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On the Ethylene-Norbornene Copolymerization Mechanism

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Summary: Results of our studies on polymerization kinetics and tests of copolymerization statistical models of ethylene-norbornene (E-N) copolymers obtained on the basis of microstructures determined by ^{13}C NMR analysis are reported. Ethylene-norbornene (E-N) copolymers were synthesized by catalytic systems composed of racemic isospecific metallocenes, *i*-Pr[(3Pr^i-Cp)(Flu)]ZrCl$_2$ or a constrained geometry catalyst (CGC) and methylaluminoxane.

Polymerization kinetics revealed that E-N copolymerization is quasi living under standard polymerization conditions. Calculations of the number of active sites and of chain propagation and chain transfer turnover frequencies indicate that the metal is mainly in the Mt-N* state, while the Mt-E* state contributes more to transfer and propagation rates.

The first-order and the second-order Markov statistics have been tested by using the complete tetrad distribution obtained from ^{13}C NMR analysis of copolymer microstructures. The root-mean-square deviations between experimental and calculated tetrads demonstrate that penultimate (second-order Markov) effects play a decisive role in E-N copolymerizations. Results show clues for more complex effects depending on the catalyst geometry in copolymers obtained at high N/E feed ratios.

Comonomer concentration was shown to have a strong influence on copolymer microstructure and copolymer properties.

The copolymer microstructure of alternating isotactic copolymers obtained with *i*-Pr[(3Pr^i-Cp)(Flu)]ZrCl$_2$ have been described at pentad level. Second-order Markov statistics better describes also the microstrucure of these copolymers.

Keywords: ^{13}C NMR analysis; copolymer microstructure; ethylene-norbornene copolymers; living polymerization; metallocene catalysts; statistical models

Introduction

Interest in addition cycloolefin polymerization has increased tremendously over the last decade, due to the discovery that *ansa*-bridged metallocenes effectively copolymerize ethylene and norbornene.[1]-[8] The importance of this new class of polymers arises from their

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special thermoplastic properties, high transparency, and high glass transition temperatures, imparted by the norbornene component. This interest led to commercialization of products such as TOPAS obtained with metallocene catalysts.

The metallocene structure plays a crucial role in the copolymerization process, the copolymer microstructure, and the copolymer properties.[9] The copolymerization mechanism consists of initiation, propagation, and termination or chain-transfer steps. It is reasonable that E-N copolymerizations begin in a manner similar to that of other α-olefin polymerizations. Detailed studies on chain termination and transfer reactions have been carried out in Prof. Brintzinger's group.[10] In order to gain deeper insights into the mechanism of these copolymerizations we have concentrated on the variables that influence the copolymer microstructure, the propagation and transfer turnover frequencies, and the presence of short and long chain branches in E-N copolymers. The present paper will review the results of our studies obtained from:

i) Polymerization kinetics
ii) Testing copolymerization statistical models from copolymer microstructures determined by ^{13}C NMR analysis.

Most recent results regarding the microstructural analysis of alternating isotactic copolymers at pental level and the influence of monomer concentration will be presented and discussed.

Results

Polymerization Kinetics

We have become interested in following the polymerization kinetics in order to understand the influence of reaction conditions and polymerization time on polymer properties. A simple sampling of the reaction mixture at different reaction times proved to be an efficient technique for studying the copolymerization kinetics, under usual conditions, that is, by using MAO and [Al]/[Zr] molar ratios as high as 2000. Both yield and molar masses grow with time. The molecular mass of E–N copolymers, obtained at low temperatures (T = 30-50°C) and high norbornene feed fractions, increases with time for up to one hour. The polydispersity can be as narrow as 1.1 at [N]/[E] feed ratios as high as 28.[11] This indicates that very little chain transfer occurs and that E-N copolymerizations are quasi-living under these conditions. Chain growth over one hour is unusual for olefin polymerization, the average lifetime of a growing ethylene and propylene polymer chain is typically less than seconds, and growth of polymer chain can only be observed with stopped-flow techniques. The type of catalyst used has a strong influence upon the quasi-living character of the reaction. The linearity of the growth of molar mass with time allows us to gain insight into the factors influencing the propagation and chain transfer reactions by using standard equations for treatment of the experimental data of the polymerization kinetics, derived from those introduced by Natta long ago. [12]

$$\frac{1}{\overline{P_n}} = \frac{M_0}{\overline{M_n}} = \frac{C^*}{R_p t} + \frac{\sum R_t^i t}{R_p t} \qquad \textbf{Eq. 1}$$

where $\overline{P_n}$ is the number average degree of polymerization, C* is the active site concentration, R_p is the polymerization rate, and R_t^i are the rates of different chain termination reactions. For a copolymerization as a first approximation, we take the weighed average of the monomer mass by using the following relationship:

$$M_0 = x_E \cdot M_E + x_N \cdot M_N \qquad \textbf{Eq. 2}$$

where x_E and x_N are the molar fractions and M_E and M_N are the molar masses of ethylene and norbornene, respectively. The calculated number-average degree of polymerization $\overline{P_n}$ can also be expressed in terms of the average turnover frequencies of monomer insertion $<f_p>$ and chain transfer or termination $<f_t>$.[13]

$$\frac{1}{\overline{P_n}} = \frac{M_0}{\overline{M_n}} = \frac{1}{<f_p>} \cdot \frac{1}{t} + \frac{<f_t>}{<f_p>} \qquad \textbf{Eq. 3}$$

The calculated [Zr*]/[Zr] and $<f_t>/<f_p>$ values for E-N copolymerization obtained with three metallocenes are summarized in Table 1.[14]

By comparing the results obtained (Table 1) for catalyst **1** at two different N/E ratios, we observe that an increase of the N/E ratio clearly gives a decrease of the monomer insertion turnover frequency. At the same time the transfer turnover frequency decreases so that the ratio $<f_t>/<f_p>$ remains constant (Table 1). Such similarity is worth noting since **1-3** catalysts produce completely different polymers: the extremes, **1**, a norbornene-rich copolymer at high N concentration and **3**, a virtually pure polyethylene over the whole feed composition range.

Table 1. Kinetic parameters of the ethylene-norbornene copolymerization.

Catalyst	N/E feed ratio	N pol (mol-%)	<f_p> (min^{-1})	<f_t> (min^{-1})	<f_t>/<f_p> '10^4	Zr*/Zr
rac-Et(Ind)$_2$ZrCl$_2$ (**1**)	28.4	59	346	0.062	1.79	0.68
rac-Et(Ind)$_2$ZrCl$_2$ (**1**)	12.5	52	634	0.109	1.72	0.66
rac-Et(4,7-Me$_2$Ind)$_2$ZrCl$_2$ (**2**)	12.5	36	185	0.032	1.73	0.94
90% *rac* /10% meso- H$_2$C(3-tert-BuInd)$_2$ZrCl$_2$ (**3**)	12.5	0.5	381	0.076	1.99	0.56

Polymerization conditions: solvent = toluene, MAO, [Al]/[Zr] = 2000; T = 30 °C, P_{C_2} = 1.01 atm.

The latter along with the activity data suggests that the decrease in activity has its origin in the interference of norbornene with the reaction mechanism.

Surprisingly, the values of <f_t>/<f_p> are very close to those reported by Busico *et al.* [13] for the stopped-flow homopolymerization of ethylene, using *rac*-Me$_2$Si(4-PhInd)$_2$ZrCl$_2$/MAO, in spite of the difference of several orders of magnitude in the ethylene polymerization.

The fraction of active sites is higher than the value of 0.1 mol/mol(Zr) reported for ethylene polymerization with *rac*-Me$_2$Si(2-methyl-4-phenyl-1-indenyl)$_2$ZrCl$_2$ at very short polymerization time under stopped flow conditions. [13] Worth to note is that under the same conditions, the number of active sites found in propene polymerization is six times higher than in ethene polymerization. The values obtained for E-N copolymerization are closer to the values recently counted by Landis (0.85-0.95 mol/mol(Zr))[15] for the polymerization of 1-hexene with dimethylmetallocene **1** by means of a new ^{2}H–tagging strategy. Each Zr* site spends a fraction of time in Zr-E* or in Zr-N* state. This depends on the norbornene content in the copolymer and on the catalyst structure.

The relatively higher concentration of Zr* active sites found in E-N copolymerization indicates that the Zr* sites that we measure are mainly in the Zr-N* state. The similarities between <f_t>/<f_p> values found in E-N copolymerization and E polymerization indicate that Zr-E* sites contribute more to chain propagation and chain transfer than the Zr-N* ones. In conclusion, the presence of norbornene both in the polymer chain and in solution plays a crucial role in the livingness of E-N copolymerization due to its steric hindrance and coordinating ability. This causes a great reduction of the propagation and chain transfer rate

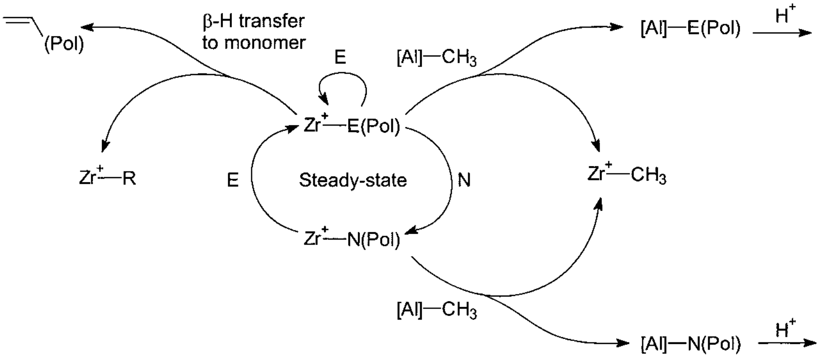

Figure 1. Reaction paths proposed to take part in the catalytic cycle during ethene-norbornene copolymerization catalyzed by metallocenes.

compared to that in the homopolymerization of α-olefins and makes the Zr* state more or less "dormant".

This agrees with the findings that the long chain branches decrease with the increasing N content in the copolymer, when using a catalyst like $Me_2Si(Me_4Cp)(N^tBu)TiCl_2$[16] which allows for incorporation of long chain branches in polyethylene: chain transfer to the monomer and the formation of the vinyl terminated polymer chain are possible only at Mt-E* sites (Figure 1).

Copolymer Microstructure and Polymerization Statistics

The scheme in Figure 1 is quite a simplified picture since penultimate inserted monomer units can be important in E-N polymerisation. When we consider second-order Markov statistics we have four copolymerization parameters linked to the probability of formation of sequences depicted in Figure 2.

A detailed knowledge of the effectiveness of catalysts in producing a given polymer structure can be achieved provided that a methodology for the detailed determination of the polymer microstructure is available. In the last few years, we have concentrated on the investigation of the microstructure of ethylene-norbornene copolymers by combining the use of NMR techniques with computational methods based on relationships between NMR spectra and conformations and an *ab initio* chemical shifts calculations.[17-20] Although some assignments

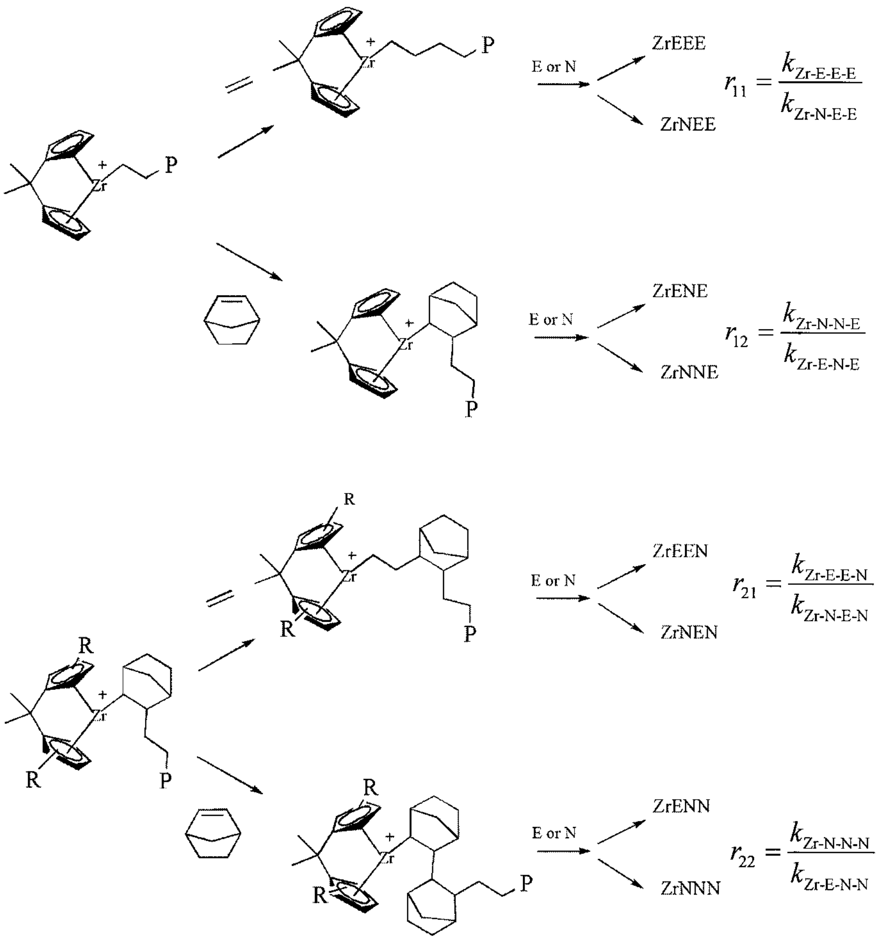

Figure 2. E-N Copolymerization reactions and reactivity ratios in the second-order Markov model.

are still controversial, there is currently a good understanding of the rather complex nature of the ^{13}C NMR spectra. This includes the assignments and quantification of isolated, alternating, and blocky norbornene sequences comprising the tacticity. Our current understanding of E-N copolymer NMR spectra yields complete tetrad sequence distributions. The analysis at tetrad level allows one to test both the first-order and the second order statistics, whilst triad distributions could allow only the fitting of the 2nd order Markov model (Figure 2). Thus, it is possible to determine the copolymerization parameters and clarify possible statistical models of copolymerization, discriminating between ultimate and penultimate effects.[22]

Reactivity Ratios and Statistical Models

The results on reactivity ratios regarding one sample per catalyst, having similar norbornene contents, are summarized in Table 2.

The C2-symmetric bridged metallocene *rac*-$Me_2Si(2\text{-}Me\text{-}[e]\text{-}benzindenyl)_2ZrCl_2$ (**5**) used in the present work is a catalyst with two homotopic sites and in principle both monomers should have the same probability of being inserted at both sides. Indeed, other C2-symmetric bridged metallocenes such as *rac*-$Me_2Si(indenyl)_2ZrCl_2$ (**4**) give rise to more random copolymers under the same conditions. However, with respect to **4**, **5** has substitutions in indenyl positions 2, 4 and 5, and the steric hindrance of the ligand structure seems to forbid two consecutive norbornene insertions at the two homotopic sites, so that a mainly alternating copolymerization occurs. However, as soon as two successive norbornene units are added some changes in the interactions occur - probably to avoid strong non-bonded interactions between the hindered growing polymer chain and the indenyl substituents - which favour the insertion of a third norbornene unit. Strong non-bonded interactions due to steric hindrance have been invoked as the cause of the formation of *rrrr* errors in isotactic polypropylene with $Me_2C\text{-}(Flu)(3\text{-}tert\text{-}butylCp)ZrCl_2$ based catalysts. [21]

Table 2. E-N copolymerization parameters calculated from tetrad analysis.

Catalyst		N pol (mol-%)	1st Fit	2nd Fit	r_{11}	r_{21}	r_{22}	r_{12}
rac-$Et(Ind)_2ZrCl_2$	(**1**)	40.16	0.010	0.004	3.041	2.191	0.018	0.030
rac-$Me_2Si(Ind)_2ZrCl_2$	(**4**)	40.73	0.017	0.001	4.414	2.339	0.026	0.066
rac-$Me_2Si(2\text{-}Me\text{-}benzindenyl)_2ZrCl_2$	(**5**)	44.1	0.034	0.027	3.373	9.931	0.039	0.005
$Me_2Si(Me_4Cp)(NBu^t)TiCl_2$	(**6**)	43.6	0.009	0.006	4.117	7.204	0.013	0.001

In general better fits are obtained with the second-order Markov statistics and this model appears to be valid. Thus, it is possible to state that the next-to-last E or N monomer unit exerts an influence on the reactivity of the propagating Mt-E* or Mt-N* species. Such an influence seems to be contingent upon the catalyst structure. The second-order Markov model must be used to describe E-N copolymerizations promoted by most of the metallocenes used.

In contrast to these results, the fits for the alternating copolymer produced from *rac*-$Me_2Si(2\text{-}Me\text{-}benzindenyl)_2ZrCl_2$ are not satisfactory either with first or with second order statistical models. A third-order or a more complex model may be required to fit the experimental data obtained with this catalyst, where more sterically hindered indene substitutions are dominant. This appears to confirm our hypothesis that various mechanisms are at work with this catalyst. Furthermore, the analysis of copolymers obtained at very high norbornene concentrations yields different values of copolymerization parameters. Thus, copolymerization obtained with all catalysts may require more complex models.

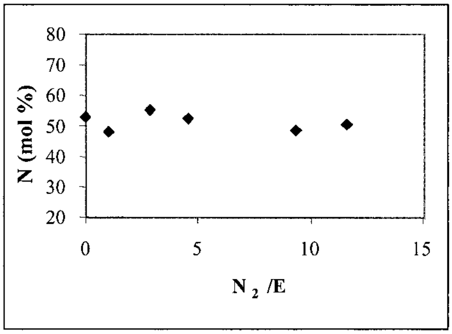

Figure 3. Plots of norbornene copolymer content of E-N copolymers obtained with 1/MAO, at constant comonomer content, as a function N_2/E.

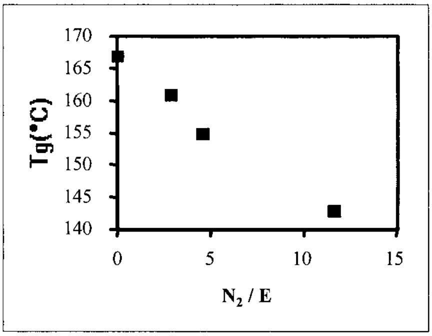

Figure 4. Plots of glass transition temperature of the E–N copolymers, obtained with 1/MAO, as a function N_2/E.

Monomer Concentration

One important variable clearly influencing the copolymerization kinetics is the comonomer concentration, thus we tested the influence of comonomer concentration on the copolymer microstructure and the copolymer properties in copolymerizations performed with catalyst *rac*-$Et(indenyl)_2ZrCl_2$ (**1**). We varied both comonomer concentrations and kept constant the comonomer feed ratio at about 28. Ethylene pressure varied from 1,1 to 0,078 atm by adding N_2 to reach 1,1 atm total pressure. By decreasing both comonomer concentrations, E-N copolymer samples with very similar N content (about 50 mol%) (Figure 3), showing differences in T_g values up to 25 °C (Figure 4), are obtained.

The analysis of copolymer spectra reveals large differences in the microstructure of these copolymers as visible in Figure 5, where the experimental tetrad distribution and those calculated according to second-order Markovian models for copolymers prepared at 1,1 and 0.078 atm ethylene pressure are compared. The sample obtained at lower comonomer concentration is more alternating and shows a much lower amount of NN blocks. Both copolymers obey second order Markov statistics.

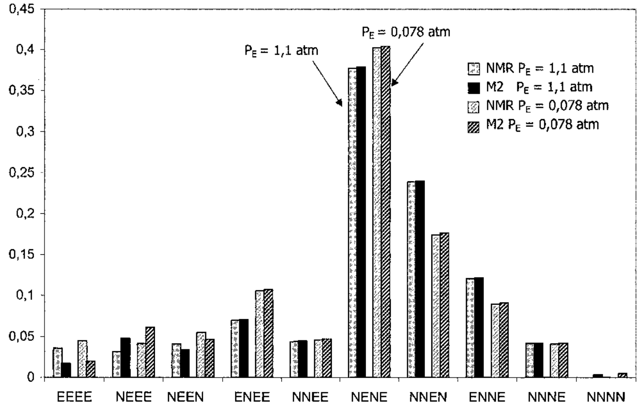

Figure 5. Tetrads distributions for E/N copolymer samples prepared with *rac*-Et(indenyl)$_2$ZrCl$_2$ (**1**), at N/E feed ratio of 28.9, ethylene pressure of 1,1 (full) and 0,078 atm (dashed), respectively; light coloured experimental data; dark coloured calculated according to second-order Markov model.

The second order Markov statistics well reproduces the major microstructural differences between the microstructure of the two samples. The lower ENNE blocks and the higher alternating NENE sequences present in the copolymer, obtained at lower E and N concentration, may explain the significantly lower T_g values observed in this sample. Indeed, the T_g differences should not arise from differences in M_n since all the copolymer samples of Figures 3 and 4 have rather high M_n values (> 70.000).

Lower PE → lower NN blocks → lower Tg values

Alternating Isotactic Copolymers

Typical catalysts which produce isotactic alternating E-N copolymers contain high steric hindered ligands such as *i*-Pr[(3-R-Cp)(Flu)]ZrCl$_2$ (R= Me, Pr^i, Bu^t).[23][24] The analysis of stereoregular alternating E-N copolymers has been used to elucidate polymerization mechanistic details such as the importance of *chain migration mechanism* vs. *chain retention mechanism*. In the case of a *chain migration mechanism* the monomer insertion occurs alternatively at one or the other coordination site. Norbornene units can be inserted only at the more open coordination site, while the small E can be inserted at both sites. This mechanism should allow only odd numbered ethylene blocks. In the case of *retention mechanism* E and N units are inserted at the same coordination site of the catalysts. This mechanism allows for the formation of odd and even numbered ethylene blocks. Arndt [23] used a statistical model which differentiates the two heterotopic sites of the catalyst *i*-Pr[(3-Bu^t-Cp)(Flu)]ZrCl$_2$: one site, always in a Zr-E* state, follows first order Markov statistics, the second can be in a Zr-N* state and follows second order Markov statistics. He concluded that E-N copolymerization follows a chain migration mechanism. On the other hand Fink *et al.* [24] have recently analyzed E-N copolymer spectra obtained with *i*-Pr[(3-Pr^i-Cp)(Flu)]ZrCl$_2$ by using their own assignments.[25] They did observe even numbered ethylene sequences and concluded that the microstructure of the copolymer is consistent with *a retention mechanism* and follows first order Markov statistics.

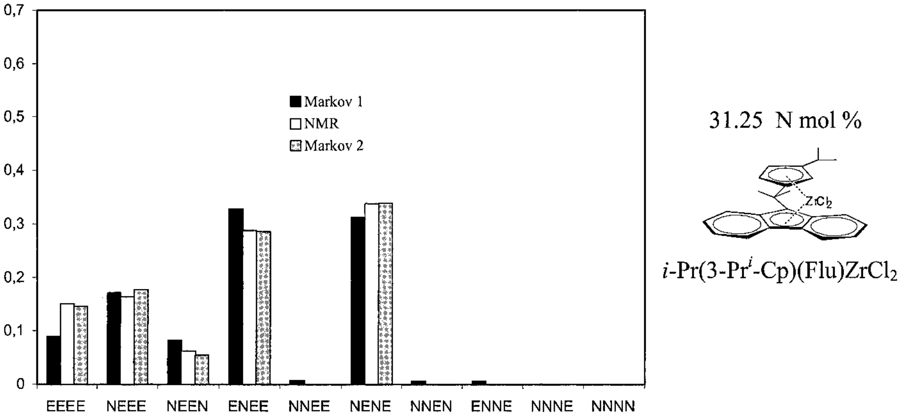

Figure 6. Experimental and calculated tetrads distributions for an E/N copolymer sample prepared with *i*-Pr[(3-Pr^i-Cp)(Flu)]ZrCl$_2$, at N/E feed ratio of 4, ethylene pressure of 1,1 atm. Black experimental data; white according to first-order Markov model; dashed according to second-order Markov model.

We have analyzed the spectra of alternating isotactic copolymers obtained with *i*-Pr[(3-Pr^i-Cp)(Flu)]ZrCl$_2$ at tetrad level (Figures 6 and 7). The comparison of experimental and calculated tetrads reveals that second Markov statistics reproduces the microstructure of this isotactic alternating copolymer more accurately than first order Markov statistics. Anyway, NEEN sequences are clearly visible in a copolymer sample containing 31.25 N-mol% (Figure 6).

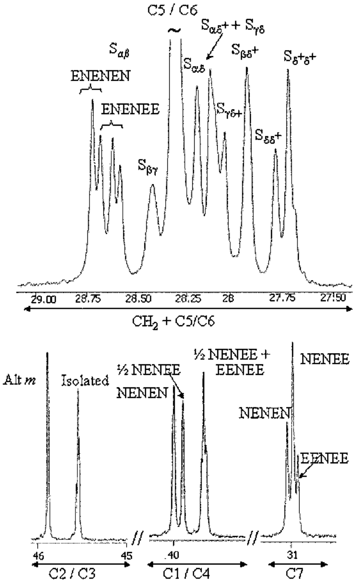

Figure 7. ^{13}C NMR spectrum performed at 100 MHz of the copolymer sample of Figure 6.

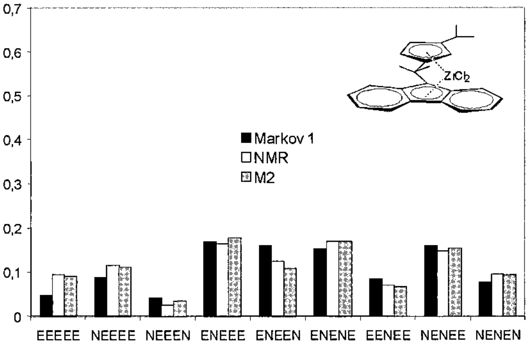

Figure 8. Experimental and calculated pentads distributions for the E/N copolymer sample of Figures 6 and 7.

Pentad Analysis

The better quality of recent NMR spectra achieved by having access to an NMR instrument at higher field (Figure 7), gives us pentad level information, which allows for even safer testing of statistical models.

This is clear in this graph where we have determined nine pentads (Figure 8), five of which are independent (only two triads and three tetrads independent). Even though there are a couple of controversies in the assignments of the CH$_2$ region, the results concerning the validity of second order statistics and the values of copolymerization parameters are practically independent from such controversies. Extension of the pentad analysis to series of E-N copolymers with a wide range of norbornene content will allow us to definitely select the best statistical model to describe E/N copolymerization with each catalyst.

Conclusions

The quasi living nature of E-N copolymerization at temperatures as low as 30 °C and high norbornene concentration in the feed allowed us to calculate the number of active sites and propagation and chain transfer turnover frequencies. We found a relatively high concentration of Zr* active sites found in E-N copolymerization. This indicates that Zr* that we measure are mostly in the in Zr-N* state. The $<f_t>/<f_p>$ values found are similar to those found for E polymerization. This is a sign that Zr-E* sites are those that contribute more to chain propagation and chain transfer turnover values. Moreover, the presence of norbornene both in the polymer chain and in solution causes a great reduction of the propagation and chain transfer rate compared to that in the homopolymerization of α-olefins and makes the Zr* state more or less "dormant".

Our understanding of E-N copolymer NMR spectra and our methodology for their analysis allows us to select the best statistical model describing E/N copolymerization with a given catalyst and to study the influence of various parameters including the catalyst symmetry and ligand substitution and the monomer concentration on the polymerization mechanism.

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