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Ethene/propene copolymerisations with *rac*-EBTHIZrR$_2$/alumoxane: σ-ligands effect

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Abstract

We report here about the role played by the σ-ligands of a metallocene in ethene/propene (E/P) copolymerisations promoted by *rac*-[ethylenebis(4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride **1**, and its corresponding dimethyl derivative *rac*-EBTHIZrMe$_2$ **2** and binaphtholate *rac*-EBTHIZr(BNP) **3** derivative, in the presence of several alumoxanes.

Alumoxanes alternative to the traditional polymethylalumoxane (MAO) were synthesised and characterised. They are based on Al(2,4,4-trimethylpentyl)$_3$ (TIOA) **4** and were prepared by reaction of **4** with water to give either tetraisooctylalumoxane (TIOAO) **5** or polyisooctylalumoxane (TAO) **6** depending on the stoichiometry of the reaction. ^{1}H NMR spectra of these products are characterised by the presence of broad bands and of resolved multiplets. Their relative amount in the region between 1.9 and 2.5 ppm was identified as the "fingerprint" of the polymerisation activity. A comparison of the results obtained in polymerisation with metallocenes having different σ-ligands allowed us to shed more light on the role played by those species.

In conclusion, the nature of the σ-ligands of a metallocene affects its catalytic activity in polymerisation, as a function of the alumoxane employed and of the relative ratio with the metallocene, and this effect is enhanced in "critical conditions," i.e. with a weakly activating cocatalyst or at a low Al/Zr ratio.

Keywords: Zirconium; Ansa-metallocenes; Ziegler–Natta catalysis; Alumoxanes; Polymerisations

1. Introduction

In the last years, metallocene-based catalytic systems [1–6] have started to find increasing industrial applications and they now play an important role in the preparation of ethene-based homo- and copolymers [7,8]. The scientific interest arises primarily from their single centre nature [1,9] and from the availability of a large variety of π-ligands structures which allows the preparation of (co)polymers with a wide range of microstructures and properties [10–16].

Their effect on the polymerisation performances can also allow a detailed study of the correlation between structure and activity of the

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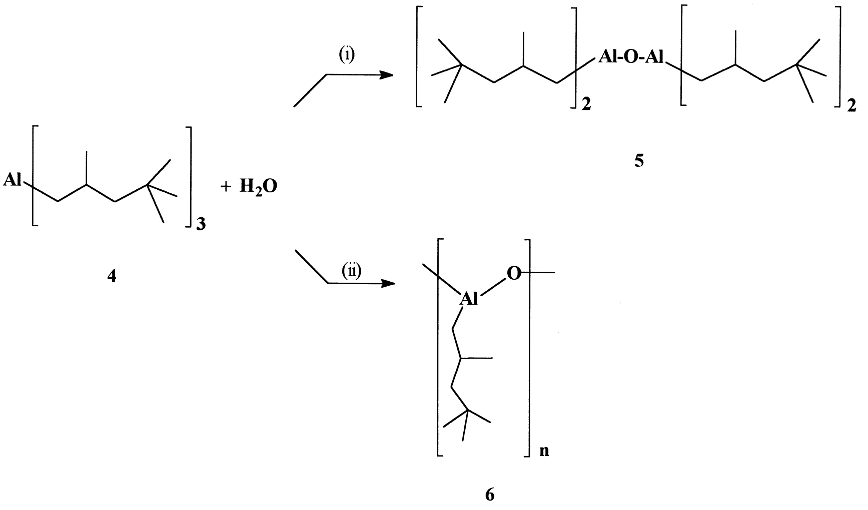


Scheme 1. Reaction of TIOA with H_2O in stoichiometric molar ratio of either 2:1 (i) and 1:1 (ii).

organometallic complexes with respect to π- and σ-ligands.

We report here about the role played by the σ-ligands in ethene/propene (E/P) copolymerisations performed in the presence of several alumoxanes. Dimethyl derivative *rac*-EBTHIZrMe$_2$ **2** [17] and binaphtholate (BNP) derivative *rac*-EBTHIZr(BNP) **3** [18,19] of *rac*-[ethylenebis(4,5,6,7-tetrahydro-1-indenyl)]zirconium dichloride (*rac*-EBTHIZrCl$_2$) **1** [20] were synthesised and used to promote E/P copolymerisations in solution.

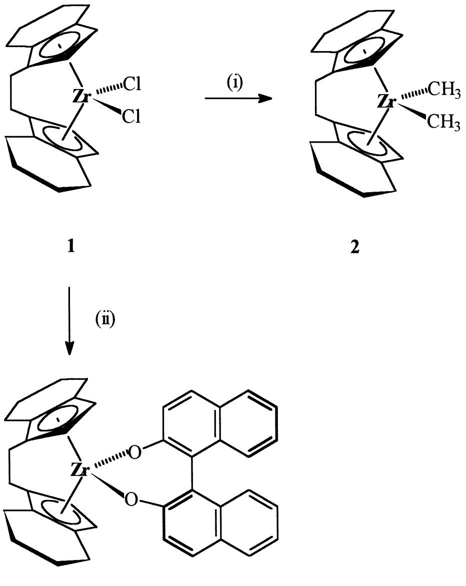
Newly developed alumoxanes alternative to the traditional polymethylalumoxane (MAO) were used as cocatalysts. They are based on Al(2,4,4-trimethylpentyl)$_3$, also called Al(iso-octyl)$_3$ (TIOA) **4**, and result from the reaction of this aluminium alkyl with water [21–23]. Depending on the TIOA/water ratio used, two alumoxanes with different formal structures were obtained: tetraisooctylalumoxane (TIOAO) **5** and polyisooctylalumoxane (TAO) **6** (Scheme 1).

The copolymerisations were performed either with TIOAO or TAO at different Al/Zr ratios. The same experiments were also repeated for comparison using MAO as cocatalyst.

2. Results and discussion

2.1. Synthesis of the zirconium complexes

The metal complexes **2** and **3** were prepared starting from commercial *rac*-EBTHIZrCl$_2$ as outlined in Scheme 2. **2** was prepared as re-



Scheme 2. (i) CH_3Li, Et_2O, −50°C; (ii) Triethylamine, 1,1′-bi-2-naphthol, toluene, 60°C.

ported in the literature by Waymouth et al. [17], while the binaphtholate derivative **3** was synthesised using 1,1′-bi-2-naphtol in toluene with triethylamine as HCl scavenger (a synthetic method which requires an easier work-up and gives higher and more reproducible yields compared to the sodium/binaphthol [18] or lithium binaphtholate [19] methods). The separation of the *rac* isomers was beyond the scope of this work; we only carefully checked that no racemisation to *meso* derivatives occurred during the reaction courses.

2.2. Synthesis of the alumoxanes

The alumoxanes were prepared (Scheme 1) by reaction of TIOA **4** with H_2O in a stoichiometric ratio of either 2:1, with the formation of

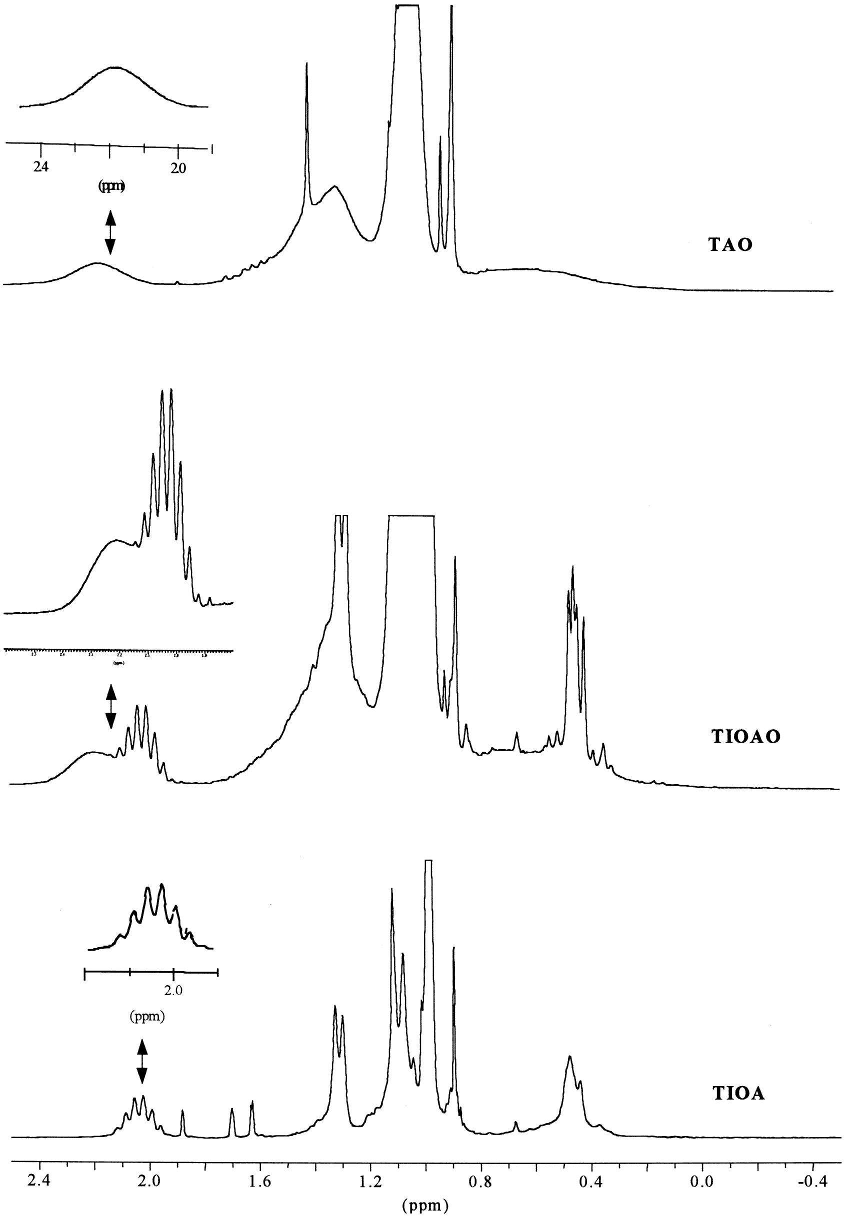


Fig. 1. ^1H NMR spectra (200.13 MHz, C_6D_6, 25°C, TMS reference) of TIOAO, TAO and TIOA.

TIOAO **5** [21,22], or 1:1, with the formation of TAO **6** [23].

2.3. NMR characterisation of the alumoxanes

The ^{1}H NMR spectra of TIOAO and TAO are shown in Fig. 1 and compared with the spectrum of TIOA.

The spectrum of TIOAO is characterised by the presence of two overlapped sets of signals in the region between 1.9 and 2.5 ppm. One set consists of broad bands typical of a polyalkylalumoxane and could be reasonably attributed to the oligomeric alumoxane; while the other, composed of sharp peaks and resolved multiplets as in TIOA, could be ascribed to the alkyl radicals belonging either to short chains of the alumoxane or to traces of residual TIOA, either in free or coordinated form.

In the TAO spectrum only a broad band is present. Based on the attributions attempted above, we can hypothesise that the TAO is only made of oligomeric alumoxane, while the presence of TIOA cannot be detected.

2.4. E/P copolymerisations

2.4.1. Copolymerisations results

Preliminary E/P copolymerisation tests were carried out using the metallocene *rac*-EBHIZrCl$_2$ with each of the alumoxanes (TIOAO, TAO or TIOA) as cocatalyst, at Al/Zr = 1000 (mol/mol). The results reported in Table 1 show that the catalytic system based on either TIOA or TAO was completely inactive, while an E/P copolymer was obtained with good catalytic activity (36 000 g polymer/g Zr) in the presence of TIOAO. The same behaviour was observed with *rac*-ethylene bis-indenyl zirconium dichloride (*rac*-EBIZrCl$_2$) in high-pressure ethene polymerisation [23].

To investigate the role played by the σ-ligands of those metallocenes, copolymerisa-

Table 1
E/P copolymerisations with *rac*-EBTHIZrR$_2$/alumoxane as catalytic system[a]

Run	Metallocene		Alumoxane	Al/Zr (mol/mol)	Yield (g)	Activity (g polymer/g Zr)	$(E)_{\text{copolymer}}$[b] (mol%)	IV[c] (dl/g)
	Type	μmol						
1	*rac*-EBTHIZrCl$_2$	1.7	TIOAO	1000	5.6	36 000	90.7	3.31
2	*rac*-EBTHIZrMe$_2$	1.7	TIOAO	1000	4.7	30 650	85.6	3.57
3	*rac*-EBTHIZr(BNP)	1.7	TIOAO	1000	2.9	19 050	94.3	3.53
4	*rac*-EBTHIZrCl$_2$	10.0	TIOAO	100	2.8	3150	89.2	n.a.[d]
5	*rac*-EBTHIZrMe$_2$	10.0	TIOAO	100	6.3	6700	89.1	4.55
6	*rac*-EBTHIZr(BNP)	10.0	TIOAO	100	0.74	800	84.7	4.48
7	*rac*-EBTHIZrCl$_2$	3.5	TIOA	1000	0	0	–	–
8	*rac*-EBTHIZrCl$_2$	3.5	TAO	1000	0	0	–	–
9	*rac*-EBTHIZrMe$_2$	3.5	TAO	1000	0.28	900	88.3	n.a.[d]
10	*rac*-EBTHIZrCl$_2$	1.7	TAO	10 000	0.71	4500	89.0	n.a.[d]
11	*rac*-EBTHIZrMe$_2$	1.7	TAO	10 000	4.7	30 100	82.2	n.a.[d]
12	*rac*-EBTHIZr(BNP)	1.7	TAO	10 000	~ 0	0	–	–
13	*rac*-EBTHIZrCl$_2$	9	MAO	100	3.35	4100	85.7	1.1
14	*rac*-EBTHIZrMe$_2$	9	MAO	100	4.05	5000	77.2	0.51
15	*rac*-EBTHIZr(BNP)	9	MAO	100	1.23	1500	84.3	1.06

[a] Polymerisation conditions: toluene = 100 ml, E/P mixture = 60/40 (wt./wt.) in gas phase; flow rate of (E + P) mixture = 1.5 l/min, $T = 50$°C, total pressure = 1.1 atm and polymerisation time = 15 min.

[b] From ^{1}H NMR analysis.

[c] Intrinsic viscosity.

[d] Not analysed.

tions were performed with each of the metallocenes (**1**, **2** or **3**) as catalyst and either with TIOAO or TAO as cocatalyst. The Al/Zr molar ratios used were 100 or 1000 for TIOAO, and 1000 or 10 000 for TAO. The results of those experiments are also reported in Table 1.

With TIOAO, at Al/Zr = 1000 (mol/mol), *rac*-EBTHIZrCL$_2$ and *rac*-EBTHIZrMe$_2$ exhibited a similar activity. However, when the Al/Zr molar ratio was reduced to 100, *rac*-EBTHIZrMe$_2$ became much more active than *rac*-EBTHIZrCl$_2$. In both cases, *rac*-EBTHIZr(BNP) was found to be the least efficient catalyst.

An important result that emphasises the role played by the σ-ligands was obtained by performing E/P copolymerisations in the presence of TAO. At a standard Al/Zr ratio (1000 mol/mol) only *rac*-EBTHIZrMe$_2$ showed catalytic activity. At higher Al/Zr ratios (10000 mol/mol) this alkylated metallocene still remained the most efficient, while also *rac*-EBTHIZrCl$_2$ began to show some activity.

E/P copolymerisations were performed also with MAO at Al/Zr = 100 (mol/mol) for comparison (see Table 1). In this case, quite similar polymerisation activities were observed with dichloride and dimethyl compounds (the dimethyl derivative showed actually a slightly higher activity), and the binaphtholate was again the least active.

From the characterisation of the E/P copolymers reported in Table 1, we can also observe that the chemical composition and the molecular mass of the copolymers are substantially independent of the nature of the σ-ligands. The molecular mass, on the contrary, seems to be affected by the nature of the cocatalyst, since MAO produces remarkably lower molecular masses in comparison with TIOAO.

2.4.2. Discussion

The role of the alumoxanes in the polymerisation mechanism has to be taken into account in the interpretation of the behaviour of the three metallocenes studied in E/P copolymerisations. In metallocene-based polymerisations, it is widely accepted that the alumoxanes have the double function of alkylating the metallocenes and of interacting with them to generate cationic metallocene-alkyl species. We can hypothesise that the aluminium alkyl (TIOA) acts as an alkylating species, while the oligomeric alumoxane plays the role of generating the ionic pair alkyl metallocene/alumoxane. It is clear that only TIOAO, which contains both TIOA and oligomeric alumoxane, is able to form catalytically active species and to produce (co)polymers. On the contrary, TIOA and TAO cannot promote polymerisations because the first lacks the species that generates the ionic pair function, and the latter lacks the alkylating agent.

In the light of this interpretation, if the presence of the aluminium alkyl in the alumoxane is undetectable (TAO), only *rac*-EBTHIZrMe$_2$, a metallocene with an alkyl group as σ-ligand, can be active. When the Al/Zr ratio increases, also *rac*-EBTHIZrCl$_2$ starts to show some activity. This result is probably due to the presence of such a small amount of aluminium alkyl that cannot be detected by NMR analysis, but which becomes significant at high Al/Zr ratios.

A similar interpretation accounts for the results obtained in the two series of TIOAO-based tests: in critical conditions (low Al/Zr ratio) only an alkylated metallocene as *rac*-EBTHIZrMe$_2$ looks favoured. Only if a strong alkylating alumoxane like MAO as cocatalyst is used can those differences be minimised.

rac-EBTHIZr(BNP) was found to be always the least active catalyst. Its low reactivity is probably due both to the presence of a bulky chelating σ-ligand that hinders the formation of the active species, and to the nature of the Zr–O bond, which is more difficult to be cleaved than the Zr–Cl bond. In fact, when experiment 6 (Table 1) was repeated, after ageing *rac*-EBTHIZr(BNP) for about 2 h and 40 min in the presence of a small amount of TIOA, its catalytic activity increased from 800 to 3000 (g polymer/g Zr) [24].

3. Conclusions

In E/P copolymerisations promoted by metallocene based catalytic system, an influence of the nature of σ-ligands of the metallorganic complex (i.e. two chloride or two methyl groups) was observed, in particular in “critical conditions”, i.e. with a weakly activating alumoxane or at a low Al/Zr ratio. This influence was remarkable with TIOAO, moderate (if any) with MAO. The metallocene with binaphtholate as σ-ligand, bidentate and sterically hindered, was less active than the other ones. We have demonstrated for the first time that a metallocene with alkyl radicals as σ-ligands is catalytically active also with an alumoxane in which the presence of an aluminium alkyl is undetectable.

It can be concluded that the nature of the σ-ligands of a metallocene affects the catalytic activity in ethene-based polymerisations depending on the alumoxane used and on its relative ratio with the metallocene. On the other hand, the σ-ligands do not seem to influence substantially the relative reactivity towards the comonomers and the molecular mass of the copolymers.

4. Experimental section

4.1. General procedures

All manipulations of air- and/or moisture-sensitive materials were carried out under inert atmosphere using a dual vacuum/nitrogen line and standard Schlenk techniques or in a dry-box under nitrogen atmosphere (<10 ppm oxygen, <20 ppm water). Nitrogen gas was purified by passage through columns containing, respectively, manganese (II) oxide suspended on vermiculite and 4-Å molecular sieves. Solvents and solutions were transferred through stainless-steel cannulae (diameter 0.5–2.0 mm) using a positive pressure of nitrogen, and mixtures were filtered in a similar way using modified cannulae which could be fitted with glass-fibre filter disks (Whatman GFC). All glassware and cannulae were thoroughly dried at 120°C, usually overnight, before use.

Unless otherwise specified, all reagents were purchased from commercial suppliers (Aldrich, Fluka and Carlo Erba) and used without further purification. *rac*-EBTHIZrCl$_2$, TIOA (1 M in hexane) and MAO (10% w/w in toluene) were purchased from Witco and used as provided by the supplier. Polymerisation-grade ethene and propene gases were received from Montell Ferrara plants. The E/P mixtures were prepared in a 5-l steel cylinder, filled with amounts of the two gases small enough to prevent their condensation. The composition of the gaseous mixture was controlled through GC analysis.

All solvents to be used under inert atmosphere were thoroughly deoxygenated and dehydrated before use. They were dried and purified by refluxing over a suitable drying agent followed by distillation under nitrogen, and stored under nitrogen in Young’s ampoules. The following drying agents were used: molten potassium for toluene, Na/K alloy for petroleum ether (b.p. 40–60°C) and diethyl ether. Triethylamine was refluxed over potassium hydroxide, distilled and stored in the dark over KOH. Toluene for polymerisations was deoxygenated by bubbling nitrogen, dried over CaCl$_2$, filtered, refluxed for 8 h over Al(isobutyl)$_3$ and distilled. Deuterated chloroform for use in NMR experiments of air-sensitive compounds was distilled over CaH$_2$ and stored under nitrogen in Young’s ampoules over 4-Å molecular sieves.

Nuclear magnetic resonance spectra were recorded on the following instruments: ^{1}H, 200.13 MHz, Bruker AC-200; ^{13}C, 50.32 MHz, Bruker AC-200. Spectra were referenced internally using the residual protio solvent resonance relative to tetramethylsilane ($\delta = 0$). All chemical shifts are quoted in δ (ppm) and coupling constants are given in Hz. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), multiplet (m).

Elemental analyses were performed using a Carlo Erba 1106 elemental analysis apparatus.

*4.2. Synthesis of (±) [ethylenebis(4,5,6,7-tetrahydro-1-indenyl)] zirconium binaphtholate **3***

1,1′-Bi-2-naphthol (1.5 mmol) was degassed, dissolved in toluene (100 ml) and added to *rac*-EBTHIZrCl_2 (1.5 mmol) suspended in 20 ml of toluene. The reaction mixture was heated to 60°C. After 2 min all solid dissolved completely. Triethylamine (1.8 mmol) was added and the solution turned cloudy immediately. The reaction mixture was stirred at 60°C for 2 h and at room temperature overnight. The resulting suspension was filtered through a cannula and the solid was washed an additional two times with toluene. Removal of the solvent from the collected liquid fractions left a foamy yellow solid, which was dried in vacuum with slight warming for about 1 h. Seventy milliliters of petroleum ether (40/60) was added and the mixture heated at 60°C for 3 h. The resulting suspension was filtered hot and the residual solid washed once with about 15 ml of petroleum ether. The NMR spectrum of the solid showed the presence of the raw binaphtholate complex, which was kept aside for further purification. The supernatant solution started to crystallise upon cooling and was stored at −15°C overnight to give the pure binaphtholate complex (yield 70%) as a yellow microcrystalline solid.

Anal. found: C, 75.8; H, 5.2. $C_{40}H_{36}O_2Zr$ (639.94) Calcd.: C, 75.1; H, 5.7%. ^{1}H NMR ($CDCl_3$): δ 1.15–2.00 (m, 12 H), 2.50–2.80 (m, 4 H), 3.10–3.4 (m, 4 H), 5.60 (d, 2 H, $J = 2.9$ Hz), 5.75 (d, 2 H, $J = 2.9$ Hz), 6.90 (d, 2 H, $J = 8.4$ Hz), 7.05 (t, 2 H, $J = 8.4$ Hz), 7.18–7.30 (m, 4 H), 7.75–7.95 (m, 4 H) ppm.

*4.3. Preparation of TIOAO **5***

The necessary amount of TIOAO was prepared each time just before use. We report here as an example the alumoxane synthesis for the preparation of sample 1. Five milliliters of toluene and 1.7 mmol (1.7 ml) of TIOA solution (1 M in hexane) were introduced in a Schlenk tube at room temperature. Then 0.85 mmol (15 μl) of distilled water were added, and the resulting solution was stirred for 10 min and siphoned off directly into the polymerisation reactor.

*4.4. Preparation of TAO **6***

The aforementioned procedure and work-up were also applied to the synthesis of TAO by using 1.7 mmol of TIOA and 1.7 mmol (30 μl) of distilled water.

4.5. Polymerisation procedures and polymer characterisation

4.5.1. E/P copolymerisation

The copolymerisations were carried out at 50°C in a 250-ml glass reactor kept in a thermostatic bath and equipped with a mechanical stirrer, a thermometer and a hose for monomer feeding. First, 100 ml of toluene and the desired amount of cocatalyst solution were introduced into the nitrogen-purged reactor. On reaching the polymerisation temperature, the nitrogen was replaced with the comonomer mixture, with a flow rate of 1.5 l/min. When the equilibrium pressure (1.1 atm) was reached, the desired amount (Table 1) of metallocene, dissolved in 5 ml of toluene in the presence of a small quantity of TIOA (or MAO, for tests 12–14 in Table 1) in $Al/Zr = 10$ mol/mol, was added to start the polymerisation. During the reaction the temperature was kept within 50 ± 0.2°C. After 15 min the polymerisation was quenched by adding 1 ml of methanol. The copolymer was recovered by precipitation in methanol/HCl, filtration and drying at 50°C under reduced pressure.

4.5.2. Polymer characterisation

The E/P mixtures were analysed using a Carlo Erba 4300 gas chromatograph, equipped with a 4 m, 6 × 4 mm, packed column in aluminium, with silicon oil "C" at 20% on Celite 22 60–80 mesh as stationary phase. A thermal conductivity detector was used.

^{1}H NMR spectra of the polymers were recorded on a DPX-200 Bruker spectrometer operating at 200.13 MHz in the Fourier transform mode at 120°C. The samples were prepared by dissolving 10 mg of copolymer in 0.5 ml of 1,1,2,2-tetrachloroethane-d_2 at 120°C. Each spectrum was acquired with a 15° pulse and 2 s of delay between pulses. About 32 transients were stored in 16 K data points using a spectral window of 2000 Hz.

Intrinsic viscosity (IV) of copolymers was determined in tetrahydronaphtalene at 135°C.

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