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LLDPE with Exclusively Ethyl Branches by Tandem Catalysis with Single-Site Zr(IV)/Co(II) Catalysts

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Abstract Semicrystalline linear low density polyethylenes (LLDPEs) with exclusively ethyl branching (from 7 to 56 branches per 1,000 carbon atoms) were prepared from ethylene by homogeneous tandem catalytic systems comprising (imino)pyridine cobalt(II) dichlorides as oligomerization precursors, bis(cyclopentadienyl)zirconium(IV) dichloride as copolymerization precursor and methylaluminoxane as activator. The activity of the tandem systems was evaluated by varying either the molar fraction of the cobalt precursors or the ethylene pressure. The latter parameter was of crucial importance to control both the productivity and the extent of 1-butene incorporation. In particular, increasing the ethylene pressure from 2 bar to 4 bar changed the "comonomer effect" from positive to negative.

Keywords Tandem catalysis · Cobalt · LLDPE · Zirconium

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1 Introduction

Tandem copolymerization catalysis, using two or more different single-site catalysts in the same reactor, is a relatively recent technique for the production of branched polyethylene (PE) from ethylene stock [1, 2]. A great variety of combinations of late and early metal catalyst precursors, under different experimental conditions, has been successfully employed in tandem processes to produce materials spanning from linear low-density polyethylene (LLDPE) to elastomeric ultra low-density polyethylene (ULDPE) [1–9]. The copolymerization step involves invariably either early metallocenes, especially of the *ansa*-type, or half-metallocenes such as the constrained geometry complex $[(\eta^5\text{-}C_5Me_4)SiMe_2(t\text{BuN})]TiCl_2$ [9–11]. These copolymerization catalysts are generally very active but not selective. Therefore, when the oligomerization catalyst produces different types of α-olefins, for example with a Schulz-Flory distribution, the LLDPE microstructure, especially in terms of length and distribution of the branches, is hardly reproducible and difficult to control [8, 9]. In order to avoid this problem, the copolymerization catalysts may be flanked by oligomerization catalysts that are able to produce a unique α-olefin [12]. As an alternative to the use of a selective ethylene oligomerization catalyst, one may employ a copolymerization catalyst that exhibits different kinetics of α-olefin incorporation into the growing copolymer chain in function of the α-olefin length as well as the experimental conditions. The first approach of this type has been described by Casagrande who reported the synthesis of LLDPE with almost exclusively ethyl branches by means of a tandem system comprising Cp_2ZrCl_2 as copolymerization catalyst, $Tp^{Ms}NiCl$ (Tp^{Ms} = hydridotris(3-mesitylpyrazol-1-yl)) as oligomerization catalyst and MAO/TMA as activator in toluene at 0 °C [3]. Notably, $Tp^{Ms}NiCl/MAO$ is
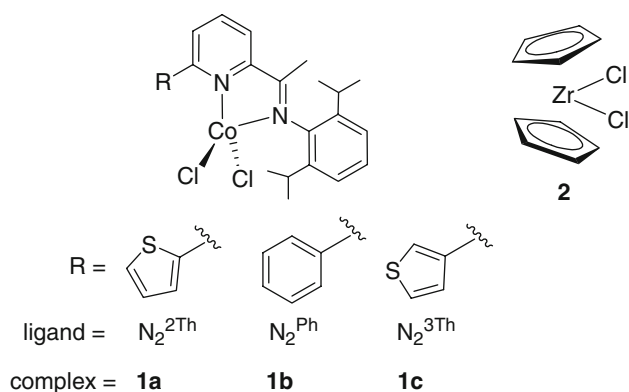
Fig. 1 (Imino)-pyridine $CoCl_2$ complexes (**1a-c**) and Cp_2ZrCl_2 (**2**) for the tandem copolymerization catalysis

able to convert ethylene into a Schulz-Flory distribution of α-olefins [13] and Cp_2ZrCl_2/MAO catalyzes the copolymerization of ethylene also with α-olefins higher than 1-butene, provided a reaction temperature ≥60 °C is used [14]. Thus, the almost selective incorporation of 1-butene (some butyl branches were detected) by the Cp_2ZrCl_2/$Tp^{Ms}NiCl$/MAO system indicates that the smallest and largely abundant 1-butene prevails over any other α-olefin for insertion into the growing copolymer chain at the experimental temperature of 0 °C.

Herein are described some new homogeneous tandem systems that allow for the conversion of ethylene into a variety of LLDPEs bearing *exclusively* ethyl branches with superior productivity and amount of branching as compared to the products obtainable with the Cp_2ZrCl_2/$Tp^{Ms}NiCl$/MAO system.

The tandem systems described in this paper comprise $CoCl_2$ modified with 6-organyl-2-(imino)pyridine ligands (**1a–c**) and Cp_2ZrCl_2 (**2**) (Fig. 1). Previous studies have demonstrated that, upon activation by MAO in toluene, **1a** oligomerizes ethylene yielding short α-olefins with a productivity as high as 6.6×10^5 mol of ethylene converted (mol of Co)$^{-1}$ h^{-1} (TOF$_{mol}$) and a Schulz-Flory α-value of about 0.08 (butenes 92.0%, hexenes 7.4%, octenes 0.6% at 30 °C) [12]. Under comparable experimental conditions, the selective ethylene dimerization to butenes (>98%) with a TOF$_{mol}$ of ca. 1.5×10^5 was achieved with the catalyst precursors **1b** and **1c** [12a, b].

2 Experimental Part

2.1 General Conditions

Argon (≥99.999% from Rivoira) was dried through a $CaCl_2$ column and deoxygenated with an oxisorb cartridge from Messer Griesheim prior to use. Ethylene N35 (Air Liquide ≥99.95%) was deoxygenated and dried through

two columns containing the BASF catalyst R3-11 and activated molecular sieves (10 Å), respectively, prior to use. Anhydrous toluene was obtained by means of a MBraun Solvent Purification Systems. The imino(pyridine) cobalt complexes $CoCl_2(N_2^{2Th})$, $CoCl_2(N_2^{3Th})$, and $CoCl_2(N_2^{Ph})$ were synthesized according to a published procedure [12b]. Cp_2ZrCl_2 was purchased from Sigma-Aldrich and used as received. Solid methylaluminoxane (MAO) was prepared by removing toluene and $AlMe_3$ under vacuum from a commercially available MAO solution (10 wt% solution in toluene, Sigma-Aldrich). 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^{-1}) was prepared by dissolving solid MAO in toluene. The solution was used within 1 week 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.

2.2 Ethylene Polymerization with the Tandem Systems **1a–c/2/MAO**

All polymerization reactions were performed in a 750 mL stainless steel reactor, constructed at the ICCOM-CNR (Firenze, Italy), equipped with a magnetic drive stirrer, a Parr 4842 temperature and pressure controller. The reactor was connected to an ethylene reservoir to maintain a constant pressure throughout the catalytic runs. The autoclave was dried under vacuum at 95 °C for 1 h and then cooled to room temperature under an argon atmosphere. Toluene (195 mL) was transferred into the autoclave under argon. Afterward, 2.4 mL of a stock toluene solution of MAO (100 mg mL^{-1}) was syringed into the autoclave, which was thermostated to 30 °C by the way of an external circulating bath and saturated with ethylene at the proper pressure. After complete temperature and pressure equilibration, the solutions/suspensions of the precatalysts in toluene (2.6 mL overall) were injected into the autoclave in rapid sequence (cobalt always first) to start the concurrent ethylene oligomerization and polymerization processes. Generally, the exotherm of the reactions led to a temperature increase of the reaction mixtures of 1 °C maximum. The catalyst (Zr + Co) concentration was generally of 6.5×10^{-5} mol L^{-1} for all polymerizations except for runs conducted with only Cp_2ZrCl_2 or at cobalt molar fractions ≤0.5. After the proper reaction time, the catalysis was terminated by cooling the reactor to 5 °C, venting off the volatiles, and introducing 2 mL of acidic EtOH (5% HCl v/v). The reaction mixture was poured into 200 mL of a solution prepared by mixing hydrochloric acid (50 mL),

ethanol (425 mL) and water (1,450 mL) and stirred over-night. When the polymer precipitated as 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, the toluene phase contained the solid was separated from water, washed with a saturated water solution of NaHCO$_3$ and then evaporated to dryness at 60 °C under vacuum.

2.3 Polymer Characterization

The ^{13}C NMR spectra of polymer materials were recorded on a Bruker Avance 300 MHz instrument (75.5 MHz) at 110 °C. Polymer samples of 150–250 mg were dissolved in 2.5 mL of a 30:70 v/v mixture of 1,1,2,2-tetrachloroeth-ane-d_2 ($\delta = 74.24$ ppm):1,2,4-trichlorobenzene in 10 mm NMR tubes. Pulse width: 30°; pulse delay: 18 s; acquisi-tion time: 1.41 s; scansion number: 1024. Melting (T$_m$) temperatures of the polymer materials were determined by differential scanning calorimetry (DSC) with a Perkin–Elmer DSC-7 instrument equipped with CCA-7 cooling device and calibrated with the melting transition of indium and n-heptane as references (156.1 and −90.61 °C, respectively). The polymer sample mass was 10 mg and aluminum pans were used. Any thermal history in the polymers was eliminated by the first heating of the speci-men at a heating rate of 20 °C min^{-1} to 200 °C, cooling at 20 °C min^{-1} to −100 °C, and then recording the second scan from −100 °C to 200 °C. Thermal gravimetric anal-yses (TGA) were obtained under nitrogen (60 mL min^{-1}) with a TGA Mettler Toledo instrument at the heating rate of 10 °C min^{-1} from 50 °C to 700 °C. The molecular weight (M$_w$) and molecular weight distribution (M$_w$/M$_n$) of the polymers were evaluated by gel permeation chroma-tography (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 solvent with an elution time of 1 mL min^{-1} and standard polystyrene as the reference.

3 Results and Discussion

All the catalytic tests were carried out in the presence of mixtures of **1a–c** and **2** under polymerization/oligomeri-zation conditions that previous studies had shown to be effective for each single-site system, taken separately. The compatibility of the oligomerization and copolymerization catalysts to each other as well as to MAO was preliminary ascertained by independent gas-uptake catalytic experi-ments: under comparable conditions, the Zr catalyst was more active than the Co catalysts, yet within the same order

of magnitude. Either single-site catalyst showed no induction period and reached the maximum activity within a few minutes, then the consumption of ethylene remained practically constant for more than half an hour.

Table 1 summarizes the experimental conditions applied to the tandem copolymerization processes catalyzed by **1a–c/2**/MAO (Fig. 2) and the relative results. The molar fraction of cobalt (χ_{Co}), ranging from 0 to 0.98, and the ethylene pressure were the only two experimental variables, while the MAO concentration and the initial temperature were fixed to 2.1×10^{-5} mol L^{-1} and 30 °C, respectively. Except for the reactions performed with only Cp$_2$ZrCl$_2$ or with cobalt molar fractions ≤ 0.5, the overall metal con-centration (Co + Ti) was fixed to 6.5×10^{-5} mol L^{-1}.

Irrespective of the oligomerization cobalt catalyst, only 1-butene was incorporated into the PE matrix to give LLDPE with exclusively ethyl branches up to 11.3 mol% of incorporated oligomer. No trace of 1-hexene enchain-ment was detected even at very high χ_{Co} values of **1a**, while no branching was observed at $\chi_{Co} < 0.5$. An inde-pendent ethylene - 1-henexe copolymerization under the experimental conditions of the tandem reaction (entry 2) showed no 1-hexene incorporation, which proves the importance of the reaction temperature to control the migratory insertion of Zr(alkyl)(α-olefin) [14]. The exclu-sive presence of ethyl branches in the LLDPE was unambiguously shown by ^{13}C{^{1}H} NMR spectroscopy. As an example, Fig. 3 reports the spectrum of the copolymer obtained under the conditions of entry 13. The ^{13}C NMR chemical shift assignments are reported in Table 2, where the nomenclature adopted for the polymer backbone and branching carbons is that defined according to Randall [15]. The 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". The carbon atoms in the ethyl chains are identified by "xB$_2$" where the "x" denotes the carbon number starting with the methyl carbon in position 1.

Both the oligomerization and copolymerization cata-lysts, taken separately, showed a linear dependence of the activity with the pressure (entries 1 vs. 11 and 3 vs. 12), indicating that the propagation and chain-transfer rates are first-order in ethylene concentration [16, 17] although with different kinetics (Fig. 4).

From a perusal of the data reported in Table 1, one may readily realize the importance of both the ethylene pressure and χ_{Co}, hence of the instantaneous concentration of the oligomers in the reactor, to control the productivity and the characteristics of the LLDPE product.

Irrespective of the oligomerization catalyst, the pro-ductivity decreased in going from 2 to 4 bar pressure (see for example entry 13 with a TOF$_{kg}$ of 25,400 vs. 7 with a TOF$_{kg}$ of 10,000). A positive "comonomer effect"

Table 1 Ethylene polymerization[a]

Entry	Prec at.	Co μmol	Zr μmol	χ_{Co}[b]	Al/Co	Al/Zr	$p(C_2H_4)$ (bar)	PE (g)	Time (h)	PE TOF_{kg}[c] 10^{-3}	PE TOF_{mol}[d] 10^{-3}	Olefin TOF_{mol}[e] 10^{-3}	M_w (kg mol^{-1})[f]	M_n (kg mol^{-1})[f]	M_w/M_n	T_m^g (°C)	ΔH_m (J g^{-1})	X (%)[h]	br.[i]	Butene (mol %)[j]
1	**2**		0.26			15908	4	2.7	0.5	20.8	740		754	193	3.91	135.7	124.2	46.0		
2[k]	**2**		0.26			15908	4	2.6	0.5	20.0	713		688	247	2.79	130.5	124.6	46.2		
3	**1a**	13.00		1.00	318		4	0.0	0.5			206								
4	**1a/2**	1.30	1.30	0.50	3182	3182	4	13.4	0.5	20.6	735		370	117	3.16	124.9	132.2	49.0	7.5	1.5
5	**1a/2**	10.40	2.60	0.80	398	1591	4	7.1	0.5	5.5	195		383	108	3.55	121.2			14.3	2.9
6	**1a/2**	12.45	0.65	0.95	332	6363	4	2.5	0.5	7.7	274		400	107	3.74	120.4	107.0	39.6	20.5	4.1
7	**1a/2**	12.74	0.26	0.98	325	15908	4	1.3	0.5	10.0	356		357	108	3.31	119.8	100.4	37.2	28.5	5.7
8	**1a/2**	12.74	0.26	0.98	325	15908	4	5.3	2.0	10.2	363		401	117	3.43	94.8	94.8	35.1	50.0	10.0
9	**1b/2**	12.74	0.26	0.98	325	15908	4	1.0	0.5	7.7	274		400	107	3.74	123.5	92.8	34.4	20.0	4.0
10	**1c/2**	12.74	0.26	0.98	325	15908	4	1.1	0.5	8.5	302		470	143	3.28	119.4	107.8	39.9	24.0	4.8
11	**2**		0.26			15908	2	1.5	0.5	11.5	411		1758	280	6.28	139.6	112.5	45.4		
12	**1a**	13.00		1.00	318		2	0.0	0.5			115								
13	**1a/2**	12.74	0.26	0.98	325	15908	2	3.3	0.5	25.4	905		280	100	2.80	87.8	82.4	30.5	56.5	11.3
14	**1b/2**	12.74	0.26	0.98	325	15908	2	2.9	0.5	22.3	795		136	64	2.13	102.6	84.1	31.2	40.0	8.0
15	**1c/2**	12.74	0.26	0.98	325	15908	2	2.8	0.5	21.5	768		320	120	2.67	112.6	97.3	36.0	32.5	6.5

[a] Reactions were performed in a stainless steel reactor (750 mL), conditions: 4,136 μmol MAO, 200 mL toluene, 450 rpm stirring rate, 30 °C initial temperature

[b] χ_{Co} = [Co]/([Co]+[Zr])

[c] Expressed as kg polymer (mol Zr)$^{-1}$ h^{-1}

[d] Expressed as mol C_2H_4 (mol Zr)$^{-1}$ h^{-1}

[e] Expressed as mol C_2H_4 (mol Co)$^{-1}$ h^{-1}

[f] Determined by GPC

[g] Determined by DSC

[h] Crystallinity calculated as $(\Delta H_f/\Delta H_{fx})*100$, where ΔH_{fx} is 269.9 Jg^{-1}. See refs. [14a and 25]

[i] Number of branches per 1,000 C atoms calculated from the ^{13}C NMR spectra

[j] Butene incorporation calculated from the ^{13}C NMR spectra
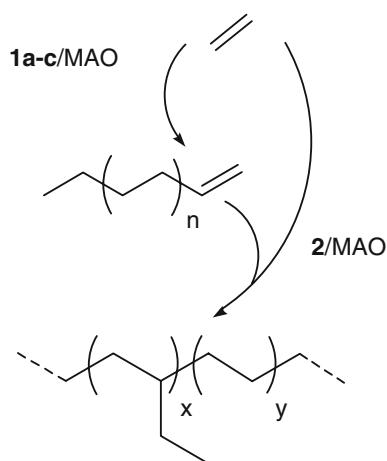
[k] Run in presence of 1.5 g of 1-hexene
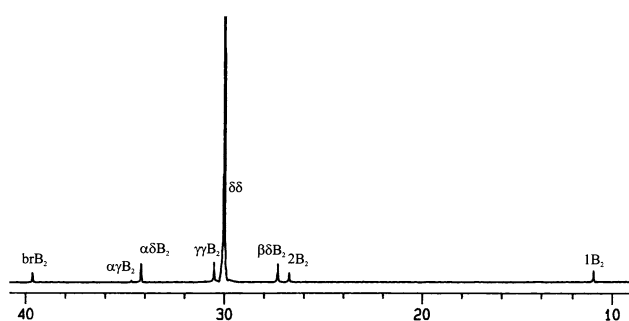
Fig. 2 The tandem copolymerization processes

Fig. 3 $^{13}C\{^{1}H\}$ NMR spectrum of the polymer produced by the tandem **1a/2**/MAO system under the conditions of entry 13

Table 2 ^{13}C NMR chemical shifts and assignments for the ethyl-branched PE obtained by the tandem **1a/2**/MAO system at χ_{Co} of 0.98 and 2 bar ethylene (100.6 MHz, 110 °C, 1,1,2,2-tetrachloroethane-d_2: 1,2,4-trichlorobenzene 30:70 v/v)

Chemical shift (ppm)	Carbon assignment	Sequence assignment
39.61	brB$_2$	EBE
34.50	$\alpha\gamma$B$_2$	EBEB+BEBE
34.34	$\alpha\delta$B$_2$	EBEE+EEBE
30.47	$\gamma\gamma$B$_2$	BEEE+EEEB
29.98	$\delta\delta$	(EEE)n
27.26	$\beta\delta$B$_2$	EBEE+EEBE
26.66	2B$_2$	EBE
11.16	1B$_2$	EBE

occurred at 2 bar (entry 13 vs. 11, a reaction catalyzed by **2**/MAO yielding PE). It is commonly agreed that the "comonomer effect", which features many copolymerization reactions of ethylene with α-olefins by early transition metal catalysts [18–22] as well as tandem catalytic processes [1, 6, 9], is originated by the improved diffusion of the monomers in the catalytic mixtures. Indeed, the reduced crystallinity caused by the α-olefin incorporation improves the solubility of both polymer and propagating
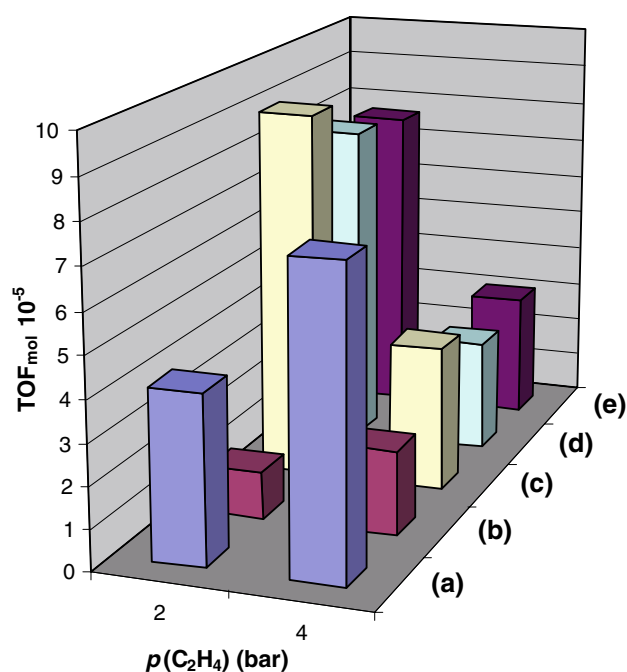

Fig. 4 TOF$_{mol}$ at different ethylene pressures: (a) **2**/MAO; (b) **1a**/MAO; (c) **1a/2**/MAO (0.98 χ_{Co}); (d) **1b/2**/MAO (0.98 χ_{Co}); (e) **1c/2**/MAO (0.98 χ_{Co})

metal alkyls [22]. In turn, a negative "comonomer effect" can be observed in copolymerization reactions when the α-olefins compete with ethylene for coordination to the unsaturated metal-alkyl moiety, thus slowing down the propagation rate. In the present reactions under 4 bar ethylene, the huge instantaneous concentration of 1-butene may hamper the regular and continuous ethylene uptake by the copolymerization catalyst (entry 7 with a TOF$_{kg}$ of 10,000 vs. 1 with a TOF$_{kg}$ of 20,800). In these conditions, it is likely that the higher solubility of the branched copolymer does not compensate enough for the negative effect on chain propagation caused by the competitive coordination of the α-olefins.

Besides affecting the productivity, the ethylene pressure has been found to influence the properties of the resulting copolymer (Table 1) as well as its physical appearance. Indeed, as shown in Fig. 5, the copolymer obtained with a χ_{Co} of 0.98 under 4 bar ethylene appeared (b) as a semi-crystalline, flexible material (entry 7), while a more amorphous, rubbery copolymer (a) was produced at lower ethylene pressure (entry 13).

In addition to the ethylene pressure, the amount of branching in the LLDPE was determined by χ_{Co}: increasing this parameter from 0.5 to 0.98, while decreasing the ethylene pressure from 4 to 2 bar, increased the 1-butene incorporation from a minimum value of 1.5 mol% up to a maximum value of 11.3 mol% with the number of branches per 1,000 carbon atoms varying from 7.5 and 56.5, respectively.

Fig. 5 Polymer materials produced by the tandem **1a/2/** MAO system (0.98 χ_{Co}) (**a**) 2 bar ethylene (entry 13), (**b**) 4 bar ethylene (entry 7)
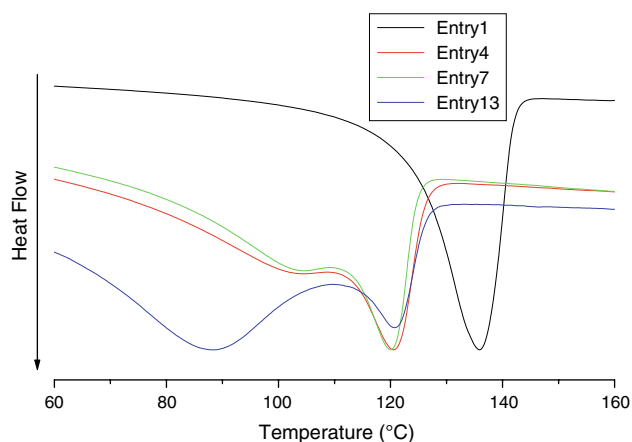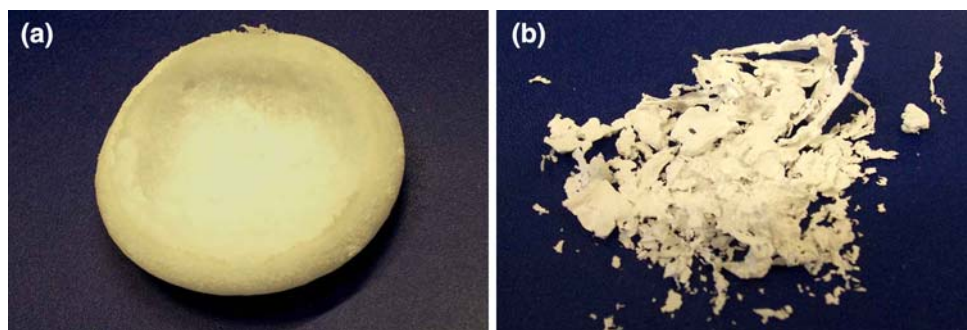

Fig. 6 DSC curves of the copolymers prepared by the tandem system **1a/2**/MAO at different χ_{Co} values and ethylene pressures
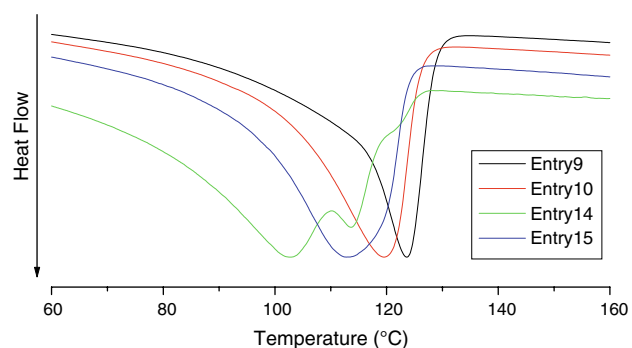
Fig. 7 DSC curves of the copolymers prepared by the tandem systems **1b/2**/MAO and **1c/2**/MAO at χ_{Co} = 0.98 and different ethylene pressures

The effects of both χ_{Co} and ethylene pressure on the copolymer properties have been also evaluated by means of DSC and GPC (Table 1).

The DSC analysis of the branched PE gave melting points between 125 °C and 88 °C which are typical values for semicrystalline LLDPE materials containing increasing branching [23]. The T_m value decreased from 139.6 °C for the PE produced by **2** (entry 11) to 87.8 °C for the LLDPE produced by the tandem system **1a/2**/MAO with χ_{Co} = 0.98 under 2 bar ethylene (entry 13). At the highest χ_{Co} investigated, the LLDPE was featured by broad or

multiple melting transitions, suggesting the presence of blocks with different ethyl-branching sequences (Figs. 6 and 7) [3].

The GPC experiments showed smaller molecular weights (M_n) for the copolymers than for the homopolymers, while no significant variation was observed by changing χ_{Co}. In all cases, the GPC curves were consistent with monomodal distributions and polydispersities ranging from 2.13 and 6.28. As expected, the TGA analysis of all copolymers showed a decrease of the thermal stability with increasing branching [24].

4 Conclusions

The new tandem system described in this work allows one to convert ethylene into LLDPE with exclusively ethyl branches, melting temperatures as low as 88 °C and productivities as high as 25,400 kg (mol Zr)$^{-1}$ h^{-1} where Zr is the simple metallocene copolymerization catalyst precursor Cp_2ZrCl_2. Cheap and largely available are also the oligomerization precursors based on $CoCl_2$ modified with (imino)pyridine ligands. The excellent branching selectivity is controlled by the metallocene catalyst that, under certain experimental conditions, is unable to copolymerize higher α-olefins than 1-butene. As a matter of fact, replacing Cp_2ZrCl_2 with $[(\eta^5\text{-}C_5Me_4)SiMe_2(t\text{BuN})]TiCl_2$, maintaining (imino)pyridine cobalt(II) dichlorides as oligomerization catalysts, generates tandem systems capable to produce not only semicrystalline LLDPE but also completely amorphous materials with Tg as low as −60 °C [9].

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