Random Propene/4-Methyl-1-pentene Copolymers Synthesized with C_2 Symmetric Highly Isospecific Metallocenes

Maria Carmela Sacchi,[1] Simona Losio,[1] Luigi Fantauzzi,[1,2] Paola Stagnaro,[3] Roberto Utzeri,[3] Maurizio Galimberti[1,4]

[1] Istituto per lo Studio delle Macromolecole ISMAC – CNR Via Bassini, 15 – 20133 Milano, Italy
[2] Università dell'Insubria, Dipartimento di Scienza e Alta Tecnologia, via Valleggio, 11 – 22100 Como, Italy
[3] Istituto per lo Studio delle Macromolecole ISMAC – CNR Via De Marini, 6 – 16149 Genova, Italy
[4] Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering G. Natta, Via Mancinelli 7 – 20131 Milano, Italy
Correspondence to: M. C. Sacchi (E-mail: sacchi@ismac.cnr.it)

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INTRODUCTION Propene (P)-based polymers are very important in the materials' world. Worldwide, about 50 million tons of semicrystalline propene homopolymers and copolymers and more than 1 million tons of ethene-propene elastomers are consumed every year.[1] Research on these materials is well active in industrial and academic laboratories: catalysts,[2–6] polymer structures, and properties[7] are investigated. In this scenario, semicrystalline propene copolymers present interesting novelties. In fact, besides products based on ethene and 1-butene, which have been known for long time, propene copolymers with higher 1-olefins find increasing applicative interest. Grades containing 1-hexene are produced for pipe, film, and healthcare segments,[8] whereas products based on 4-methyl-1-pentene (Y) show good flexibility, shape followability, and stress absorbing properties.[9] Propene copolymers with contents up to about 3% by moles of a comonomer, such as ethene or higher 1-olefins are known as "random" copolymers: the term random is actually used to indicate the absence of comonomer sequences along the polymer chain, rather than a particular value of the product of copolymerization reactivity ratios. They are traditionally prepared with heterogenous isospecific titanium-based catalysts, whose multisite nature intrinsically gives rise to a multiplicity of copolymer microstructures.[10] It is widely acknowledged that single site metallocene and post-metallocene-based catalysts are the ideal systems for controlling the comonomer incorporation in the polymer chain.[11] It could be thus expected that single site catalyst(s) should be available for preparing real random P/Y copolymers. However, results available in the literature demonstrate that single site metallocene-based catalysts not

In memory of Prof. Adolfo Zambelli who passed away on 21th January 2015. We would like to recognize his outstanding contribution to the field of macromolecular chemistry. Many research groups around the world draw inspiration from his groundbreaking work and, to this day, new lines of research build on some early intuitions that he had as a young and bright scientist. Prof. Zambelli's rigorous approach, vivid curiosity and keen observation of reality have been and continue to be an example for fellow researchers and a testimony to his genuine passion for science and, ultimately, for truth.

necessarily prepare 1-olefins copolymers with random distribution of comonomers. Indeed, sterically hindered highly isospecific metallocenes promoted E/P copolymerizations with high r_1r_2 product ($r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$),[12–15] due not only to r_1 value much larger than 1 but also, in most cases, to unusually high r_2 values. The comparison between meso and racemic sterically hindered metallocenes allowed to identify the high isospecificity of the catalytic system as the key feature to obtain such high r_1r_2 values.[13] When a bulky comonomer, such as Y, was used, high r_1r_2 values were obtained even with moderately isospecific metallocenes: E/Y copolymerizations were characterized by r_2 values larger than those detected in the case of E/P copolymerizations, regardless of the isospecificity of the catalytic system.[16,17]

In the field of insertion polymerization, it is widely acknowledged that the enantioselectivity of the catalytic site is given by the cooperation of the organometallic complex and of the growing chain.[18,19] The presence of a bulky comonomer such as Y in α or in β position with respect to the transition metal, that indeed occurs in the case of E/Y copolymerizations, thus enhances the isoselectivity of the catalytic site. In the case of E/1-olefin copolymerization, it was forecasted that the trend for a reactivity ratio “should be rationalized in terms of nonbonded interactions of the incoming monomer with some carbon atoms of the growing chain, for example, the carbon in β- or even γ-position from the metal.”[19] Even in the presence of such wide prior art, a reasonable forecast of the comonomer distribution in the propene-based copolymer appears not possible. Thus, in order to prepare P/Y copolymers with tailor made properties, it appears to be of great importance to elicit the correlation between enantioselectivity of catalytic centre and reactivity ratios of comonomers.

Herein we report on P/Y copolymerizations promoted by three metallocenes characterized by different enantioselective ability in propene homo-polymerization: the stereospecificity increases from the moderately isospecific *rac*-Et(IndH$_4$)$_2$ZrCl$_2$ (**EBTHI**), to *rac*-Me$_2$Si(2-Me-BenzInd)$_2$ZrCl$_2$ (**MBI**) and up to the highly isospecific *rac*-CH$_2$(3-^{t}BuInd)$_2$ ZrCl$_2$ (**TBI**). Copolymers were prepared in solution, over a wide range of chemical composition, determining their molar mass by size exclusion chromatography (SEC) and the comonomer sequences, at the triad level, through ^{13}C NMR analysis.[20] Statistical elaboration of copolymerization data, by applying first- and second-order Markovian models, allowed to calculate the reactivity ratios of the copolymerizations.

EXPERIMENTAL

General Experimental Details

All experiments and manipulations involving air-sensitive compounds were carried out under dry nitrogen atmosphere in glovebox or by using standard Schlenk line techniques. Methylaluminoxane (MAO) (Sigma-Aldrich) was used after removing all volatiles and drying the resulting powder at 50 °C for 3 h under reduced pressure (0.1 mmHg), in order to improve its storage stability. **EBTHI** complex was provided by Basell Poliolefine Italia. **MBI** complex was donated by Targor. **TBI** complex was kindly donated by L. Resconi. Toluene (Fluka > 99.5% pure) was refluxed over Na for about 8 h and stored over molecular sieves under nitrogen. 4-methyl-1-pentene (Aldrich, ≥ 99% pure) was refluxed over LiAlH$_4$, then distilled trap-to-trap and, finally, stored under nitrogen and kept at 0 °C. Nitrogen and propene gases were dried and deoxygenated by passage over columns of CaCl$_2$, molecular sieves, and BTS catalysts. Deuterated solvent for NMR measurements (C$_2$D$_2$Cl$_4$) (Cambridge Isotope Laboratories) was used as received.

Copolymerizations

The copolymerizations were performed at 50 °C, in a 250 mL glass reactor equipped with a magnetic stirrer according to a standard procedure. Run M1 is reported as an example: 100 mL of anhydrous toluene, the proper amounts of Y, and MAO were added in the said order. After thermal equilibration of the reactor system, propene was continuously added until saturation. The polymerization was typically started by adding 2 μmol of the metallocene to the mixture via syringe. A small amount of MAO (10 wt % of the total) is added to the metallocene to preactivated it. The final Al/Zr molar ratio was in the range between 1200 and 3000, depending on the experiment. The pressure of propene was kept constant at 1.08 bar for all the experiments. The copolymerization was terminated after 15 min by adding a small amount of ethanol and dilute hydrochloric acid, and polymers were precipitated by addition of the whole reaction mixture to ethanol (1000 mL) to which concentrated hydrochloric acid (5 mL) had been added. In most experiments, under the reaction conditions adopted, a Y conversion lower than 10% was obtained, which means that the ratio Y/P can be considered basically constant throughout the polymerization. The copolymer samples were collected by filtration and dried under vacuum at 70 °C.

Nuclear Magnetic Resonance

For ^{13}C NMR, about 100 mg of copolymer was dissolved in C$_2$D$_2$Cl$_4$ in a 10 mm tube. HDMS (hexamethyldisiloxane) was used as internal chemical shift reference. The spectra were recorded on a Bruker NMR AVANCE 400 Spectrometer equipped with a SEX 10 mm probe with automatic matching and tuning, operating at 100.58 MHz (^{13}C) in the PFT mode working at 103 °C. The applied conditions were the following: 10 mm probe, 14.30 μs as 90° pulse angle; 64 K data points; acquisition time 5.56 s; relaxation delay 20 s; 3−4 K transient. Proton broad-band decoupling was achieved with a one-dimensional sequence using bi_waltz_16_32 power-gated decoupling.

Molecular Analysis

The weight average molar mass (M_w) and the molar mass distribution (M_w/M_n) were obtained by a high temperature Waters GPCV2000 SEC system using two online detectors: a differential viscometer and a refractometer. The experimental conditions consisted of three PL Gel Olexis columns, *o*-DCB

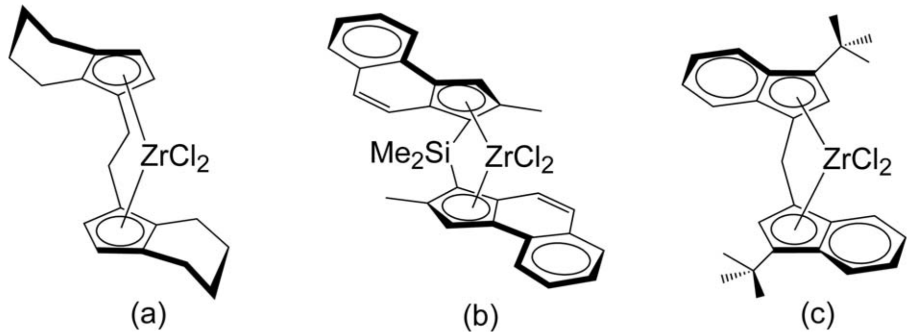


FIGURE 1 C_2 symmetric metallocenes under investigation: (a) **EBTHI**, (b) **MBI**, and (c) **TBI**.

as the mobile phase, 0.8 mL min^{-1} flow rate, and 145 °C temperature. The calibration of the SEC system was constructed using eighteen narrow M_w/M_n polystyrene standards with molar masses ranging from 162 to 5.6 × 10^6 g mol^{-1}. For SEC analysis, about 12 mg of polymer was dissolved in 5 mL of *o*-DCB with 0.05% of BHT as antioxidant.

RESULTS AND DISCUSSION

Copolymerizations

Figure 1 shows the metallocene complexes used in this work. Namely, **EBTHI**, **MBI**, and **TBI** that belong to the class of C_2-symmetric metallocenes were selected, as mentioned in the "Introduction" section, as they are endowed with different stereospecificity.

Table 1 collects data available in the literature on microstructure of polypropene (PP) prepared with such metallocenes. Both stereospecificity and regiospecificity decrease in the order **TBI** > **MBI** > **EBTHI**.[21–25]

Three series of P/Y copolymerization reactions were conducted with MAO activated **EBTHI**, **MBI**, and **TBI**. Copolymerization and molecular characterization data are shown in Table 2. [Y]/[P] feed ratio varied from 0.03 to 3.00 mol/mol and this allowed the preparation of copolymers in wide ranges of chemical composition, from about 3 to about 90 as Y mol %. To maintain nearly constant the comonomer concentration in solution throughout the reaction course, low Y conversion was adopted (up to about 15%).[15] Catalyst concentrations and polymerization times were thus adjusted in order to obtain reasonable copolymer yields. In particular, with **MBI**, catalyst amounts up to 10 μmol were used and polymerization times up to 2 h were adopted. Rigorous comments on catalytic activities cannot be made, as the polymerization conditions were not exactly reproduced. It is only possible to observe the decrease of the catalytic activity as the Y content in the polymerization bath increases for copolymerizations promoted by all of the three metallocenes and, in particular, by **MBI**. Catalytic activities in homopolymerization and copolymerization of metallocenes adopted for the present work are reported in the literature.[11(a),21]

TABLE 1 Microstructure of PP Obtained with the Three Different Metallocene Complexes and MAO as the Cocatalyst

Catalyst	I.I.^{a} (mmmm%)	Regiomistakes (%)	Ref.
EBTHI	91.5	1.0	15
MBI	93.0	0.3	21
TBI	97.0	0.0	15

^{a} I.I.: Isotactic index.

Polydispersity index values (in most cases equal to about 2) are in accordance with the single centre nature of the metallocene-based catalytic systems. One can observe that **MBI** leads to fairly high molar mass values, while samples produced from **TBI** and **EBTHI** exhibit lower molar masses. Moreover, it can be noticed that with **MBI**, the copolymer molar mass decreases as the Y content increases.

^{13}C NMR Analysis

Comonomer content and microstructure of the copolymers were determined by means of ^{13}C NMR spectroscopy. The general structure of P/Y copolymer is shown in Scheme 1.

Carbons are labeled according to the nomenclature first defined by Carman and Wilkes[26] and modified by Dorman et al.,[27] and Randall,[28] where P, S, and T refer to the primary (methyl), secondary (methylene), and tertiary (methine) carbons of the main chain, respectively. Methylene carbons along the backbone were identified by a pair of Greek letters to indicate the distance to branches in either directions. Methyl, methylene, and methine carbons in the side chain were designated, respectively, by the symbols CH_3(sc), CH_2(sc), and CH(sc).

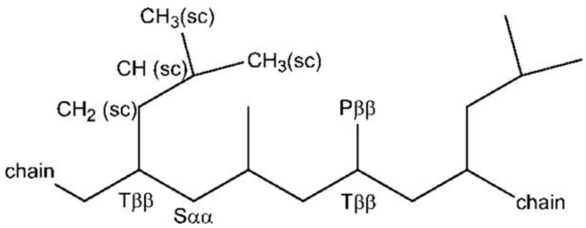
Figure 2 shows the ^{13}C NMR spectra of P/Y copolymers with similar comonomer content (about 15 mol %) from **EBTHI**, **MBI,** and **TBI** catalysts. Figures 3 and 4 show the expanded methylene regions of copolymers having higher Y content (about 60 and about 80 mol %, respectively). In Figure 2(a), the complete spectrum assignment according to ref. 20 is shown. Because of the low molar masses, several small signals are detected in the spectra of the copolymers obtained with **EBTHI** and **TBI** as catalyst precursors, that are assigned to a variety of chain end groups (starred signals in spectra a and c).[29,30]

TABLE 2 Copolymerization Data for P/Y System with Different Metallocene Catalysts[a]

Catalyst	Run	Y/P[b] (mol/mol)	*t* (min)	[catalyst] μmol	Al/Zr (mol/mol)	Activity[c]	Y[d] (mol %)	Conversion%	M_w[e] ($\times 10^3$)	M_w/M_n[e]
EBTHI	E1	0.04	10	1.1	3,000	2,406	1.88	2.9	20	2.1
	E2	0.08	10	1.1	3,000	2,345	3.57	2.5	16	1.9
	E3	0.12	10	2.5	3,000	2,213	5.70	5.8	10	1.8
	E4	0.22	10	2.6	3,000	503	9.92	1.3	10	1.8
	E5	0.33	15	6.0	3,000	754	15.74	5.8	7	1.8
	E6	0.42	15	4.1	3,000	1,202	18.72	5.9	8	1.8
	E7	0.86	15	3.5	3,000	1,166	35.88	3.6	11	1.9
	E8	1.21	30	3.0	3,000	388	43.00	2.0	7	1.8
	E9	1.75	45	3.4	3,000	562	53.27	4.2	7	1.8
	E10	1.84	45	3.3	3,000	146	60.75	1.1	6	1.9
	E11	2.43	90	7.0	3,000	136	67.21	2.9	10	2.1
	E12	3.00	60	5.0	3,000	506	85.81	5.4	43	2.1
MBI	M1	0.03	15	2.0	3,000	1,246	3.00	7.6	133	2.5
	M2	0.05	15	1.1	3,000	1,286	5.27	6.5	130	2.1
	M3	0.06	15	2.2	3,000	1,195	8.79	9.7	69	2.3
	M4	0.07	15	2.2	3,000	1,019	10.10	8.2	66	2.3
	M5	0.17	15	1.6	3,000	586	14.86	3.7	62	1.9
	M6	0.30	15	2.6	3,000	173	22.82	1.4	40	2.1
	M7	0.46	30	3.9	3,000	90	29.72	1.8	25	2.0
	M8	0.60	90	10.0	1,200	82	51.95	13.6	20	2.2
	M9	1.19	60	10.0	1,200	46	62.77	2.9	47	3.9
	M10	1.74	90	10.0	1,200	70	73.53	5.0	44	3.2
	M11	1.84	120	10.0	1,200	111	76.94	10.4	18	2.6
	M12	2.43	90	10.0	1,200	70	81.06	3.8	24	2.9
	M13	3.00	60	10.0	1,200	130	88.70	4.0	15	1.9
TBI	T1	0.03	10	2.0	3,000	2,493	2.95	15.0	12	1.5
	T2	0.05	25	2.0	3,000	936	4.99	13.2	19	2.3
	T3	0.11	12	5.0	1,200	1,436	10.60	14.2	10	1.8
	T4	0.17	10	2.0	3,000	927	15.10	4.5	15	2.1
	T5	0.30	12	5.0	1,200	390	22.72	5.8	12	1.8
	T6	0.46	18	5.0	1,200	786	32.32	12.1	12	2.1
	T7	0.86	15	5.0	1,200	482	43.88	4.4	12	1.8
	T8	1.19	30	5.0	1,200	861	59.57	13.2	13	1.9
	T9	1.74	18	5.0	1,200	923	68.39	6.3	18	1.8
	T10	2.43	15	5.0	1,200	531	82.58	2.4	10	1.7
	T11	3.00	15	5.0	1,200	446	90.81	1.7	38	2.1

[a] Polymerization conditions: total volume = 100 mL, T = 50 °C, P = 1.08 atm, Al/Zr = 3,000–1,200 (mol/mol), **EBTHI**: T = 30 °C, Al/Zr = 3,000.
[b] Y/P feed ratio in liquid phase.
[c] $mg_{pol}/(mmol_{Zr}\ h)$.
[d] From ^{13}C NMR analysis.
[e] Molar mass and polydispersity index from SEC analysis.

Spectra reported in Figures 2–4 allow some qualitative comments on the comonomer distributions obtained with the three different catalyst precursors. Copolymers having low Y content (around 15 mol %) have apparently similar ^{13}C NMR spectra, as shown in Figure 2. Clear differences are not appreciable among their patterns. The differences become detectable by increasing Y content, as revealed by the inspection of the expanded region of Y side chain methylene carbon (Figs. 3 and 4). In fact, the relative intensity of the signal due to CH_2(sc) of Y$\underline{YYY}$Y pentad (43.65 ppm) with respect to that of the signal due to CH_2(sc) of P$\underline{YYY}$Z pentad (Z means P or Y) is higher in copolymers from **MBI** and **EBTHI** compared to copolymers from **TBI**.



SCHEME 1 Structure and carbon labeling of P/Y copolymer.

Analogously, the relative intensity of the signal due to the centered αα-methylene of YYYY tetrad at 40.05 ppm with respect to the signal of the PYYZ tetrad at 39.90 ppm is lower in copolymers from **TBI**. These comments arise by observing the spectra of copolymers with 60 mol % as Y content (shown in Fig. 3) and, in particular, the spectra of copolymers with about 80 mol % as Y content (shown in Fig. 4). Thus, **EBTHI** and **MBI** seem to reveal a higher ability to form Y homosequences with respect to **TBI**.

Triad molar fractions for copolymers from **EBTHI**, **MBI**, and **TBI** up to about 70% in comonomer content are reported in Table 3.[3131] These values were obtained from ^{13}C NMR spectra, applying a best fitting procedure.[20(a)] The analysis of the data of Table 3 shows that, in general, the relative content of YYY triad is higher in copolymers prepared with **MBI** and **EBTHI** rather than in copolymers from **TBI**. In fact, by examining, as an example, data of copolymers with about 60% by moles as Y content, whose ^{13}C NMR spectra are shown in Figure 3, it appears that copolymer from **TBI** with 59.57 mol % as Y content (Run T8) has 21.6 mol % as YYY triad, whereas copolymers from **MBI** with 62.77 mol % as Y content (Run M9) and from **EBTHI** with 60.75 mol % as Y content (Run E10) have 30.2 mol % and 33.7 mol % as YYY triad content, respectively.

Statistical Analysis of Copolymerization Data

Data on polymer bath composition, reported in Table 2, and on triad molar fractions, reported in Table 3 (obtained according to a best-fitting procedure described in Supporting

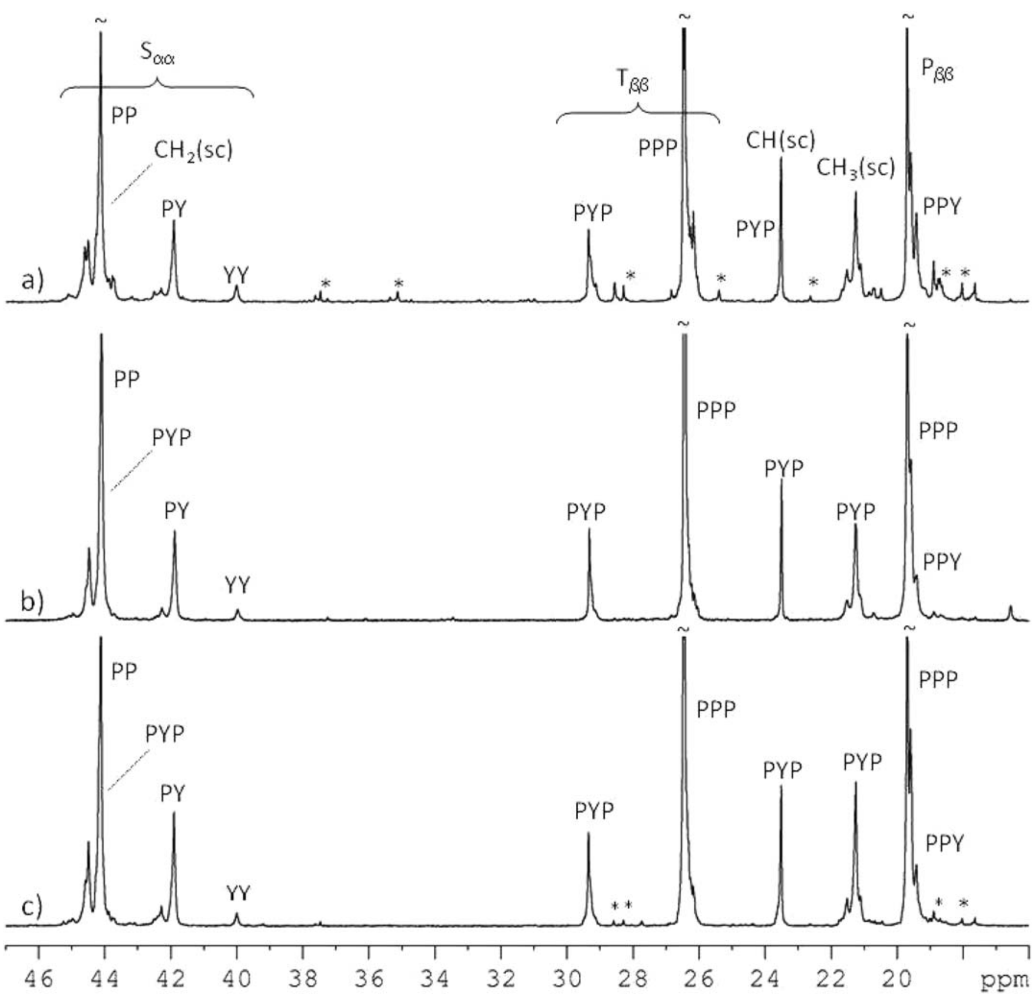


FIGURE 2 ^{13}C NMR spectra of P/Y copolymers with similar comonomer content: (a) 15.74 mol % content prepared with **EBTHI** (run E5 in Table 2), (b) 14.86 mol % content prepared with **MBI** (run M5 in Table 2), and (c) 15.10 mol % content prepared with **TBI** (run T4 in Table 2).

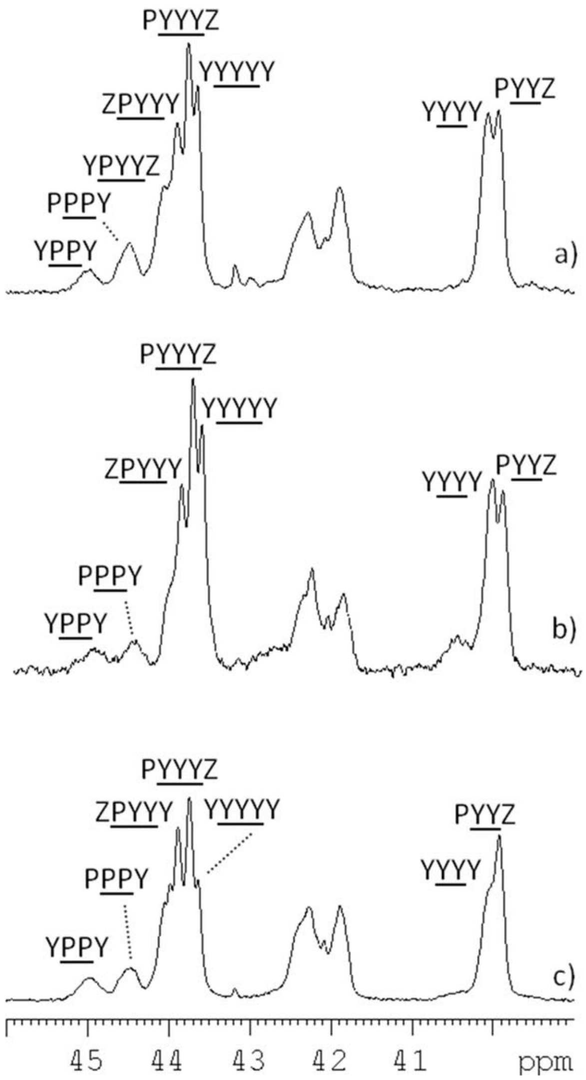


FIGURE 3 ^{13}C NMR spectra of P/Y copolymers with similar comonomer content: (a) 60.75 mol % content prepared with **EBTHI** (run E10 in Table 2), (b) 62.77 mol % content prepared with **MBI** (run M9 in Table 2), and (c) 59.57 mol % content prepared with **TBI** (run T8 in Table 2). Z means P or Y.

Information for selected samples), were elaborated with a statistical method,[12] already applied to E/P[13–15] and E/Y[15–17(a)] copolymerizations, that allows to estimate the copolymerization reactivity ratios as well as their product. The first-order Markovian model was applied to obtain the values, reported in Table 4, of r_1 and r_2 reactivity ratios, with their confidence intervals, and of the product of reactivity ratios r_1r_2. The reactivity ratios are defined as follows:

$$r_1 = k_{11}/k_{12}$$

$$r_2 = k_{22}/k_{21}$$

where k_{ij} is the rate constant of the reaction for the addition of the comonomer j to a growing chain bearing the comonomer i as the ultimate inserted unit.

The lowest value of product of reactivity ratios r_1r_2, not far from 1, was obtained with **TBI** as the catalyst precursor. More in particular, copolymerizations from **TBI** revealed the lowest value of r_1 and a value of r_2 close to the lowest one. The most random distribution of the comonomers appears thus to be obtained with the most isospecific metallocene.

The highest value of r_1r_2 product was obtained with the least isospecific metallocene, **EBTHI**, and was mainly due to a high value of r_1. It is worth observing that the value of r_2 is larger than 1 for copolymerizations from all of the three metallocenes and is larger than the r_1 value for copolymerizations from **MBI** and **TBI**. In the literature, r_2 value higher

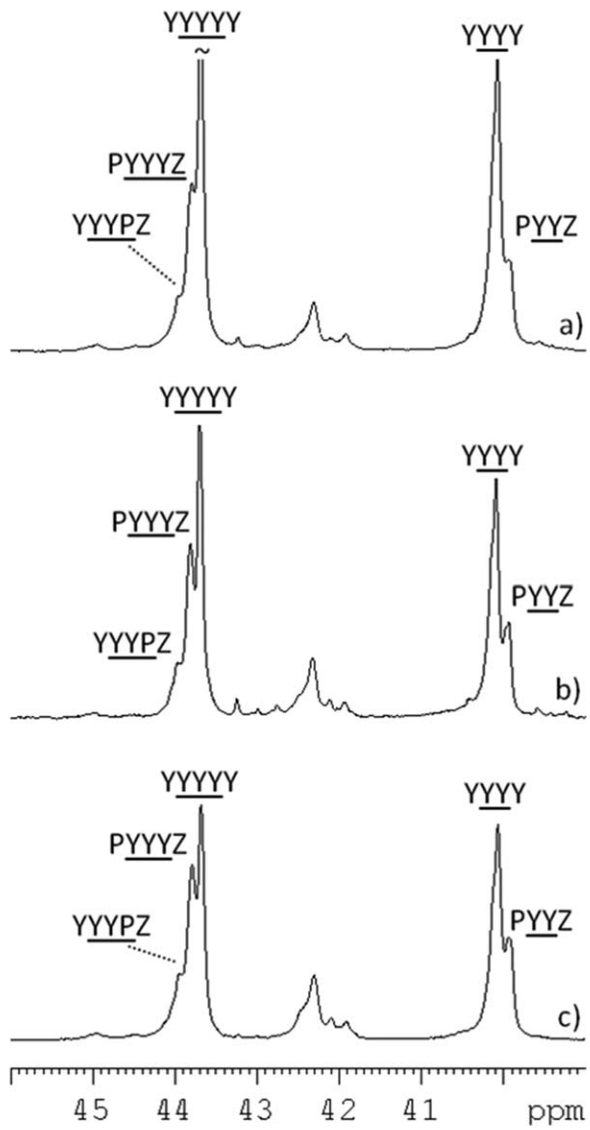


FIGURE 4 ^{13}C NMR spectra of P/Y copolymers with similar comonomer content: (a) 85.81 mol % content prepared with **EBTHI** (run E12 in Table 2), (b) 81.06 mol % content prepared with **MBI** (run M12 in Table 2), and (c) 82.98 mol % content prepared with **TBI** (run T10 in Table 2). Z means P or Y.

TABLE 3 Triad Molar Fractions from ^{13}C NMR Spectra of P/Y Copolymers Prepared with **EBTHI**, **MBI**, and **TBI** as Catalyst Precursors

				Triad					
Run	Y/P	Y (mol%)[a]	R^{2b}	PPP	PPY	YPY	PYP	PYY	YYY
E3	0.12	5.70	99.68	0.847	0.088	0.008	0.049	0.006	0.002
E4	0.22	9.92	99.92	0.739	0.139	0.016	0.067	0.037	0.004
E5	0.33	15.74	99.75	0.629	0.177	0.028	0.091	0.052	0.022
E7	0.86	35.88	99.84	0.312	0.244	0.072	0.078	0.232	0.062
E8	1.21	43.00	99.79	0.198	0.265	0.077	0.120	0.179	0.160
E9	1.75	53.27	99.74	0.108	0.241	0.089	0.126	0.168	0.267
E10	1.84	60.75	99.86	0.095	0.219	0.091	0.142	0.116	0.337
E11	2.43	67.21	99.93	0.042	0.172	0.098	0.133	0.102	0.451
M1	0.03	3.00	99.59	0.907	0.062	0.000	0.030	0.001	0.000
M2	0.05	5.27	99.86	0.856	0.086	0.005	0.045	0.006	0.001
M3	0.06	8.79	99.84	0.770	0.130	0.012	0.072	0.010	0.005
M4	0.07	10.03	99.68	0.732	0.154	0.013	0.087	0.007	0.007
M5	0.17	14.86	99.85	0.612	0.210	0.029	0.125	0.018	0.005
M6	0.30	22.82	99.41	0.479	0.256	0.036	0.135	0.059	0.034
M7	0.46	29.72	99.82	0.428	0.198	0.077	0.100	0.151	0.046
M8	0.60	51.95	99.87	0.136	0.237	0.108	0.020	0.313	0.187
M9	1.19	62.77	99.44	0.121	0.122	0.130	0.057	0.268	0.302
M10	1.74	73.53	99.83	0.046	0.080	0.139	0.031	0.296	0.408
T1	0.03	2.95	99.65	0.917	0.051	0.002	0.025	0.005	0.000
T2	0.05	4.99	99.87	0.868	0.075	0.008	0.043	0.005	0.003
T3	0.11	10.60	99.84	0.742	0.134	0.018	0.071	0.028	0.007
T4	0.17	15.10	99.40	0.573	0.236	0.023	0.116	0.051	0.001
T5	0.30	22.72	99.78	0.490	0.238	0.045	0.133	0.062	0.032
T6	0.46	32.32	99.86	0.313	0.248	0.084	0.131	0.159	0.064
T7	0.86	47.88	99.90	0.143	0.250	0.129	0.188	0.133	0.157
T8	1.19	59.57	99.81	0.031	0.163	0.175	0.096	0.320	0.216
T9	1.74	68.39	99.78	0.085	0.091	0.139	0.053	0.265	0.367

[a] From diad distribution.

[b] Total discrepancy function.[20(a)]

than 1 has not been reported for E/P copolymerizations.[13] Moreover, the r_2 values appear higher than those reported for metallocene catalyzed copolymerizations of propene with higher 1-olefins,[32] suggesting a particularly easy formation of Y homosequences. The r_2 value appears also higher than that observed in the literature for the same pair of comonomers in the presence of *rac*-$Me_2Si(4\text{-Ph-2MeInd})_2ZrCl_2$ where the comonomer content was very low (up to 7 mol %). In previous works,[13–17(a),33–36] the correlation between catalytic system and copolymer microstructure was elucidated taking into consideration the effect of both the two last inserted units (ultimate and penultimate effect).[37] Copolymerization data were thus elaborated with the second-order Markovian model, that takes into account also the penultimate effect. As a consequence of the adoption of the second-order Markovian model, the following reactivity ratios are derived:

$$r_{11} = k_{111}/k_{112,}$$

$$r_{21} = k_{211}/k_{212}$$

$$r_{22} = k_{222}/k_{221}$$

$$r_{12} = k_{122}/k_{121}$$

TABLE 4 Reactivity Ratios for P/Y Copolymerizations with Different Metallocene Catalysts

Catalyst	r_1	r_2	r_1r_2
EBTHI	2.20 ± 0.28	1.33 ± 0.38	2.93 ± 1.12
MBI	1.13 ± 0.11	1.97 ± 0.23	2.25 ± 0.48
TBI	0.96 ± 0.10	1.27 ± 0.17	1.22 ± 0.29

TABLE 5 R Parameter, r_{ij} Reactivity Ratios and CDI, Calculated with a Second-Order Markovian Model for P/Y Copolymerizations from Isospecific Organometallic Complexes

	r_{11}	r_{21}	r_{12}	r_{22}	CDI[a]	R[b]
EBTHI	2.029 ± 0.199	2.034 ± 0.511	0.445 ± 0.111	2.012 ± 0.307	2.47 ± 0.82	4.40
MBI	1.198 ± 0.139	0.705 ± 0.170	1.364 ± 0.343	1.923 ± 0.233	1.72 ± 0.55	0.76
TBI	1.014 ± 0.075	0.681 ± 0.108	0.968 ± 0.163	1.548 ± 0.183	1.18 ± 0.28	0.86

[a] CDI calculated according to the formula $CDI=\sqrt[3]{r_{11}^2 r_{22}^2 r_{12} r_{21}}$

[b] $R = (P/Y)_{copolymer}/(P/Y)_{feed}$.

where k_{ijk} is the rate constant of the reaction for the addition of the comonomer k to a growing chain bearing the comonomers i and j as the penultimate and the ultimate inserted units, respectively. Values for r_{ij} reactivity ratios as well as for comonomer distribution index (CDI) are reported in Table 5. CDI index corresponds to the r_1r_2 product of reactivity ratios derived from the first-order Markovian model and has the same meaning: a high CDI value indicates the presence of relatively long sequences of comonomers.[38]

At a first sight, data reported in Table 5 confirm that, in the P/Y copolymerization promoted by **TBI**, the comonomer distribution is close to the random one, as indicated by the value of the CDI (CDI $\sim$ 1). The larger CDI values, observed for **MBI** and **EBTHI**, indicate that copolymers with prevailingly sequential enchainment of comonomers are obtained with metallocenes with lower isospecificity, in particular with **EBTHI**. Data in Table 5 allow to investigate the relative reactivity of P with respect to Y, as a function of chain end sequences. In fact, the values of r_{11}, r_{21}, $1/r_{12}$, and $1/r_{22}$ provide the relative reactivity of P versus Y when chain end sequences are PP, YP, PY, and YY, respectively. Such relative reactivities are shown in the bar chart of Figure 5.

For **TBI** as the catalyst precursor, P and Y have almost the same reactivity when PP is the sequence on the Zr atom (r_{11} value is about 1) and the Y reactivity increases to a minor extent when at least one of the two last inserted units is Y (r_{21} as well as $1/r_{12}$ and $1/r_{22}$ values are not so far from 1 and are rather close to each other). It appears that two comonomers such as P and Y, though endowed with different steric encumbrance, have very similar reactivity toward a catalytic site based on a highly isospecific metallocene. Similar findings are observed with **MBI** as the catalyst precursor. However, the P/Y reactivity ratios is higher than 1 when PP are the two last inserted comonomer units, whereas the Y reactivity becomes prevailing when Y is one of the two last inserted units and, in particular, when YY is the sequence on the Zr atom. The least isospecific metallocene, **EBTHI**, shows remarkably different behavior. The P/Y relative reactivity is much higher when P is one of the two last inserted units and only the homo YY sequence promotes a higher Y reactivity.

As reported in the Introduction, highly isospecific metallocenes were found able to promote E/P copolymerizations with high r_1r_2 product.[12–15] Also moderately isospecific metallocenes were demonstrated able to give rise to ethene copolymerization with high r_1r_2 product, when Y was the 1-olefin. This latter result was explained with the enhanced isoselectivity of the catalytic system, thanks to the cooperation between the organometallic complex and the growing chain containing the bulky Y comonomer.[16(a)]

Rationalization of the results reported in this work can be attempted, taking into account such prior art. It can be hypothesized that, in the case of the metallocene with the lowest isospecificity, **EBTHI**, the different bulkiness of P and

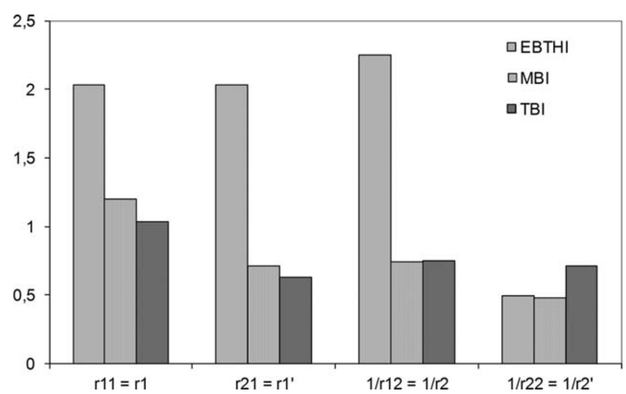


FIGURE 5 P/Y relative reactivity (r_1, $r_{1'}$, $1/r_2$, and $1/r_{2'}$) obtained from second-order ($r_1 \neq r_{1'}$ and $r_2 \neq r_{2'}$) reactivity ratios for copolymerizations promoted by **MBI**, **TBI**, and **EBTHI**.

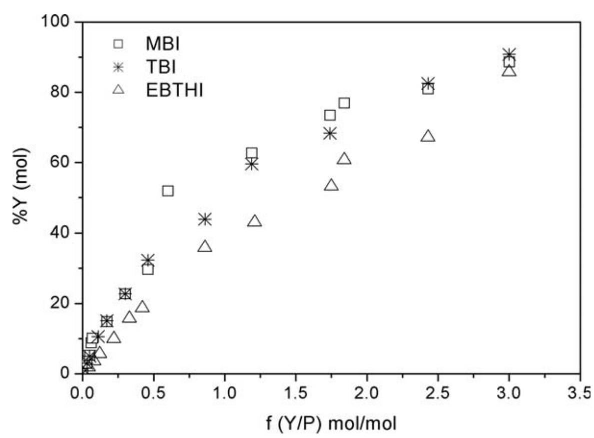


FIGURE 6 Y molar content in P/Y copolymer as a function of Y/P molar ratio in the polymerization bath.

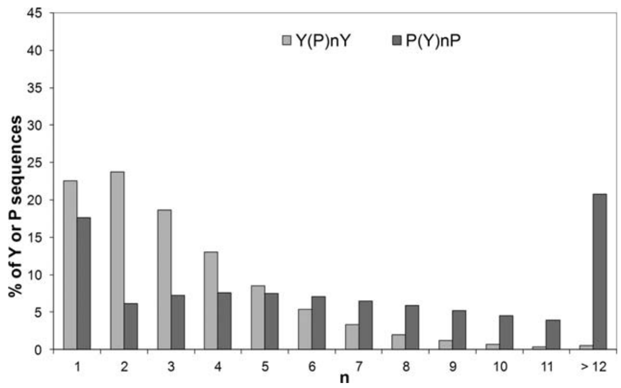


FIGURE 7 Probabilities of sequences of *n* comonomer units for run E10 in Table 2 (Y = 60.75 mol %).

Y favors the formation of P sequences. The tendency to form Y sequences could be explained with the insertion of Y unit(s) that causes the enhancement of the isospecificity of the catalytic site. In the case of **EBTHI**, two Y units are required to observe the increase of probability of a further Y insertion. To explain why Y insertion, in the polymer chain growing on the **EBTHI**-based site, occurs to such an extent to justify sequences formation, the P/Y relative reactivity toward the catalytic centre can be taken into consideration. This reactivity is indicated by the *R* parameter, given by the expression reported above, where 1 and 2 are P and Y, respectively.

By examining the *R* values shown in Table 5, it is clear that **EBTHI** has much higher reactivity for P, whereas **MBI** and **TBI** show slightly higher reactivity for Y. Figure 6 shows the Y content in the copolymer as a function of the P/Y molar ratio in the polymerization bath. Hence, to prepare P/Y copolymers with a given comonomer content, larger Y concentration in the polymerization bath has to be used in the case of **EBTHI**. The formation of long sequences of both P and Y, in P/Y copolymers from **EBTHI**, could be thus explained as follows: the preferential reactivity of **EBTHI** for P and the increase of Y relative reactivity after Y insertions that occur as a consequence of the larger Y concentration in the polymerization bath.

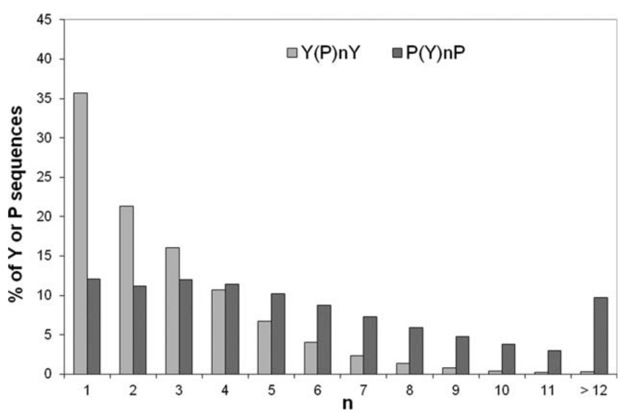


FIGURE 8 Probabilities of sequences of *n* comonomer units for run M9 in Table 2 (Y = 62.77 mol %).

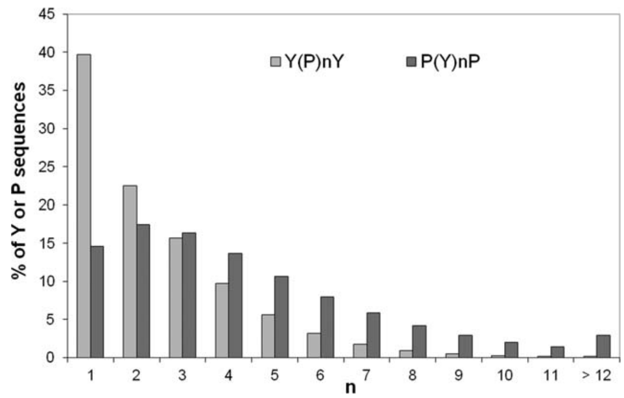


FIGURE 9 Probabilities of sequences of *n* comonomer units for run T8 in Table 2 (Y = 59.57 mol %).

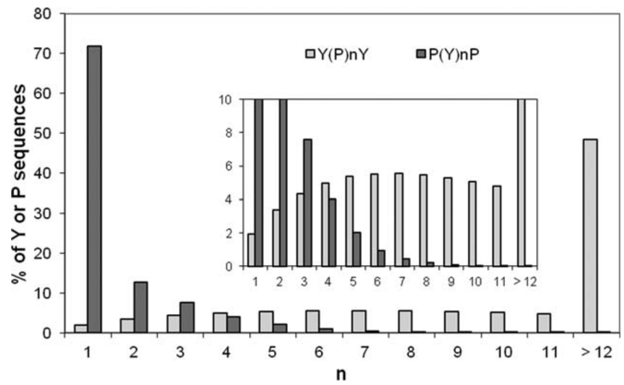


FIGURE 10 Probabilities of sequences of *n* comonomer units for run E5 in Table 2 (Y = 15.74 mol %). In the inset the relative abundance of Y sequences [P(Y)$_n$P] in the 0–10% range is reported.

Appreciably lower value of the CDI index was calculated for P/Y copolymers from **MBI**. Taking into account the similar

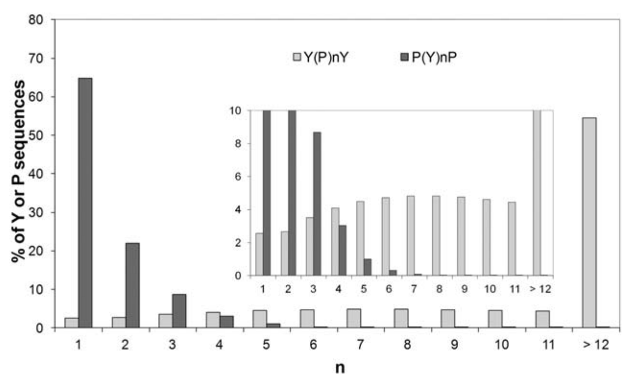


FIGURE 11 Probabilities of sequences of *n* comonomer units for run M5 in Table 2 (Y = 14.86 mol %). In the inset the relative abundance of Y sequences [P(Y)$_n$P] in the 0–10% range is reported.

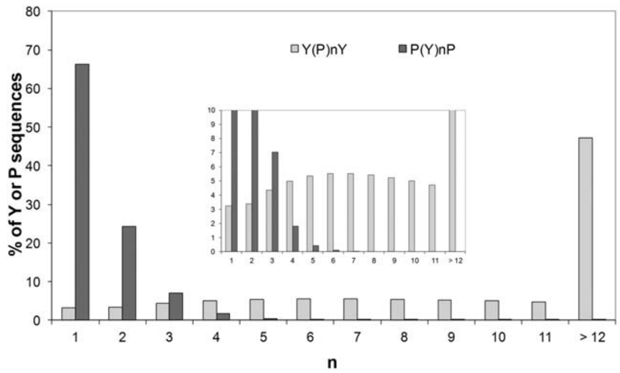


FIGURE 12 Probabilities of sequences of *n* comonomer units for run T4 in Table 2 (Y = 15.10 mol %). In the inset the relative abundance of Y sequences [P(Y)$_n$P] in the 0–10% range is reported.

isospecificity of **MBI** and **EBTHI**, this finding could be first ascribed to the much closer reactivity of **MBI** for P and Y, revealed by the *R* parameter and, as a consequence, to the more similar concentration of P and Y in the polymerization bath. P/Y copolymers from **TBI** are characterized by an almost random distribution of comonomers. In particular, it is worth observing the very similar values of r_{11} and r_{12} reactivity ratios: P and Y have almost the same probability to be inserted in the polymer chain, when either P or Y is the last inserted units and Y is in the penultimate position. The only reactivity ratio appreciably larger than 1 is r_{22}: two Y as the last inserted units make further Y insertion more probable than the P insertion. These findings are in line with what observed in the case of E/Y copolymerizations:[16(a),17] Y insertion has higher probability when Y is one or both of the last inserted units. In the light of the similar *R* values of **MBI** and **TBI**, results obtained with the latter metallocene could be ascribed to its higher isospecificity.

In the bar charts of Figures 7–9, are shown the relative contents of comonomer sequences made by *n* units, with *n* ranging from 1 to values ≥ 12, for copolymers from **EBTHI**, **TBI**, and **MBI**, and having Y content around 60% by moles. Y sequences [P(Y)$_n$P] and P sequences [Y(P)$_n$Y] were calculated, according to a method reported in ref. 17, for P/Y copolymers, whose ^{13}C NMR spectra are shown in Figure 4: run E10 from **EBTHI** (Y = 60.75 mol %), run M9 from **MBI** (Y = 62.77 mol %), and run T8 from **TBI** (Y = 59.57 mol %). Calculations were performed using the experimental values of reactivity ratios (r_{11}, r_{12}, r_{21}, and r_{22}) given in Table 5.[39] Isolated unit ($n = 1$) and short sequences (n = 2–5) of P are present in all of the three P/Y copolymers but, in particular, in the sample from **TBI** (Fig. 9). Isolated P units are about 40%, 35%, and 20% by moles in copolymers from **TBI**, **MBI**, and **EBTHI**, respectively. Copolymer from **TBI** shows as well prevailing short Y sequences: only less than 5% of Y form homosequences equal or longer than 12 units. Vice versa, [P(Y)$_n$P] sequences with more than 12 Y units are about 10% of the total Y amount in the copolymer from **MBI** (Fig. 8), and more than 20% in the sample from **EBTHI** (Fig. 7).

To elucidate the differences among the microstructures of copolymers with Y content around 15% by moles, not appreciable in ^{13}C NMR spectra of Figure 2, Y sequences [P(Y)$_n$P] and P sequences [Y(P)$_n$Y] are shown in the bar charts of Figures 10–12, for E5, M5, and T4 copolymers, respectively. In the inset in the Figures, the relative abundance of Y sequences [P(Y)nP] in the 0–10% range is emphasized. P(Y)$_n$P with $n \geq 4$ are about 3%, 5%, 8% by moles in copolymers from **TBI**, **MBI**, and **EBTHI**, respectively, thus confirming the different comonomer distribution also at low comonomer content.

CONCLUSIONS

In this work, copolymers of P with Y were prepared with metallocene-based catalytic systems. For the first time, it is shown that a catalytic system endowed with a very high isospecificity, based on a metallocene such as **TBI**, prepares copolymers with almost random distribution of P and Y, whereas sequences of both comonomers are increasingly obtained with metallocenes with minor enantioselectivity, such as **MBI** and, in particular, **EBTHI**. The synthesis of a random copolymer of P and a branched 1-olefin such as 4-methyl-1-pentene, with a highly isospecific catalytic system is, to some extent, unexpected, at least on the basis of previous results on ethene/Y copolymerization, that revealed the formation of E and Y sequences by using highly isospecific catalytic systems. In the case of the P/Y copolymers reported in this work, the obtainment of random comonomer distribution appears to be due to the easy propagation of both comonomers, thanks to the high enantioselectivity of **TBI**, to the similar reactivity of P and Y toward **TBI**, that leads to have similar concentrations of the two comonomers in the polymerization bath. This result can open the way for the preparation on a large scale of random propene-based copolymers by playing on the stereospecificity of the metallocene and on the steric hindrance of the comonomer.

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