Macromolecules **1998,** *31,* 3409−3416

Ethene/Propene Copolymerization with High Product of Reactivity Ratios from a Single Center, Metallocene-Based Catalytic System

Maurizio Galimberti,* Fabrizio Piemontesi, Ofelia Fusco, Isabella Camurati, and Mara Destro

Montell Italia S.p.A., G. Natta Research Center, P.le G. Donegani 12, 44100 Ferrara, Italy

Received November 24, 1997; Revised Manuscript Received February 17, 1998

ABSTRACT: Ethene and propene were copolymerized using a metallocene-based catalytic system, composed of *rac*-isopropylidenebis(3-*tert*-butylcyclopentadienyl) zirconium dichloride, and poly(methylalumoxane) (MAO). Ethene/propene copolymers were prepared in a broad range of chemical composition, from 17% to 92% as ethene molar content. The use of an isospecific metallocene allowed the preparation of *bi*polymers composed of ethene and propene with regioregular propene units inserted, in a single macromolecular chain, with the same enantioface, whereas the careful control of the polymerization conditions led to the preparation of copolymers with a very narrow distribution of the chemical composition. A careful analysis of the copolymers microstructure was performed, essentially aimed at the investigation of the comonomers distribution. A statistical treatment of the ^{13}C NMR data brought to the determination of the reactivity ratios (r_1 and r_2) of the comonomers. Data are reported and discussed to demonstrate that a single center homogeneous catalyst is able to prepare ethene/propene copolymers with long sequences of both comonomers.

Introduction

The discovery of suitable cocatalysts, first MAO[1] and then boranes[2] and AlR_3/H_2O systems,[3] has allowed metallocenes to give rise to highly active catalytic systems for the homo- and copolymerization of ethene and 1-olefins.[1b,4]

In the world of Ziegler−Natta catalysis, metallocenes have marked a clear, dramatic difference with respect to traditional catalytic systems, heterogeneous titanium based and homogeneous vanadium based. Single center catalysts with defined chemical structure, in most cases endowed with high catalytic activity, have become for the first time available for the preparation of polyolefins.

In particular, in the field of ethene/propene copolymers, metallocenes have allowed the preparation of a large variety of copolymers[5] and of a new generation of elastomers.[6] The single center nature of metallocene-based catalytic systems set them clearly apart from the heterogeneous titanium-based ones, characterized by the multiplicity of the catalytic centers.[7] With metallocenes, copolymers with narrow intermolecular distribution of the molecular properties can be prepared. This result was actually already achieved by using homogeneous vanadium-based catalysts that, as already discussed elsewhere,[6d,7,8] can behave as single center catalysts. The key feature of metallocenes that marks a dramatic change with respect to the traditional vanadium catalysis and, actually, to the whole past state of the art is thus the nature of the catalytic centers, characterized not only by the high homogeneous nature but also, most of all, by the presence of π-ligands of defined chemical structure that remain coordinated to the transition metal atom during the course of the polymerization.[4] This allows one to steer the behavior of the copolymerization and the characteristics of the copolymer, by playing with the structure of the ligands. The opportunity to design the structure of the π-ligands has allowed the preparation of a large variety of organometallic complexes. A correlation between the structure and the performances of the organometallic complex can be established or, at least, attempted.

The results obtained in the frame of our research, already reported,[5q,6] have demonstrated the large variety of copolymer microstructure afforded by metallocene based catalytic systems. The product of reactivity ratios (r_1r_2) ranges from about 0.02 to about 3, the propene sequences can be highly isotactic, atactic, or highly syndiotactic, and 2,1-inserted propene units are not detectable or present up to a level of about 3−4% by mole. All these results arise from copolymers characterized by the very narrow distribution of the molecular properties, so that the intramolecular distribution of the comonomers can be described by the same statistical law for all the macromolecular chains.[5q,6,9] The results reported in the scientific literature by other authors[5] confirm the versatility of metallocenes as catalysts for ethene/propene copolymers, at a level unknown for the traditional catalysis.

The present paper is focused on the intramolecular distribution of the comonomers. In the field of ethene/propene copolymers and, in particular, for the one of the elastomeric copolymers, it is well-known that heterogeneous titanium-based catalysts prepare products with a high product of reactivity ratios, whereas homogeneous vanadium-based catalysts give rise to copolymers with r_1r_2 ranging from about 0.2 to about 1.[7] Studies reported in the literature have already shown that the high product of reactivity ratios of titanium-based copolymers is related to the multiplicity of the catalytic centers, rather than to their intrinsic nature, being essentially due to the presence in the copolymer of macromolecular chains with very different chemical compositions.[10] Furthermore, there is a sort of general assumption that a homogeneous single center catalyst is intrinsically unable to generate long sequences of both comonomers. As a matter of fact, some authors have already commented on the ability of metallocenes to prepare ethene/propene copolymers with random dis-

S0024-9297(97)01724-5 CCC: $15.00

Table 1. Ethene/Propene Copolymerization with *rac*-$Me_2C(3\text{-}^tBuCp)_2ZrCl_2$ and MAO as the Catalytic System[a]

run	E/P[b] gas phase	E/P[b] liquid phase	yield (g)	$(E)_{copolymer}$ (% mol)	I.V. (dL/g)	$(E + P)_{feed}/(E + P)_{polymer}$[c] (mol/mol)	$(E)_{feed}/(E)_{polymer}$[d] (mol/mol)
1	0.099	0.020	1.7	19.8	n.d.[e]	23	12
2	0.22	0.053	2.0	38.3	0.3	18	9
3	0.43	0.099	0.6	66.4	0.6	54	23
4	1.13	0.27	0.9	85.8	n.d.[e]	33	21
5	1.50	0.37	2.52	86.5	2.3	12	10
6	1.6	0.38	1.00	87.1	2.5	33	21
7	2.57	0.61	4.05	91.9	n.d.[e]	7.2	7

[a] Polymerization conditions: toluene = 100 mL, *rac*-$Me_2C(3\text{-}^tBuCp)_2ZrCl_2$ = 3.5 μmol, Al/Zr = 1000 (mol/mol), T = 50 °C, total pressure = 1.1 atm, flow rate of (E + P) mixture = 1.5 L/min, and polymerization time = 15 min. [b] Feed ratio (mol/mol). [c] Ratio between the monomers fed to the reactor and those converted into the polymer. [d] Ratio between ethene fed to the reactor and that converted into the polymer. [e] Not determined.

tribution of the comonomers (see, for example, refs 5i,g,p,w).

This paper discusses the ability of a single center homogeneous metallocene-based catalytic system to prepare ethene/propene copolymers with a high product of reactivity ratios. Preliminary results, obtained with selected metallocenes, have been already reported in the past few years.[5q,6a,c] More recently, a metallocene has been identified as able to prepare ethene/propene copolymers whose microstructure is suitable for an accurate determination of comonomers distribution. Preliminary results were already presented elsewhere.[6d,11] A thorough description of experimental activity, polymerization results, and statistical treatment of ^{13}C NMR data is here presented.

Results and Discussion

Ethene/Propene Copolymerizations. Ethene and propene were copolymerized in solution using a catalytic system composed of a metallocene, *rac*-isopropylidenebis-(3-*tert*-butylcyclopentadienyl) zirconium dichloride [*rac*-$Me_2C(3\text{-}^tBuCp)_2ZrCl_2$] and polymethylalumoxane (MAO). *rac*-$Me_2C(3\text{-}^tBuCp)_2ZrCl_2$ was designed and developed in Montell as a suitable metallocene for the preparation of isotactic polypropene. A fully isotactic pentad content as high as 99.4% was obtained in bulk at 50 °C.[12] An accurate NMR analysis confirmed the pure racemic structure of the metallocene sample employed in this work.

The ethene/propene copolymerizations reported here were performed so as to maintain constant, to the greatest possible extent, the relative concentration of the comonomers during the polymerization tests. In particular, the samples analyzed for the determination of r_1 and r_2 were obtained applying the concepts expressed by Crespi et al.[13] in the early days of the copolymerizations promoted by Ziegler−Natta catalysts: “To maintain a constant monomer concentration, continuous feeding and discharge of the monomers with very high space velocities of the circulating gases can be adopted”.[13] This approach was already followed by some of the authors.[5j] Details are in the Experimental Section. The use of a solution process allowed us to bypass the issues, typical of a suspension process,[14] related to the actual physical status of the polymer crumbs in the polymerization medium, which affect, to a great extent, fundamental aspects of the polymerization, such as, for example, the diffusion of the monomers toward the catalytic centers, not to mention the possible occurrence of fouling phenomena. Furthermore, the low concentrations adopted in this work for the copolymers in the polymerization solution (less than 4% w/v), their low molecular mass, the relatively high polymerization temperature (50 °C) and the use in most cases of a good solvent such as toluene allow us to disregard any limitation for the diffusion of the comonomers toward the catalytic centers, thanks to the low viscosity of the solution and, as a consequence, any variation of the concentration of the monomers. It is therefore reasonable to apply thermodynamic methods to calculate the composition of the polymerization solution, assumed to be constant all over the polymerization time. It is worth underscoring that a particular attention to the physical aspects of the copolymerization has to be paid when a highly active catalytic system, as a metallocene/MAO one, is used.[15]

Data of the copolymerizations performed with *rac*-$Me_2C(3\text{-}^tBuCp)_2ZrCl_2$ and MAO are shown in Table 1.

The ratio between the monomers fed to the polymerization system and those converted into the copolymer was well above the value traditionally accepted in the literature.[16] No efforts were made to reproduce the results, in terms of catalytic activity. Hence, only a comment about the order of magnitude can be spent: a catalytic activity as high as 1100 (kg of polymer)/(mol of Zr) in 15 min was achieved. However, as discussed below, the copolymer microstructure and the copolymerization parameters (r_1 and r_2) were found to be independent of the catalytic activity. A wide range of ethene/propene ratios in the polymerization bath was explored, from 2/98 to 38/62 as the molar ratio. This allowed the preparation of ethene/propene copolymers with an ethene content ranging from about 17 mol % to about 92 mol %, as detected from ^{13}C NMR analysis. $\bar{M}_w/\bar{M}_n$ values close to 2, detected for samples 1, 3, and 7, are typical of a metallocene-based (co)polymer and indicate the single center[17] nature of the catalytic system. This result was expected on the basis of the isomeric purity of the metallocene and leads us to exclude any possible isomerization reaction, even if unlikely, occurring during the polymerization. To further confirm the homogeneity of the investigated copolymers, a “macrosample” was prepared in a polymerization carried out in solution adopting a procedure, described in the Experimental Section, different from that of runs 1−7 and nevertheless characterized by the nearly constant composition of the polymerization bath. To investigate the distribution of the chemical composition (CCD), sample 8 was fractionated by applying a method based on the use of mixtures of poor and good solvents in different relative amounts and with a standard extraction time.[18] The selected solvents were proven to be able to extract fractions with different chemical composition from ethene/propene copolymers of similar comonomer content. Data and results of the fractionation are collected in Table 2.

Table 2. Fractionation of an Ethene/Propene Copolymer Prepared with $Me_2C(3\text{-}^tBuCp)ZrCl_2$/MAO as the Catalytic System

fraction no.	solvent type and relative amounts[a]	fraction (wt %)	E (mol %)	r_1r_2[b]
raw polymer			68.1	4.29
1	MEK / Hept = 70/30	3.0	62.0	n.d.[c]
2	MEK / Hept = 60/40	8.0	64.7	3.86
3	MEK / Hept = 50/50	26.8	66.0	n.d.[c]
4	MEK / Hept = 45/55	48.8	67.9	n.d.[c]
5	MEK / Hept = 40/60	13.4	68.8	3.77
av.		100	67.1	

[a] MEK = 2-butanone, Hept = *n*-heptane; relative amount expressed as wt/wt. [b] Evaluated as $r_1r_2 = 1 + F(\chi + 1) - (F + 1)(\chi + 1)^{1/2}$, where $F = [E]/[P]$ (mol/mol in the copolymer) and $\chi = ([EEE] + [PPP])/[EPE]$ (see ref 22). [c] Not determined.

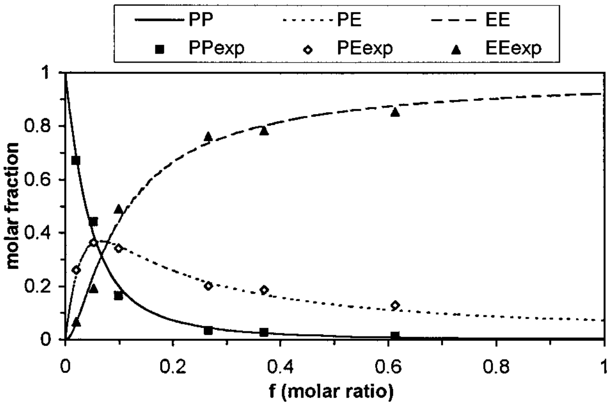


Figure 1. Diad distribution vs *f* for ethene/propene copolymers from rac-$Me_2C(3\text{-}^tBu\text{-}Cp)_2ZrCl_2$/MAO. Comparison of experimental and theoretycal data.

The fractions have a very similar chemical composition, to demonstrate the very narrow CCD of a copolymer from *rac*-$Me_2C(3\text{-}^tBuCp)_2ZrCl_2$.

These findings allowed to investigate the ethene/propene copolymers under the assumption that the collected results are really representative of the microstructure of every single macromolecule, at least on a statistical basis.

The results of the ^{13}C NMR characterization of samples 1−8 are collected in Table 3. The ethene content as well as the comonomer distribution (diads and triads) are reported. Even a simple inspection of diad and triad distributions reveals that the relative amount of the homosequences is higher than the one traditionally reported for metallocenes based copolymers.[5q,9] The propene sequences are fully isotactic. Not even for PPP content as high as 55% by mole was it possible to detect the presence of stereoerrors. The substantial absence of regio- and stereoirregularities in the propene placement allows the quantitative evaluation of the comonomer distribution at a triad level from ^{13}C NMR spectra[19] (see Experimental Section). Moreover, the copolymers can be regarded as *bi*polymers[20] composed of ethene and propene with regioregular propene units inserted in a single macromolecular chain with the same enantioface. In Table 3, a comparison is also shown between two copolymers (samples 5 and 6) obtained with the same polymerization bath composition but with a different catalytic activity. The triad distribution demonstrates that, as anticipated above, a single center catalyst gives rise to the same copolymer microstructure over a range of catalytic activity, provided that the activity is not high enough to remarkably affect the concentration of the monomers on the catalytic center. This result can be explained by assuming that, in a single center catalyst, the amount of active catalytic centers may change, for example as a result of the effect of poisons, whereas their nature remains the same. Moreover, the comparison between samples 3 and 8 shows that *rac*-$Me_2C(3\text{-}^tBuCp)_2ZrCl_2$ does not afford a different comonomer distribution also in the presence of different solvents such as, respectively, toluene and hexane.

Determination of r_1 and r_2. The reactivity ratios r_1 and r_2 for ethene/propene copolymerizations were determined using a statistical approach based on a pure Markovian copolymerization model.[21] The method is thoroughly explained in the attached Appendix. The fitting between experimental data and the Markovian model is represented in Figure 1 and in Figure 2, for diad and triad distributions, respectively.

In the graphs, the points refer to experimental data, whereas the curves were drawn on the basis of the optimized parameters of the statistical model. The very good agreement between experimental and theoretical data allows us to conclude that the ethene/propene copolymerizations from *rac*-$Me_2C(3\text{-}^tBuCp)_2ZrCl_2$ can be described by a first-order Markovian statistical model, i.e., a model that implies an effect on the monomer insertion of the last inserted monomeric unit (ultimate effect). The values obtained for r_1 and r_2 are shown in Table 4, together with their product as well as with the estimated error.

Most of the r_1 and r_2 values reported in the literature were obtained by applying the Finemann and Ross equation.[22] To have a comparison with the literature data, the Finemann/Ross approach was followed also for the copolymers from *rac*-$Me_2C(3\text{-}^tBuCp)_2ZrCl_2$. This comparison could be attempted, as the Finemann/Ross method is based on the assumption of the validity of the ultimate effect. The r_1 and r_2 values from this

Table 3. ^{13}C NMR Characterization of Ethene/Propene Copolymers Prepared with *rac*-$Me_2C(3\text{-}^tBuCp)_2ZrCl_2$/MAO as the Catalytic System

sample no.[a]	*f*[b]	E[c]	PPP	PPE	EPE	PEP	EEP	EEE	E[d]	PP	PE	EE
1	0.0204	0.1982	0.5488	0.2371	0.0158	0.0842	0.0906	0.0234	0.1979	0.671	0.2623	0.0668
2	0.0526	0.3831	0.3045	0.2678	0.0446	0.0899	0.1925	0.1007	0.3751	0.4427	0.3643	0.193
3	0.0989	0.6642	0.0793	0.1758	0.0807	0.0428	0.2551	0.3663	0.6621	0.1661	0.3436	0.4903
4	0.2658	0.8584	0.0132	0.0626	0.0658	0.0099	0.1813	0.6672	0.8631	0.0351	0.2036	0.7613
5	0.3699	0.8645	0.0083	0.0617	0.0655	0.0099	0.1629	0.6917	0.8779	0.0279	0.1884	0.7837
6	0.38	0.8713	0.0129	0.0510	0.0649	0.0107	0.1575	0.7031	0.8729	0.0387	0.1770	0.7844
7	0.6129	0.9194	0.000	0.0321	0.0484	0.0036	0.1289	0.7869	0.9199	0.0145	0.1313	0.8543
8	0.079	0.6810	0.0846	0.1671	0.0673	0.0350	0.2196	0.4265	0.6813	0.1650	0.3074	0.5276
8 fract 2		0.6467	0.1007	0.1824	0.0703	0.0443	0.2090	0.3934	0.6425	0.1957	0.3237	0.4806
8 fract 5		0.6882	0.0918	0.1467	0.0733	0.0326	0.2269	0.4287	0.6876	0.1350	0.3547	0.5102

[a] The numbers of the samples are those of the corrisponding runs. [b] E/P feed ratio (mol/mol) in liquid phase. [c] From triad distribution as E = PEP + EEP + EEE. [d] From diad distribution as E = EE + 0.5EP.

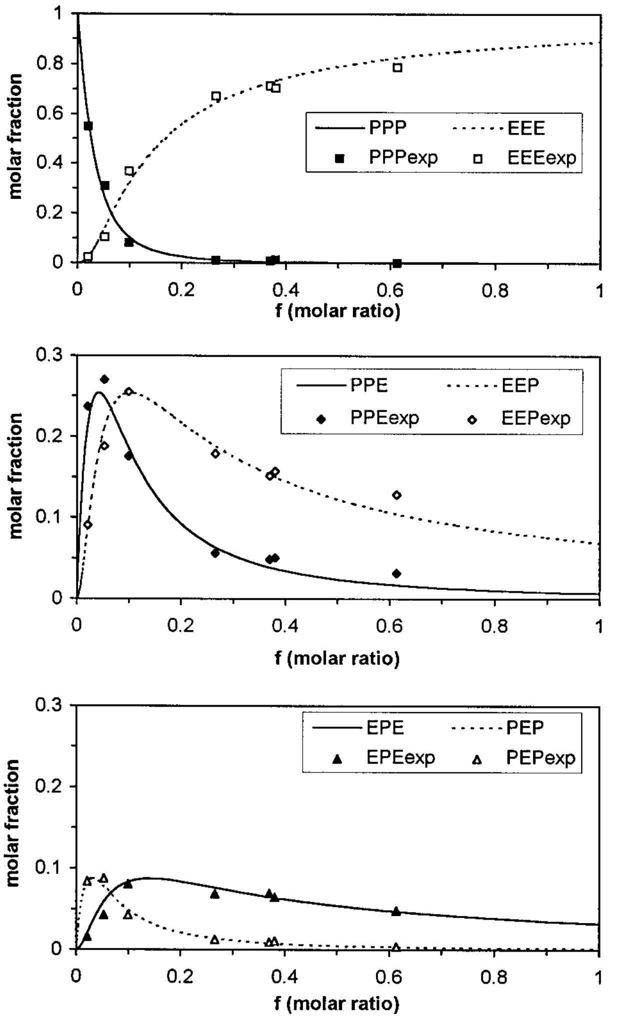


Figure 2. Triad distribution vs *f* for ethene/propene copolymers from rac-Me$_2$C(3-^{t}Bu-Cp)$_2$ZrCl$_2$/MAO. Comparison of experimental and theoretycal data.

Table 4. Reactivity Ratios for Ethene/Propene Copolymerization with *rac*-Me$_2$C(3-^{t}BuCp)$_2$ZrCl$_2$/MAO as the Catalytic System

method	$r_1 \pm \delta r_1$	$r_2 \pm \delta r_2$	$r_1r_2 \pm \delta(r_1r_2)^a$	LS$_{tot}$	ν^b
diad fitting	25.5 ± 2.7	0.109 ± 0.014	2.8 ± 0.7	0.0117	10
triad fitting	25.6 ± 1.5	0.110 ± 0.008	2.8 ± 0.4	0.0129	28
Finemann /Ross plot	19.3 ± 4.8	0.074 ± 0.08	1.4 ± 1.9	0.00896	4

[a] $\delta(r_1r_2) = r_1\delta r_2 + r_2\delta r_1$. [b] Number of degrees of freedom.

approach are also shown in Table 4. The very low ν value (see Table 4) in the application of the Finemann and Ross method brings about a very high error (as a 95% confidence limit from the linear regression) on the evaluated r_1 and r_2 parameters, introducing a large uncertainty in the evaluation of their product (r_1r_2 = 1.4 ± 1.9). The statistical approach affords more reliable results as narrow confidence interval are obtained (see Table 4). The r_1r_2 values, definitively higher than 1, reported in the two first lines of Table 4 are a numerical evidence of the presence of long sequences of both comonomers in ethene/propene copolymers from *rac*-Me$_2$C(3-^{t}BuCp)$_2$ZrCl$_2$. In Figure 3, the relative amount of the propene homodiads is plotted as a function of the chemical composition of the copolymers.

A comparison is shown with copolymers characterized by a random distribution ($r_1 = 1/r_2$), as well as by an almost alternate distribution, ($r_1r_2 = 0.2$)[5q,x,6a,c,d,11a,b] of

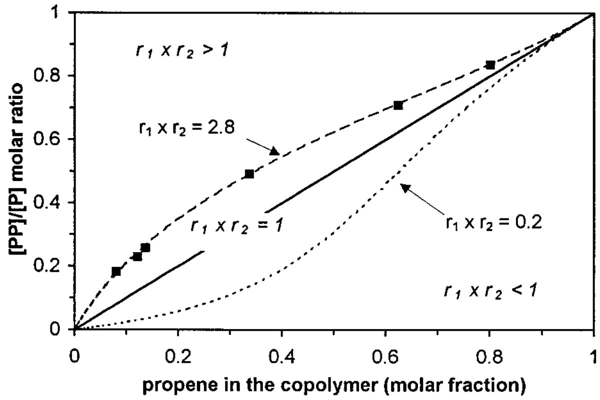


Figure 3. PP/P vs P in ethene/propene copolymers, as a function of r_1r_2. The theoretycal curves refer to, from top to bottom, r_1r_2 = 2.8, 1, and 0.2 (see text). The experimental points refer to ethene/propene copolymers from rac-Me$_2$C(3-^{t}-Bu-Cp)$_2$ZrCl$_2$/MAO.

the comonomers. The curves clearly show that the comonomer distribution afforded by *rac*-Me$_2$C(3-^{t}BuCp)$_2$-ZrCl$_2$ is not compatible with a random copolymer and thus indicate that any insertion of a comonomer is definitely dependent on the type of the last inserted monomer. As already mentioned in the Introduction, a class of metallocenes was selected by some of the authors to obtain an E/P copolymers with high r_1r_2. A typical representative was *rac*-ethylenebis(4,7-dimethylindenyl)zirconium dichloride [*rac*-(EBDMI)ZrCl$_2$]. The present work was not based on the copolymers from *rac*-(EBDMI)ZrCl$_2$ as this metallocene gives rise to a clearly detectable amount of 2,1-propene insertions that affects, to some extent, the quantitative determination of the comonomers distribution. However, it is worth observing that, similar to *rac*-Me$_2$C(3-^{t}BuCp)$_2$ZrCl$_2$, *rac*-(EBDMI)ZrCl$_2$ is a bridged stereorigid racemic metallocene with bulky substituents on the Cp ring.

In the scientific literature devoted to ethene/propene copolymers from metallocenes, only one example of an ethene/propene copolymer with a high r_1r_2, obtained with Cp$_2$HfCl$_2$/MAO is reported.[4f] To compare copolymers prepared under the same experimental conditions, three samples of ethene/propene copolymers were prepared with this catalytic system. The selected polymerization bath compositions were among those adopted for *rac*-Me$_2$C(3-^{t}BuCp)$_2$ZrCl$_2$ or close to them. Data and results are in Table 5.

r_1 and r_2 values were evaluated by adopting the method described in this manuscript, moving from the triad distribution: $r_1 = 13.48 \pm 0.91$, $r_2 = 0.041 \pm 0.016$, and $r_1r_2 = 0.55 \pm 0.26$. These values seem to exclude the possibility that this catalytic system can prepare copolymers with long sequences of both comonomers, at least under the applied experimental conditions. On the other side, many examples of ethene/propene copolymers with long ethene sequences are reported in the literature.[5c] However, these copolymers are also characterized by the very limited amount of 1-olefin sequences (in some cases almost undetectable), i.e., by the low values of r_2. In fact, it is generally observed that a catalyst keen to give long ethene sequences has a very low reactivity toward a larger monomer as propene. In the Introduction, it was also reported that ethene/propene copolymers with high product of reactivity ratios of the comonomers are typically obtained from heterogeneous titanium-based catalytic systems, as the result of the analysis of a blend of macromolecules

Table 5. Ethene/Propene Copolymerization with Cp_2HfCl_2/MAO as the Catalytic System[a]

run	E/P[b] gas phase	*f*	yield (g)	(E)$_{copolymer}$ (% mol)	PPP	PPE	EPE	PEP	EEP	EEE	PP	PE	EE
9	0.55	0.18	0.31	70.0	0.0308	0.0702	0.1990	0.1137	0.2523	0.3340	0.0749	0.4597	0.4654
10	2.2	0.53	1.02	89.6	0.000	0.0146	0.0906	0.0232	0.1490	0.7227	0.0064	0.1930	0.8006
11	5.4	1.28	4.6	93.2	0.000	0.0078	0.0604	0.0077	0.1003	0.8238	0.0061	0.1165	0.8784

[a] Polymerization conditions: toluene = 100 mL, Cp_2HfCl_2 = 3.5 μmol (run 10) or 5.0 μmol (runs 9 and 11), Al/Zr = 1000 (mol/mol), T = 50 °C, total pressure = 80 mm Hg, flow rate of (E + P) mixture = 1.5 L/min, and polymerization time = 15 min. [b] Feed ratio (mol/mol).

having a different or even a very different chemical composition. For the copolymers prepared with *rac*-$Me_2C(3\text{-}^tBuCp)_2ZrCl_2$ this possibility has to be excluded on the basis of the above-mentioned results, i.e., the narrow molecular mass and chemical composition distribution and, most of all, the chance of using a single site statistical model to describe the comonomer distribution. Moreover, it is worth observing that any of the investigated fractions of copolymer sample 8 shows a r_1r_2 product higher than 1 (see Table 2). A detailed study is in progress to understand how a single center homogeneous Ziegler–Natta catalyst can prepare ethene/propene bipolymers with long sequences of both comonomers, i.e., how an insertion polymerization carried out under constant polymerization conditions can generate long sequences of two very different monomers such as ethene and propene. The following aspects are mainly considered, to investigate their influence on r_1 and r_2: the stereospecificity of the metallocene, the role played by steric and electronic effects, and the role of the cocatalyst. Some results will be reported in forthcoming papers.[15]

Experimental Section

General Procedures and Materials. All reactions and manipulation were carried out under dry nitrogen atmosphere using the Schlenk tube technique. All the chemicals were stored under nitrogen.

Toluene (Carlo Erba RPE) was deoxygenated by bubbling dry nitrogen, maintained overnight under nitrogen in the presence of $CaCl_2$, filtered, refluxed for 8 h over $Al(isobutyl)_3$, and finally distilled.

Hexane (Carlo Erba, RPE) was refluxed for 8 h over $Al(isobutyl)_3$ and distilled.

Polymerization grade ethene and propene were received directly from Montell Ferrara plants. Ethene/propene mixtures were prepared in a 5 L steel cylinder, filled with quantities of the two gases small enough to prevent their condensation.

MAO (Witco, 10% w/w in toluene) was used without any further treatment.

rac-$Me_2C(3\text{-}^tBuCp)_2ZrCl_2$, was synthesized following the reported procedure.[12]

Cp_2HfCl_2 (Strem) was used without any further purification.

Determination of the Concentration of the Polymerization Solutions. The vapor–liquid equilibrium for ethene/propene/toluene and ethene/propene/hexane mixtures was estimated from the Redlich Kwong Soave equations. This set of thermodynamic equations was selected, on the basis of a comparison with experimental results, among those available in Aspen Plus (Release 9), commercialized by Aspen Technology Inc. The concentrations of the comonomers were hence calculated.

Low-Pressure Polymerizations. Polymerizations were performed at 50 °C, in a 250 mL glass reactor, equipped with a mechanical stirrer, a thermometer, and a pipe for monomer feeding. Then 100 mL of toluene and 2 mL of MAO solution (3.45 mmol of aluminum) were introduced into the nitrogen-purged reactor, kept in a thermostatic bath. At the polymerization temperature, the monomer mixture was fed with a flow of 1.5 L/min. When the equilibrium pressure (80 mmHg of overpressure) was reached, 1.45 mg (3.5 μmol) of *rac*-$Me_2C(3\text{-}^tBuCp)_2ZrCl_2$, dissolved in 5 mL of toluene in the presence of 0.05 mmol of MAO, was added to start the polymerization. During the polymerization, the temperature was kept within ±0.2 °C. The polymerization was stopped after 15 min by adding 1 mL of methanol, and the copolymer was recovered by precipitation in methanol/HCl and filtration and finally dried at 50 °C under reduced pressure.

Polymerizations with Cp_2HfCl_2 were performed by following the same procedure. Data are in Table 5.

High-Pressure Polymerization. Polymerization was performed in a 4 L steel autoclave, equipped with a mechanical stirrer, an external jacket for the circulation of a mixture of steam and water to regulate internal temperature, a glass window to have a visual control of the reaction, and valves for the introduction of liquids and gases. Temperature, pressure, and monomer feeding were regulated and controlled by an nXL YOKOGAWA process system.

First 1355 g of hexane, 24 g of ethene, 420 g of propene, and 1.3 mL of the toluene solution of MAO (2.25 mmol) were introduced into the autoclave at room temperature. The reactor was heated at 50 °C, and a solution prepared by dissolving 1 mg of *rac*-$Me_2C(3\text{-}^tBuCp)_2ZrCl_2$ in 7 mL of toluene containing 2.25 mmol of MAO was injected.

During the polymerization, the pressure was kept constant by feeding ethene and the temperature was maintained within ±0.1 °C. A homogeneous polymer solution was formed. After 70 min the reaction was stopped by injecting CO. Monomers and solvent were purged out, and the copolymer was recovered by precipitation in acetone and filtration and dried under reduced pressure at 60 °C for 3 h. A 46.5 g yield of copolymer was weighed.

Polymer Analysis. Intrinsic viscosities were determined in tetrahydronaphthalene at 135 °C. GPC mesurements were performed on a Waters 150-C GPC equipped with TSK columns (Model GM-HXL-HT) with 1,2-dichlorobenzene as solvent, at 135 °C. Monodisperse fractions of polystyrene were used as standards.

Copolymer Fractionation. The fractionation of the copolymers was performed by successively using solvents (pure or a mixture) with increasing solubility power, at their boiling point. In a round-bottomed flask, equipped with mechanical stirrer, 600 mL of solvent(s) and 6.0 g of polymer were introduced, under nitrogen. The mixture was allowed to reflux for 6 h and then to reach room temperature under stirring. The solution was then separated from the unsolved polymer by filtration. The solvent was removed by evaporation at reduced pressure and the recovered polymer was dried at 40 °C, at reduced pressure, for about 12 h.

NMR Analysis. ^{13}C NMR spectra were obtained with a DPX-200 spectrometer operating at 50.32 MHz in the Fourier transform mode at 120 °C. The peak of the $S_{\delta\delta}$ carbon (nomenclature according to Carman[23]) was used as internal reference. The samples were dissolved in 1,1,2,2-tetrachloroethane-d_2 at 120 °C with a 8 w%/v concentration. Each spectrum was acquired with a 90° pulse, with 12 s of delay between pulses and CPD (waltz16) to remove $^1H-^{13}C$ coupling. About 5000 transients were stored in 32K data points using a spectral window of 3000 Hz.

The molar mm % was calculated through the following equation: mm % = $100T_{\beta\beta}(mm)/[T_{\beta\beta}(mm) + T_{\beta\beta}(mr + rr)]$.

Triad distribution was calculated according to Kakugo.[24] At high propene content it is more difficult to obtain a correct evaluation of the PPE triad from the direct integration of $T_{\beta\delta}$ owing to the presence of $S_{\gamma\gamma}$ as a shoulder of $T_{\beta\delta}$.[19] To obtain

Table 6. Diad and Triad Distributions for an E/P Copolymer Expressed through the First-Order Markovian Probabilities

diad	triad
PP $NP(\mathrm{P}|\mathrm{M{-}E})[1 - P(\mathrm{E}|\mathrm{M{-}P})]$	PPP $NP(\mathrm{P}|\mathrm{M{-}E})[1 - P(\mathrm{E}|\mathrm{M{-}P})]^2$
PE $2NP(\mathrm{P}|\mathrm{M{-}E})P(\mathrm{E}|\mathrm{M{-}P})$	PPE $2NP(\mathrm{P}|\mathrm{M{-}E})P(\mathrm{E}|\mathrm{M{-}P})[1 - P(\mathrm{E}|\mathrm{M{-}P})]$
EE $NP(\mathrm{E}|\mathrm{M{-}P})[1 - P(\mathrm{P}|\mathrm{M{-}E})]$	EPE $NP(\mathrm{P}|\mathrm{M{-}E})P(\mathrm{E}|\mathrm{M{-}P})^2$
	PEP $NP(\mathrm{P}|\mathrm{M{-}E})^2P(\mathrm{E}|\mathrm{M{-}P})$
	PEE $2NP(\mathrm{P}|\mathrm{M{-}E})P(\mathrm{E}|\mathrm{M{-}P})[1 - P(\mathrm{P}|\mathrm{M{-}E})]$
	EEE $NP(\mathrm{E}|\mathrm{M{-}P})[1 - P(\mathrm{P}|\mathrm{M{-}E})]^2$
$N = 1/[P(\mathrm{P}|\mathrm{M{-}E}) + P(\mathrm{E}|\mathrm{M{-}P})]$	

a correct estimation of the $T_{\beta\delta}$ area, all the peaks between 31.0 and 29.0 ppm were integrated together and their relative amounts were obtained applying a deconvolution program (Bruker WINNMR).

Acknowledgment. The authors gratefully acknowledge the important contributions given by Giovanni Baruzzi, who performed the thermodynamic elaborations, and by Marcello Colonnesi, who ran the NMR experiments.

Appendix: Statistical Approach for the Determination of r_1 and r_2

Hayashi analyzed ethene-propene copolymers from heterogeneous Ziegler–Natta catalytic systems using a two-site first-order Markovian model to fit the experimental triad distribution. The r_1 and r_2 values for the two catalytic sites were obtained from the probability parameters found for each copolymer sample using the expressions

$$\mathrm{r}_1 = \frac{p_{11}}{p_{12}f} \qquad r_2 = \frac{p_{22}f}{p_{21}} \tag{1}$$

where p_{mn} represents the probability of a n-monomer insertion in a m-ended chain.

Cheng reported the possibility to evaluate the r_1 and r_2 values of different catalytic sites present in a heterogeneous ZN catalyst using a “statistical mixture model” based on the combination of different first-order Markovian models used to fit in the same time all the ^{13}C NMR triad distributions of copolymers obtained starting from different bath compositions, but in the paper he discussed only the application of mixed Bernoullian models.[25]

As we deal with a single center catalyst, we use here a statistical approach based on a pure Markovian copolymerization model.[26]

It is well-known that the Markovian probabilities $P(\mathrm{E}|\mathrm{M{-}P})$ (probability of ethene insertion in a metal–propene bond) and $P(\mathrm{P}|\mathrm{M{-}E})$ (probability of propene insertion in a metal–ethene bond) depend on the copolymerization bath composition f (mole ratio between ethene and propene) and on the reactivity ratios according to the following equations:

$$P(\mathrm{P}|\mathrm{M{-}E}) = \frac{1}{1 + r_1 f} \qquad P(\mathrm{E}|\mathrm{M{-}P}) = \frac{f}{f + r_2} \tag{2}$$

The combination of these two probability parameters generates the theoretical Markovian expressions for comonomer sequences (diads or triads) which are shown in Table 6.

With a given catalytic system and given polymerization conditions (e.g. temperature, solvent, and total monomer pressure), the $P(\mathrm{E}|\mathrm{M{-}P})$ and $P(\mathrm{P}|\mathrm{M{-}E})$ probability parameters depend only on the polymerization bath composition, as the reactivity ratios r_1 and r_2 are expected to be constant. Therefore, the reactivity ratios r_1 and r_2 can be treated as the parameters to be optimized through the fitting of the experimental diad or triad distributions, using the equations reported in Table 6.

The ethene content and the comonomer distributions (diads and triads) for all copolymer samples, obtained from ^{13}C NMR, are reported in Table 3.

The fitting procedure is as follows.

(1) For each copolymerization bath composition f_i, two probability parameters $P(\mathrm{E}|\mathrm{P})_i = P(\mathrm{E}|\mathrm{M{-}P})_i$ and $P(\mathrm{P}|\mathrm{E})_i = P(\mathrm{P}|\mathrm{M{-}E})_i$ are evaluated using two initial values for r_1 and r_2 and eq 2.

(2) The related diad or triad distributions are then calculated from the expressions reported in Table 6 using the starting parameters $P(\mathrm{E}|\mathrm{P})_i$ and $P(\mathrm{P}|\mathrm{E})_i$.

(3) The sum of the squares of the deviations between experimental and calculated distribution (triads, for example) for each copolymer sample is evaluated as

$$\begin{aligned}\mathrm{LS}_i = {} & (\mathrm{PPP_{exp}} - \mathrm{PPP_{calc}})^2 + (\mathrm{PPE_{exp}} - \mathrm{PPE_{calc}})^2 + \\ & (\mathrm{EPE_{exp}} - \mathrm{EPE_{calc}})^2 + (\mathrm{PEP_{exp}} - \mathrm{PEP_{calc}})^2 + \\ & (\mathrm{PEE_{exp}} - \mathrm{PEE_{calc}})^2 + (\mathrm{EEE_{exp}} - \mathrm{EEE_{calc}})^2\end{aligned}$$

(4) All the values of LS_i are collected in the summation over all copolymer samples, as follows:

$$\mathrm{LS_{tot}} = \sum\nolimits_i \mathrm{LS}_i$$

(5) $\mathrm{LS_{tot}}$ is minimized by changing the values of r_1 and r_2.

This calculation was done in the present work using the Solver macro in the MS Excel program (7.0 version). A diagram is reported in Scheme 1 to show the fitting procedure for diad distributions.

The degrees of freedom (ν) are also calculated through the equation

$$\nu = n_{\mathrm{obs}} - r_{\mathrm{obs}} - n_{\mathrm{par}} \tag{3}$$

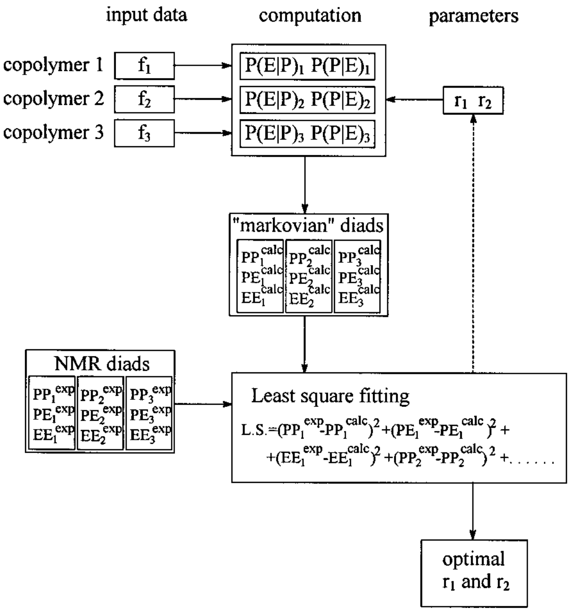
where n_{obs} is the number of experimental data points (for the triad fitting $n_{\mathrm{obs}} = 6 \times 6$), r_{obs} is the number of dependencies in the data (the sum of the triads for each sample is equal one, $r_{\mathrm{obs}} = 6$), and n_{par} is the number of estimated parameters ($n_{\mathrm{par}} = 2$).

The confidence intervals for the estimated parameters are evaluated on the basis of Student's distribution using the relationship[27]

$$\hat{r}_i - t_\alpha(\nu)\sqrt{\frac{C_{ii}(\mathrm{LS_{tot}})}{\nu}} < r_i^* < \hat{r}_i + t_\alpha(\nu)\sqrt{\frac{C_{ii}(\mathrm{LS_{tot}})}{\nu}} \tag{4}$$

where is the estimated value for r_i, ν is the number of degrees of freedom, $t_\alpha(\nu)$ is the Student-t value (for a

Scheme 1



95% confidence interval we use $\alpha = 0.025$ with the ν values reported in Table 4) and C_{ii} is the *i*,*i*-element of the covariance matrix $\boldsymbol{C}$ of the estimated parameters vector (r_1, r_2). The matrix $\boldsymbol{C}$ is the inverse of the Hessian matrix $\boldsymbol{H}$ at the point where $\mathrm{LS}_{\mathrm{tot}}$ is a minimum

$$\boldsymbol{H} = \begin{bmatrix} \dfrac{\partial^2 (\mathrm{LS}_{\mathrm{tot}})}{\partial {r_1}^2} & \dfrac{\partial^2 (\mathrm{LS}_{\mathrm{tot}})}{\partial r_1 \partial r_2} \\ \dfrac{\partial^2 (\mathrm{LS}_{\mathrm{tot}})}{\partial r_1 \partial r_2} & \dfrac{\partial^2 (\mathrm{LS}_{\mathrm{tot}})}{\partial {r_2}^2} \end{bmatrix} \tag{5}$$

The second-order derivatives were calculated using a numerical method.[28] As an example we report here the formulas used for the estimation of one of the elements of $\boldsymbol{H}$:

$$\frac{\partial[\mathrm{LS}_{tot}(\hat{r}_1 + h,\hat{r}_2)]}{\partial r_1} = \frac{\mathrm{LS}_{tot}(\hat{r}_1 + 2h,\hat{r}_2) - \mathrm{LS}_{tot}(\hat{r}_1,\hat{r}_2)}{2h} \tag{6}$$

$$\frac{\partial[\mathrm{LS}_{tot}(\hat{r}_1 - h,\hat{r}_2)]}{\partial r_1} = \frac{\mathrm{LS}_{tot}(\hat{r}_1,\hat{r}_2) - \mathrm{LS}_{tot}(\hat{r}_1 - 2h,\hat{r}_2)}{2h} \tag{7}$$

$$\frac{\partial^2[\mathrm{LS}_{tot}(\hat{r}_1,\hat{r}_2)]}{\partial {r_1}^2} = \frac{\dfrac{\partial[\mathrm{LS}_{tot}(\hat{r}_1 + h,\hat{r}_2)]}{\partial r_1} - \dfrac{\partial[\mathrm{LS}_{tot}(\hat{r}_1 - h,\hat{r}_2)]}{\partial r_1}}{2h} \tag{8}$$

h is selected in the interval $0.1 > h > 0.0001$ to have constant derivatives for further changes of the h value.

References and Notes

(1) Kaminsky W.; Hansen, H. DE 3,240,383, 1982. (b) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99.

(2) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728. (b) Turner, H. W. *Eur. Pat. Appl.* 277004, 1988; *Chem. Abstr.* **1989**, 110, 58290a; (c) Turner, W.; H. Hlatky, G. G. *Eur. Pat. Appl.* 277003, 1988; *Chem. Abstr.* **1989**, *110*, 58290b.

(3) Resconi, L.; Giannini, U.; Albizzati, E. EP 0384171 to Montell Technology B. V., 1990. (b) Resconi, L.; Galimberti, M.; Piemontesi, F.; Guglielmi, F.; Albizzati, E. EP 0575875 to Montell Technology B.V., 1993. (c) Dall'Occo, T.; Galimberti, M.; Resconi, L.; Albizzati, E.; Pennini, G. WO 96/02580 to Montell Technology B.V., 1996.

(4) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99. (b) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325. (c) Gupta, V. K.; Satish, S.; Bhardway I. S. J. *Macromol. Sci. Rev. Macromol. Chem. Phys.* **1994**, *C34*, 439. (d) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (e) Huang J.; Rempel, G. L. *Prog. Polym. Sci.* **1995**, *20*, **459**. (f) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 225.

(5) Busico, V.; Mevo, L.; Palumbo, G.; Zambelli, A.; Tancredi, T. *Makromol. Chem.* **1983**, *184*, 2193. (b) Kaminsky, W.; Miri, M. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, 23, 2151. (c) Ewen, J. A. In *Catalytic Polymerization*; Kei, T.; Soga, K. Kodansha: Tokyo 1986; p 271. (d) Kaminsky, W.; Schlobohm, M. *Makromol. Chem., Macromol. Symp.* **1986**, *4*, 103. (e) Drögemüller, H.; Heiland, K.; Kaminsky, W. In: *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Kaminsky, W.; Sinn, H. Springer-Verlag: Berlin 1988; p 303. (f) Chien, J. C. W.; He, D. J. *Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1585. (g) Chien, J. C. W.; He, D. J. *Polym. Sci. Part A: Polym. Chem.* **1991**, *29*, 1595. (h) Chien, J. C. W.; He, D. J. *Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1603. (i) Chien, J. C. W.; He, D. J. *Polym. Sci. Part A: Polym. Chem.* **1991**, *29*, 1609. (j) Zambelli, A.; Grassi, A.; Galimberti, M.; Mazzocchi, R.; Piemontesi, F. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 523. (k) Soga, K.; Park, J. R.; Shiono, T. *Polym. Commun.* **1991**, *32*, 310. (l) Soga, K.; Uozomi, T. *Makromol. Chem.* **1992**, *193*, 823. (m) Soga, K.; Kaminaka, M. *Macromol. Chem. Phys.* **1994**, *195*, 1369. (n) Soga, K.; Uozumi, T.; Saito, M.; Shiono, T. *Macromol. Chem. Phys.* **1994**, *195*, 1503. (o) Pietikainen, P.; Seppala, J. V. *Macromolecules* **1994**, *27*, 1325. (p) Koivumaki, J.; Seppala, J. V. *Eur. Polym. J.* **1994**, *30*, 1111. (q) Galimberti, M.; Martini, E.; Piemontesi, F.; Sartori, F.; Resconi, L.; Albizzati, E. *Macromol. Symp.* **1995**, *89*, 259. (r) Banzi, V.; Angiolini, L.; Caretti, D.; Carlini, C. *Angew. Makromol. Chem.* **1995**, *229*, 113. (s) Mitani, M.; Ouchi, K.; Hayakawa, M.; Yamada, T.; Mukaiyawa, T. *Polym. Bull.* **1995**, *35*, 677. (t) Marques, M.; Yu, Z.; Rausch, M. D.; Chien, J. C. W. *J. Polym. Sci.; Part A: Polym. Chem.* **1995**, *33*, 2787. (u) Yu, Z.; Marques, M.; Rausch, M. D.; Chien, J. C. W.; *J. Polym. Sci.: Part A: Polym. Chem.* **1995**, *33*, 2795. (v) Dolatkhani, M.; Cramail, H.; Deffieux, A. *Macromol. Chem. Phys.* **1996**, *197*, 2481. (w) Lehtinen, C.; Löfgren, B. *Eur. Polym. J.* **1997**, *33*, 115. (x) Karol, F. J.; Kao, S.-C.; Wasserman, E. P.; Brady, R. C. *New J. Chem.* **1997**, *21*, 797.

(6) Galimberti, M.; Martini, E.; Sartori, F.; Piemontesi, F.; Albizzati, E. *Proceedings of MetCon '94*; Houston, TX, May 25–27, 1994 (available from The Catalyst Group, P.O. Box 637, Spring House, PA, 19477). (b) Galimberti, M.; Dall'Occo, T.; Camurati, I.; Sartori, F.; Piemontesi, F. *Proceedings of MetCon '95*; Houston, TX May 17–19, 1995 (available at: see ref 6a). (c) Galimberti, M.; Dall'Occo, T.; Piemontesi, F.; Camurati, I.; Collina, G.; Battisti, M. *Proceedings of MetCon '96*; Houston, TX, June 12–13, 1996 (available at: see ref 6a). (d) Galimberti, M.; Baruzzi, G.; Camurati, I.; Fusco, O.; Piemontesi, F., Vianello, M.; *Proceedings of Metallocenes Europe '97, The 3rd International Congress on Metallocenes Polymers*; Dusseldorf, Germany, April 8–9, 1997 (available at Schotland Business Research, Inc., Skillman, NJ 08558). (e) Galimberti, M.; Ferraro, A.; Baruzzi, G.; Sgarzi, P.; Camurati, I.; Piemontesi, F.; Mingozzi, I.; Vianello, M. *Proceedings of MetCon '97*; Houston, TX, June 4–5, 1997 (available at: see ref 6a). (f) Ferraro, A.; Galimberti, M.; Baruzzi, G.; Di Diego, M. *Proceedings of MetCon '97*; Houston, TX, June 4–5, 1997 (available at: see ref 6a).

(7) Zucchini, U.; Dall'Occo, T.; Resconi, L. *Indian J. Of Technol.* **1993**, *31*, 247 and references therein.

(8) McGeary, C. A.; Wortman, W. A.; Karpelkes, R., Kontos, E. G. *Proceedings of Flexpo 96*; Houston, TX, June 26–28, 1996 (available at Chemical Market Resources, Inc. 1120 NASA Rd. 1, Suite 340, Houston, TX 77058-3320).

(9) Herfert, N., Fink, H. *Polym. Mater. Sci. Eng.* **1992**, *67*, 31. (b) Herfert, N.; Montag, P.; Fink, G. *Makromol. Chem.* **1993**, *194*, 3167 (c) Randall J. C.; Rucker, S. P. *Macromolecules*, **1994**, *27*, 2120.

(10) Albizzati, E.; Giannini, U.; Collina, G.; Noristi L.; Resconi, L. Catalysts and Polymerizations. In *Polypropylene Hand-*

book; Moore, Edward P., Jr. Ed.; Hanser Publishers: Munich, Vienna, New York, 1996; p 11 and refs 505, 506 therein.

(11) Galimberti, M.; Piemontesi, F.; Fusco, O.; Camurati, I. Communication at the Workshop on Recent advances in homogeneous Ziegler–Natta polymerizaton, IIASS, Vietri sul Mare (SA), Italy; September 19–20, 1996. (b) Galimberti, M.; Destro, M.; Fusco, O.; Piemontesi, F.; Camurati, I.; Communication at XIII Convegno Italiano di Scienza e Tecnologia delle Macromolecole, AIM, Genova, Italy, September 21–25, 1997.

(12) Resconi, L.; Piemontesi, F.; Nifant'ev, I.; Ivchenko, P.; Albizzati, E. WO 96/22995 to Montell Technology B.V., 1995.

(13) Crespi, G.; Valvassori, A.; Sartori, G. In *Copolymerization*; Ham, G. E., Ed.; Interscience Publishers: New York, London, Sidney, 1964; p 240.

(14) Hoel, E. L.; Cozewith, C.; Byrne, G. D. *AIChE J.* **1994**, *40*, 1669.

(15) Galimberti, M.; Destro, M.; Piemontesi, F.; Fusco, O.; Camurati, I. Manuscripts in preparation.

(16) Sacchi, M. C.; Shan, C.; Forlini, F.; Tritto, I.; Locatelli, P. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 231.

(17) Resconi, L.; Fait, A.; Piemontesi, F.; Colonnesi, M.; Rychlicki, H.; Zeigler, R. *Macromolecules* **1995**, *28*, 6667.

(18) Balbontin, G.; Dall'Occo, T.; Galimberti, M. *Polym. Adv. Technol.* **1992**, *4*, 429.

(19) Tritto, I.; Fan, Z.; Locatelli, P.; Sacchi, M. C.; Camurati, I.; Galimberti, M. *Macromolecules* **1995**, *28,* 3342.

(20) The term *bi*polymer is here used to indicate a copolymer composed of only two comonomers. In fact the prefix “co-“, that comes from the Latin *cum* and indicates the union of more subjects without specifying their number, has been substituted with the prefix “bi-“, that comes from the Latin “*bis*” and mainly signifies twice.

(21) Odian G. *Principles of Polymerization*, 3rd ed.; Wiley & Sons: New York, 1991; p 455.

(22) Odian G. *Principles of Polymerization*, 3rd ed.; Wiley & Sons: New York, **1991**; p 469.

(23) Carman, C. J.; Harrington, R. A.; Wilkes, C. E. *Macromolecules* **1977**, *10,* 537. (b) Wilkes, C. E.; Carman, C. J.; Harrington, R. A. *J. Polym. Sci.: Symp.* **1973**, *43,* 237.

(24) Kakugo, M.; Naito, Y.; Mizunuma, K.; Miyatake, T. *Macromolecules* **1982**, *15,* 1150.

(25) Cheng, H. N. In *New Advances in Polyolefins*; Chung, T. C., Ed.; Plenum Press: New York, 1993; p 159.

(26) Natta G.; Mazzanti G.; Valvassori A.; Sartori G.; Morero D. *Chim. Ind. (Milan)* **1960**, *42*, 125.

(27) Van der Burg, M. W.; Chadwick, J. C.; Sudmeijer, O.; Tulleken, H. J. A. F. *Makromol. Chem., Theory Simul.* **1993**, *2*, 399.

(28) See, for example: *Numerical Recipes in C: The Art of Scientific Computing*, 2nd ed.; Cambridge University Press: Cambridge, England, 1992; p 187.

MA9717247