olefins, whereas the PE is selectively obtained by an insertion reaction at the CGC catalyst. In terms of macromolecular topology, the present tandem systems promote a better control as compared to the so-called "chain walking" catalysts, which generally lead to the production of low density polyethylene with long branching and non-linear structure [26].

## CONCLUSIONS

Tandem catalysis for the production of branched PE has grown considerably since its discovery by Bazan and coworkers in 1998 [27]. By an appropriate choice of catalysts and experimental conditions, it is now possible to exert a control over the polymer microstructure and topology, which is hardly achievable by traditional systems involving ethylene/α-olefin copolymerization by metallocenes or ethylene polymerization by chain-walking Ni and Pd catalysts [26, 28].

The new tandem systems described in this work allow one to produce a variety of branched polyethylenes, ranging from semicrystalline LLDPE to amorphous, rubbery products, under experimental conditions that allow for an actual industrial scale-up. It is noteworthy that, for the first time, linear polyethylene rubbers have been produced by tandem copolymerization catalysis, with a precise control of branching.

Studies are in progress to develop other (imino)pyridyl cobalt catalysts that are capable of producing α-olefins with different Schulz–Flory distributions in order to form new tandem systems in conjunction with either **4** or other copolymerization catalysts.

## REFERENCES

1. Bianchini, C., Miller, H., and Ciardelli, F., *Modification and Blending of Synthetic and Natural Macromolecules*, Ciardelli, F. and Peneczek, S., Eds., Dordrecht: Kluwer, 2004, p. 15.
2. *Metallocene-Based Polyolefines*, Scheirs, J. and Kaminsky, W., Eds., Chichester: Wiley, 2000.
3. Wang, W., Yan, D., Charpentier, P.A., Zhu, S., Hamielec, A., and Sayer, B.G., *Macromol. Chem. Phys.*, 1998, vol. 199, p. 409.
4. Whiteley, K.S., in *Ullmann's Encyclopedia of Industrial Chemistry*, Gerhatz, W. and Elvers, B., Eds., Weinheim: VCH, 1992, vol. A21, p. 488.
5. Johnson, L.K., Killian, C.M., and Brookhart, M., *J. Am. Chem. Soc.*, 1995, vol. 117, p. 6414.
6. Komon, Z.J.A. and Bazan, G.C., *Macromol. Rapid Commun.*, 2001, vol. 22, p. 467.
7. McKnight, A.L. and Waymouth, A.L., *Chem. Rev.*, 1998, vol. 98, p. 2587.
8. Boussie, T.R., Diamond, G.M., Goh, C., Hall, K.A., LaPointe, A.M., Leclerc, M., Lund, C., Murphy, V., Shoemaker, J.A.W., Tracht, U., Turner, H., Zhang, J., Uno, T., Rosen, R.K., and Stevens, J.C., *J. Am. Chem. Soc.*, 2003, vol. 125, p. 4306.
9. Eur. Pat. Appl. EP 416 815, 1991.
10. Bianchini, C., Giambastiani, G., Mantovani, G., Meli, A., and Mimeau, D., *J. Organomet. Chem.*, 2004, vol. 689, p. 1356.
11. Ye, Z., AlObaidi, F., and Zhu, S., *Macromol. Rapid Commun.*, 2004, vol. 25, p. 647.
12. Wang, J., Li, H., Guo, N., Li, L., Stern, C.L., and Marks, T.J., *Organometallics*, 2004, vol. 23, p. 5112.

13. Li, L., Metz, M.V., Li, H., Chen, M.-C., Marks, T.J., Liable-Sands, L., and Rheingold, A.L., *J. Am. Chem. Soc.*, 2002, vol. 124, p. 12725.
14. Abramo, G.P., Li, L., and Marks, T.J., *J. Am. Chem. Soc.*, 2002, vol. 124, p. 13966.
15. Wang, H., Ma, Z., Ke, Y., and Hu, Y., *Polym. Int.*, 2003, vol. 52, p. 1546.
16. Chien, J.C.W. and Nozaki, T., *J. Polym. Sci., Part A: Polym. Chem.*, 1993, vol. 31, p. 227.
17. Philipp, W., Trinkle, S., Lilge, D., Friedrich, C., and Mülhaupt, R., *Macromol. Mater. Eng.*, 2001, vol. 286, p. 309.
18. Philipp, W., Trinkle, S., Suhm, J., Mader, D., Friedrich, C., and Mülhaupt, R., *Macromol. Chem. Phys.*, 2000, vol. 201, p. 604.
19. Galland, G.B., Seferin, M., Mauler, R.S., and Dos Santos, J.H.Z., *Polym. Int.*, 1999, vol. 48, p. 660.
20. Xu, G. and Ruckenstein, E., *Macromolecules*, 1998, vol. 31, p. 4724.
21. Sperber, O. and Kaminsky, W., *Macromolecules*, 2003, vol. 36, p. 9014.
22. Usami, T. and Takayama, S., *Macromolecules*, 1984, vol. 17, p. 1756.
23. Randall, J.C., *J. Macromol. Sci., Rev. Macromol. Chem. Phys*, 1989, vol. C29, p. 201.
24. Galland, G.B., de Souza, R.F., Mauler, R.S., and Nunes, F.F., *Macromolecules*, 1999, vol. 32, p. 1620.
25. Peacock, A., in *Handbook of Polyethylene: Structures, Properties, and Applications*, New York: Marcel Dekker, 2000.
26. Guan, Z., *Chem. Eur. J.*, 2002, vol. 8, no. 14, p. 3086.
27. Barnhart, R.W. and Bazan, G.C., *J. Am. Chem. Soc.*, 1998, vol. 120, p. 1082.
28. Gates, D.P., Svejda, S.A., Onate, E., Killian, C.M., Johnson, L.K., White, P.S., and Brookhart, M., *Macromolecules*, 2000, vol. 33, p. 2320.