DOI: 10.1002/masy.200650217

rac-[CH_2(3-tert-butyl-1-indenyl)$_2$]$ZrCl_2$/MAO in the Copolymerization of Olefins and Dienes

*Stefania Pragliola, Chiara Costabile, Mariagrazia Napoli, Gaetano Guerra, Pasquale Longo**

Summary: Olefin-diene copolymerizations in the presence of C_2 symmetric zirconocene *rac*-[CH_2(3-tert-butyl-1-indenyl)$_2$]$ZrCl_2$/MAO catalytic system have been reported and rationalized by experimental and molecular modeling studies. Ethene gives 1,2-cyclopropane and 1,2-cyclopentane, 1,3-cyclobutane, and 1,3-cyclopentane units in copolymerization with 1,3-butadiene, 1,4-pentadiene, and 1,5-hexadiene, respectively. Propene-1,3-butadiene copolymerizations lead to 1,2 and 1,4 butadiene units and to a low amount of 1,2-cyclopropane units.

Keywords: copolymerization; NMR; Ziegler-Natta catalyst

Introduction

C_2 symmetric zirconocene *rac*-[CH_2(3-tert-butyl-1-indenyl)$_2$]$ZrCl_2$ (**1**) shows a substantially complete regioselectivity and stereoselectivity in the polymerization of propene leading to an isotactic polymer through a primary 1,2 insertion.[1,2]. As for (**1**), a different mechanism of regioselectivity, with respect to other isospecific zirconocenes which lead to a substantial amount of regioirregularities,[3] involves the inhibition of secondary monomer coordination, through suitable substitutions of the π-ligand.[1,4]

Recent polymerization studies have shown that only this latter regioselectivity, due to π-ligand substitution, is retained for other hydrocarbon monomers, forcing them to unusual reaction paths also leading to new polymeric structures. (**1**)/MAO, employed as catalyst in the ethene-styrene copolymerization, produces block copolymers, whereas the homogeneous catalytic systems, known to copolymerize these monomers, preferentially give rise to pseudorandom copolymers without styrene homosequences. The polystyrene blocks are isotactic and an unusual primary insertion of styrene,[5] rather than the usual secondary insertion is observed.[6]

(**1**)/MAO is also active in the polymerization of conjugated dienes, promoting 1,4 polymerization of 1,3-butadiene and (Z)-1,3-pentadiene and 1,2 polymerization of (E)-1,3-pentadiene and 4-methyl-1,3-pentadiene.[7] It is worth noting that **1** is an isospecific catalytic precursor, at least in the polymerization of 1-olefins,[2] while it produces, probably with chain-end steric control,[8] 1,2-syndiotactic polymers with (E)-1,3-pentadiene and 4-methyl-1,3-pentadiene.

In this paper, the behaviour of (**1**)/MAO catalytic system in olefin-diene copolymerizations have been reported and rationalized by experimental and molecular modeling studies. It worth noting that copolymerization of olefins and dienes is of particular importance since the resulted unsaturated copolymers may exhibit interesting properties, e.g. cross-linking efficiency or rubber compatibility.

^{13}C NMR Analysis

1,3-Butadiene-ethene Copolymers

Copolymerization runs of 1,3-butadiene and ethene in the presence of catalyst (**1**)

Dipartimento di Chimica, Università di Salerno. Via S. Allende, I-84081 Baronissi, Salerno (Italy)
E-mail: plongo@unisa.it

Table 1.

Copolymerizations 1,3-butadiene–ethene (run 1–2), 1,3-butadiene–propene (run 3–4), 1,4-pentadiene–ethene (run 5), and 1,5-hexadiene–ethene (run 6), in the presence of (1)/MAO.

Run[a]	[D][b] (mol/L)	[O][c] (mol/L)	Time (h)	T (°C)	Y[d] (g)	X_D[e]	$f_{1,2\text{-}\Delta}$[f]	$f_{1,2\text{-⌂}}$[f]	$f_{B1,1}$[f]	$f_{B1,3}$[f]	$f_{B1,2}$[f]	$f_{B1,4}$[f]	$f_{1,3\text{-}\square}$[f]	$f_{1,3\text{-⌂}}$[f]
1	1,3-BD[g] (0.52)	E[g] (0.16)	16	20	3.5	0.03	0.64	0.36	—	—	—	—	—	—
2	1,3-BD[g] (0.51)	E[g] (0.16)	1.5	50	2.0	0.04	0.14	0.04	0.61	0.20	—	—	—	—
3	1,3-BD[g] (0.51)	P[g] (1.2)	20	20	0.06	0.09	0.11	0.08	—	—	0.56	0.25	—	—
4	1,3-BD[g] (0.15)	P[g] (6.8)	20	50	0.32	0.03	—	0.11	0.20	0.08	0.13	0.48	—	—
5	1,4-PD[g] (0.50)	E[g] (0.16)	1.5	50	1.90	0.03	—	—	—	—	—	—	0.30[h]	—
6	1,5-HD[g] (0.14)	E[g] (0.16)	1.5	50	2.0	0.03	—	—	—	—	—	—	—	1

[a] Polymerizations were carried out in toluene by using a concentration $1 \cdot 10^{-3}$ M of zirconocene and 1 M of MAO (based on Al).

[b] Concentration of diene in the feed.

[c] Concentration of olefin in the feed.

[d] Yield.

[e] Molar fraction of diene units in the copolymer chains.

[f] Fraction of diene leading to 1,2-cyclopropane ring units ($f_{1,2\text{-}\Delta}$), 1,2-cyclopentane ring units ($f_{1,2\text{-⌂}}$), 1,1 units ($f_{B1,1}$), 1,3 units ($f_{B1,3}$), 1,2-butadiene units ($f_{B1,2}$), 1,4-butadiene units ($f_{B1,4}$),1,3 cyclobutane ring units ($f_{1,3\text{-}\square}$) and 1,3-cyclopentane ring units ($f_{1,3\text{-⌂}}$).

[g] 1,3-butadiene (1,3-BD), 1,4-pentadiene (1,4-PD), 1,5-hexadiene (1,5-HD), ethene (E), propene (P).

[h] The remaining 70 % of inserted 1,4-pentadiene units gives crosslinks.

are described in rows 1–2 of Table 1.[9–11] The ^{13}C NMR spectrum of sample 1 (see Figure 1 a) does not show any signal in the region of the unsaturated carbons, while the aliphatic region includes, beside the intense peak placed at 27.8 ppm related to methylene sequences, three resonances placed at 10.1, 17.1, and 32.5 ppm which can be attributed to *trans* 1,2-disubstituted cyclopropane rings as well as five resonances of *trans* 1,2-disubstituted cyclopentane rings and minor resonances which can be attributed to *cis* 1,2-disubstituted rings (see Table 2).

For the copolymer obtained at higher polymerization temperature (sample 2 of Table 1), the ^{13}C NMR spectrum of Figure 1b shows the presence of a polyethene, containing *E* propenyl branches and *E* double bonds along the main chains with methyl branches in (position, which correspond to 1,1 and 1,3 constitutional units from butadiene, respectively (see Table 2).

1,3-Butadiene-propene Copolymers

Copolymerization runs of 1,3-butadiene and propene in the presence of catalyst (**1**)/MAO are described in rows 3–4 of Table 1.[12]

The copolymers obtained at room temperature (see run 3 reported in the Table 1) are polypropenes containing prevailingly 1,2-butadiene units and a lower amount of 1,4-butadiene units, cyclopropane and cyclopentane units (see Figure 1 c). The copolymers obtained at higher temperature as well as higher propene concentration also contain 1,1 and 1,3-butadiene units (see Figure 1 d).

Resonances analysis of the spectra of sample 3 and 4 clearly indicates that the propene homosequences are in isotactic arrangement and that 1,4-butadiene units are in cis configuration and in homosequence, since propene-1,4-butadiene heterosequence signals are not detectable. Moreover, the ^{13}C NMR analysis shows that the 1,2-butadiene units take place in the polymer chain as isolate units between propene units and the regiochemistry of insertion is the same for both monomers. In particular, since, as largely reported in literature, the propene regiochemistry of insertion is primary,[13,14] it has to be unusually primary for butadiene inserting as 1,2 units, too.

It is worth noting that in the propene homosequences, some regioirregularities are present; in fact signals at 13.6 and

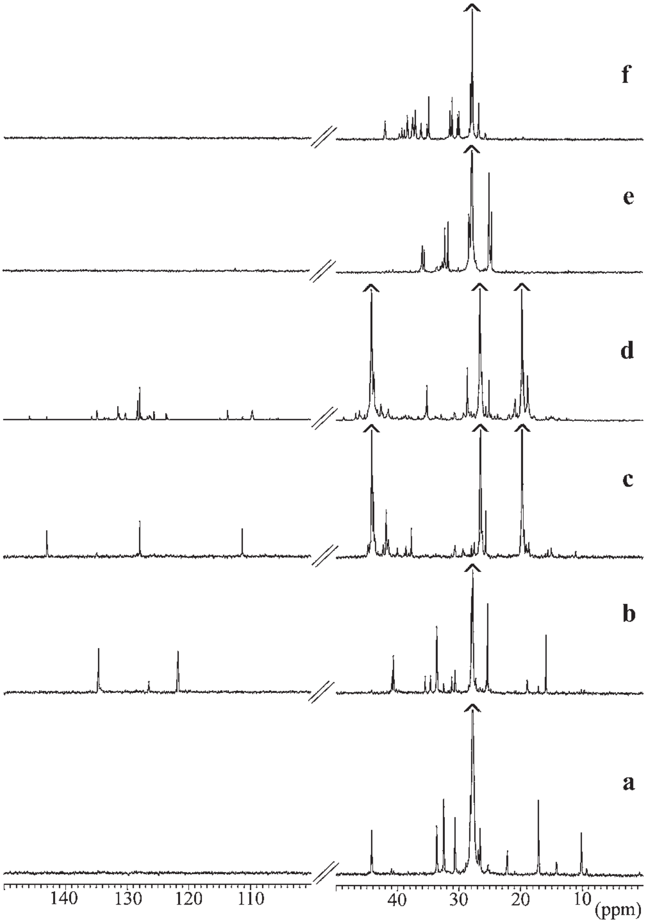


Figure 1.
^{13}C NMR of sample 1–6 (spectra a–f, respectively) of Table 1. Tetrachlorodideuteroethane was used as a solvent. Hexamethyldisiloxane scale.

15.6 ppm attributable to methyl groups of tail to tail propene sequences were relieved.

1,4-Pentadiene-ethene Copolymers

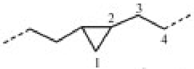
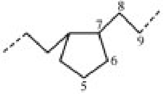
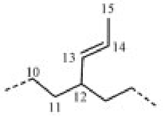
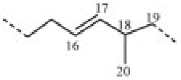
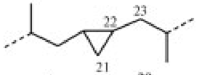
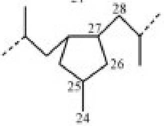
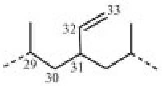
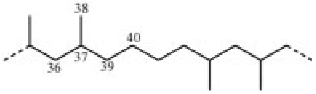
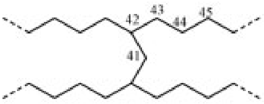
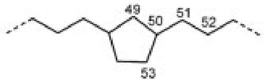
The ^{13}C NMR spectrum of sample 5 of Table 1,[15] relative to the ethene-1,4-pentadiene copolymer, does not present signals in the unsaturated region proving that both double bonds of 1,4-pentadiene units are always involved in an addition reaction. In the saturated region, three signals at 30.2_8, 33.1_7, 34.7_0 ppm attributable to 1,3 cyclobutane units as well as five resonances (see Table 2) relative to cross-linked structures can be observed (see Figure 1 e).

1,5-Hexadiene-ethene Copolymers

The spectrum of sample 6 of Table 1, that is a ethene - 1,5-hexadiene copolymer sample, shows only the resonances expected for a polyethene containing 1,3-cyclopentane units,[16–20] (see Figure 1 f).

The resonances of all recognized structural units have been attributed on the basis of the data reported in the literature for carbon in similar environments,[16–21] by Distortionless Enhancement by Polarisation Transfer 90 and 135 (DEPT-90 and DEPT-135) ^{13}C NMR experiments, and by using additivity rules.[22,23] All recognized substructures and the assignments of the main resonances are reported in Table 2.

Table 2.
^{13}C NMR assignments of all recognized structures of copolymer samples 1–6.

diene units	chemical shift$^{a)}$		
	carbon	observed	calculated
	1	10.08	9.8$^{10)}$
	2	17.06	16.8$^{10)}$
	3	32.45	32.5$^{10)}$
	4	27.77	27.8$^{10)}$
	$1'^{a}$	9.28	9.8$^{10)}$
	$2'$	14.12	14.3$^{10)}$
	$3'$	30.54	30.7$^{10)}$
	$4'$	24.57	25.1$^{10)}$
	5	22.22	22.2$^{10)}$
	6	33.91	33.6$^{10)}$
	7	44.22	44.3$^{10)}$
	8	30.54	30.8$^{10)}$
	9	26.22	26.2$^{10)}$
	10	25.31	25.3$^{10)}$
	11	33.61	33.6$^{10)}$
	12	40.92	40.0$^{10)}$
	13	134.77	134.7$^{10)}$
	14	121.75	121.7$^{10)}$
	15	15.78	15.7$^{10)}$
	16	126.47	126.5$^{10)}$
	17	134.62	134.2$^{10)}$
	18	35.48	34.3$^{10)}$
	19	34.54	34.5$^{10)}$
	20	18.85	18.8$^{10)}$
	21	11.02	11.1$^{12)}$
	22	14.98	15.0$^{12)}$
	23	40.04	39.5$^{12)}$
	24	18.71	18.8$^{12)}$
	25	30.64	31.5$^{12)}$
	26	41.44	41.2$^{12)}$
	27	41.56	39.7$^{12)}$
	28	38.63	38.4$^{12)}$
	29	27.52	27.6$^{12)}$
	30	41.84	40.1$^{12)}$
	31	37.74	37.4$^{12)}$
	32	142.97	143.0$^{12)}$
	33	111.21	111.3$^{12)}$
	34	127.87	127.8$^{12)}$
	35	25.66	25.6$^{12)}$
	36	43.85	43.8$^{12)}$
	37	28.65	28.7$^{12)}$
	38	18.81	18.8$^{12)}$
	39	35.22	35.2$^{12)}$
	40	25.1	25.3$^{12)}$
	41	35.49	37.3$^{15)}$
	42	35.94	33.9$^{15)}$
	43	32.37	32.6$^{15)}$
	44	25.01	25.1$^{15)}$
	45	28.25	28.2$^{15)}$
	46	30.28	30.1$^{15)}$
	47	33.17	32.1$^{15)}$
	48	34.70	34.7$^{15)}$
	$46'$	32.20	32.2$^{15)}$
	$47'$	33.67	32.9$^{15)}$
	$48'$	35.55	35.2$^{15)}$
	49	37.46	37.3$^{18)}$
	50	37.40	37.2$^{18)}$

(***Continued***)

Table 2.
(*Continued*)

diene units	chemical shift[a]		
	carbon	observed	calculated
	51	35.17	35.0[18)]
	52	26.79	27.0[18)]
	53	31.12	31.2[18)]
	49′	39.15	39.0[18)]
	50′	38.35	38.6[18)]
	51′	34.91	35.0[18)]
	52′	26.79	27.0[18)]
	53′	30.21	30.1[18)]

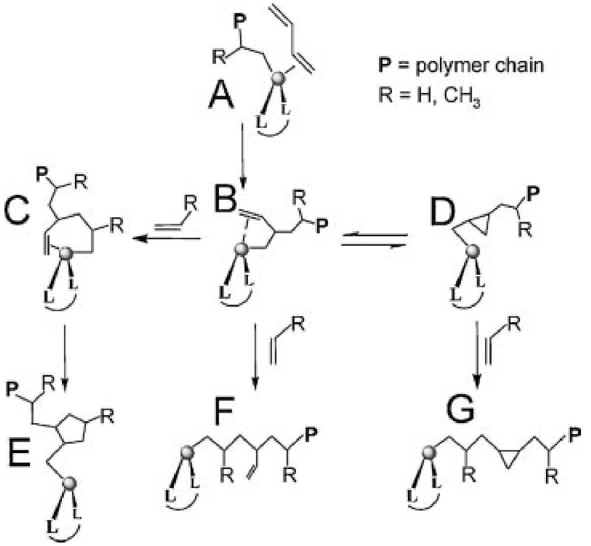
[a] The primed numbers are referred to cis configuration structures.

Mechanism Schemes

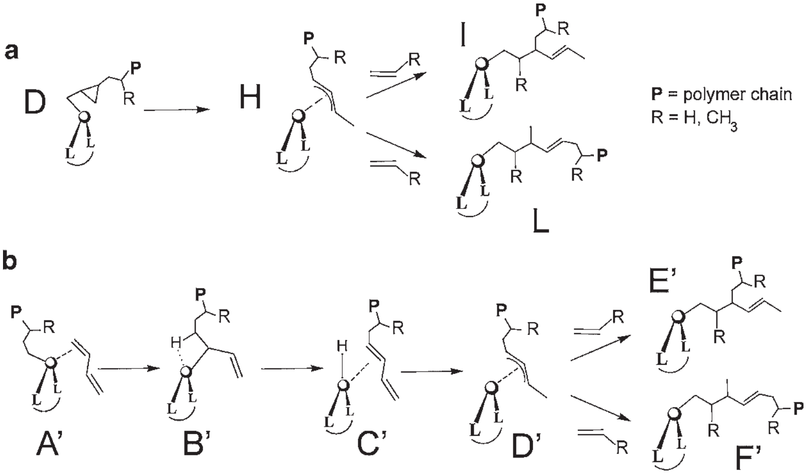
The formation of 1,2-cyclopentane and 1,2-cyclopropane units from butadiene, can be rationalized by the mechanism sketched in Scheme 1.[9,12]

According to this reaction scheme, a primary butadiene coordination (A in Scheme 1) would give rise, through a 1,2-insertion into the σ metal-polymer bond, to a primary growing chain, that is bound to the metal by a methylene group (B). The resulting 1,2-inserted butadiene unit would be bonded to the metal also by a back-biting coordination of the closest double bond of the chain. This four carbon atoms back-biting chain could give rise to a six carbon atoms back-biting chain (C), through olefin (ethene or propene) insertion. Both kinds of back-biting chains (B and C) could give rise to cyclization reactions leading to formation of 1,2-cyclopropane (D) and cyclopentane (E) rings, respectively, through intramolecular insertion of the coordinated double bond into the σ metal-alkyl bond. Insertion of an olefin on intermediate B can also lead to an intermediate (F) without a back-biting coordination that would give 1,2 units along the chain.

(*E*)-1,1- and (*E*)-1,3-constitutional units from butadiene[10] could arise from both mechanism a or b shown in Scheme 2.



Scheme 1.



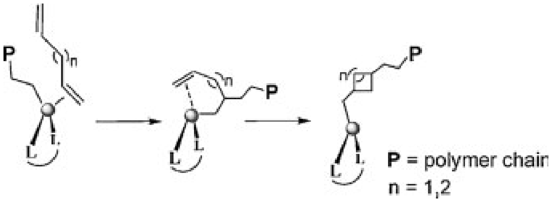
Scheme 2.

Mechanism a, starting from intermediate (D) (already sketched in Scheme 1) presents a γ-H migration from methylene carbon of the cyclopropane to the methylene carbon bound to the metal and the simultaneous breaking of the cyclopropane bond between methine carbons, leading to intermediate (H). The obtained allyl coordination intermediate would generate 1,1- (I)) or 1,3- (L) units after an olefin insertion.

Alternatively, the formation of (*E*)-1,1- and (*E*)-1,3-butadiene units could be justified hypothesizing a reaction mechanism b that involves a secondary coordination (A′) and insertion of butadiene (B′). This plausible pathway involves β-H elimination to afford a diene species (C′)/(D′), followed by 1,4-reinsertion of the diene into the metal-H bond to form the syn η^3-allyl species (D′). The insertion of an olefin unit into the external allyl carbons, which are bound to the growing chain or to the methyl substituent, would produce 1,1 and 1,3 constitutional units, respectively, both with (*E*) configuration of the double bond.

1,4-Pentadiene and 1,5-hexadiene also give cyclization reaction in copolymerization with ethene conducted by using (**1**)/MAO as catalyst.[15]

1,3-Cyclobutane units arise from 1,2-addition of 1,4-pentadiene into metal-polymeryl σ-bond followed by coordination and intramolecular insertion of pendant vinyl group. Analogously it occurs for 1,5-hexadiene (see Scheme 3). In this case 1,3-cyclopentane units are generated. Cross-links likely arise from coordination of pendant double bond, of 1,4-pentadiene units inserted in a polymer chain, to another catalytic centre followed, by insertion in other propagating chain. It is worth noting that, while 1,5-hexadiene inserts in the polymer chains giving exclusively cyclization reaction, the insertion of 1,4-pentadiene leads to only 30% of 1,3



Scheme 3.

cyclobutane units and almost 70% of crosslinks.

Mechanism Study with Labeled Butadiene

In order to experimentally discriminate between the two proposed a and b mechanisms, for the formation of 1,1 and 1,3 butadiene units, as well as cyclic units, we have co-polymerized ethene in the presence of ^{13}C labeled 1,3-butadiene by using specific reaction conditions such as to obtain both cyclization reaction and 1,1- and 1,3-insertions of butadiene.[24]

1,3-Butadiene enriched only on carbon 1 was synthesized and used in copolymerization with ethene. This clearly means that, being 1,3-butadiene a symmetric molecule, both carbon 1 and carbon 4 of the units generating from butadiene result ^{13}C enriched along the polymer chain. The ^{13}C NMR spectrum of the resulting polymer, obtained by using 4% ^{13}C enriched 1,3-butadiene, was examined and compared with that of a copolymer sample obtained using the same reaction conditions and commercial monomers. This experiment clearly allowed to check, without any doubt, if the 1,1- and 1,3-butadiene constitutional units derive from a primary or secondary monomer insertion. In fact, a secondary insertion of butadiene would induce an enrichment in ^{13}C of the carbons of the methyl group and of the saturated methine of the 1,1-butadiene units (E′) and of methyl group and of the unsaturated methine farther from the methyl group of the 1,3-butadiene units (F′).

A primary insertion of butadiene would enrich in ^{13}C the carbons of the methyl group and of the unsaturated methine farther from the methyl group of the 1,1-butadiene units (I) and the carbons of the methyl group and of the methine closest to the methyl group of the 1,3 butadiene units (L).

The ^{13}C NMR spectra of a copolymer sample obtained by using ^{13}C enriched butadiene (Figure 2**a**) and of a copolymer sample obtained in the same reaction conditions by using commercial butadiene

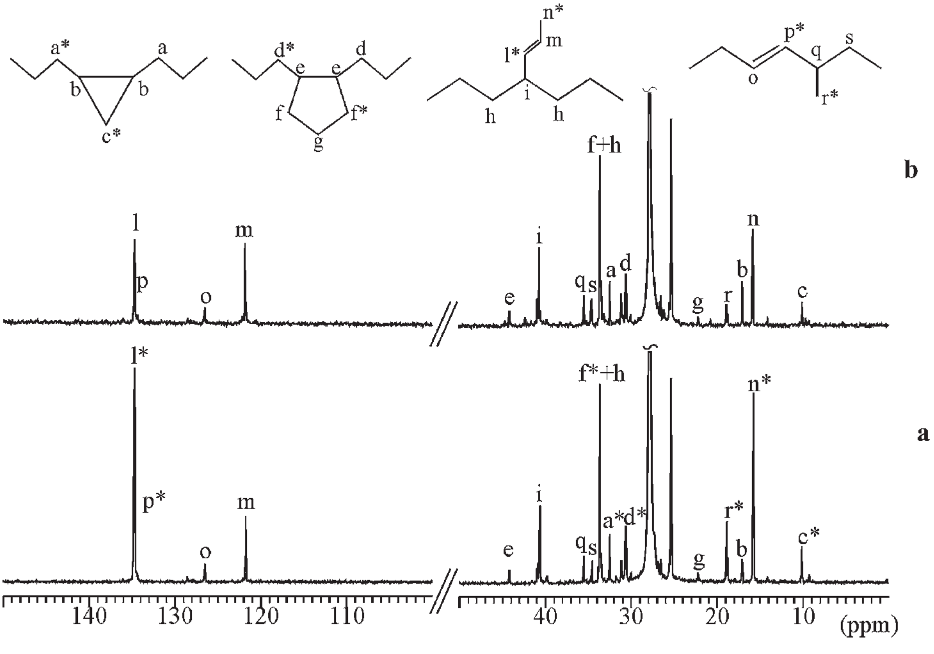
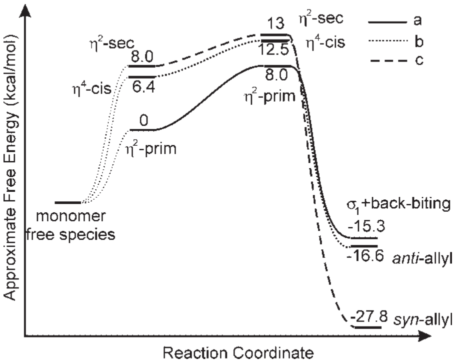


Figure 2.
^{13}C NMR spectra of a copolymer sample obtained by using ^{13}C enriched butadiene (**a**) and of a copolymer sample obtained in the same reaction conditions by using commercial butadiene (**b**) (Hexamethyldisiloxane scale).

(Figure 2**b**) are reported in Figure 2, where all the recognized units generated from butadiene are also shown.

The comparison between the intensities of the peaks related to the 1,1- and 1,3-butadiene constitutional units shows that those at 15.7_8, 134.7_7 ppm (diagnostic of the carbons of the methyl group and of the unsaturated methine farther from the methyl group of the 1,1 butadiene units) and those at 18.8_5 and $134{,}6_2$ ppm (diagnostic of the carbons of the methyl group and of the methine closest of the methyl group of the 1,3-butadiene units) are increased with respect to the peaks relative to the other carbons of such units.

Thus, the ^{13}C enriched carbons of 1,1- and 1,3-butadiene units are those expected for a primary coordination, insertion, cyclization of butadiene followed by cyclopropane breaking and consequent carbon skeleton isomerization (mechanism a, Scheme 2). Comparison of the intensities of the signals related to the 1,2-cyclopentane and cyclopropane units shows that the peaks at 10.0_8 and 32.4_5 ppm, related to the carbons of the methylene of the 1,2-disubstituted cyclopropane ring and the methylene closest to the cyclopropane rings, and those at 33.9_1 and 30.5_4 ppm, related to the two methylenes closest to the methine of the cyclopentane units, result increased with respect to the peaks relative to the other carbons of cyclic units. These results are also consistent with the pathway we already proposed for the butadiene cyclization reaction.



Scheme 4.

Molecular Modeling Studies

Molecular modeling calculations were able to rationalize most of the observed behaviour for copolymerizations of 1,3-butadiene with ethene catalyzed by (**1**)/MAO.[11,15]

Three possible insertion mechanisms of a butadiene monomer on a σ chain have been considered. In particular, minimum energy coordination intermediates and insertion transition states have been located for the primary η^2 coordination of butadiene, which leads through a primary vinyl insertion to a σ-coordinated growing chain (step A–> B, in Scheme 1, pathway **a** in Scheme 4), for a η^4-s-*cis* coordination of butadiene leading to an *anti*-η^3-coordinated growing chain (pathway **b**) and for a η^2 secondary coordination of butadiene leading to a *syn*-η^3-coordinated growing chain (pathway **c**). It is worth noting that only a primary η^2 coordination and insertion of butadiene can give rise, after further steps, to cyclopropane or cyclopentane units, while pathways **b** and **c** could only give rise to 1,4-cis, 1,4-trans or 1,2 butadiene units along the chain.

The energy profiles of Scheme 4 clearly show that pathway **a** involving a η^2 primary butadiene insertion is largely favored. In fact, its activation energy relative to butadiene insertion is at least 4.5 kcal/mol smaller than for the other two competing pathways. This is in good agreement with the polymerization results of Table 1 (run 1,2), since (**1**)/MAO, for all the considered polymerization conditions, does not produce the usual 1,4 or 1,2 butadiene constitutional units but produces only constitutional units generated by the common intermediate, which presents a σ-coordinated back-biting growing chain (B in Scheme 2).

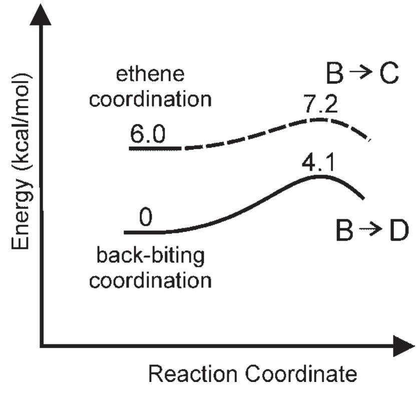
As reported in the *Mechanism Schemes* section, the σ-coordinated back-biting growing chain (B) can give rise, after the back-biting insertion (B → D), to a 1,2-cyclopropane unit, or, after an ethene insertion (B → C) followed by the back-biting insertion, to a 1,2-cyclopentane unit (E).

The percentage of 1,2-cyclopropane and 1,2-cyclopentane depends first of all on the competition between B → D and B → C (see Scheme 1). The intermediates and the transition states for those two pathways were modeled, [15] and the results are reported in Scheme 5.

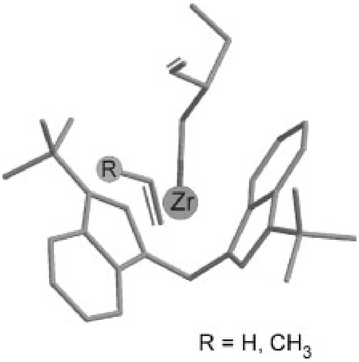
The transition state relative to the formation of a 1,2-cyclopropane unit presents an energy which is 3.1 kcal/mol lower than the ethene insertion transition state. The ethene would also hardly displace the back-biting coordination which is largely favored (about 6 kcal/mol).

As for copolymerizations butadiene-propene at room temperature, 25% of butadiene inserts as a 1,4 unit, whereas 75% (11% of cyclopropane, 8% of cyclopentane and 56 % of 1,2 units) arises from a primary 1,2 insertion. The energy gap between primary 1,2 and 1,4 insertion transition states is probably lower than the corresponding gap in the ethene-butadiene copolymerization. It is not surprising that increasing the temperature up to 50 °C, the percentage of 1,4 units increases up to 48 %.

Moreover the σ-coordinated back-biting growing chain intermediate, arising from a primary 1,2 insertion, only partially evolves to 1,2-cyclopropane units at room temperature. In fact, 56 % of butadiene gives 1,2 units. Since propene is more nucleofilic than ethene, propene coordination would probably be favored with respect to the ethene coordination, although the ethene polymerization is faster. Density functional theory calculations, which compare the energy coordination of propene and ethene for the model reported in Chart 1, confirm these hypothesis. In particular, propene presents a coordination energy 2.1 kcal/mol lower than ethene. As a consequence, the easier displacement of the back-biting in the presence of propene would slow down the formation of 1,2-cyclopropane rings mainly leading to 1,2 units.



Scheme 5.

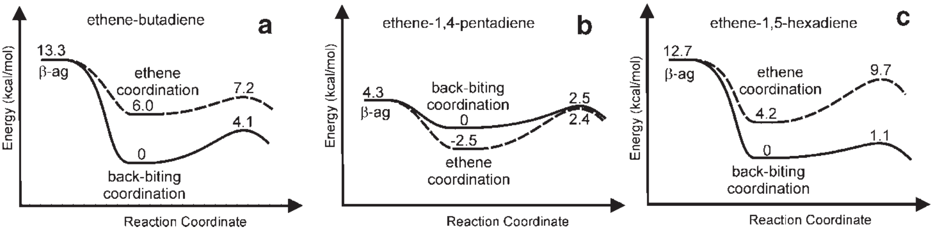


R = H, CH$_3$

Chart 1

As for higher temperatures, the presence of 20 % of 1,1 units and 8 % of 1,3 units can be rationalized considering that the propene coordination would be entropically less favored than at room temperature and the σ-coordinated back-biting growing chain intermediate would give rise to a 1,2-cyclopropane intermediate, that, being unstable, would evolve to 1,1 and 1,3 units.

Finally, the ethene-butadiene copolymerization in the presence of (**1**)/MAO has been compared with the ethene-1,4-pentadiene and 1,5-hexadiene copolymerizations. Both 1,3-butadiene and 1,5-hexadiene generate, under specific conditions, only cyclic units, arising from primary 1,2 diene insertion, followed by back-biting coordination and insertion (Scheme 3). Similarly 1,4-pentadiene gives primary 1,2 insertion, followed for 30% by coordination and insertion of the back-biting and for



Scheme 6.

70% by the insertion of ethene units. The origin of the easy formation of 1,2-cyclopropane and 1,3-cyclopentane units compared to the formation of 1,3-cyclobutane units have been investigated.[15] The competition between the ethene insertion and the back-biting double bond insertion would be responsible of the percentage of rings in the polymer.

Minimum energy pathways (coordinations and insertion transition states) for these two kinds of insertions are sketched in Scheme 6. Coordination energies are also compared with the ß-agostic interaction intermediates of the terminal growing chain after the diene insertion (ß-ag of Scheme 6).

The **a**, **b** and **c** letters of Scheme 6 refer to intermediates relative to the copolymerization of ethene with 1,3-butadiene, 1,4-pentadiene and 1,5-hexadiene, respectively. According to these calculations, while the cyclization reaction is clearly favored in the ethene-1,3-butadiene and ethene-1,5-hexadiene copolymerizations, the ethene insertion competes with the cyclization reaction in the ethene-1,4-pentadiene copolymerization ($\Delta\Delta E^{\neq} \approx 0$ kcal/mol), due to the low stability of the back-biting coordination intermediate. These results are in agreement with the experimental data reported in the *^{13}C NMR analysis* section.

Conclusions

Olefin-diene copolymerizations in the presence of (**1**)/MAO catalytic system have been reported and rationalized by experimental and molecular modeling studies. Results can be resumed as follows:

- Ethene-1,3-butadiene copolymerizations give rise to a polyethene containing 1,2-disubstituted cyclopropane rings as well as 1,2-disubstituted cyclopentane rings at room temperature, and to 1,1 and 1,3 butadiene units at 50 °C.
- The propene-1,3-butadiene copolymers obtained at room temperature are polypropenes containing prevailingly 1,2-butadiene units and a low amount of 1,4-butadiene units, cyclopropane and cyclopentane units, whereas those obtained at higher temperature as well as higher propene concentrations also contain 1,1 and 1,3–butadiene units.
- Ethene-1,4-pentadiene copolymerizations give a polyethene presenting cyclobutane units and crosslinks, while ethene-1,5-hexadiene copolymerizations give a polyethene with 1,3-disubstituted cyclopentane units.

According to molecular modeling studies, a cyclization would occurs when 1) the primary 1,2 diene regiochemistry insertion is favoured with respect to other possible regiochemistry; 2) the back-biting coordination and insertion are favoured with respect to an olefin coordination and insertion.

Polyolefins with cyclic groups are excellent materials with high glass transition temperature and high transparency. Polyethene containing 1,2-cyclopropane rings can be easily functionalized, by opening cyclopropane units through acetylation, hydrohalogenation and esterification reactions. Furthermore, the high reactivity of cyclopropane rings allows the easy formation of radicals, e.g. by heating, able to polymerize monomers as styrene and methylmethacrylate. The products can result grafted copolymers suitable as compatibilizers for polymer blends.

[1] L. Resconi, F. Piemontesi, I. Camurati, O. Sundmeijer, I.E. Ninfant'ev, P.V. Ivchenko, L.G. Kuz'mina, *J. Am. Chem. Soc.* **1998**, *120*, 2308.

[2] L. Resconi, D. Balboni, G. Baruzzi, C. Fiori, S. Guidotti, *Organometallics* **2000**, *19*, 420.

[3] A. Grassi, A. Zambelli, L. Resconi, E. Albizzati, R. Mazzocchi, *Macromolecules* **1988**, *21*, 617.

[4] (a) W. Röll, H.H. Brintzinger, B. Rieger, R. Zolk, *Angew. Chem. Int. Ed. Engl.* **1990**, *102*, 339; (b) M. Toto, L. Cavallo, P. Corradini, G. Moscardi, L. Resconi, G. Guerra, *Macromolecules* **1998**, *31*, 3431.

[5] L. Caporaso, L. Izzo, I. Sisti, L. Oliva, *Macromolecules* **2002**, *35*, 4886.

[6] C. Pellecchia, P. Longo, A. Grassi, P. Ammendola, A. Zambelli, *Makromol. Chem., Rapid Commun.* **1990**, *8*, 277.

[7] S. Pragliola, E. Forlenza, P. Longo, *Macromol. Rapid Commun.* **2001**, *22*, 783.

[8] D. Seebach, V. Prelog, *Angew. Chem. Int. Ed. Engl.* **1982**, *19*, 857.

[9] S. Pragliola, G. Milano, G. Guerra, P. Longo, *J. Am. Chem. Soc.* **2002**, *124*, 3502.

[10] P. Longo, S. Pragliola, G. Milano, G. Guerra, *J. Am. Chem. Soc.* **2003**, *125*, 4799.

[11] P. Longo, M. Napoli, S. Pragliola, C. Costabile, G. Milano, G. Guerra, *Macromolecules* **2003**, *36*, 9067.

[12] S. Pragliola, C. Costabile, F. Di Bartolomeo, P. Longo, *Macromol. Rapid Commun.* **2004**, *25*, 995.

[13] L. Resconi, G. Cavallo, A. Fait, F. Piemontesi, *Chem. Rev.* **2000**, *100*, 1253.

[14] P. Longo, A. Proto, A. Grassi, P. Ammendola, *Macromolecules* **1991**, *24*, 4624.

[15] M. Napoli, C. Costabile, S. Pragliola, P. Longo, *Macromolecules* **2005**, *38*, 5493.

[16] L. Resconi, R.M. Waymouth, *J. Am. Chem. Soc.* **1990**, *112*, 4953.

[17] G.W. Coates, R.M. Waymouth, *J. Am. Chem. Soc.* **1991**, *113*, 6270.

[18] T.N. Choo, R.M. Waymouth, *J. Am. Chem. Soc.* **2002**, *124*, 4188.

[19] G.W. Coates, R.M. Waymouth, *J. Mol. Cat.* **1992**, *76*, 189.

[20] G.W. Coates, R.M. Waymouth, *J. Am. Chem. Soc.* **1993**, *115*, 91.

[21] M. Pooter, P.R. Smith, K.K. Dohrer, K.F. Bennet, M.D. Meadows, C.G. Smith, H.P. Schouwenaars, R.A. Geerards, *J. Appl. Polym. Sci.* **1991**, *42*, 399.

[22] M.W. Duch, D.W. Grant, *Macromolecules* **1970**, *3*, 165.

[23] D.M. Grant, E.G. Paul, *J. Am. Chem. Soc.* **1964**, *86*, 2984.

[24] S. Pragliola, C. Costabile, M. Magrino, M. Napoli, P. Longo, *Macromolecules* **2004**, *37*, 238.