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Penultimate-Unit Effect in Ethene/4-Methyl-1-pentene Copolymerization for a "Sequential" Distribution of Comonomers

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ABSTRACT: This paper presents a novel microstructure for an ethene/1-olefin copolymer. Ethene/4-methyl-1-pentene copolymers were found to be essentially made of sequences of ethene alternating with sequences of 4-methyl-1-pentene, with a minor amount of isolated ethene units distributed in the 1-olefin sequence. This microstructure is produced by highly isospecific catalytic sites and can be explained on the basis of a penultimate unit effect in copolymerization. Two isospecific organometallic complexes were used to prepare said copolymer: a sterically hindered, highly regio- and stereospecific metallocene, *rac*-[methylenebis(3-*tert*-butyl-1-indenyl)]-zirconium dichloride [*rac*-H_2C-(3-^{t}BuInd)$_2$ZrCl$_2$] (TBI), and the prototypical moderately isospecific hydrogenated metallocene without any substituent on the indenyl ligand, *rac*-ethylenebis(tetrahydroindenyl)zirconium dichloride [*rac*-(EBTHI)ZrCl$_2$] (EBTHI). As a comparison, copolymers were also prepared with the so-called "constrained geometry" half-sandwich complex, {η^1:η^5- [(*tert*-butyl-amido)dimethylsilyl)(2,3,4,5-tetramethyl-1-cyclopentadienyl)}-titanium dichloride [Me$_2$Si(Me$_4$Cp)(N-^{t}Bu)TiCl$_2$] (CG). Comonomer sequences at the triad level were determined through ^{13}C NMR analysis, and reactivity ratios of copolymerizations were elaborated through a statistical method, investigating the effect of ultimate and penultimate inserted comonomer units. Values of r_1r_2 products larger than 1 were calculated for copolymerizations from both the isospecific metallocenes, with relatively high values of both r_1 and r_2. The investigation of the penultimate-unit effect brought to calculate high values of both r_{11} and r_{22} and unprecedented contemporary low values of r_{12} and, surprisingly, r_{21} to indicate the occurring of comonomer sequences and the unusual absence of alternate comonomers. In particular, the low r_{21} value indicates that the 4-methyl-1-pentene unit in the penultimate position causes a remarkable decrease of the ethene reactivity, with the insertion of a minor amount of isolated units in 4-methyl-1-pentene sequences. A product of reactivity ratios r_1r_2 close to 1 was obtained with CG as the catalyst precursor, not only confirming the tendency of this organometallic complex to promote almost random ethene/1-olefin copolymerizations, already observed with propene as the 1-olefin, but also suggesting that the isospecificity of the catalytic site plays a key role in affording the novel copolymer microstructure. With 4-methyl-1-pentene as the comonomer, for the first time long 1-olefin sequences are observed in an ethene copolymer obtained with a catalytic system poorly isospecific in propene homopolymerization, such as EBTHI. This seems to suggest that the branched comonomer 4-methyl-1-pentene contributes to the formation of a highly isospecific site, whose stereospecificity is once more confirmed to arise from the cooperation of the catalyst and of the growing chain. These findings seem also to indicate that when a catalytic site becomes highly isospecific, it is likely to form sequences of both comonomers in an ethene/1-olefin copolymer.

Introduction

The development of the so-called single center catalysts (SSC) has paved the way for the production of ethene (E) copolymers with homogeneous comonomer distribution,[1] along with controlled comonomer content, even when nonconventional bulky and/or branched comonomers, such as 4-methyl-1-pentene (Y), are used.[2] In previous works, it was shown that highly isospecific metallocenes were able to give rise to copolymers of ethene and propene (P) with a high product of reactivity ratios r_1r_2 and, as a consequence, with the contemporary presence of long sequences of both comonomers.[3] In particular, with a highly isospecific metallocene, such as *rac*-[methylenebis(3-*tert*-butyl-1-indenyl)]zirconium dichloride (*rac*-H_2C-(3-^{t}BuInd)$_2$ZrCl$_2$) (TBI), it was possible to prepare an E/P copolymer with sequences of both comonomers long enough to give rise to crystalline domains even in a composition range typical for the formation of fully amorphous elastomeric materials.[4] Results

Scheme 1

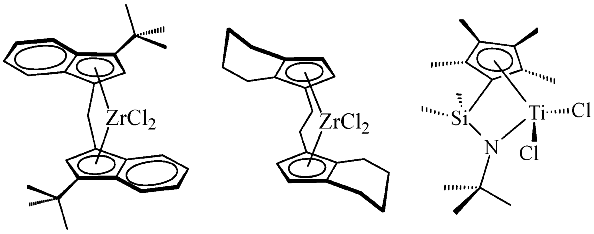

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Table 1. Ethene/4-Methyl-1-pentene (E/Y) Copolymerization with Different Organometallic Complexes and MAO as the Catalytic System[a]

catalyst	run	f^b (mol/mol)	yield (g)	activity × 10^{-3} ($mg_{pol}/(mmol_{Mt}$ h))	Y%[c] (mol)	PDI[d]	monomer conv (%)
rac-H_2C-(3-^{t}BuInd)$_2ZrCl_2$	1	1.883	0.659	790.8	1.18	n.d.[e]	1.69
	2	0.932	0.370	888.0	2.76	n.d.[e]	0.90
	3	0.457	0.680	136.3	5.19	n.d.[e]	1.81
	4	0.224	0.338	67.7	8.49	n.d.[e]	0.79
	5	0.131	0.072	7.2	13.66	n.d.[e]	0.15
	6	0.075	0.096	38.4	33.66	2.3	1.35
	7	0	0.659	134.4	100	1.9	-
rac-(EBTHI)$ZrCl_2$	8	1.885	1.215	2917.2	0.94	2.2	2.32
	9	0.934	0.402	964.8	2.16	2.1	0.77
	10	0.470	0.387	121	5.21	n.d.[e]	0.92
	11	0.146	2.037	815	5.57	n.d.[e]	3.09
	12	0.111	4.073	1629	10.8	2.3	5.59
	13	0.072	1.245	498.0	28.85	2.0	2.29
	14	0	4.475	894.3	100	n.d.[e]	-
[$Me_2Si(Me_4Cp)$(N-^{t}Bu)$TiCl_2$]	15	3.510	0.531	106.2	3.92	2.8	3.19
	16	1.887	0.367	73.4	8.18	n.d.[e]	2.25
	17	1.249	0.502	100	9.28	1.9	2.51
	18	0.693	0.386	77	15.48	n.d.[e]	1.90
	19	0.466	0.191	19.1	18.43	2.8	0.73
	20	0.310	0.482	96	24.83	n.d.[e]	1.70
	21	0.226	0.556	27.8	34.46	2.0	1.89
	22	0.107	0.527	52.7	43.93	2.7	1.25

[a] Polymerization conditions: toluene = 100 mL, Al/Mt = 1000 (mol/mol), T = 45 °C, [catalyst] = 10 μmol; t = 5−30 min. [b] E/Y feed ratio (mol/mol) in liquid phase. [c] From ^{13}C NMR analysis. [d] PDI = polydispersity index. [e] n.d. = not determined.

suggested that the key role was played by the isospecificity of the catalytic system and that copolymers with relatively long sequences of both comonomers could be prepared only with catalytic systems able to prepare a polypropene with an isotacticity index as high as at least 91%.[1a,3] In the present work, we have studied the copolymerization of E and Y promoted by two metallocenes, greatly differing in isospecificity, representative of different copolymerization statistics and also endowed with different catalytic activity. They are the following: the stereorigid, racemic, and sterically hindered (*rac*-H_2C-(3-^{t}BuInd)$_2ZrCl_2$) (TBI), designed by Resconi for the synthesis of highly regio- and stereo(iso)specific polypropene[5] and able to promote ethene/propene copolymerization with relatively high reactivity ratio product (r_1r_2 = 1.8),[6] and the prototypical hydrogenated metallocene without any substituent on the indenyl ligand, *rac*-ethylenebis(tetrahydroindenyl)zirconium dichloride [*rac*-(EBTHI)$ZrCl_2$] **(**EBTHI**)**, moderately isospecific and that gives rise to relatively low reactivity ratio product (r_1r_2 = 0.49)[3] in E/P copolymerization. EBTHI appeared to be more active than TBI,[4] and this could allow the investigation of a potential effect due to monomer diffusion phenomena. The main objective of the work here presented was to further investigate the correlation between the isospecificity of the catalytic system and the microstructure of an ethene/1-olefin copolymer, when the 1-olefin was higher than propene. In particular, the determination of copolymerization reactivity ratios was seen as a tool to describe and hence to tune at the nanoscale level the structure of the copolymers, eventually with the aim to prepare polymers with different crystalline phases. To better clarify the role of the stereospecific ability of the catalytic system, a further single center catalyst was used for E/Y copolymerization, the so-called "constrained geometry" half-sandwich complex, {η^1:η^5-[(*tert*-butyl-amido)dimethylsilyl](2,3,4,5-tetramethyl-1-cyclopentadienyl)}titanium dichloride [$Me_2Si(Me_4Cp)$(N-^{t}Bu)-$TiCl_2$] (CG),[7,8] that gives rise to an essentially atactic (slightly syndiotactic) polypropene and to E/P copolymerizations with a reactivity ratio product very close to 1, which indicates a tendency of this catalyst to give a nearly random comonomer distribution.[9]

The investigation of copolymer microstructure at the triad level, through ^{13}C NMR analysis, is presented as well as the application of a statistical method able to investigate the influence of the ultimate and of the penultimate inserted comonomer units.

Results and Discussion

Three series of E/Y copolymers in a wide range of chemical composition were synthesized with the organometallic complexes shown in Scheme 1, in combination with polymethylalumoxane (MAO).

In Table 1, data on E/Y copolymerizations and on the obtained copolymers are reported.

Copolymerization conditions were optimized to obtain copolymer samples with homogeneous comonomer composition, suitable for microstructure investigation. In particular, to maintain nearly constant the comonomer concentration in solution throughout the whole course of the reaction, conversion of both comonomers was kept in most cases below 2% and had a maximum value of 5%, following an experimental approach already reported.[3,6,9] A wide range of E/Y ratios in the polymerization bath was adopted allowing the preparation of copolymers with a Y content ranging from about 1 to about 44 mol %. M_w/M_n values close to 2 were determined for samples prepared with any of the catalytic system and for different chemical compositions, as clear indication of the single center nature of the three catalytic systems.

^{13}C NMR Characterization of Copolymers. All copolymers were carefully examined through ^{13}C NMR analysis. A restricted number of E/Y copolymer sequences had been assigned in a pioneering work by Kimura et al.,[10] through the analysis of a copolymer obtained with an isospecific heterogeneous titanium-based Ziegler−Natta catalyst: the raw copolymer, containing about 2 mol % of Y, and the solvent-extracted fractions that had a maximum Y content of 19 mol % were investigated.

Recently, some of the authors reported on a wide ^{13}C NMR analysis of E/Y copolymers synthesized with TBI/MAO catalyst, as fully regioregular and highly isotactic Y sequences are ideal for spectral assignment analysis. In fact, the spectral multiplicity could be ascribed only to differences in comonomer sequences, and an exhaustive assignment of NMR signals was performed.[11]

In Figure 1, the spectra of three copolymers with about 30 mol % of Y obtained with TBI (a), EBTHI (b), and CG (c)

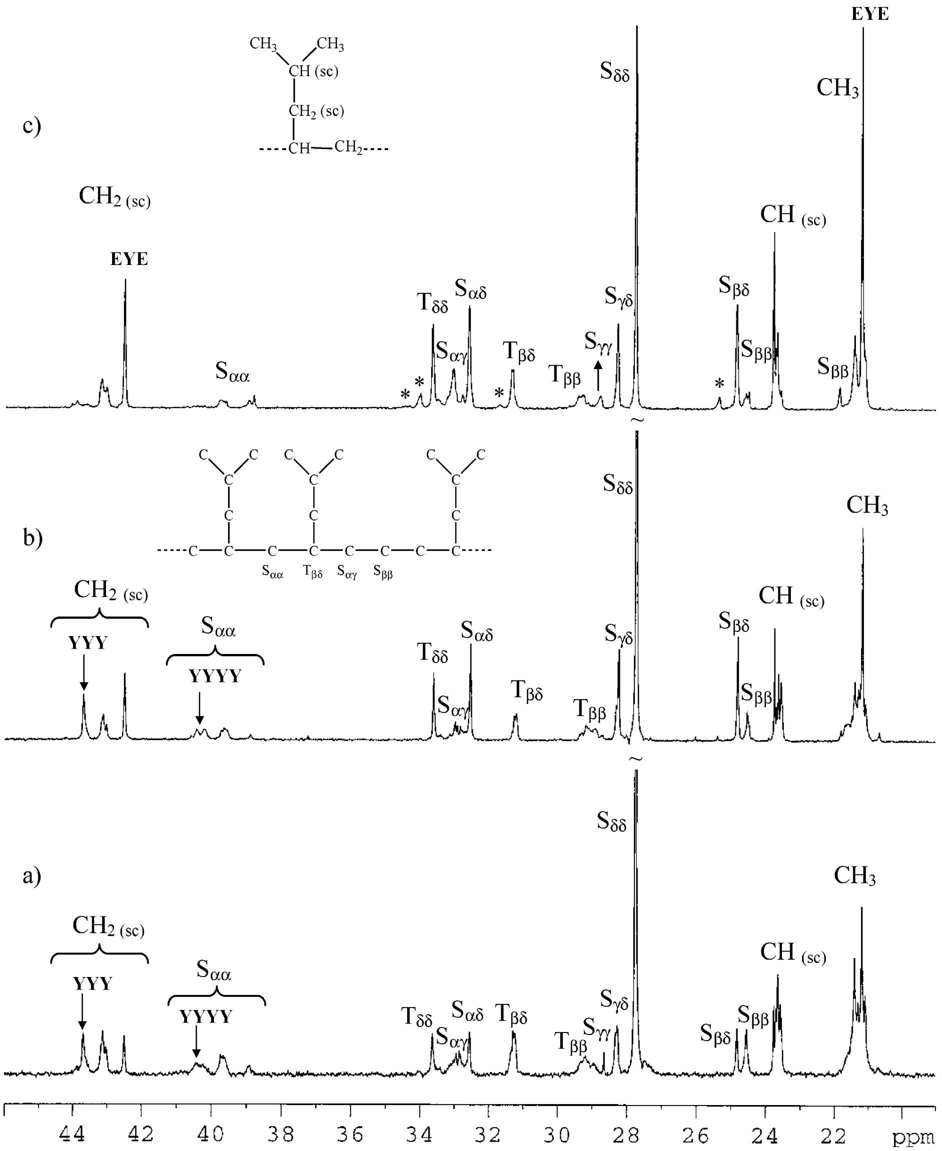

Figure 1. ^{13}C NMR spectra of ethene/Y copolymers with similar comonomer content: (a) 33.66 mol % content prepared with *rac*-H$_2$C-(3-^{t}BuInd)$_2$ZrCl$_2$/MAO catalyst (run 6 in Table 1), (b) 28.85 mol % content prepared with [*rac*-(EBTHI)ZrCl$_2$]/MAO (run 13 in Table 1), and (c) 34.46 mol % content prepared with [Me$_2$Si(Me$_4$Cp)(N-^{t}Bu)TiCl$_2$]/MAO (run 21 in Table 1).

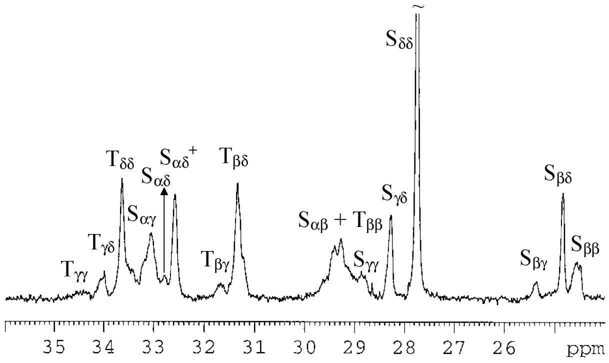

Figure 2. Expanded plot of ^{13}C NMR spectrum of ethene/Y copolymer with 43.93 mol % prepared with [Me$_2$Si(Me$_4$Cp)(N-^{t}Bu)TiCl$_2$]/MAO (run 22 in Table 3).

based catalytic systems are shown (runs 6, 13, and 21 of Table 1). Denomination of resonance peaks follows that of Carman and Wilkes: primary (methyl), secondary (methylene), and tertiary (methine) carbons are denoted as P, S, and T, respectively.[12] The position of a carbon relatively to its nearest methine group was labeled by two Greek subscripts, where δ indicates all methines four bonds far from the methylene carbon of interest and $\delta+$ farther than four bonds. Methylene and methine carbons in the side chains are designated by the symbols CH$_2$(sc) and CH(sc).[13]

Noticeable differences appear between the spectra of copolymers obtained with the two isospecific metallocenes (Figure 1a,b) and the spectrum of the copolymer obtained with CG catalyst (Figure 1c), particularly as far as the relative abundance of comonomer sequences is concerned. The resonance at 42.50 ppm, corresponding to EYE sequence (centered on the CH$_2$ of Y side chain), has a minor intensity in the spectra of copolymers from the isospecific metallocenes, whereas it is clearly evident in the spectrum of the copolymer obtained with CG catalyst. This alternate EYE sequence gives also rise to the signal at 21.18 ppm (centered on the two methyls of Y side chain), which is evidently less intense in the spectra of E/Y copolymers from the isospecific metallocenes. On the other hand, the signals at 43.66 and 40.22 ppm, assigned to YYY and YYYY homosequences, respectively, are intense in the spectra of the copolymers obtained with TBI and EBTHI catalysts and hardly detectable in the spectrum of the copolymer from the CG catalyst. Also, the EEE sequence is definitely more abundant

Chart 1

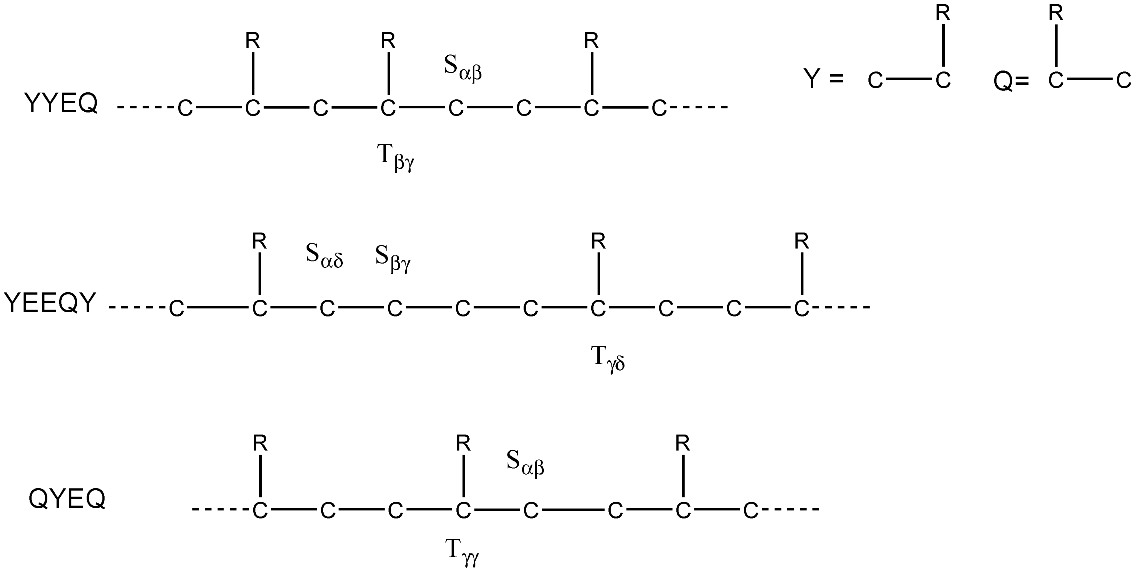

Table 2. ^{13}C NMR Characterization of E/Y Copolymers Prepared with Metallocenes and MAO as the Catalytic System

metallocene	sample no.	f^a (mol/mol)	Y%^{b} (mol)	YYY	YYE	EYE	YEY	YEE	EEE
rac-H_2C-(3-^{t}BuInd)$_2$$ZrCl_2$	1	1.883	1.18	0.00	0.23	0.95	0.69	1.99	96.14
	2	0.932	2.76	0.00	0.68	2.02	0.50	3.42	93.39
	3	0.457	5.19	0.35	1.96	2.88	1.84	4.93	88.03
	4	0.224	8.49	1.32	3.89	3.28	3.6	5.47	82.07
	5	0.131	13.66	3.52	6.05	4.09	4.13	4.97	77.24
	6	0.075	33.66	12.44	14.63	6.59	10.60	7.23	48.51
rac-(EBTHI)$ZrCl_2$	8	1.885	0.94	0.00	0.00	0.94	0.00	1.80	97.26
	9	0.934	2.16	0.60	0.00	1.56	0.00	2.98	94.86
	10	0.470	5.21	1.28	1.21	2.72	0.85	4.63	89.31
	12	0.111	10.8	1.66	2.95	6.19	2.59	10.94	75.97
	13	0.072	28.85	10.72	8.87	9.26	6.94	13.55	50.66

[a] E/Y feed ratio (mol/mol) in liquid phase. [b] From triad distribution as Y = (YYY + EYY + EYE).

Table 3. ^{13}C NMR Characterization of E/Y Copolymers Prepared with "Constrained Geometry" Half-Sandwich Catalyst and MAO as the Catalytic System

sample no^a	f^b (mol/mol)	Y%^{c} (mol)	Q%^{d} (mol)	YYY	YYE	EYE	QEE	QEY	YEY	YEE	EEE	regioirreg^e (%)
15	3.510	3.92	0.29	0.00	0.31	3.61	0.10	0.20	1.04	6.28	88.15	3.3
16	1.887	8.18	0.47	0.00	1.02	7.15	0.07	0.39	1.41	11.46	77.99	1.7
17	1.249	9.28	0.89	0.00	1.48	7.80	0.63	0.25	2.82	12.67	73.45	5.1
18	0.693	15.48	1.92	0.00	3.39	12.09	1.40	0.51	4.71	16.72	59.25	4.2
19	0.466	18.43	2.39	1.92	6.07	10.42	1.79	0.59	6.92	12.70	57.17	7.5
21	0.226	34.46	5.19	3.91	11.87	17.12	4.09	0.86	12.38	17.83	26.94	9.4

[a] The numbers of the samples are those of the corresponding runs. [b] E/Y feed ratio (mol/mol) in liquid phase. [c] From triad distribution as Y = (YYY + EYY + YEE). [d] Q = 2,1 4-methyl-1-pentene inserted unit. [e] Calculated according to Randall as $[100(^1/_2S_{\alpha b} + ^1/_2S_{\beta g})/(S_{\alpha\alpha} + ^1/_2S_{\alpha b} + S_{\beta\beta} + ^1/_2S_{\beta g} + S_{\gamma\gamma} + ^1/_2S_{\gamma\delta})$ from ^{13}C NMR spectrum.

in copolymers from isospecific metallocenes, as it can be appreciate in the three spectra by the relative intensity of the signal at 27.73 ppm.

Besides, one can easily observe that the spectrum of Figure 1c shows a few supplementary resonances (starred in the figure) that are completely absent in the spectrum of the copolymer from TBI catalyst and only hardly detectable in that of the copolymer from EBTHI: these never reported resonances are assigned to regioirregularities.[14] These signals become even more evident in the expanded plot of Figure 2 of a copolymer with higher Y content (43.93 mol %, run 22 of Table 1) prepared with the same CG catalyst. In Chart 1, the possible sequences arising from the inverted Y units are reported; the exhaustive assignment of regio- and stereoirregular sequences will be the subject of a forthcoming paper.[14]

Triad distribution data arising from ^{13}C NMR analysis of all the three series of copolymers are collected in Table 2 for the isospecific metallocenes and in Table 3 for the CG catalyst. Table 3 also shows the E-centered regioirregular triads QEE and QEY (where Q indicates the 2,1 comonomer inserted unit). The QEE triad is easily evaluated from the integrated peak area of the $T_{\gamma\delta}$ carbon. The QEY triad is calculated as $S_{\alpha\beta}/4$, when the Y content is below 20 mol %; at higher Y content, as being $S_{\alpha\beta}$ partially unresolved from the $T_{\beta\beta}$ carbon (see Figure 2), the QEY triad is evaluated from the $T_{\gamma\gamma}$ carbon. The index of regioirregularity, i.e., the sum of the relative concentration of even (2 and 4) methylenes sequences, was calculated according to Randall, from eq 1:[15]

$$X_2 + X_4 = \frac{^1/_2(S_{\alpha\beta} + S_{\beta\gamma})}{S_{\alpha\alpha} + ^1/_2S_{\alpha\beta} + S_{\beta\beta} + ^1/_2S_{\beta\gamma} + S_{\gamma\gamma} + ^1/_2S_{\gamma\delta}} \times 100 \quad (1)$$

Table 4. Reactivity Ratios for E/Y Copolymerizations with Different Organometallic Complexes and MAO as the Catalytic System

metallocene	comonomers	$r_1 \pm \delta r_1$	$r_2 \pm \delta r_2$	$r_1r_2 \pm \delta(r_1r_2)$[a]	ref
rac-H_2C-(3-^{t}BuInd)$_2ZrCl_2$	E/Y	93.9 ± 15.6	0.18 ± 0.05	17.2 ± 8.1	this work
	E/P	17.4 ± 1.3	0.10 ± 0.02	1.8 ± 0.5	6
rac-(EBTHI)$ZrCl_2$	E/Y	91.2 ± 16.1	0.11 ± 0.05	9.8 ± 6.2	this work
	E/P	10.4 ± 0.7	0.05 ± 0.01	0.5 ± 0.1	3
[$Me_2Si(Me_4Cp)$(N-^{t}Bu)$TiCl_2$]	E/Y	7.5 ± 1.3	0.11 ± 0.04	0.8 ± 0.4	this work
	E/P	1.3 ± 0.1	0.82 ± 0.05	1.1 ± 0.1	9

[a] $\delta(r_1r_2) = r_1\delta r_2 + r_2\delta r_1$.

^{13}C NMR spectra and the derived calculated triad distributions collected in Tables 2 and 3 indicate that E/Y copolymers from TBI and EBTHI isospecific metallocenes are characterized by relatively long homosequences of both comonomers, with only a minor presence of alternate comonomer units, whereas a more evenly distributed abundance of comonomer sequences that will be herein below demonstrated as random seems to describe a copolymer from the CG catalyst, thus suggesting that, at least for the explored catalysts, there could be a correlation between the stereospecific ability of the catalyst and the E/Y comonomer distribution.

Determination of Reactivity Ratios of Comonomers. Data on comonomer sequences were elaborated through a statistical method, reported in previous publications,[3,9] successfully applied to E/P copolymerizations from a single center catalytic system, based either on a metallocene or on a constrained geometry complex. Said method allows one to identify the statistical model suitable for describing the copolymerizations as well as for deriving the reactivity ratios between the comonomers. It is known that when the insertion of a comonomer is influenced by the last (ultimate) inserted unit, a first-order Markovian statistical model (ultimate effect) is adopted to determine the reactivity ratios.[16] From the first-order Markovian model, r_1 (= k_{11}/k_{12}) and r_2 (= k_{22}/k_{21}) reactivity ratios are derived, 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 last inserted one. In particular, 1 and 2 indicate E and Y, respectively. A second-order Markovian model describes a copolymerization when the insertion of a comonomer is influenced by both the two last inserted units (penultimate effect).[17] As a consequence of the adoption of the second-order Markovian model, the following reactivity ratios can be derived:

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

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

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

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

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.

The presence of regioirregularities in copolymers from the CG catalyst sensibly affects the correct determination of triad distribution. Therefore, the statistical treatment was applied only to samples with relatively low regioirregularity content, less than 10%.

In Table 4, r_1 and r_2 values are collected together with the confidence intervals from the least-squares at the minimum point and are compared with those reported in the literature for E/P copolymerization carried out under comparable experimental conditions.

For any of the catalysts, r_1 and r_2 values are respectively higher and lower than 1, thus indicating a preferred insertion of ethene regardless of the last inserted comonomer unit. However, a remarkable difference can be observed between the reactivity ratios of the isospecific metallocenes and those of the CG catalyst. In fact, much higher values of r_1 are obtained with metallocenes, with a noticeable increase with respect to ethene/propene copolymerizations, whereas the r_1 value obtained with the constrained geometry catalyst is 1 order of magnitude lower. This CG catalyst was reported as a first example of a catalytic system able to give a true random E/P copolymerization.[9] In a random copolymerization, the insertion of a comonomer is independent of the last inserted comonomer unit, and hence $k_{11}/k_{12} = k_{21}/k_{22}$, i.e. $r_1 = 1/r_2$, which brings to $r_1r_2 = 1$. With the CG catalyst, r_1 and $1/r_2$ for E/P copolymerization were found to be 1.3 and 1.2, respectively, thus indicating an almost ideal copolymerization. But also in the case of Y as the 1-olefin, r_1 and $1/r_2$ are very close to each other, being 7.5 and 9, respectively, and this reveals that the ability of CG catalyst to give rise to random ethene/1-olefin copolymerizations holds moving from propene to a higher branched 1-olefin.

Another remarkable difference, definitely more intriguing for the interpretation of the copolymerization mechanism, appears from the comparison of the reactivity ratios obtained with metallocenes and with the CG catalyst. While with the CG catalyst, moving from E/P to E/Y copolymerization, the increase of r_1 value goes along with a reduction of r_2 value, with metallocenes both r_1 and r_2 increase to values that indicate a higher presence of sequences of both comonomers along the macromolecular chain, as clearly experimentally observed and above commented in the ^{13}C NMR spectra. As mentioned in the Introduction, highly isospecific metallocenes, such as TBI, were already reported as able to give rise to sequences of both comonomers, i.e., to a high product of reactivity ratios, in E/P copolymers.[6] Conversely, this result is definitely surprising for copolymerizations promoted by EBTHI, as the tendency to the formation of 1-olefin sequences was not observed when propene was the 1-olefin, not even at a high polymerization temperature, when the increase of r_1r_2 value was a consequence of the increase of r_1.[4] By considering all the data available on ethene/1-olefin copolymerizations, one can say that once more a high r_1r_2 value with relatively high values of both r_1 and r_2 arise from an isospecific metallocene, but for the first time, in the case of EBTHI, the organometallic complex is moderately isospecific in propene homopolymerization.

Penultimate Unit Effect in Ethene/4-Methyl-1-pentene Copolymerization. With the aim to base any consideration on parameters with a better fitting of the experimental data and, most of all, to have a better insight into the copolymerization mechanism, triads of Table 2 were elaborated through a second-order Markovian model. This approach was not applied to copolymerizations from CG catalysts, which were already commented as nearly random. Table 5 reports thus the values of the second-order Markovian reactivity ratios for copolymerizations from the two isospecific metallocenes together with the

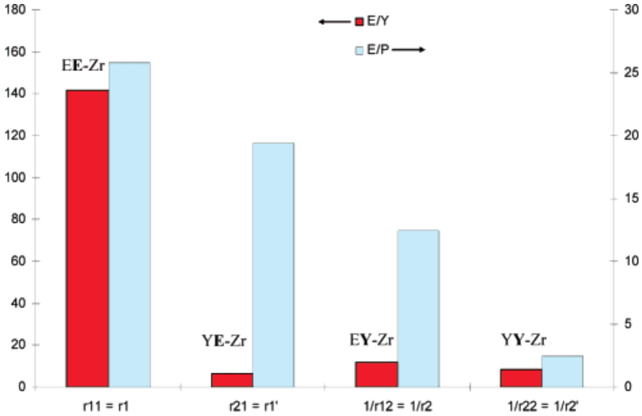

Figure 3. Comparison of ethene/comonomer relative reactivity (r_{11}, r_{21}, $1/r_{12}$, and $1/r_{22}$) obtained for E/Y and E/P copolymerizations promoted by [*rac*-H_2C-(3-^{t}BuInd)$_2$ZrCl_2]/MAO.

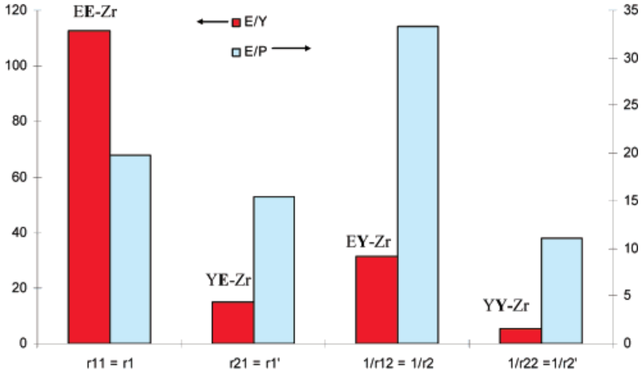

Figure 4. Comparison of ethene/comonomer relative reactivity (r_{11}, r_{21}, $1/r_{12}$, and $1/r_{22}$) obtained for E/Y and E/P copolymerizations promoted by [*rac*-(EBTHI)ZrCl_2]/MAO.

comonomer distribution index (CDI), i.e., an index derived from r_{11}, r_{21}, r_{22}, and r_{12} that has the same meaning of the classical product of reactivity ratios r_1r_2, derived from the first-order parameters.[3]

One can first comment an evident increase of data fitting. Moreover, CDI values larger than 1 are observed for both metallocenes, analogously to what reported by elaborating data with the first-order Markovian model. More interesting hints on copolymerization mechanism obviously arise from the examination of reactivity ratios. The values of r_{11} and r_{22}, larger than those of r_{21} and r_{12}, confirm the tendency of both isospecific metallocenes to give an E/Y copolymer with a prevailingly sequential enchainment of comonomers. To help the interpretation of data of Table 5, the relative reactivity of E with respect to Y is shown in the bar chart of Figure 3 and Figure 4 for TBI and EBTHI, respectively, as a function of chain end sequences, i.e., when the chain end sequences are EE−Zr, YE−Zr, EY−Zr, YY−Zr, and is compared to values obtained in a previous work for E/P copolymerization.[4] This type of representation was selected as a fingerprint of the sequential nature of an ethene/1-olefin copolymer.[4] In fact, for E/P copolymerizations promoted by TBI, the ethene reactivity was found to decrease in the following order: EE−Zr, PE−Zr, EP−Zr, PP−Zr, as shown in Figure 3: propene as the last inserted unit(s) favors the insertion of further propene units. However, this trend was not observed for E/P copolymers from EBTHI, as shown in Figure 4.

As a first remarkable difference between E/P and E/Y copolymerizations, it is evident in the bar charts of Figures 3 and 4 that the relative reactivity of ethene decreases when Y is inserted for both the isospecific metallocenes. Moreover, an unusual low value of r_{21} can be observed for copolymers from both the metallocenes and particularly from TBI. This indicates that the relative reactivity of ethene with respect to 4-methyl-1-pentene dramatically decreases not only when two Y comonomer units are the last inserted ones, as shown by the low $1/r_{22}$ values, but also and very interestingly when one Y unit is located only in the penultimate position. These findings clearly reveal that a penultimate effect steers the microstructure of an ethene copolymer with 4-methyl-1-pentene, when isospecific metallocenes are used to promote the copolymerization. These values of the reactivity ratios are unusual in the field of ethene/1-olefin copolymerization and seem to suggest that a novel copolymer microstructure has been formed. In particular, for E/Y copolymers from TBI, values of reactivity ratios typical for alternate sequences are extremely low. To have a visual representation of the copolymer microstructure, chain generation was performed adopting the Monte Carlo approach[18] (see Supporting Information). A chain segment having 200 units and a 50/50 molar composition was generated, using the reactivity ratios determined for TBI, reported in Table 5, and a corresponding theoretical copolymerization bath composition $f = 0.0516$. A picture of the generated copolymer chain is shown in Figure 5. Two main features strike the attention. Sequences made of ethene and essentially of 4-methyl-1-pentene alternate themselves along the macromolecular chain. Moreover, a 4-methyl-1-pentene sequence is interrupted by only isolated units of ethene.

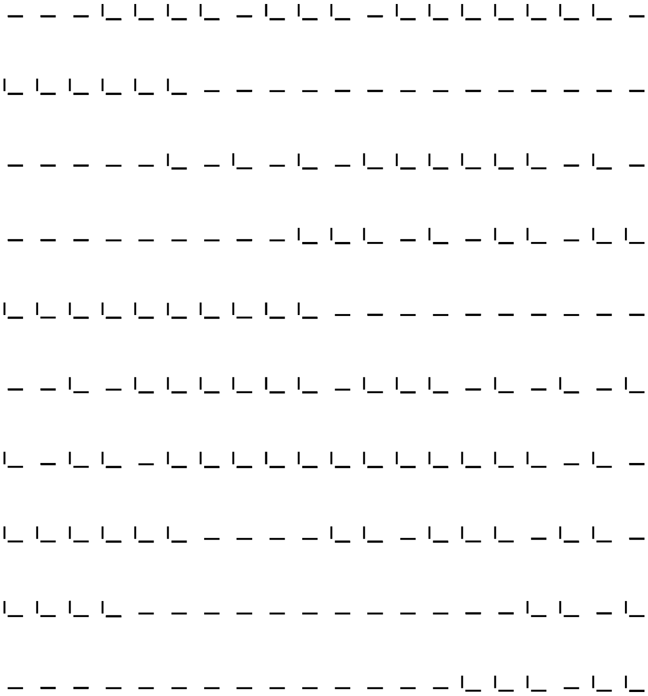

Figure 5. Chain segments generated using the Markovian parameters obtained from the reactivity ratios of Table 5 relative to TBI catalyst. f_1/f_2 ratio was set at 0.0506 mol/mol to produce a chain with 50/50 comonomer molar ratio.

Rationalization of Results and Statistical Elaborations. To attempt a rationalization of these experimental findings and statistical elaborations, taking also into account the results obtained in the case of E/P copolymers,[4] one can comment as follows. (i) Sequences of both comonomers in ethene/1-olefin copolymers, and thus copolymers with a high product of reactivity ratios, are obtained only when a highly isospecific organometallic complex is employed because only a highly isospecific catalyst allows an easy propagation of the 1-olefin and thus increases its probability in the presence of ethene. (ii)

Table 5. Reactivity Ratios Calculated Using a Second-Order Markovian Model for Ethene/Y Copolymerizations with *rac*-H_2C-(3-^{t}Bu-Ind)$_2$ZrCl$_2$ and *rac*-(EBTHI)ZrCl$_2$/Alumoxane as the Catalytic System[a]

catalyst	comonomer	reactivity ratios[b]				CDI[c]
		r_{11}	r_{22}	r_{21}	r_{12}	
rac-H_2C-(3-^{t}Bu-Ind)$_2$ZrCl$_2$	E/Y	141.7 ± 28.4	0.12 ± 0.04	6.6 ± 2.4	0.08 ± 0.03	5.5 ± 3.8
	E/P	25.8 ± 2.8	0.40 ± 0.05	19.4 ± 6.3	0.08 ± 0.02	5.5 ± 1.8
rac-(EBTHI)ZrCl$_2$	E/Y	112.6 ± 12.6	0.19 ± 0.06	14.8 ± 4.2	0.03 ± 0.01	6.0 ± 3.3
	E/P	19.8 ± 1.7	0.09 ± 0.01	15.4 ± 1.8	0.03 ± 0.004	1.1 ± 0.2

[a] The experimental conditions are indicated in Table 1. [b] Calculated with the method described in ref 3 using a second-order Markovian model. [c] Comonomer distribution index calculated according to the formula CDI = $(r_{11}^2\, r_{22}^2 r_{12} r_{21})^{1/3}$.[3]

It is of a high interest to observe that when Y is the 1-olefin, also a moderately isospecific catalyst, such as EBTHI, is able to give rise to a sequential copolymer, whereas this ability was not observed in any of the experimental conditions adopted for E/P copolymerization. (iii) It is known that the stereospecificity of a catalyst in 1-olefin insertion polymerization arises from the cooperation of the catalytic system and of the growing chain.[18] (iv) It is thus clear that a key role is played by the inserted branched 1-olefin that much contributes to the stereospecific ability of the catalytic system: EBTHI becomes a more isospecific catalyst when Y is inserted in the growing chain, and the branched 1-olefin exerts a powerful isospecific induction also when occupies the penultimate position. When the 1-olefin hydro(deuterium) oligomerization promoted by metallocene-based catalytic systems was applied to 4-methyl-1-pentene, the highest value of enantiomeric excess was calculated,[20] to confirm that this monomer favors per se a higher isospecificity. (v) The very high isospecificity of the catalytic site, which promotes 1-olefin propagation, could be in line with the unusually low alternate distribution of comonomers, key features of the novel copolymer microstructure here presented.

A penultimate styrene effect has been recently reported for the copolymerization of ethylene and styrene promoted by constrained geometry catalysts.[21] The authors propose the hypothesis that the styrene reactivity is enhanced by the presence of aromatic moieties in close proximity to the active site. It is thus evident that the mechanism suggested for ethylene/styrene copolymerizations by CG catalysts is different from the one presented in this paper, which moves from the high isospecificity of the catalytic site to justify the formation of 1-olefin sequences, rather than the increase of its relative reactivity.

In conclusion, these findings seem to suggest that a typical feature of a highly isospecific catalytic site is the formation, in an ethene/1-olefin copolymer, of relatively long sequences of the two comonomers, which, at least in principle, should be both able to crystallize in a broad range of copolymer composition. The presence of ethene and 4-methyl-1-pentene crystalline phases is under investigation and will be reported in a future work.

Experimental Section

General Remarks. 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 drybox under nitrogen atmosphere (<10 ppm oxygen, <20 ppm water). Toluene was dried by distillation from sodium under a nitrogen atmosphere. Methylaluminoxane (MAO) (Witco, 10 wt % solution in toluene) was used after drying in vacuum to remove the solvent and unreacted trimethylaluminum (TMA) and was stored under nitrogen. [Me$_2$Si(Me$_4$Cp)-(N-^{t}Bu)TiCl$_2$] was provided by Boulder Scientific, [*rac*-H_2C-(3-^{t}BuInd)$_2$ZrCl$_2$] was used as kindly donated by Resconi, and [*rac*-(EBTHI)ZrCl$_2$] was provided by Basell Poliolefine Italia S.r.l. Nitrogen and ethene were purified by passage through columns of BASF RS-11 (Fluka) and Linde 4 Å molecular sieves.

Ethene/4-Methyl-1-pentene Polymerizations. In a typical polymerization reaction, a 0.25 L Büchi autoclave equipped with a mechanical stirrer was charged under nitrogen with a solution of the proper amount of 4-methyl-1-pentene and 7.5 mmol of dry methylaluminoxane (MAO) in 100 mL of anhydrous toluene. A 25 mL injector was charged with 10 mL of a solution of 10 μmol of catalyst and 2.5 mmol of MAO in toluene (total MAO/Mt molar ratio = 1000). After thermal equilibration of the reactor system at 45 °C, ethene was continuously added until saturation. When the equilibrium pressure (2.47 atm) was reached, the injector with the metallocene solution was pressurized with nitrogen, and the solution was injected into the reactor. The reaction was terminated by addition of a small amount of ethanol, and the polymer was precipitated upon pouring the whole reaction mixture into ethanol (500 mL) to which concentrated hydrochloric acid (5 mL) had been added. The polymer was collected by filtration and dried under vacuum at 70 °C.

Nuclear Magnetic Resonance (NMR). ^{13}C NMR spectra of the polymers were recorded in $CDCl_2CDCl_2$ at 103 °C on a Bruker Avance-400 spectrometer operating at 100.58 MHz, (internal chemical shift reference: 1% hexamethyldisiloxane). Conditions: 10 mm probe; 90° pulse angle; 64K data points; acquisition time 5.56 s; relaxation delay 20 s; 3K−4K transients. Proton broad-band decoupling was achieved using bi_waltz16_32 power-gated decoupling.

Determination of the Concentration of the Polymerization Solutions. The vapor−liquid equilibrium for E/Y toluene mixture was calculated from the Redlich−Kwong−Soave equations.[22] This set of thermodynamic equations was selected among those available in Aspen Plus (commercialized by Aspen Technology Inc. Release 9) on the basis of a comparison with the experimental results. The concentrations of the comonomers were hence calculated.

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Supporting Information Available: Description of the procedure adopted for the chain generation reported in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For recent reviews, see, for example: (a) Resconi, L.; Fait, A.; Piemontesi, F.; Cavallo, G. *Chem. Rev.* **2000**, *100*, 1253−1345 and references therein. (b) Kaminsky, W.; Arndt, M. *Adv. Polym. Sci.* **1997**, *127*, 143−187 and references therein. (c) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255−270. (d) Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143−1170 and references therein.

(2) (a) Mulhaupt, R.; Ovenall, D. W.; Ittel, S. D. *J. Polym. Sci., Polym. Chem.* **1988**, *26*, 2487−2500. (b) Tincul, I.; Smith, J.; van Zyl, P. *Macromol. Symp.* **2003**, *193*, 13−28. (c) Tait, P. J. T.; Berry, I. G. In *Comprehensive Polymer Science*; Eastmont, G. C., Ledwith, A., Russo,

S., Sigwalt, P., Eds.; Pergamon Press: Oxford, UK, 1989; Vol. 4, p 575. (d) Ver Strate, G. *Encycl. Polym. Sci. Eng.* **1986**, *6*, 522. (e) Boor, J., Jr. *Ziegler-Natta Catalysts and Polymerization*; Academic Press: New York, 1979.

(3) (a) Galimberti, M.; Destro, M.; Fusco, O.; Piemontesi, F.; Camurati, I. *Macromolecules* **1999**, *32*, 258−263. (b) Galimberti, M.; Piemontesi, F.; Mascellani, N.; Camurati, I.; Fusco, O.; Destro, M. *Macromolecules* **1999**, *32*, 7968−7976.

(4) Losio, S.; Piemontesi, F.; Forlini, F.; Sacchi, M. C.; Tritto, I.; Stagnaro, P.; Zecchi, G.; Galimberti, M. *Macromolecules* **2006**, *39*, 8223−8228.

(5) Resconi, L.; Balboni, D.; Baruzzi, G.; Fiori, C.; Guidotti, S. *Organometallics* **2000**, *19*, 420−429.

(6) Locatelli, P.; Losio, S.; Forlini, F.; Sacchi, M. C.; Tritto, I.; Galimberti, M.; Piemontesi, F. Communication at "European Polymer Conference on Stereospecific Polymerization and Stereoregular Polymers"-EUPOC 2003, Milano, Italy, 8−12 June, 2003.

(7) (a) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587−2598 and references therein. (b) McKnight, A. L.; Masood, M. A.; Waymouth, R. M.; Straus, D. A. *Organometallics* **1997**, *16*, 2879−2885. (c) Braunschweig, H.; Breitling, F. M. *Coord. Chem. Rev.* **2006**, *250*, 2691−2720.

(8) Lanza, G.; Fragala, I. L.; Marks, T. J. *Organometallics* **2002**, *21*, 5594−5612.

(9) Galimberti, M.; Mascellani, N.; Piemontesi, F.; Camurati, I. *Macromol. Rapid Commun.* **1999**, *20*, 214−218.

(10) Kimura, K.; Yuasa, S.; Maru, Y. *Polymer* **1984**, *25*, 441−446.

(11) Losio, S.; Tritto. I.; Zannoni, G.; Sacchi, M. C. *Macromolecules* **2006**, *39*, 8920−8927.

(12) Carman, C. J.; Wilkes, C. E. *Rubber Chem. Technol.* **1971**, *44*, 781−804.

(13) In the spectrum of Figure 1c, peaks at 21.80 and 24.57 ppm are both assigned to the $S_{\beta\beta}$ methylene carbon of the YEY sequence. The peak at 21.80 ppm has been already assigned to the $S_{\beta\beta}$ carbon in the literature (ref 10), for E/Y copolymer from a heterogeneous Ti-based catalytic system. The assignment of the peak at 24.57 ppm to the $S_{\beta\beta}$ carbon has been also reported in the literature (ref 11) for E/Y copolymers from a metallocene-based catalytic system (TBI). Copolymers reported in this work from CG- and EBTHI-based catalytic systems show for the first time the contemporary presence of both peaks. This aspect is elsewhere investigated and discussed (ref 14).

(14) Losio, S.; Boccia, A. C.; Sacchi, M. C. *Macromol. Chem. Phys.*, submitted.

(15) Randall, J. C. *Macromolecules* **1978**, *33*, 11−13.

(16) Odian, G. *Principles of Polymerization*, 3rd ed.; Wiley & Sons: New York, 1991; pp 455−458.

(17) Odian, G. *Principles of Polymerization*, 3rd ed.; Wiley & Sons: New York, 1991; pp 503−505.

(18) http://office.microsoft.com/en-us/excel/HA011118931033.aspx.

(19) Zambelli, A.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. *Macromolecules* **1982**, *15*, 211−212.

(20) Pino, P.; Prada, P.; Galimberti, M. *Frontier of Macromolecular Science*; Saegusa, T., Higashimura, T., Abe, A., Eds.; 1989; pp 43−48.

(21) Arriola, D. J.; Bokota, M.; Campbell, R. E., Jr.; Klosin, J.; LaPointe, R. E.; Redwine, O. D.; Shankar, R. B.; Timmers, F. J.; Abboud, K. A. *J. Am. Chem. Soc.* **2007**, *129*, 7065−7076.

(22) (a) Soave, G. *Chem. Eng. Sci.* **1972**, *27*, 1197−1203. (b) Peneloux, A.; Rauzy, E.; Freze, R. *Fluid Phase Equilib.* **1982**, *8*, 7−23. (c) Schwartzentruber, J.; Renon, H. *Ind. Eng. Chem. Res.* **1989**, *28*, 1049−1055.

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