

# Cyclic olefin polymerization and relationships between addition and ring opening metathesis polymerization

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## Abstract

Results of our work concerning: (i) the elucidation of the role of the ionic species  $[\text{Cp}_2\text{Ti}^{13}\text{CH}_3]^+[\text{Cl} \cdot \text{MAO}]^-$  and of precursors of alkylidene  $\text{Cp}_2\text{Ti}=\text{CH}_2$  species in addition alkene polymerization, (ii) the synthetical strategies for converting the living active titanacyclobutanes into  $\sigma$ -titanocene complexes, and (iii) the evidence for the synthesis of polyethylene polynorbornene *di*-block copolymer are briefly summarized.  $^{13}\text{C}$  NMR spectra of ethylene–norbornene copolymers, prepared with addition catalysts based on *ansa*-zirconocenes and methylaluminoxane as cocatalyst, and assignments of comonomer pentads in ethylene–norbornene (EN) copolymers are reported. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Polymerization; Copolymers; Cyclic olefin

## 1. Introduction

Strained cyclic olefins can be polymerized by transition metal-based catalysts either by ring opening metathesis polymerization (ROMP) [1] or by addition polymerization [2]. Although examples of living polymerization catalyzed by transition metals are quite rare, since 1986 several living ROMP of strained cyclic olefins have been reported for well-defined titanium, tantalum, tungsten, molybdenum, and ruthenium metathesis catalytic systems [3,4]. Traditional titanium-based catalysts ( $\text{TiCl}_4/\text{AlEt}_3$  1/2.5) are reported to yield very low molecular weight addition norbornene polymers without ring opening [5]. The new metallocene-based catalysts [6] allow the addition homopolymerization of cyclic olefins and synthesize high molecular weight norbornene polymers which are insoluble in hydrocarbons [7]. Late transition metal catalysts such as palladium and nickel-based catalysts homopolymerize via addition functionalized norbornenes also [8–12]; moreover, some palladium-based catalysts give living addition norbornene polymerization [13]. However, structures of these addition norbornene polymers have not been unequivocally clarified so far.

We wish to briefly summarize results of our work related to cyclic olefin polymerization and to relationships between metathesis and addition polymerization. Our interest in this field originates

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from the fact that the same combination of catalyst/cocatalyst can provide addition or metathesis polymerization of cyclic olefins depending on the polymerization conditions [1]. We also wish to briefly report on some recent results regarding ethylene–norbornene copolymerization with zirconocene-based catalysts. These copolymers constitute a new class of interesting transparent thermo-plastic materials which are suitable for optical applications.

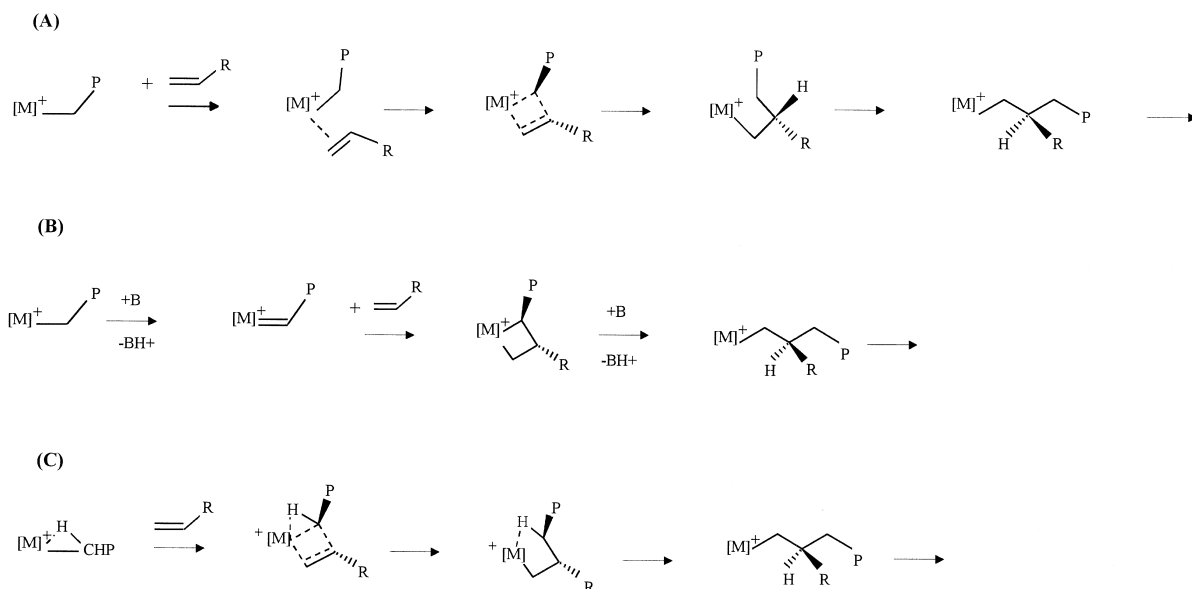
## 2. Relationships between addition and ROMP polymerizations

### 2.1. Olefin polymerization mechanism

Addition polymerization of  $\alpha$ -olefins by Ziegler–Natta catalysts proceeds through successive insertions of a coordinated olefin into a metal–carbon bond formed by reacting the transition metal catalyst and the cocatalyst. Several mechanisms have been suggested for the olefin insertion.

One of the best accepted is the Cossee–Arlman mechanism which involves a direct migration of the coordinated olefin to the metal–alkyl bond [14–16]. Scheme 1A reports a modified Cossee–Arlman mechanism for ionic metallocene-based catalysts. Among the other mechanisms which have emerged, the Green–Rooney mechanism (Scheme 1B) [17] suggests the formation of a carbene and a metallacyclobutane as intermediates for addition polymerization as in the accepted mechanism for metathesis polymerization [1].  $\alpha$ -agostic interactions have also been hypothesized as assisting olefin insertion by reducing the activation energy during the transition state (Scheme 1C) [18–20].

During our studies of the equilibria of  $\text{Cp}_2\text{Ti}^{13}\text{CH}_3\text{Cl}$  **1** and  $\text{Cp}_2\text{Ti}(\text{CH}_3)_2$  **2** with methylaluminoxane (MAO) we observed cation-like species  $[\text{Cp}_2\text{Ti}^{13}\text{CH}_3]^+[\text{Cl} \cdot \text{MAO}]^-$  **3** along with precursors of alkylidene  $\text{Cp}_2\text{Ti}=\text{CH}_2$  species **4** [21–24]. Different ratios of cation-like species and of alkylidene related species are formed depending on the temperature. To elucidate whether or not alkylidene



Scheme 1. (A) Modified Cossee–Arlman mechanism for olefin polymerization by cationic metallocene-based catalysts. (B) Modified carbene mechanism for olefin polymerization by cationic metallocene based catalysts: B is a base. (C) Insertion mechanism, assisted from  $\alpha$ -agostic interactions, for olefin polymerization by cationic metallocene based catalysts.

Table 1  
Ethylene polymerization activities of Cp<sub>2</sub>Ti<sup>13</sup>CH<sub>3</sub>Cl/MAO system<sup>a</sup>

T (°C)	Al/Ti	Reaction products <sup>b</sup>	Activity [gPE/(gTi h)]	M <sub>w</sub> · 10 <sup>-3</sup>	Chain-end groups b/c <sup>c</sup>
-20	15	<b>3</b> (56), <b>4</b> (0)	1920	554	1.0
0	15	<b>3</b> (47.4), <b>4</b> (12.1)	1380	354	1.0
20	10	<b>3</b> (32.0), <b>4</b> (45.5)	670	160	1.0

<sup>a</sup> Polymerization conditions: [Ti] = 5.0 · 10<sup>-4</sup> mol/l; solvent = toluene, 80 ml; ethylene pressure = 1 atm; t = 30 min.

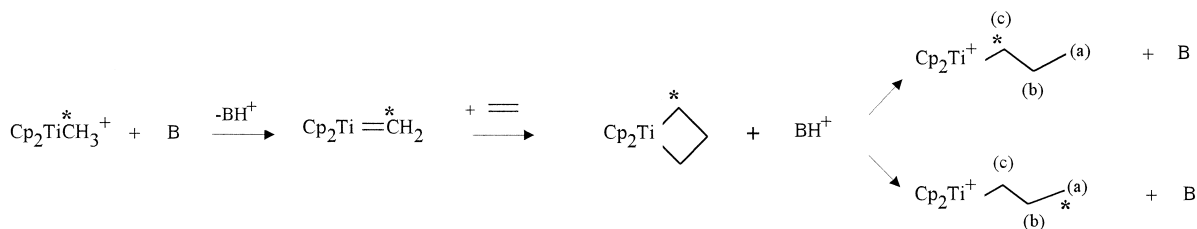
<sup>b</sup> Molar fractions of titanocene compounds calculated by the integrated peak areas from the <sup>13</sup>C NMR spectra obtained at the same temperature and at Al/Ti = 10.

<sup>c</sup> The molar ratios between methylenes b and c of chain-end groups (Scheme 2) were measured from the <sup>13</sup>C NMR spectra of isolated polyethylene samples obtained at 105°C in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>.

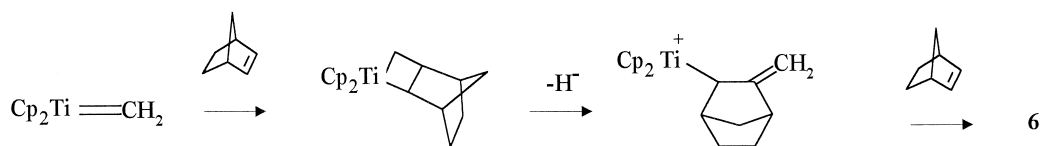
complexes which are typically active for metathesis polymerization play a role in the addition polymerization mechanism, we employed the following experimental approaches: (i) <sup>13</sup>C NMR in situ <sup>13</sup>C<sub>2</sub>H<sub>4</sub> polymerization and in situ norbornene oligomerization in the presence of both alkylidene-related species and cation-like species; (ii) <sup>13</sup>C NMR analysis of chain-end groups of polyethylene produced from Cp<sub>2</sub>Ti<sup>13</sup>CH<sub>3</sub>Cl/MAO system [25].

In the in situ ethylene polymerization experiments, the appearance of polyethylene signals is concurrent with the decrease of cationic [Cp<sub>2</sub>Ti<sup>13</sup>CH<sub>3</sub>]<sup>+</sup>[Cl · MAO]<sup>-</sup> signals but is not related to the intensity of the alkylidene 'Cp<sub>2</sub>Ti = <sup>13</sup>CH<sub>2</sub>' signals. The <sup>13</sup>C NMR analysis of polyethylene chain-end groups (Table 1) shows that the <sup>13</sup>C enrichment of Cp<sub>2</sub>Ti<sup>13</sup>CH<sub>3</sub>Cl is present in the methyl chain-end group (a) and not in the methylene of the *n*-propyl chain-end group (c), as should have been the case if the polymerization occurred through a carbene mechanism (Scheme 2).

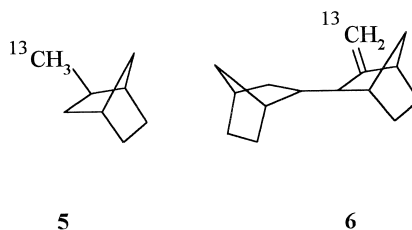
Moreover, in the in situ norbornene oligomerization 2-<sup>13</sup>C enriched-methyl-norbornane **5** produced from the addition of norbornene to Ti-<sup>13</sup>CH<sub>3</sub> bond of cation **3** at 0°C was identified. A <sup>13</sup>C enriched methylidene-norbornane dimer **6** at 20°C was identified and revealed the possibility of norbornene addition to titanium carbenes through the formation of titanacyclobutane without the opening of the norbornene ring (Scheme 3). This process requires higher energies (2–3 kcal/mol) with respect to the Cossee type insertion and thus higher temperatures, at which the alkylidene species tend to decompose.



Scheme 2.



Scheme 3.



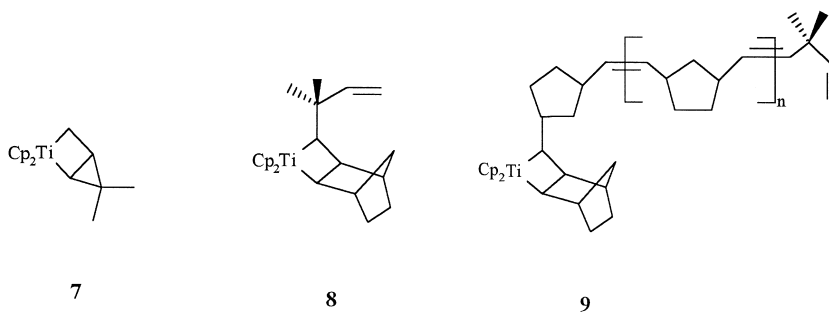
All these data showed that the carbene mechanism does not operate in the addition polymerization of olefins with these titanocene-based catalysts.

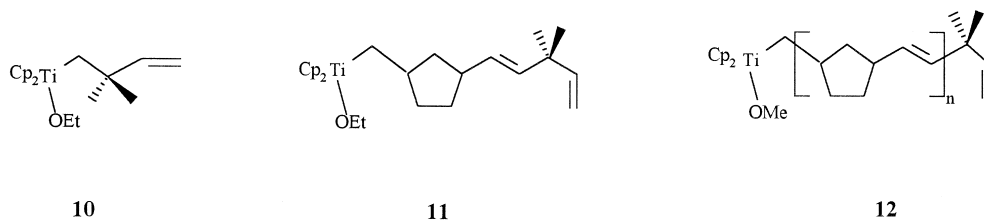
In addition, it seems that  $\alpha$ -agostic interactions are not necessary for the ethylene polymerization with titanium-based catalysts, although isotope effects in propylene polymerization catalyzed by zirconocene-based catalysts were observed and explained by  $\alpha$ -agostic interactions [26]. A mechanistic pathway in which the  $\alpha$ -agostic interaction might lower the activation barrier to olefin insertion was proposed (Scheme 1C). In a recent review of literature on isotope labeling studies to probe the transition state nature in olefin insertion, Grubbs and Coates [27] give a unified interpretation of the different isotope effects observed in various catalytic systems.

## 2.2. Transformation of titanacyclobutanes into $\sigma$ -alkyl titanocene complexes

Among all the catalysts which have been reported to catalyze living ring opening metathesis polymerizations, titanacyclobutanes have the distinguishing feature of containing a metal which gives complexes that can catalyze  $\alpha$ -olefin polymerization. For this reason, we explored synthetic strategies to convert the titanium metathesis active catalyst into a Ziegler–Natta catalyst, with the aim of obtaining *di*-block copolymers which may have desirable physical properties not obtainable from a blend of the respective homopolymers.

We first reported on the synthetic pathways for the transformation of titanacyclobutanes into  $\sigma$ -alkyl titanocene complexes [28,29]. 3,3-dimethylcyclopropene-titanacycle **7**, and titanacyclobutanes **8** and **9** were converted into  $\sigma$ -alkyl titanocene complexes such as **10**, **11** and **12**. Complex **7** is the best initiator of these norbornene ROMP polymerizations; **8** and **9** are the living metathesis active titanacyclobutanes, formed after one or more norbornene ROMP steps [30].





Then, the  $\sigma$ -alkyl titanocene complexes **11** and **12** in the presence of AlEtCl<sub>2</sub> as cocatalyst have been shown to be able to add ethylene to Ti-polynorbornyl bonds by a study of <sup>13</sup>C<sub>2</sub>H<sub>4</sub> (1-<sup>13</sup>C, 90% enriched) polymerization, performed by <sup>13</sup>C NMR spectroscopy. Therefore, it should be possible to obtain polyethylene–polynorbornene block copolymers by combining olefin metathesis and Ziegler–Natta polymerizations.

We synthesized this block copolymer in batch reactors also. Yields are very low due to the need of using very low amounts of AlEtCl<sub>2</sub> (Al/Ti = 2) in order to avoid chain transfer reactions. However, we have characterized the copolymer by <sup>13</sup>C NMR analysis. The spectrum of the polymer obtained with complex **12** is shown in Fig. 1.

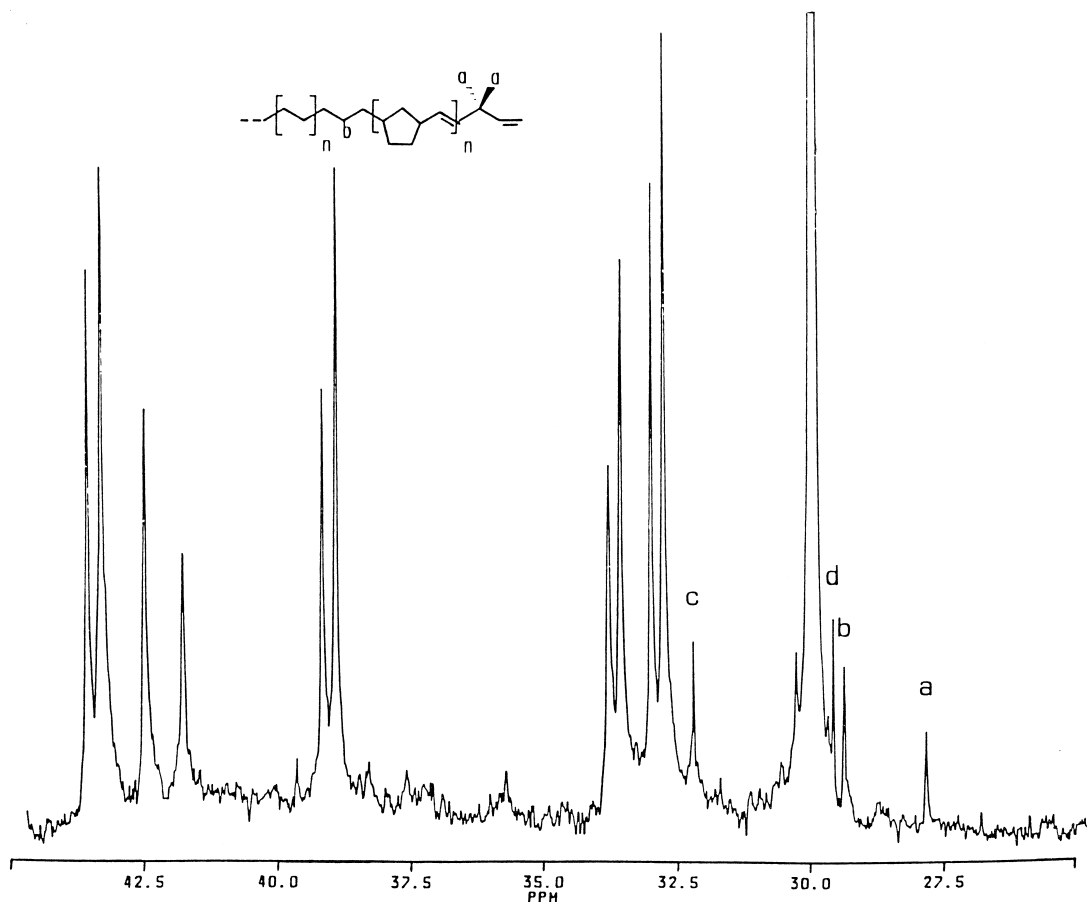


Fig. 1. <sup>13</sup>C NMR spectrum at 105°C in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> of the polymer obtained from ethylene polymerization with the catalyst **7**/AlEtCl<sub>2</sub>. Polymerization conditions: solvent = C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>; [Ti] = 5 mmol/l, [Al]:[Ti] = 2.00; T = 0°C; t = 30'.

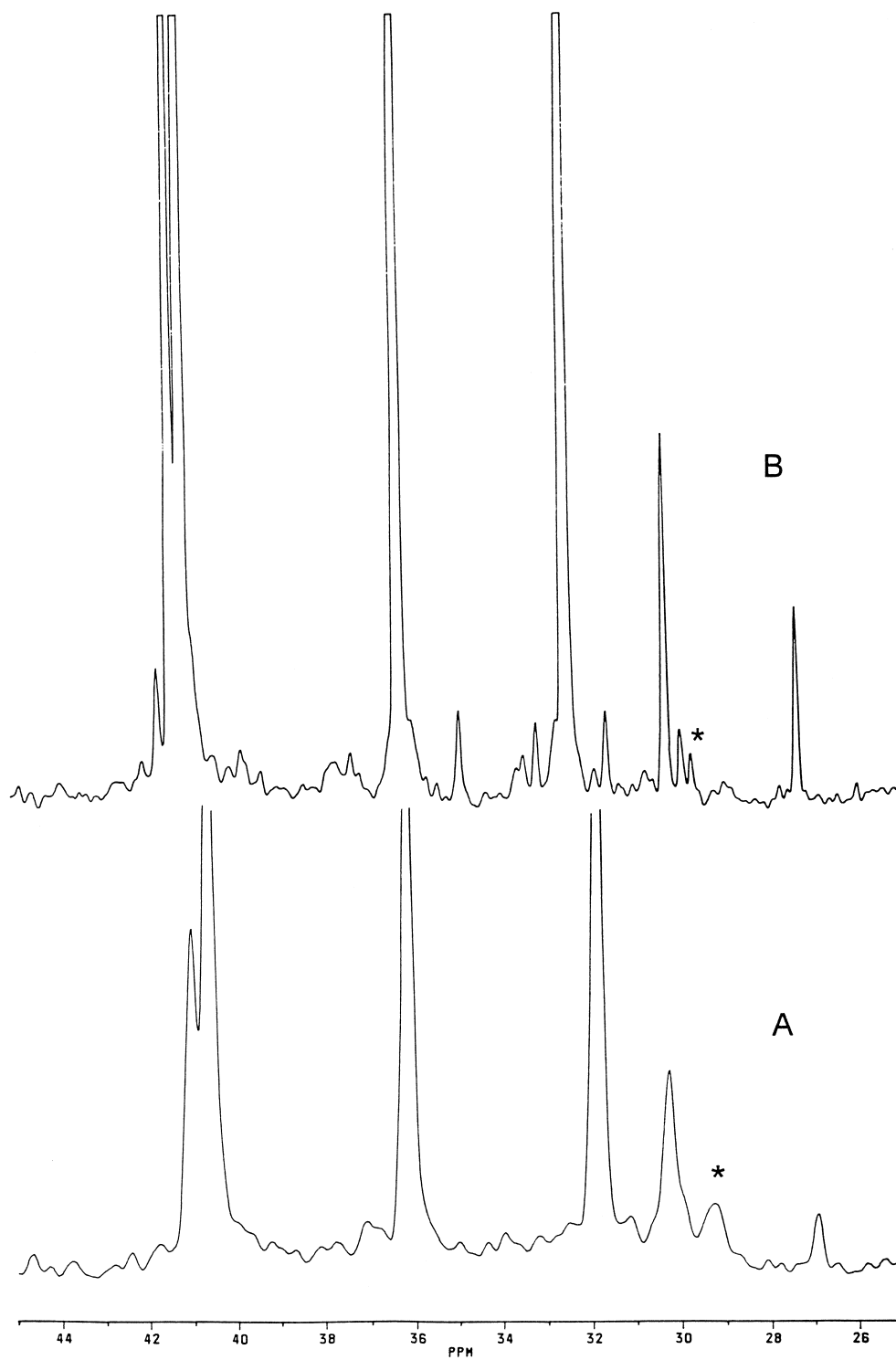
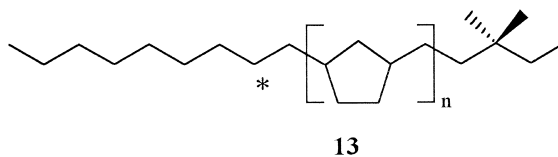


Fig. 2.  $^{13}\text{C}$  NMR spectrum at  $105^\circ\text{C}$  of the model compound **13** in  $\text{toluene-}d_8$  at  $-20^\circ\text{C}$  (A) and in  $\text{C}_2\text{D}_2\text{Cl}_4$  at  $105^\circ\text{C}$  (B).

The most interesting features are: (i) the (a) signal at 28.20 ppm of the two geminal methyls of the chain-end groups due to the ROMP initiator **7**; (ii) the high polyethylene peak at 30.33 ppm; (iii) a (b) peak at 29.65 ppm which is not observed in the spectrum of a low molecular weight polyethylene, and that we assigned to the first methylene carbon of polyethylene bonded to the polynorbornyl group. This peak is shifted 0.69 ppm upfield with respect to the polyethylene peak (PE) while the signal due to the same carbon in the low temperature in situ NMR experiments is shifted 1.0 ppm upfield with respect to the PE peak. This difference has been shown to be due to the different temperatures and solvents used in the two experiments, as confirmed from  $^{13}\text{C}$  NMR analysis of the model compound **13**.



**13** was synthesized by hydrogenation of the olefin obtained by reaction between complex **9** and *n*-octaldehyde. The comparison of the  $^{13}\text{C}$  NMR spectra of the model in the same conditions as in the NMR tube polymerization (toluene- $d_8$  at  $-20^\circ\text{C}$ ) Fig. 2A, and in the conditions like those of NMR analysis of the polymer sample ( $\text{C}_2\text{D}_2\text{Cl}_4$  at  $105^\circ\text{C}$ ) Fig. 2B, proved that the above assignment is correct.

We concluded that it is possible to convert titanacyclobutanes into  $\sigma$ -alkyltitanocene complexes and that polyethylene can grow on Ti-polynorbornyl bonds. Moreover, there is a possibility of obtaining polyethylene–polynorbornene block copolymers provided that chain transfer reactions do not occur.

### 3. Ethylene–norbornene copolymerization with zirconocene catalysts

The new metallocene-based catalysts yield addition norbornene homopolymers which are insoluble in hydrocarbons. The insertion of linear segments among the cyclic units of the polymer chain modifies structures and leads to increases in the polymer solubility. Indeed, ethylene–norbornene (EN) copolymers are soluble, transparent, and amorphous materials [7,31]. In the framework of a wider research project on homo- and copolymers of norbornene derivatives, we synthesized series of ethylene–norbornene copolymers in the presence of different metallocenes and methylaluminumoxane as cocatalyst [32]. The comparison of the  $^{13}\text{C}$  NMR spectra of these copolymers containing different norbornene amounts allowed us to make new comonomer sequence assignments. The assignments have been based on: (i) the assumption that norbornene insertion is 1,2-*exo* in copolymers rich in norbornene also; (ii) the correlation of chemical shifts and intensities of signals of copolymer samples with different composition.

In Fig. 3 the complete spectrum of a EN copolymer prepared with  $\text{Me}_2\text{C}(\text{Flu})(\text{Cp})\text{ZrCl}_2$  precatalyst is reported. The  $^{13}\text{C}$  NMR chemical shifts of the carbons of a norbornene unit isolated among ethylene units are already known<sup>1</sup> and we observe them at 28.30 ppm ( $S_{\alpha\beta}$ ), 30.91 ppm ( $S_{\alpha\alpha}$ ), 39.50

<sup>1</sup> Carman and Wilkes terminology, where S and T refer to secondary and tertiary carbons, is used. The two greek subscripts indicate the distances of the observed carbon from the closest tertiary carbons.

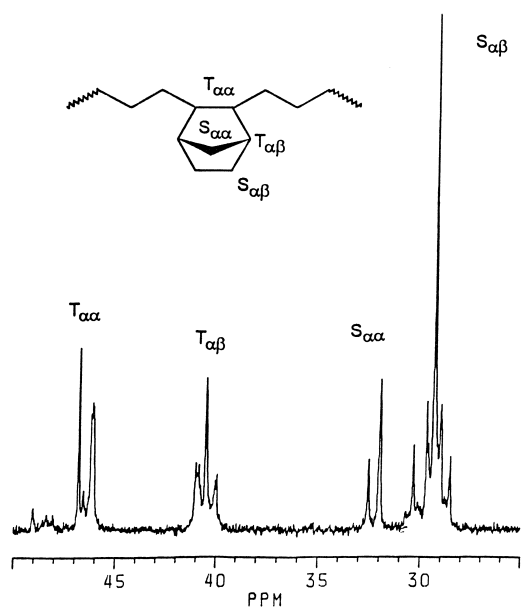
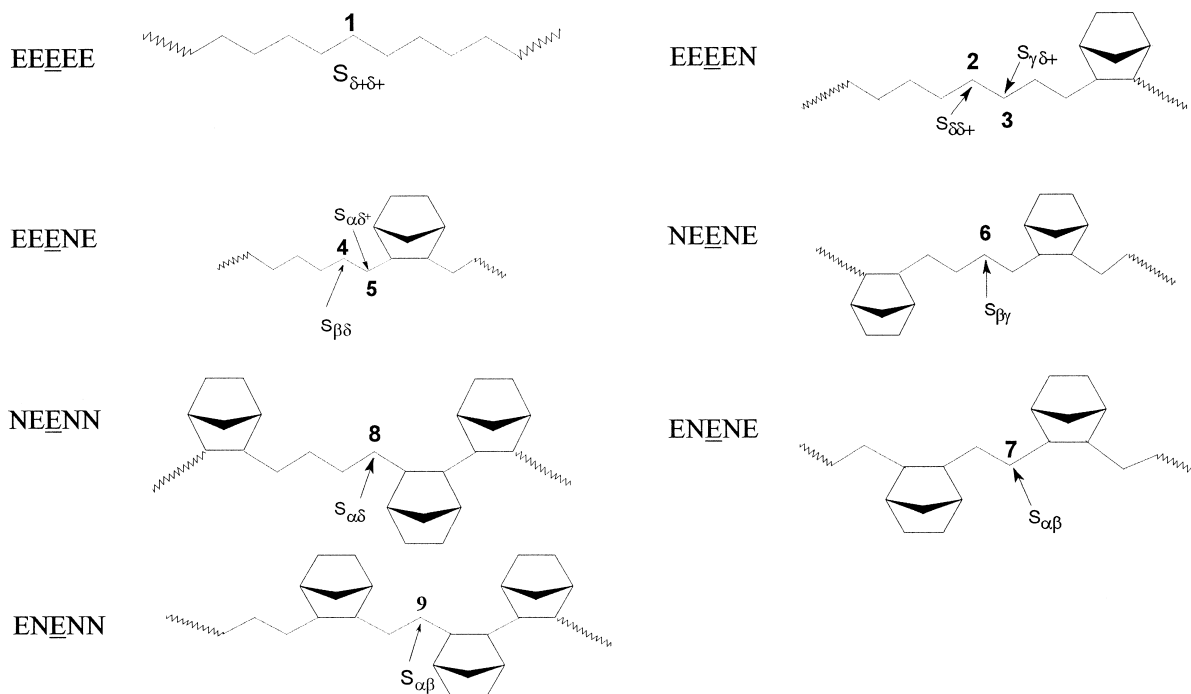


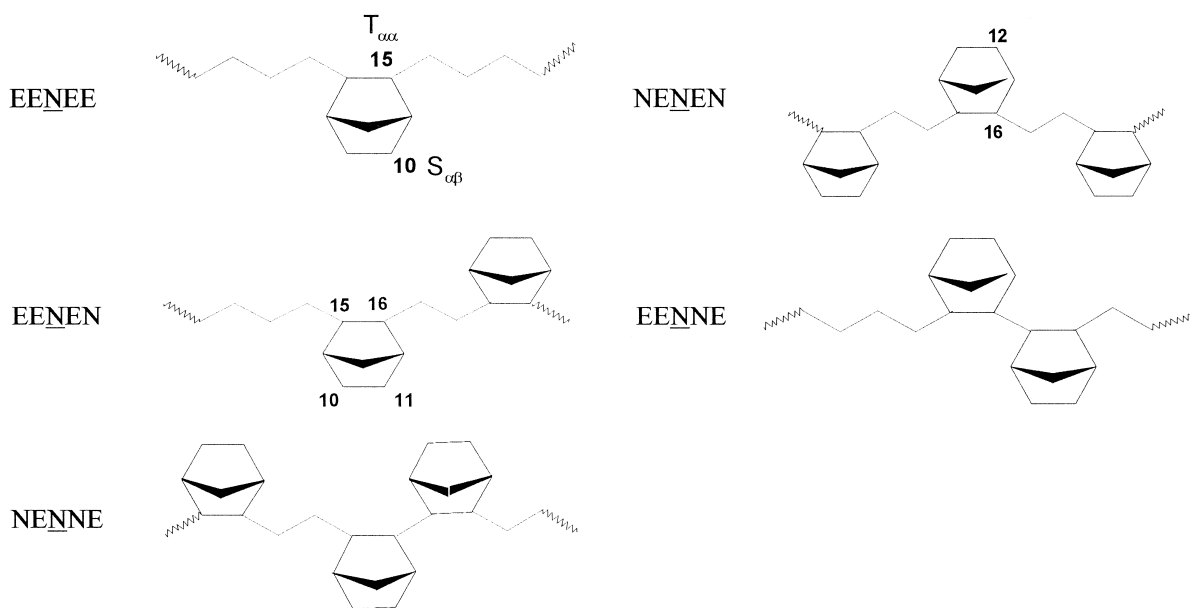
Fig. 3.  $^{13}\text{C}$  NMR spectrum of a EN copolymer prepared with  $\text{Me}_2\text{C}(\text{Flu})(\text{Cp})\text{ZrCl}_2$  and methylaluminoxane. Polymerization conditions: solvent = toluene;  $[\text{Zr}] = 8 \cdot 10^{-5}$  mol/l,  $[\text{MAO}]:[\text{Zr}] = 1000$ ;  $T = 40^\circ\text{C}$ ;  $t = 30'$ ;  $[\text{N}]:[\text{E}] = 44$ .

ppm ( $T_{\alpha\beta}$ ), and 45.03 ppm ( $T_{\alpha\alpha}$ ) [33]. The microstructural environments of carbons of norbornene units and of the methylenes of ethylene units in EN copolymer pentads, identified by NMR, are represented in Schemes 4 and 5, respectively. In Tables 2 and 3 pentad assignments are summarized.



Scheme 4. Microstructural environments of methylenes of ethylene units in comonomer sequences discernible by  $^{13}\text{C}$  NMR.



Scheme 5. Microstructural environments of carbons of norbornene units in comonomer sequences discernible by  $^{13}\text{C}$  NMR.Table 2  
Assignments for the methylene carbons of ethylene in EN copolymers

Carbon	Sequence	No.	Chemical shift (ppm)	$\Delta\delta$ (ppm)
$S_{\delta+\delta+}$	EEEEE	1	27.74	0.00
$S_{\delta\delta+}$	EEEN	2	27.80	0.06
$S_{\gamma\delta+} - S_{\gamma\delta}$	EEEN	3	27.93	0.19
$S_{\beta\delta+}$	EEENE	4	28.07	0.33
$S_{\alpha\delta+} - S_{\alpha\delta}$	EEENE + NEENE	5	28.13	0.39
$S_{\beta\gamma}$	NEENE	6	28.19	0.45
$S_{\alpha\beta}$	ENENE	7	28.39	0.65
$S_{\alpha\beta}$	ENENE	7	28.39	0.00
$S_{\alpha\delta}, S_{\alpha\beta}$	NEENN, ENENN	8,9	27.55 <sup>a</sup> , 27.72 <sup>a</sup>	-2.16, -1.85

<sup>a</sup> =  $\text{Me}_2\text{C}(\text{Flu})(\text{Cp})\text{ZrCl}_2$ .Table 3  
Assignments for the carbons of norbornene units in EN copolymer

Carbon	Sequence	No.	Chemical shift (ppm)	$\Delta\delta$ (ppm)
$S_{\alpha\beta}$	EE/NEE	10	28.30	0.00
$S_{\alpha\beta}$	EE/NEN	11	28.59, 28.61	0.29, 0.31
$S_{\alpha\beta}$	NENEN	12	28.69, 28.72	0.39, 0.42
$S_{\alpha\beta}$	EE/NNE, NE/NNE	13, 14	29.31, 29.67	1.01, 1.37
$T_{\alpha\alpha}$	EE/NEE	15	45.03	0.00
$T_{\alpha\alpha}$	NENEN, EE/NEN	16	45.74	0.71
$T_{\alpha\alpha}$	EE/NNE, NE/NNE	17, 18, 19	46.05, 47.12, 48.07 <sup>a</sup>	1.47, 2.09, 3.04

<sup>a</sup>  $\text{Me}_2\text{C}(\text{Flu})(\text{Cp})\text{ZrCl}_2$ .

Chemical shift additive rules are very helpful for determining chemical structures of non-cyclic alkanes, while constrained structure of bicyclic norbornene units makes it difficult to determine chemical shift additive rules. In Tables 2 and 3 a  $\Delta\delta$  of chemical shifts with respect to a carbon taken as reference point is reported in the attempt to roughly evaluate the effect of the vicinity of norbornene units on the observed carbon. In Fig. 4, the region of methylene carbons of ethylene units and of the  $S_{\alpha\beta}$  carbons of norbornene units (Fig. 4A–D) and of  $T_{\alpha\alpha}$  carbons of norbornene units (Fig. 4A'–D') of the spectra of EN copolymers with different compositions are shown. The samples of the spectra reported in Fig. 4(A, A', B and B') were prepared in the presence of *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> and those of the spectra reported in Fig. 4 (C, C', D and D') were prepared with Me<sub>2</sub>C(Flu)(Cp)ZrCl<sub>2</sub> precatalyst.

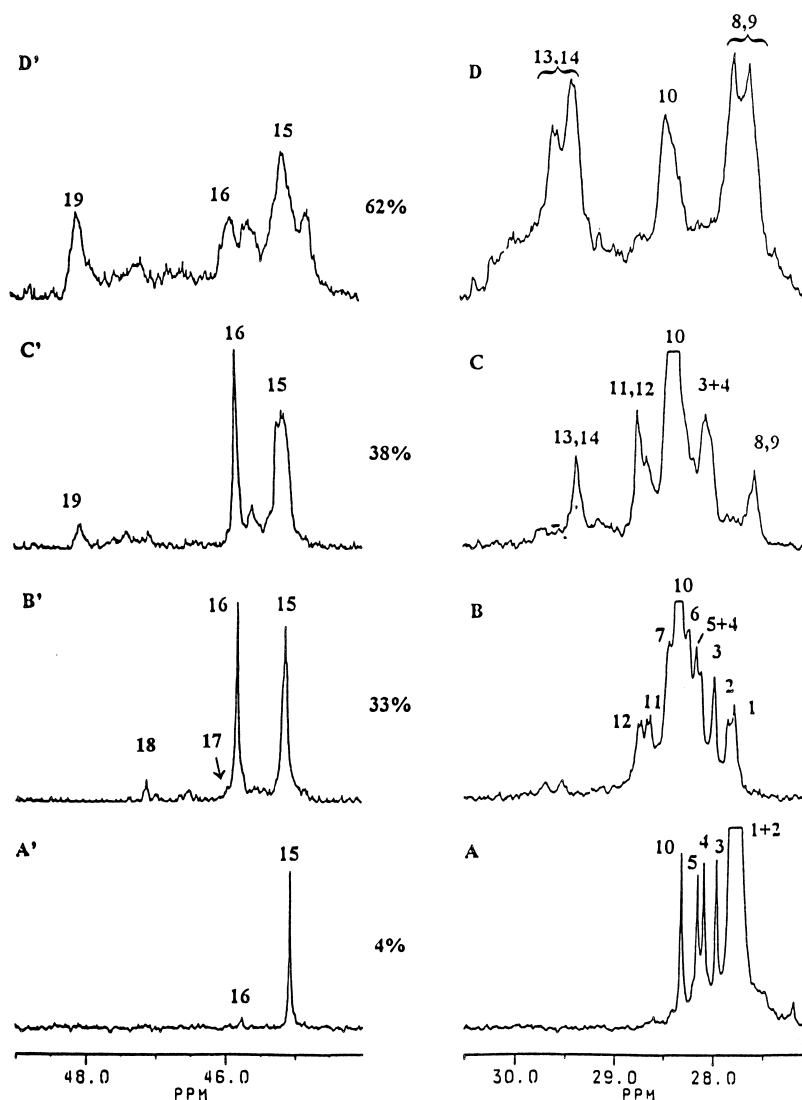


Fig. 4. Expansions of <sup>13</sup>C NMR spectra of EN copolymers prepared with *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> (A, A', B, B') and with Me<sub>2</sub>C(Flu)(Cp)ZrCl<sub>2</sub> (C, C', D, D') and methylaluminoxane. Polymerization conditions: solvent = toluene; [Zr] = 8. 10<sup>-5</sup> mol/l, [MAO]:[Zr] = 1000; T = 40°C.

As to the methylene carbons of ethylene units, the spectrum of the copolymer with the highest ethylene content in Fig. 4A shows, besides the signal at 27.74 ppm (1) of the  $S_{\delta+\delta+}$  carbons in long ethylene sequences, three signals at 27.93 ppm (3) at 28.07 ppm (4) and 28.13 ppm (5). They have been assigned to  $S_{\gamma\delta+}$ ,  $S_{\beta\delta+}$ ,  $S_{\alpha\delta+}$  carbons of the EEEEN sequence on the basis of the changes in their intensity with norbornene content. In this sequence the vicinity of a norbornene unit causes a downfield shift for the methylene carbons. The signals at 28.19 ppm (6) and 28.39 ppm (7) (Fig. 4B) have been assigned to  $S_{\beta\gamma}$ , and  $S_{\alpha\beta}$  carbons of the ethylene unit in NEENE and ENENE sequences.

In the spectrum of a sample of a copolymer with higher norbornene content (38 mol%) in Fig. 4C signals (8 and 9) at 29.37 and at 27.55 ppm become evident, and they appear very intense in the spectrum of the copolymer containing the highest norbornene content (Fig. 4D). These signals are related to the presence of norbornene diads. We have tentatively assigned signals 8 and 9 to the  $S_{\alpha\beta}$  and to  $S_{\alpha\delta}$  methylene of ENENN and NEENN sequences. It seems that the vicinity of an NN diad, that is, the substitution of the second last ethylene unit with a norbornene unit, causes an upfield shift. Signals (13 and 14) at 29.31 and 29.67 ppm are due to  $S_{\alpha\beta}$  carbons of norbornene units of NN diads which appear in this region between 28.3 and 30.0 ppm (Table 3). The signal at 28.30 ppm (10) is due to the  $S_{\alpha\beta}$  carbon of norbornene isolated among ethylene units EENEE. The pair of signals 11 (Fig. 4B) which increases in intensity with norbornene content has been assigned to the same carbon in the EENEN sequence. The pair of signals (12) which become more intense in Fig. 4C has been assigned to norbornene units in NENEN sequence.

The expansions between 44 and 50 ppm (Fig. 4A'–D') show the signals due to  $T_{\alpha\alpha}$  carbons which are the norbornene signals most sensitive to comonomer environment. On the basis of the criteria used for the assignments of methylene carbons and of the  $S_{\alpha\beta}$  carbons, we have assigned the signals at 45.03 ppm (15), and 45.74 ppm (16), to EENEE, and to EENEN + NENEN sequences, respectively. Signals 17, 18, and 19 at 46.05 ppm, 47.12 ppm and 48.07 ppm have to be assigned to the  $T_{\alpha\alpha}$  carbons of sequences containing NN diads such as EENNE and NEENE. It is worth considering that NN diads can be meso or racemic and that the spectrum of the copolymer prepared with  $\text{Me}_2\text{C}(\text{Flu})(\text{Cp})\text{ZrCl}_2$  we observe a strong signal (19) at 48.07 ppm, while in the spectrum of a copolymer with similar norbornene content prepared with *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> we observe that one of the strongest signals appears at 47.12 ppm. These and other differences might be due either to the prevalence of different comonomer sequences or of diads with different tacticity since these two catalysts are known to yield prevalingly isotactic or syndiotactic polypropene [6]. Moreover, Fig. 4D' shows the appearance of two strong signals between 45.03 and 45.74 which might also be due to the effect of the presence of NN diads on norbornene units of other sequences.

We will report elsewhere the description of copolymer microstructure of ethylene–norbornene copolymers prepared in the presence of metallocenes with different ligand pattern. This will allow us to provide a more complete sequence assignments which can be used to determine copolymerization parameters.

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