Investigation of Ethylene/Butadiene Copolymers Microstructure by ^{1}H and ^{13}C NMR

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ABSTRACT: Ethylene and butadiene are copolymerized with neodymocene catalysts. In this paper, a complete ^{1}H and ^{13}C NMR analysis of ethylene/butadiene copolymers is reported for the first time. The results of this study show that the microstructure of copolymers depends on the cyclopentadienyl ligands of the catalyst. The presence of the *trans*-1,2-cyclohexane structure, formed by intramolecular cyclization, is detected and fully investigated by 2D NMR ^{1}H/^{13}C direct and long-range correlation.

Introduction

Copolymers of conjugated dienes monomers and olefins have practical applications but they are difficult to obtain since the two classes of monomers behave very differently on a given catalytic system. As a result, they are commonly homopolymerized with different precursors.

Olefin/butadiene alternating copolymers have been obtained with titanium and vanadium based catalysts. However, these catalysts must be prepared at very low temperatures (i.e., −70 °C), and the subsequent polymerizations are performed at temperatures under 0 °C.[1] Other vanadium systems are able to copolymerize butadiene and olefins at higher temperatures.[2] The ^{13}C NMR analysis performed by Bruzzone et al. showed that the copolymers synthesized have a block-type structure. Block copolymers have also been obtained with heterogeneous Ziegler−Natta catalysts.[3] Mechanistic studies done by Robert et al. tend to prove that the polymerization is induced by a "double coordination" mechanism and that chain growth takes place on different active centers according to the monomer type.[4]

A significant decrease in activity is usually observed in the presence of butadiene with group IV metallocene catalysts and only small amounts of butadiene are inserted.[5] However some workers have recently claimed to have developed efficient systems based on cyclopentadienylamido and phenoxy complexes.[6]

Lanthanide-based catalysts are known for their efficiency in stereospecific polymerization of conjugated dienes. It has been shown that some precursors of diene polymerization can insert small quantities of α-olefin in polybutadiene—or polyisoprene—chain.[7] Mixed Ti/Nd systems have also been investigated for olefin/butadiene copolymerization, but it seems that the reaction takes place principally on the titanium.[8]

For our part, we developed a new catalytic system based on neodymocene complexes which copolymerize ethylene and butadiene (up to 40 mol % butadiene in the copolymer).[9] A series of original polymers with a wide variety of microstructures, have been obtained under different conditions (precatalyst, alkylating agent, monomer feed, ...). Since the final properties and performance of copolymers are strongly determined by both the comonomer content and the comonomer distribution along the chain, complete ^{1}H and ^{13}C NMR analyses have been done on these copolymers in order to elucidate their different structures. Of course, the NMR microstructural analysis is more complex than in a strictly binary monomer system because of the versatility of the butadiene insertion (1,4-*trans*, 1,4-*cis*, 1,2). Moreover, the presence of insertions followed by a rearrangement giving rise to formation of cycles along the chain is a typical feature of some of the catalysts investigated. This cyclization has been fully investigated by 2D NMR ^{1}H/^{13}C direct and long-range correlations. Since the nature of the terminal unit sheds light on the polymerization mechanism, resonances related to chain ends have also been assigned.

A complete NMR assignment is reported here for these new copolymers. Of course the spectra presented are only few examples of the diverse situations encountered during this study. Concerning the few ethylene/butadiene copolymers and the related NMR observations previously reported in the literature, it is worth adding that the current work sheds light on and rationalizes some of results which remained unexplained for that class of copolymers as well.

Results and Discussion

The experimental conditions and polymerization yields are summarized in Table 1.

1,4-*trans*-Butadiene Insertion. Figure 1 shows the ^{13}C NMR spectrum of a ethylene/butadiene copolymer containing 3.5 mol % of inserted 1,4-butadiene units (from ^{1}H NMR). This copolymer is obtained with the catalytic system $(Me_3SiC_5H_4)_2NdCl$ (**1**)/BuLi/HAl(^{i}Bu)$_2$ (ratio 1/10/10; run 1). The main resonance at $\delta = 30.06$ corresponds to the methylene carbons of a polyethylene chain. In our case, it corresponds to all carbons that are far enough from both terminal units and butadiene units. The resonances corresponding to the butyl and isobutyl end groups are easily assigned (Scheme 1).

The chemical shifts of the characteristic aliphatic carbons of the 1,4-butadiene insertion can be predicted

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Table 1. Polymerization Conditions and Yields

run	complex ([Nd] μM)	alkylating agent ratio/Nd	butadiene feed (mol %)	yield (g)	time (min)
1	**1** (235)	BuLi + HAl(^{i}Bu)$_2$ 10/10	3.9	3.7	80
2	**1** (264)	BuLi + HAl(^{i}Bu)$_2$ 10/10	21	2.0	270
3	**2** (196)	BuLi + HAl(^{i}Bu)$_2$ 10/10	43	4.8	120
4	**3** (75)	BuLi + HAl(^{i}Bu)$_2$ 10/10	5	1.4	60
5	**3** (107)	BOMAG[a] 20	5	2.7	60
6	**4** (284)	BuLi + HAl(^{i}Bu)$_2$ 10/10	5	8.7	90[b]
7	**5** (153)	BuLi + HAl(^{i}Bu)$_2$ 10/10	20	3.0	120
8	**5** (100)	BuMgCl 20	19	2.8	60

[a] BOMAG: butyloctylmagnesium. [b] Polymerization occurs only in the presence of hydrogen.

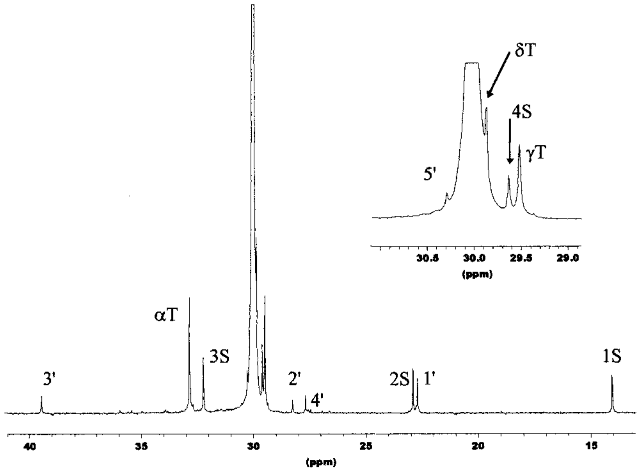
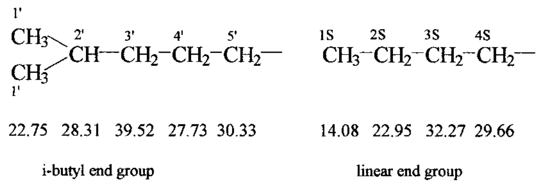


Figure 1. ^{13}C NMR spectrum of E/B copolymer (run 1) synthesized with the catalytic system $(Me_3SiC_5H_4)_2NdCl$/BuLi/HAl(^{i}Bu)$_2$ (ratio: 1/10/10); overall mol % B = 3.5; high-field resonance region.

Scheme 1. Terminal End Groups and Related Observed ^{13}C Chemical Shifts



using a classical incremental approach which rationalizes effects of the double bonds (cis and trans) on the chemical shifts of the neighboring carbons in the α, β, γ, or δ positions. On the basis of this classical additivity scheme, δ_{ij}, the chemical shift of a carbon which is in i and j positions to two different double bonds is given by the expression $\delta_{ij} = \delta_0 + i + j$, with $\delta_0 = 30.06$ and i (or j) being the increments which rationalize the influence of a double bond. For example, Bruzzone et al.[2] used the incremental values α(trans) = 3, α(cis) = − 2.4, β(trans or cis) = 0, and γ(trans or cis) = − 0.5 to calculate the chemical shift values (δ) in polyalkenamers $[-CH{=}CH-(CH_2)_n-]$ compared to the δ_0 value of the CH_2 in a polyethylene chain (PE). These commonly used increments are only approximations established with alkene models compared with the corresponding alkanes, since the ideal model should be precisely ethylene/1,4-*trans*-butadiene (E/T) and ethylene/1,4-*cis*-butadiene (E/C) copolymers which are not available at this time. Exact increment values for the influence of a trans double bond can be obtained from E/T copolymer with isolated 1,4-*trans*-butadiene units (T).

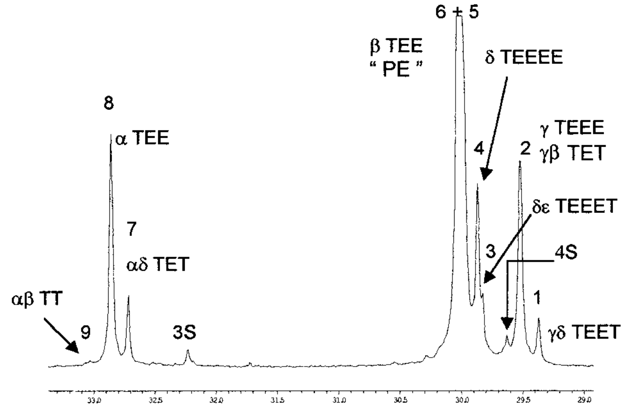
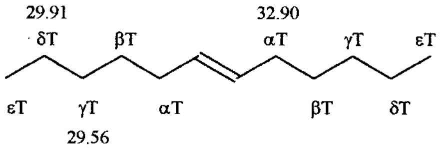


Figure 2. ^{13}C NMR spectrum of E/B copolymer (run 2) synthesized with the catalytic system $(Me_3SiC_5H_4)NdCl$/BuLi/HAl(^{i}Bu)$_2$ (ratio: 1/10/10); overall % mol B = 16.4; high-field resonance region.

Scheme 2. ^{13}C NMR Resonances for "Isolated" 1,4-*trans*-Butadiene Unit (T) in a Polyethylene Chain (Observed Chemical Shift Values)



If we initially consider an ethylene/butadiene copolymer with isolated butadiene units, carbons in α position to the double bond are expected at $\delta = 33.06$ for a trans insertion and at $\delta = 27.66$ for a cis insertion. In both cases, carbons in β position should overlap with the main resonance at $\delta = 30.06$ ("PE"), and carbons in γ position are also expected at $\delta = 29.56$. As shown in Figure 1, the first copolymer spectrum contains three characteristic methylenic carbon resonances expected for "strictly isolated" 1,4-*trans*-butadiene units (T) in a polyethylene chain. From high-field to low-field, these three resonances correspond to carbons in γ, δ, and α positions (Scheme 2). The α-carbon at $\delta = 32.90$ is the only one which is specific to this isolated *trans*-butadiene insertion.

By finding the difference between the main resonance at $\delta = 30.06$ and these three chemical shift values, we can calculate the exact incremental values which rationalize the influence of a trans double bond. The following values are obtained

$$\alpha(\text{trans}) = 2.84,\ \beta(\text{trans}) = 0;\ \gamma(\text{trans}) = -0.5,\ \text{and}\ \delta(\text{trans}) = -0.15$$

which can be compared with approximate values used previously by Bruzzone et al.[2]

The absence of any other resonance due to simultaneous influences of two double bonds is a strong evidence that at least three ethylene units (E) are inserted between *trans*-butadiene units (T). The term "isolated butadiene units" denotes the absence of such simultaneous effects.

Figure 2 shows the ^{13}C NMR spectrum of a ethylene/butadiene copolymer containing 16.4 mol % of inserted 1,4-butadiene units. This copolymer is obtained with the same catalytic system $(Me_3SiC_5H_4)_2NdCl$ (**1**)/BuLi/HAl(^{i}Bu)$_2$ (ratio 1/10/10; run 2). New resonances related to cumulated effects of two trans double bonds can be observed here. On the basis of additive effects, Scheme

Scheme 3. Saturated Carbons Influenced by Two Neighboring Trans Double Bonds

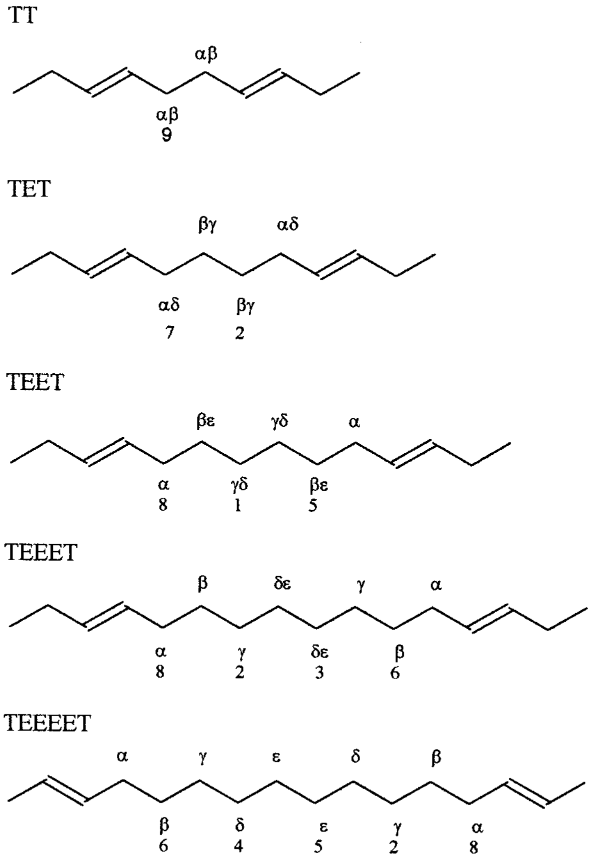


Table 2. Complete Assignment of Saturated Carbons in E/B Copolymers with 1,4-*trans*-Butadiene Insertion

peak no.	carbon type and sequence assignment	δ (ppm) calcd[a]	δ (ppm) obsd
1	$\gamma\delta$ TEET	29.41	29.42
2	γ TEEE $\beta\gamma$ TET	29.56	29.56
3	$\delta\epsilon$ TEEET	29.91	29.87[b]
4	δ TEEEE	29.91	29.91
5	ϵ TEEEE $\beta\epsilon$ TEET	30.06	30.02[b]
6	"PE" and β TEEE	30.06	30.06
7	$\alpha\delta$ TET	32.75	32.76
8	α TEE	32.90	32.90
9	$\alpha\beta$ TT	32.90	33.06

[a] Calculated values are obtained with the additivity scheme using individual increment values α, β, γ, and δ determined in this work (see above). [b] Peaks which are well rationalized by assuming an effect of the double bond on the carbon in ϵ position to this double bond (peak 5 is observable on the spectrum given in Figure 3).

3 gives all possible sequences—and carbons—concerned. A complete assignment of saturated carbons based on perfect additivity using the α to δ increment values calculated above is given in Table 2. The agreement between calculated and observed chemical shift values is excellent, except in the case of the αβ TT resonance (peak 9) due to the close position of the two double bonds. Nevertheless, the assignment of peak 9 is correct since it is also supported by the $\delta = 33.02$ value observed for polybutadiene analyzed in exactly the same conditions (solvent, temperature). Additional splittings observed with low E content (peak 3 in Figure 2, and peaks 3 and 5 in Figure 3 for example) are well rationalized by an ϵ effect with $\epsilon(\text{trans}) = -0.04$.

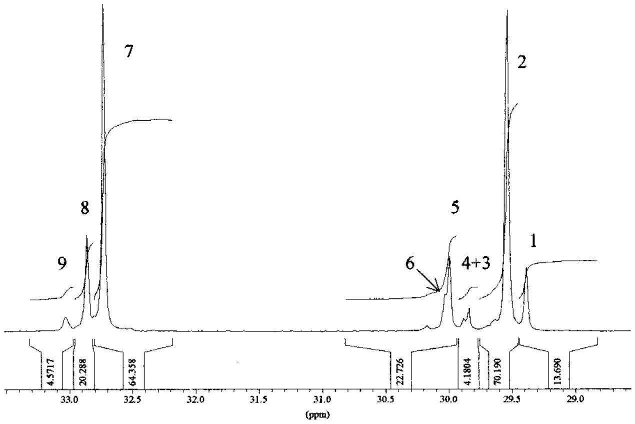


Figure 3. ^{13}C NMR spectrum of E/B copolymer (run 3) synthesized with the catalytic system [$Me_2Si(Me_3SiC_5H_3)_2$]-$NdCl/BuLi/HAl(^iBu)_2$ (ratio: 1/10/10); overall mol % B = 43; high-field resonance region.

Some ethylene/butadiene copolymers obtained with modified vanadium catalysts were previously analyzed by Bruzzone et al.[2] Their spectra, obtained at lower frequency (25.14 MHz), were poorly resolved, so an assignment was only possible in terms of dyads since peaks [1 + 2] and peaks [3 + 4 + 5 + 6] overlapped, which was consistent with a rationalization in terms of $\beta = \delta = 0$. Concerning α carbons, the TT dyad [9] was rationalized with α = 3 and $\beta = 0$ (and perfect additivity), but chemical shifts observed for TE dyads—depending on the type of copolymer obtained, block or alternated—were observed but not explained. With polymers obtained with catalyst systems based on supported Ti^{3+} species,[10] three badly resolved peaks in the low-field region [corresponding to 7, 8, 9] were observed. Nevertheless, the complete lack of resolution in the high-field region meant that a full assignment and a consistent rationalization of the effects of a trans double bond on all neighboring carbons were not possible.

The internal consistency of present assignments is first quantitatively validated through a series of relations between sequences, then both the 1,4-*trans*-butadiene content (mol %) and the dyad distribution of T and E units are calculated (TT, TE and EE).

If we take the number of identical carbons related to a given sequence (two carbons for TT, TET, TEET and one for all other sequences) into account, the following identities are obtained:

$$\{1\} = 2\text{TEET}, \quad \{2\} = \text{TEEE} + 2\text{TET}$$

$$\{3\} = 2\text{TEEET}, \quad \{4\} = \text{TEEEE}, \quad \{7\} = 2\text{TET}, \quad \{8\} = \text{TEE}, \quad \{9\} = 2\text{TT}$$

$$\{2 - 7\} = \{3 + 4\} = \text{TEEE}$$

where $\{N\}$ is the integral value of the peak number N.

Then, for the lower-field region ($\delta = 32.4$ to 33.3 ppm)

$$\{7 + 8 + 9\} = \text{all } \alpha \text{ carbons from T units} = 2\text{T} = 2\text{TT} + \text{TE} = S_0$$

$\{9\} = 2\text{TT}$, and then the relation $\{7 + 8\} = \text{TE} = S_{01}$ is expected since this integral corresponds to all α carbons in TE dyads, one by dyad, whatever their orientation, $\overrightarrow{TE}$ or $\overrightarrow{ET}$.

Table 3. Comparison of Polymer 3 (Figure 3) Microstructure (Experimental) with Random and Pseudo-alternate Copolymers (Calculated) of the Same Overall mol % T Ratio

	% EE	% TE	% TT	% T	η
polymer 3	13.45	84.25	2.30	44.6	1.70
random	30.70	49.40	19.90	44.6	1
pseudo-alternate[a]	10.80	89.20	0	44.6	1.80

[a] If [T]<[E] a copolymer is pseudo-alternate if all T units are "isolated" (absence of TT dyad and then [TE] = 2[T]) and $\eta = 1/[E]$. If [T] = [E] and [TT] = [EE] = 0, the polymer is perfectly alternate.

The internal consistency of the assignment is checked by

$$\{7 + 8\} = 2\mathrm{TET} + \mathrm{TEE} = (\overrightarrow{TET} + \overrightarrow{TEE}) + (\overrightarrow{TET} + \overrightarrow{EET}) = \overrightarrow{TE} + \overrightarrow{ET} = \mathrm{TE}$$

At higher-field ($\delta = 29.2$ to 30.5 ppm)

$$\{1 \text{ to } 6\} = \text{all carbons other than } \alpha\text{, i.e. all carbons from E units} = 2\mathrm{E} = 2\mathrm{EE} + \mathrm{TE} = \mathrm{S}_1$$

$$\{1 + 2\} = \text{all } \gamma \text{ carbons in sequences which include them, i.e. in TE dyads} = \mathrm{TE} = \mathrm{S}_{10}$$

The internal consistency of the assignment is again checked by

$$\{1 + 2\} = 2\mathrm{TEET} + \mathrm{TEEE} + 2\mathrm{TET} = (\overrightarrow{TEET} + \overrightarrow{TEEE}) + (\overrightarrow{TEET} + \overrightarrow{EEET}) + 2\overrightarrow{TET} = (\overrightarrow{TEE} + \overrightarrow{TET}) + (\overrightarrow{EET} + \overrightarrow{TET}) = \overrightarrow{TE} + \overrightarrow{ET} = \mathrm{TE}$$

An equal number of α and γ carbons is expected in sequences which include them, i.e. TE dyads. The corresponding integrals are found almost equal $\{7 + 8\} = \{1 + 2\}$ on all spectra, with $\{2\} \neq \{7\}$ particularly in E-rich copolymers, and $\{7 + 8\} + \{1 + 2\} = \mathrm{S}_{01} + \mathrm{S}_{10} = 2\mathrm{TE}$.

Since $\{1 \text{ to } 6\} = 2\mathrm{E}$ and $\{1 + 2\} = \mathrm{TE}$, it then holds by difference $\{3 \text{ to } 6\} = 2\mathrm{EE}$, which is not directly established.

The mol % 1,4-*trans*-butadiene content is

$$\%\,\mathrm{T} = \mathrm{T}/(\mathrm{T} + \mathrm{E}) = \{7 \text{ to } 9\}/\{1 \text{ to } 9\} = \mathrm{S}_0/(\mathrm{S}_0 + \mathrm{S}_1)$$

The dyad distribution of T and E units (%TT, %TE, %EE) is obtained from

$$\{9\} = 2\mathrm{TT}, \quad \mathrm{S}_{01} + \mathrm{S}_{10} = \{7 + 8\} + \{1 + 2\} = 2\mathrm{TE}, \text{ and } \mathrm{S}_1 = \{3 \text{ to } 6\} = 2\mathrm{EE}$$

$$\text{and} \qquad 2(\mathrm{TT} + \mathrm{TE} + \mathrm{EE}) = 2(\mathrm{E} + \mathrm{T}) = \{1 \text{ to } 9\}$$

Copolymerization with [$Me_2Si(3-Me_3SiC_5H_3)_2$]NdCl: Example of Reactivity Ratio Calculation. A copolymer with high butadiene content (run 3) is synthesized with a catalytic system based on the silylene-bridged complex [$Me_2Si(3-Me_3SiC_5H_3)_2$]NdCl (**2**). Table 3 gives the dyad distribution obtained from the ^{13}C spectrum of this copolymer (Figure 3) compared with the calculated distributions in a random copolymer and in a pseudo alternated copolymer with the same overall composition (mol % T). It is worth noting that the mol % T calculated from the ^{13}C NMR dyad distribution is found to be slightly higher than the overall mol % butadiene insertion obtained by ^{1}H NMR, as it does not take account many of the carbon resonances out of 29.4−32.9 ppm resonance region: i.e., carbons from ethylene units which are generated by chain ends or which are adjacent to 1,2-butadiene insertion. The observed microstructure indicates a strong tendency of the catalytic system to form an alternating copolymer. More precisely, the measure of the blocky character of a copolymer may be given by the ratio of observed frequency of ET dyad appearance with respect to that predicted by Bernouillian statistics in a copolymer of the same composition;[11] i.e., $\eta = [\mathrm{ET}]/2[\mathrm{E}][\mathrm{T}]$. As shown by Table 3, a high value of η is found ($\eta = 1.70$), not far from the value corresponding to a pseudo-alternating copolymer of the same composition ($\eta = 1.80$).

In the case of a catalytic system which gives mostly one type of butadiene insertion, the microstructure of the E/B copolymer can be described in terms of a true binary copolymer. In terms of a microstructural description, the E/B copolymer corresponding to run 3 is a terpolymer "T/V/E" (42% 1,4-*trans*-butadiene, 1% 1,2-butadiene and 57% ethylene) but can be considered as a binary T/E copolymer due to its very low 1,2-butadiene ratio. For that purpose, r_B refers to the reactivity ratio of the butadiene in its 1,4-*trans* inserted form.

In this context, if the catalyst is "monosite", and if the monomer composition $(\mathrm{E/B})_m$ is constant during the polymerization, a more complete analysis of the system is possible and allows us to calculate the individual reactivity ratios r_E and r_B.

On the basis of the above assignment, the following expressions are calculated:

$$\overrightarrow{EE}/\overrightarrow{ET} = 2\mathrm{EE}/\mathrm{ET} = 2\{3 \text{ to } 6\}/\{1 + 2 + 7 + 8\} = \mathrm{A}$$

$$\overrightarrow{TEE}/\overrightarrow{TET} = 0.5\mathrm{TEE}/\mathrm{TET} = \{8\}/\{7\} = \mathrm{B}$$

$$\overrightarrow{TEEE}/\overrightarrow{TEET} = 0.5\mathrm{TEEE}/\mathrm{TEET} = \{2 - 7\}/\{1\} \text{ or } \{3 + 4\}/\{1\} \text{ C and D, with D being more reliable.}$$

$$\overrightarrow{TT}/\overrightarrow{TE} = \mathrm{TT}/0.5\mathrm{TE} = \{9\}/\{1 + 2\} = \mathrm{E}$$

A very good agreement is found between A, B, and D values obtained from different sequence levels which indicates that the polymer is homogeneous (single site catalyst and constant monomer composition). Thus, the system can be fit with a two reactivity ratio model:

$$\overrightarrow{EE}/\overrightarrow{ET} = \overrightarrow{TEE}/\overrightarrow{TET} = \overrightarrow{TEEE}/\overrightarrow{TEET} = r_\mathrm{E}(\mathrm{E/B})_m \text{ and } \overrightarrow{TT}/\overrightarrow{TE} = r_\mathrm{B}(\mathrm{B/E})_m$$

The following values of reactivity ratios: $r_\mathrm{B} = 0.08 \pm 0.03$, $r_\mathrm{E} = 0.25 \pm 0.05$ and $r_\mathrm{B}\, r_\mathrm{E} = 0.02 \pm 0.005$ have been determined from ^{13}C analysis of several copolymers obtained with catalytic system based on the complex [$Me_2Si(3-Me_3SiC_5H_3)_2$]NdCl, and different constant monomer compositions.

1,2-Butadiene Insertion. Low butadiene insertion (runs 4, 5) is obtained with the complex $(C_5Me_5)_2NdCl_2Li(OEt)_2$ (**3**). However, an unexpected increase of 1,2-butadiene (V) insertion is obtained by changing the alkylating agent. When butyloctylmagnesium (BOMAG) is used instead of BuLi + $HAl(^i Bu)_2$ this produces an increased ratio of 1,2-butadiene (V) insertion. The copolymer obtained with a 5 mol % butadiene monomer feed contains 0.7 mol % B with 33% 1,4-butadiene units and 67% 1,2-butadiene units (^{1}H NMR). The ^{13}C spectrum (Figure 4) shows the typical saturated carbon resonances related to 1,4-*trans* (T) insertion (see above assignment) and new carbons—one methine and three

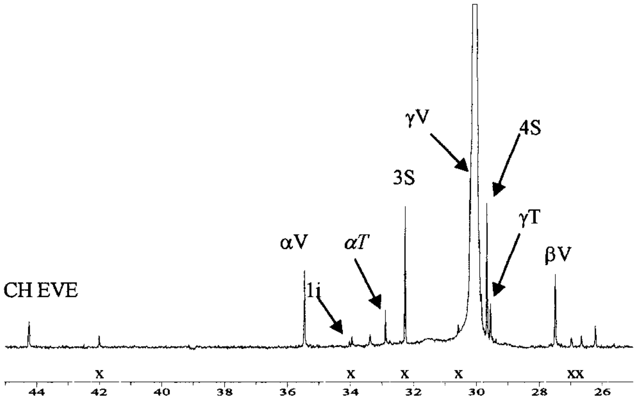
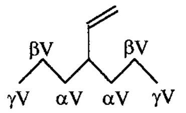


Figure 4. ^{13}C NMR spectrum of E/B copolymer (run 5) synthesized with the catalytic system $(C_5Me_5)_2NdCl_2Li(OEt_2)_2$/BOMAG (ratio: 1/20); overall mol % B = 0.7; high-field resonance region.

Scheme 4. Isolated 1,2 Units (EVE) and Assignment of Related ^{13}C Chemical Shifts

Carbon type	δ (ppm) Calc.[a]	δ (ppm) Obs.	
CH (EVE)	44.96	44.27	
αV	34.46	35.48	
βV	27.86	27.51	
γV	30.26	30.22	

[a] Calculated values are obtained with increment values given by Kalinowski et al.[16] for substitution of an H atom by X = $-CH{=}CH_2$ in an alkane.

methylene—assigned to 1,2 isolated units in EVE sequences (Scheme 4).

Terminal End Groups. Ethylene-rich copolymers show typical butyl end groups (EEE*, Scheme 1), as well as vinyl chain ends (EEVt) coming from β-H elimination after an ethylene insertion. VE* terminal units are observed in 1,2-butadiene rich copolymer. In copolymers with high 1,4-*trans*-butadiene content, terminal end groups TEE*, TE*, and occasionally EET* are detected. All related carbons have been observed and assigned (Scheme 5).

A special case is the copolymerization of ethylene and butadiene with the system $(Me_3CC_5H_4)_2NdCl$ (**4**)/BuLi/HAl(^{i}Bu)$_2$ (run 6). In the initial stages of the reaction, no activity is observed due to the formation of a stable η^3-allyl bond after the insertion of a butadiene unit.[9] Addition of hydrogen allows the synthesis of polyethylene oligomers with vinylene chain end EET*. A specific carbon ($\mathbf{C}H_3$) resonance is observed at $\delta = 17.77$.

Formation of Cycles. The ^{13}C NMR spectra of copolymers (runs 7, 8) obtained with catalysts based on the complex $[Me_2Si(C_{13}H_8)_2]NdCl$ (**5**) show six intense new signals (Figure 5). These signals are present in the 1,2-butadiene-rich copolymer previously described (Figure 4, denoted as x), but they are only trace signals.

These six peaks are related to a structure which has been fully identified as *trans*-(1,2)-cyclohexane by 1D (^{1}H and ^{13}C) and 2D (H−H and H−C) NMR correlations (Scheme 6). Two preliminary remarks concerning these six peaks provide a guideline to the follow investigation.

(1) One of these peaks ($\delta = 42.01$ ppm) corresponds to a methine carbon, and the others are CH_2 carbons as shown by DEPT spectrum. These new peaks are not associated with a new type of double bond as the (T + V) mol % in the copolymer obtained by ^{13}C NMR from $\mathbf{C}H_2\alpha$ carbons is nearly equal to the result obtained by ^{1}H NMR from $-C\mathbf{H}{=}$ resonances. This allows us to rule out the presence of a significant amount of EVVE; the methine carbon should be expected at nearly the same chemical shift ($\delta CH_{EVVE} = \delta CH_{EVE} - 2.2 = 42.07$).

(2) Two of these six peaks ($\delta = 33.96$ and 32.26) are very close to δ values already assigned to **1i** ($\delta = 34.05$) and **3S** ($\delta = 32.27$) for V_t and saturated chain end EEE*, respectively (Schemes 5 and 1 respectively). However, these peaks remain even in the absence of any detectable V_t chain ends by ^{1}H NMR or saturated chain ends by ^{13}C NMR. Moreover, these six peaks are simulta-

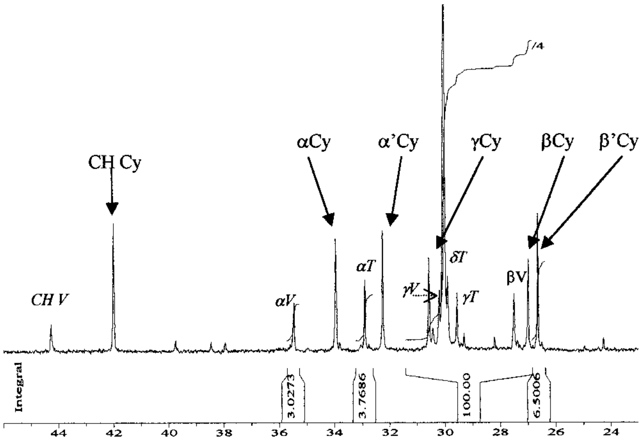
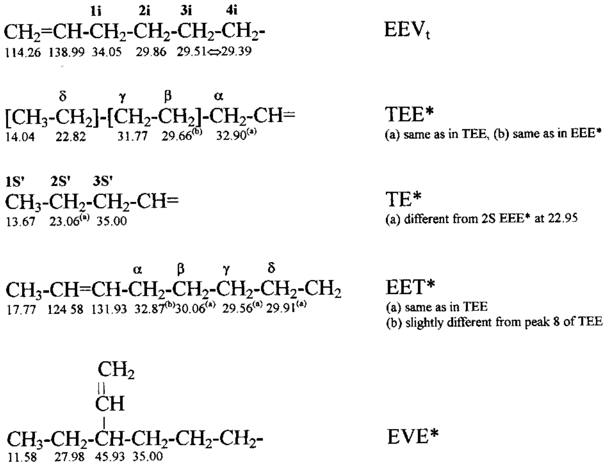


Figure 5. ^{13}C NMR spectrum of E/B copolymer (run 7) synthesized with the catalytic system $[Me_2Si(C_{13}H_8)_2]NdCl$/BuLi/HAl(^{i}Bu)$_2$ (ratio: 1/10/10); overall mol % B = 10.4; high-field resonance region.

Scheme 5. Terminal End Groups and Related Observed ^{13}C Chemical Shifts



Scheme 6. Isolated Cyclic Units (ECyE) and Assignment of Related ^{13}C Chemical Shifts

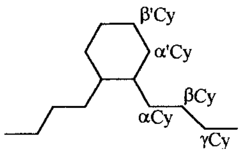
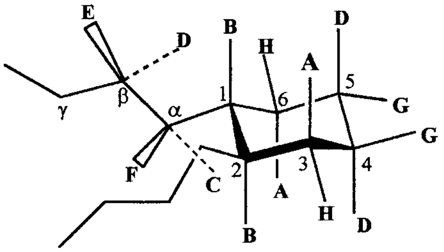
Carbon type	δ (ppm) Obs.	
CH (cycle)	42.01	
αCy + 1i	33.96	
α'Cy + 3S	32.26	
γCy	30.59	
βCy	27.00	
β'Cy	26.66	

Table 4. ^{1}H and ^{13}C Assignment of Isolated Cyclic Units (ECyE) in E/B Copolymers

$\delta(^1H)$ (343K)^a		^{1}H assignment^b	$\delta^{13}C$ (343K)^a	^{13}C assignment
H	1.76	α′e	32.21	3 and 6 (α′Cy)
G	1.66	β′e	26.67	4 and 5 (β′Cy)
F	1.51	α_2	33.85	α
E	1.34	β_2	26.89	β
D	1.20	$\beta_1 + \beta'$a		
C	1.10	α_1	33.85	α
B	1.0	H1a + H2a	41.89	1 and 2 (CH Cy)
A	0.96	α′a	32.21	3 and 6 (α′Cy)

[a] All chemical shift values given in the frame of this work have been obtained at 363 K, except 2D NMR data (343 K), so chemical shift values given here are slightly different from those given in Scheme 6 for the same structure. [b] Key: e, equatorial; a, axial; and δe > δa on a given carbon.

Scheme 7. Trans 1−2 Cyclohexane Structure with ^{1}H and ^{13}C Assignments.



neously present and their integral values are almost equal for high molecular weight polymers, when overlapped chain end resonances are not suspected. For all of these reasons, the presence of cycles has been considered.

At this stage, an analysis by both 1D and 2D NMR appeared to be essential. Homonuclear (^{1}H−^{1}H) and heteronuclear (^{13}C−^{1}H) 2D NMR correlations have been examined. The complete description of the structure has been achieved by comparing direct and long-range ^{1}H/^{13}C correlations.

Except for the two protons bound to the carbon at $\delta = 30.56$, which are not precisely localized since they are located in the region of the main ^{1}H resonance, eight different ^{1}H resonances (from A to H, Table 4, Scheme 7) are localized for nine protons ($4CH_2 + 1CH$), which clearly indicates the overlapping of two resonances. The 2D ^{13}C−^{1}H HMQC (^1J C−H correlations) allows us to identify carbon at $\delta = 32.21$ bound to A and H protons and carbon at $\delta = 33.85$ bound to C and F protons. An expansion of the region 26−27 ppm shows that the carbon at $\delta = 26.67$ is bound to the two protons (D + G), and the carbon at $\delta = 26.89$ is bound to the two protons (D + E). As this correlation is not very clear, it seems it is area D which contains the two overlapping proton resonances bound to two different carbons. The ^{1}H−^{1}H 2D COSY correlation shows the expected (GD), (AH), and (CF) geminal couplings but fails to clearly reveal the (ED) geminal coupling which should correspond to protons bound to the carbon at $\delta = 26.89$. Vicinal coupling correlations are also observed between G and H protons, which proves that carbons referred as α′ and β′ are neighboring partners. By using the weak correlation between F and E protons, it seems possible to suggest that carbons α and β are also neighboring partners, but these observations are not enough for a complete description of the structure.

Highly typical features are given by complementary observation of ^{1}H−^{13}C 2D HMQC and HMBC correlations. By definition, the first one (HMQC) provides $^1J_{CH}$ connectivities, whereas the second one (HMBC) indicates relationship through both two and three bonds ($^2J_{CH}$ and $^3J_{CH}$ connectivities also called long-range connectivities), and $^1J_{CH}$ connectivities are suppressed. In our case, CH at $\delta = 41.89$ and CH_2 at $\delta = 26.67$ show typical features which are "fingerprints" of a 1,2-substituted cyclohexane structure.

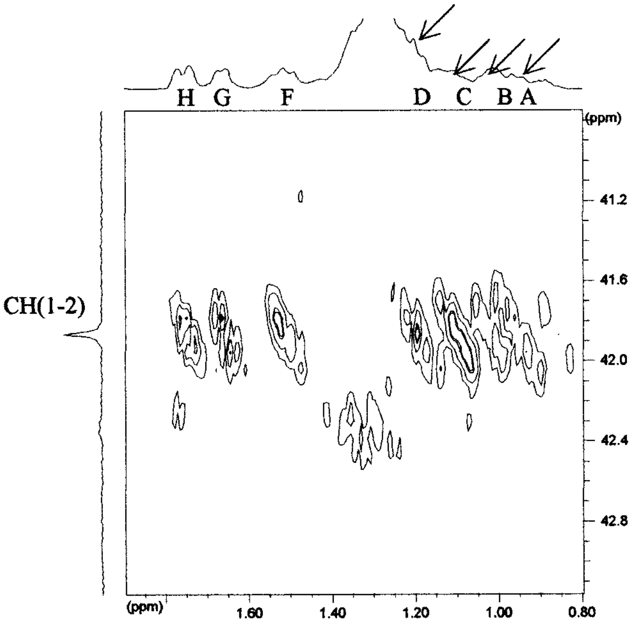


Figure 6. Two-dimensional heteronuclear NMR correlations: ^{13}C−^{1}H HMBC-GS contour plot of polymer 8 (run 8): expansion of the correlations related to the methine carbon of the cycles (343K) [correlations via two and three bonds].

Concerning CH carbon at $\delta = 41.89$, HMQC shows a $^1J_{CH}$ connectivity with a proton B at $\delta = 1.0$ and HMBC shows a long-range connectivity ($^2J_{CH}$) with a proton at the same chemical shift. This clearly indicates that the structure has two neighboring and identical CH carbons (and protons B). These two CH moieties being referred to as 1 and 2, the HMQC connectivity corresponds to **C_1-H1** and **C_2-H2** ($^1J_{CH}$) since the HMBC long-range connectivity corresponds to **C_1-C_2-H2** and **C_2-C_1-H1** ($^2J_{CH}$). Exactly the same observation holds for the CH_2 at $\delta = 26.67$, which shows both short-range and long-range connectivity with protons G and D. This structure has two neighboring and identical CH_2 at $\delta = 26.67$, which are referred to as 4 and 5. If one, or both of the aforementioned long-range couplings were ^3J and not ^2J, then other structures should be considered, namely 1,2- and 1,3-cycloheptane and 1,3-cyclooctane. The fact that the six carbon resonances typical of the structure show equal integral values allows us to rule out these last structures where all carbon and protons are not represented twice.

All 1D and 2D NMR data are consistent with a *trans*-1,2-cyclohexane structure (Scheme 7). Of course, the *cis*-1,2-(axial,equatorial)-cyclohexane structure is ruled out, particularly because H1 and H2 should not be magnetically equivalent in such a structure. Note that the only portion of the NMR data we show here are the complete HMBC connectivities (seven correlations) observed for C_1 with five ^2J proton coupling partners H_2(B), A, H, C, and F and two ^3J coupling partners G and D (Figure 6).

The formation of cyclohexane rings is attributed to a cyclization which happens after a 1,2-butadiene inser-

Scheme 8

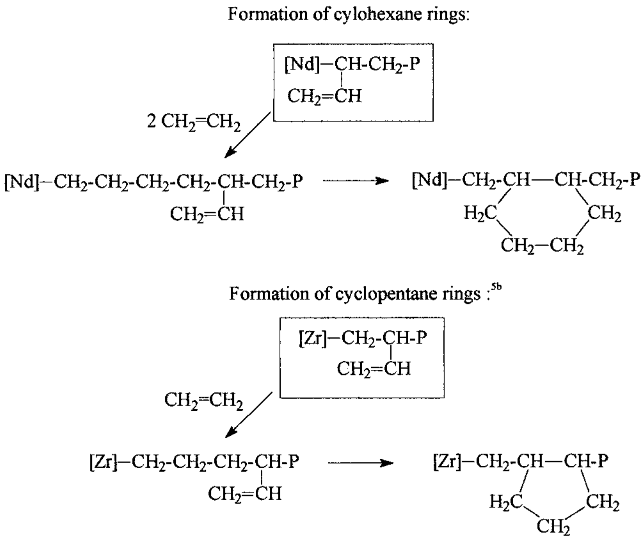


Table 5. E/B Copolymers: Composition and Microstructure

run	mol % B (ballast)	mol % B (polymer)	microstructure		
			1,4-trans	1,2	cycles
1	3.9	3.5	96	4	0
2	21	16.4	97	3	0
3[a]	43	43.0	97.5	2.5	0
4	5	0.6	76	24	0
5	5	0.7	34	66	traces
6[b]	5	1.9	100	0	0
7	20	10.4	28	23	49
8	19	14.3	22	28	50

[a] Polybutadiene[9] obtained with the same catalytic system has the following microstructure: 88.4% 1,4-trans, 5.6% 1,2, 6% 1,4-cis. [b] 90% of the butadiene inserted is in terminal position (T*).

tion, followed by two ethylene units insertions (Scheme 8). This intramolecular cyclization mechanism can be compared to the formation of 1,3-cyclopentane rings previously observed in the homo- and copolymers of 1,5-hexadiene with olefins.[12] It is worth noting the presence of cyclohexane rings in a polyethylene chain, since cyclohexene is not copolymerized with ethylene by zirconocene catalyst.[13] Moreover, it is the first time that cyclohexane rings are detected in copolymers of olefin and butadiene. Until now, only cyclopentane rings have been observed in copolymers obtained with zirconocene/methylaluminoxane catalysts.[5b] These cyclization reactions provide important information on the polymerization mechanism. With lanthanocene catalysts, the cyclization happens after a "normal" 1,2-butadiene insertion (formation of a η^3-coordinated butenyl anion), but in the case of zirconocene catalysts (formation of cyclopentane rings), the butadiene is inserted like an olefin (Scheme 8). These results may be related to the better ability of lanthanocene catalysts to copolymerize ethylene and butadiene.

Overall % Butadiene Insertion and Microstructure (Table 5). Except when cycles are present, ^{1}H NMR spectra give the overall butadiene content in the copolymers (mol % B), and the distribution of these B units in 1,4 linear (L) insertion (L = 1,4-*cis* + 1,4-*trans*) and 1,2 insertion (V). A typical spectrum is presented in Figure 7. An exact determination of the 1,2-butadiene (V) insertion needs to take into account the contribution of vinyl chain ends (V_t) to integral I_2 ($I_2 = 2V + 2V_t$). In that case, $I_5 = V_t$ is a direct measure of vinyl chain ends and I_4 gives a direct measure of 1,2-butadiene insertion (I_4 = V) and 2L = I_3; if I_3 and I_4 are not well resolved then 2V = $I_2 - 2I_5$ and 2L = $\{I_3 + I_4 + I_5\} - 0.5I_2$. In both cases, the number of ethylene units is 2E = $[I_1 - 4L - 3V + 4V_t]/2$, and then B/(B + E) is easily obtained.

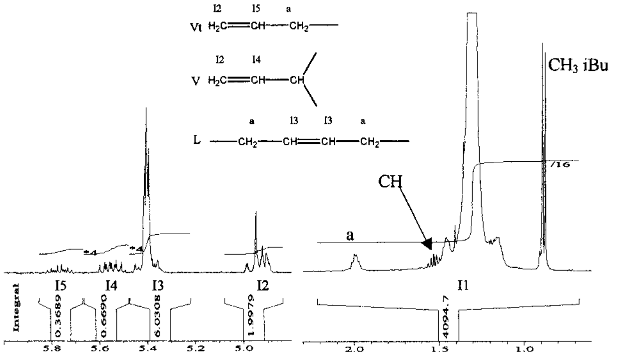


Figure 7. Typical ^{1}H NMR spectrum of a E/B copolymer without cycles: overall mol % B = 0.4; distribution of B units: 18% 1,2 and 82% 1,4 units (exclusively trans from the ^{13}C spectrum).

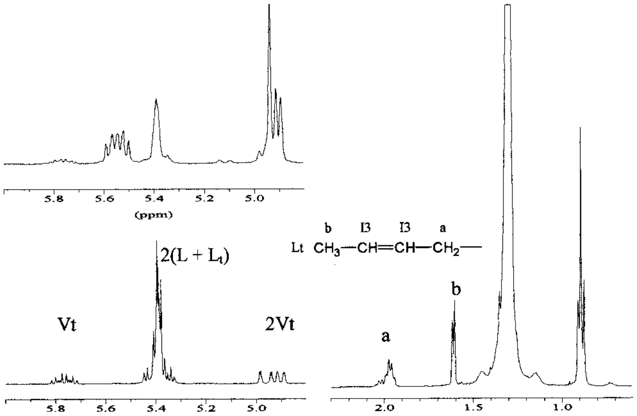


Figure 8. ^{1}H NMR spectrum of E/B copolymers: (bottom) (run 6) copolymer, overall mol % B = 1.9 (exclusively 1,4-*trans* from ^{13}C spectrum), distribution of B units 10% internal T and 90% terminal T*; (top) double bond resonance region of a 1,2-butadiene rich copolymer without cycles (run 5) overall mol % B = 0.7, distribution of B units 66% 1,2 and 34% 1,4-*trans*.

Direct ^{1}H NMR determination of the butadiene inserted remains valid even when a noticeable ratio of the butadiene inserted provides vinylene chain end. In this case, a CH_3 resonance is observed at δ = 1.6 (b) (Figure 8 bottom), whereas in the α position to the double bonds the CH_2 α resonances are observed at δ = 2.0 (a) regardless of the position of the 1,4-butadiene insertion, internal or terminal. Figure 8 (top) shows the olefinic region of a 1,2-butadiene-rich copolymer (run 5).

On the other hand, when *trans*-1,2-cyclohexane moieties are detected in both the ^{1}H and ^{13}C spectra, ^{1}H spectra can no longer be used for the determination of the overall butadiene insertion since double bonds disappear with the cyclization in this type of butadiene insertion. In that case ^{13}C NMR gives the total butadiene insertion (B), and the distribution of 1,4-*trans* (T), 1,2 (V), and 1,2 followed by cyclization (Cy) microstructures. From our present assignments, the following expressions are obtained:

$$2B = 2T + 2V + 2Cy = \{7 + 8 + 9\} + \alpha V + \beta' Cy$$

$$2E = \{26.8 \text{ to } 31.5 \text{ ppm}\} + \alpha V/2 + 2\beta' Cy$$

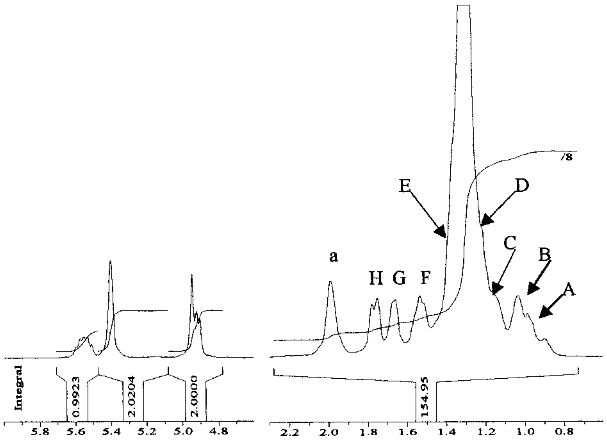


Figure 9. ^{1}H NMR spectrum of E/B copolymer (run 7) containing *trans*-1,2-cyclohexane cycles: overall mol % B = 10.4; distribution of B units 28% 1,4-*trans*, 23% 1,2, and 49% cycles (from ^{13}C spectrum).

Concerning V units, among the nine carbons giving six peaks, five of them coming from E units, four are already included in the region 26.8−31.5 (βV and γV) to which αV/2 is added. Concerning cycles, among the 12 carbons giving six peaks, eight come from E units, four are already included in the region 26.8−31.5 (βCy and γCy) to which 2β'Cy is added. Peaks αCy and α′Cy are not used due to overlapping with chain end peaks 1i and 3S, respectively.

As shown in Figure 9, if cycles are not taken into account, it should have been concluded that polymer from run 7 has 5.3 mol % inserted butadiene (from double bonds at low field and an erroneous evaluation of ethylene units at high field), whereas the ^{13}C spectra gives a global insertion of 10.4 mol % with the following microstructure: 28% 1,4-*trans*, 23% 1,2, and 49% cycles.

Conclusion

In a previous paper, we reported an original synthesis of poly(ethylene-*co*-1,3-butadiene) with neodymocene catalysts.[9] The polymerization is performed at elevated temperature (80 °C) and yields copolymers with high butadiene content without gel formation. The overall butadiene insertion and the microstructure of the copolymers are investigated here by both ^{1}H and ^{13}C NMR analysis. This complete NMR study of the copolymers shows the wide variety of microstructures obtained according to the ligands of the metallic complex and lays the foundations of future investigations in this field.

Experimental Section

All reactions were carried out under pure dry argon using standard Schlenk techniques. THF was distilled from sodium benzophenone under argon. Toluene was dried on molecular sieves (3 Å). All reagents were purchased from commercial suppliers and used without further purification. $(C_5Me_5)_2NdCl_2Li(OEt_2)_2$ [**3**][14] was prepared according to the literature. Syntheses of $(Me_3SiC_5H_4)_2NdCl$ [**1**], $[Me_2Si(3\text{-}Me_3SiC_5H_3)_2]NdCl$ [**2**], $(Me_3CC_5H_4)_2NdCl$ [**4**], and $[Me_2Si(C_{13}H_8)_2]NdCl$ [**5**] have been reported previously.[9,15]

Polymerizations were performed in a 0.5 L glass reactor, equipped with a stainless steel blade. The alkylating agent and the neodymium complex were introduced in a flask containing 300 mL of toluene. The mixture was stirred for 15 min and then transferred into the reactor under a stream of argon. Argon was then pumped out, and the reactor was charged with butadiene−ethylene mixture. The pressure was kept constant (4 bar) during the entire reaction. The polymer was then precipitated in 800 mL of methanol, washed, and dried under vacuum.

High-resolution liquid NMR spectroscopy was carried out with a Bruker DRX 400 spectrometer operating at 400 MHz for ^{1}H and 100.6 MHz for ^{13}C. 1D spectra were obtained with a 5 mm QNP probe at 363 K. For 2D spectra, a broad-band probe with field gradient on *z*-axis was used, with a COSY-GS sequence for ^{1}H−^{1}H correlation and HMQC-GS and HMBC-GS for ^{1}H−^{13}C correlations. Polymer samples were examined as 10−15% (w/v) solutions. A mixture of tetrachloroethylene (TCE) and perdeuteriobenzene (C_6D_6) (2/1 by volume) was used as solvent. Chemical shift values (δ) are given in ppm in reference to internal tetramethylsilane (TMS); in absence of TMS the resonance of polyethylene ("PE" at δ = 30.06) is used as internal reference. Typical accumulations included the following: 70° rf pulse; TD = 64K; 4.5 s recycle time. Typical accumulations with gated proton decoupling were about 10 000 scans (12 h). No significant difference in relative integrals, for the carbons of interest to us (CH_2), was observed between acquisition made under these conditions and those made in absence of the nuclear Overhauser effect (NOE).

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