Propene-Norbornene Copolymers: Synthesis and Microstructure

L. Boggioni, I. Tritto, M. Ragazzi, P. Carbone, D. R. Ferro*

Istituto per lo Studio delle Macromolecole del C.N.R., Via E. Bassini 15, 20133-Milano, Italy
E-mail: l.boggioni@ismac.cnr.it

Summary: Series of propene–norbornene (P–N) copolymers were synthesized in the presence of two C_2 symmetric zirconocenes, *rac*-Et(Indenyl)$_2$ZrCl$_2$ (**1**) and *rac*-Me$_2$Si(Indenyl)$_2$ZrCl$_2$ (**2**), and of the C_s symmetric zirconocene Me$_2$C(Cp)(Fluorenyl)ZrCl$_2$ (**3**) with MAO as cocatalyst. P–N copolymers were characterized by ^{13}C NMR spectroscopy, SEC, and DSC. A first assignment of the main ^{13}C NMR signals of P–N copolymers obtained with **1** and **2** containing isolated N units was obtained on the basis of DEPT experiments and by comparison with isotactic polypropene (*i*-PP) and E–N copolymer spectra. *Ab initio* theoretical ^{13}C NMR chemical shifts, combined with R.I.S. statistics of the P–N chain, gave important detailed indications for the assignment of the complex ^{13}C spectra of these copolymers. Such assignments were used to estimate the N copolymer content. The comparison of N content values obtained from the areas of different regions of the spectra reveals that 1,3 propene misinsertions are formed in greater amount as the [N]/[P] ratio of the feed increases. This may be due to the steric hindrance of the Mt–tertiary carbon bond when N is the last inserted unit, which makes difficult the next propene insertion and causes the low polymerization activities, molecular masses and T_g. The spectra of P—N copolymers obtained with **3** revealed to be even more complex. A limited assignment of the spectrum has been achieved. This allowed us to evaluate the N content in the copolymers and to evidence the low tendency of the C_s symmetric **3** to give 1,3 propene misinsertions in P–N copolymers. This is in agreement with the results observed with this catalyst in propene homopolymerization.

Keywords: *ab-initio* ^{13}C NMR chemical shifts; microstructure; propene-norbornene copolymerization

Introduction

Cycloolefin copolymers, which were made possible by the introduction of new *ansa*-metallocene based catalysts, may provide interesting materials endowed with such properties as excellent transparency, good heat resistance and high glass transition temperature.[1] The

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properties of ethene–norbornene (E–N) copolymers can be modulated by varying and controlling their composition and microstructure; e.g., their glass transition temperature (T_g) can reach values as high as 220 °C. The incorporation of norbornene into the isotactic polypropene chain was expected to feature higher T_g than E–N copolymers with the same N content and molar mass (MM) since polypropene (PP) has a higher T_g than polyethene. Since such properties depend greatly on the composition and the microstructure of the polymer chain, considerable effort has been devoted in the last few years to elucidate the microstructure of the E–N copolymers, mainly on the basis of the interpretation of their ^{13}C NMR spectra. Significant contributions to assign the complex ^{13}C NMR spectra can be provided by the knowledge of the conformational characteristics of the polymer chain.[2] No interpretation of P–N copolymer spectra has been attempted so far. Indeed, such a study meets greater difficulties than those met with E–N copolymers, since differences in stereo- and regioregularity of propene units as well as in the comonomer distribution and the stereoregularity of the bicyclic units originate complex microstructures of the polymer chain and complex spectra. Given the great general interest in norbornene copolymers, we have undertaken the study of P–N copolymerization with specific regards to the elucidation of the copolymer microstructure. In this paper we will summarize the studies on P–N copolymers prepared with two C_2 symmetric zirconocenes, namely *rac*-Et(Indenyl)$_2$ZrCl$_2$ (**1**) and *rac*-Me$_2$Si(Indenyl)$_2$ZrCl$_2$ (**2**) (Figure 1), with methylaluminoxane (MAO) as cocatalyst. P–N copolymers were characterized by ^{13}C NMR spectroscopy, SEC, and DSC.[3] Novel results on synthesis and microstructural characterization of P–N copolymers with one C_s symmetric zirconocene catalyst, namely Me$_2$C(Cp)(Fluorenyl)ZrCl$_2$ (**3**) (Figure 1) with MAO, will be presented and compared.

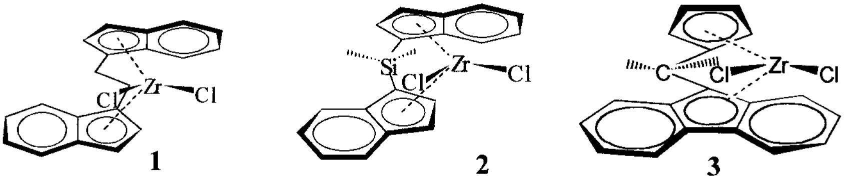

Figure 1. Molecular structures of C_2 (**1** and **2**) and C_s (**3**) precatalysts.

Experimental part

All experiments involving air-sensitive compounds were performed using standard glovebox and Schlenk techniques. **1**, **2**, and **3** (Figure 1) were obtained from Boulder Scientific. Methylaluminoxane (MAO), purchased from Witco, was dried under vacuum and stored as a powder. Toluene was distilled over sodium under a nitrogen atmosphere. Norbornene was distilled over potassium under a nitrogen atmosphere and used as a stock-solution in toluene. Propene was passed over molecular sieves (4Å) and BTS to remove oxygen and water.

To a thoroughly dried round bottom flask (250 mL), toluene and a norbornene stock solution were transferred to give the desired amounts of norbornene and a total liquid volume of 100 mL after addition of MAO and **1**, **2** or **3**. Temperature was kept constant at 30 °C. The stirring rate (700 - 1000 rpm) and propene pressure (1.01 atm) were set and kept constant during the runs, and equilibration was allowed. Finally, MAO (4 mmol) and catalyst (2 μmol), both dissolved in small amounts of toluene, were injected ([Al]/[Zr] = 2000). Polymerization was allowed for a period of time, from 0.5 to 4.00 hrs, to assure low norbornene conversion before the polymer was precipitated in an ethanol (0,8 L)/HCl (10 mL) mixture, stirred overnight, filtered, stirred with ethanol overnight, filtered, and dried at 70 °C under vacuum above.

The copolymers were dissolved in $C_2D_2Cl_4$ with hexamethyldisiloxane (HMDS) as internal standard. The spectra were recorded on a Bruker AM-270 spectrometer operating at 67.89 MHz (^{13}C) in the PFT mode operating at 103 °C. Further experimental details on ^{13}C DEPT NMR spectra were as reported earlier.[2],[3]

The molar mass distribution (MMD) and polydispersity were measured on a high-temperature dual-detector size exclusion chromatography (SEC) system. The SEC system was a GPCV2000 from Waters (Milford, MA, USA) that uses two on-line detectors: a differential viscometer (DV) and a differential refractometer (DRI) as concentration detector. The description of this SEC-DV system has been reported elsewhere.[4]

DSC measurements were performed using a Perkin Elmer Pyris 1 equipped with signal subambient devices. The copolymer sample (3-6 mg) was first cooled to –80 °C and kept there for 1 min. Then the sample was heated to 200 °C (20 °C/min), cooled to –80 °C (20 °C/min), heated to 200 °C (20 °C/min). The sample was kept under a He flow (30 ml/min) during the whole run, and the glass transition temperature T_g was taken from the second heating.

Synthesis of propene-norbornene copolymers with C_2 and C_s symmetric catalysts

Catalysts **1** and **2** were selected as *ansa*-metallocenes of C_2 symmetry that have proven effective for producing prevailingly isotactic and regioregular polypropene[5],[6] as well as E–N copolymers with a tendency to alternate.[2] Catalyst **3** was selected as a metallocene of C_s symmetry which yields prevailingly syndiotactic polypropene[6] and is very active in E–N copolymerization.[1] Figure 2 shows that as the feed ratio ([N]/[P]) increases the productivity decreases, as expected.

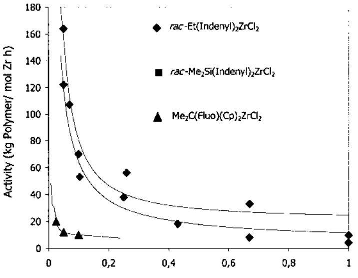

Figure 2. P–N Copolymerization activity obtained with **1**/MAO, **2**/MAO, and **3**/MAO at 30°C, P_P = 1,01 atm, MAO (4 mmol) and catalyst (2 μmol), in 100 mL toluene.

The polymerization activities of **1** and **2** were found to be quite low especially when compared to those obtained for E–N copolymerization under analogous experimental conditions.[2],[3] This may result from the difficulty of inserting a propene in the Mt–tertiary carbon bond formed after the norbornene insertion (Mt-N).

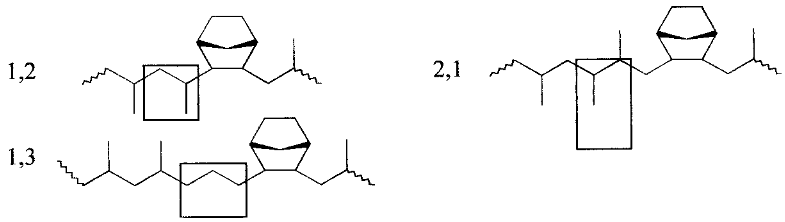

Figure 3. Possible 1,2-, 2,1-, and 1,3- propene insertions into Mt–N carbon bond.

Indeed, such a situation is even more sterically crowded than the sites formed after a propene (2,1) regioirregular insertion (Figure 3), which have a lower reactivity with respect to sites with a primary growing polypropene chain.[5],[6] The very low polymerization activities obtained with **3** seems to be indicative of even greater difficulties of insertion of propene into the Mt-N bond of this catalyst than into the Mt-N carbon bond of catalysts **1** and **2**.

Microstructure of propene-norbornene copolymers with C_2 symmetric catalysts

1D ^1H and ^{13}C NMR methods are considered the most useful ones for quantitative evaluation of polymer stereochemistry and copolymer content, although modern multidimensional NMR techniques could provide further information on polymer stereochemistry.[7] The research approach of this work for elucidating the unkown P–N copolymer structure combines 1D ^{13}C NMR experiments and computational techniques with information on the catalyst behavior in P homopolymerization and E–N copolymerization.

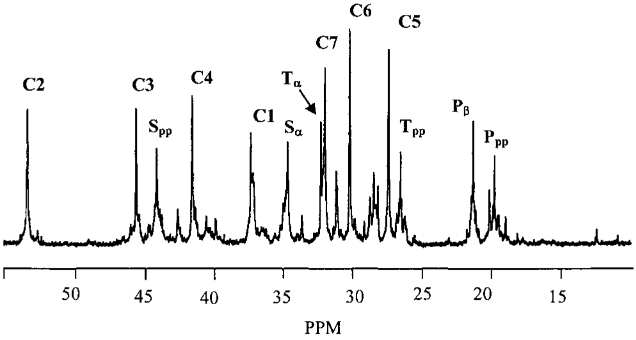

Figure 4. ^{13}C NMR spectrum of P-N copolymers prepared, at [N]/[P] feed ratio = 0.26, in the presence of **1**/MAO.

Figure 4 displays the ^{13}C NMR spectrum of a P–N copolymer prepared with **1**/MAO, at [N]/[P] feed ratio of 0.26, along with the final signal assignment. The structure and carbon numbering of an isotactic poly(P-*co*-N) are sketched in Figure 5. 2,3-*exo* norbornene insertion is considered to occur into the metal-carbon bond as in E–N copolymerization. All propene consecutive monomer units have the methyls in erythro relationships as in an isotactic polypropene chain.

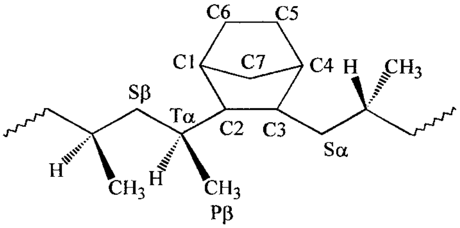

Figure 5. Structure and carbon numbering of an isoctatic poly(P-*co*-N).

A first general assignment of the ^{13}C NMR spectra of two P–N copolymers with different norbornene contents has been based on distortionless enhancement by polarization transfer (DEPT) ^{13}C spectra and on comparison with isotactic PP and E–N copolymer spectra.[3] The spectrum in Figure 4 shows seven groups of signals with comparable areas, which should be due to the norbornene carbons. The number of signals indicates that there is no symmetry in the norbornene unit in agreement with the general structure depicted in Figure 5. DEPT experiments showed that signals at 31.90, 30.09, and 27.33 ppm are secondary carbons and have to be assigned to C7 and C5/C6 norbornene carbons. The comparison of the chemical shifts of these signals with those of E–N copolymers allowed us to make a further step in assignments (Table 1).

Table 1. Comparison between ^{13}C chemical shifts of propene units in isotactic PP and P–N copolymer and between ^{13}C chemical shifts of norbornene units in P–N and E–N copolymer.

Carbon	Chemical shifts (ppm)	
	Propene	
	P–N	PP
CH_3 **(P)** *(mmmm)*	18.43-20.43	18.89-21.69
	(19.69)	*(19.67)*
CH **(T)** *(mmmm)*	26.10-26.80	26.26-26.82
	(26.56)	*(26.40)*
CH_2 **(S)** *(mmmm)*	43.64-44.69	43.81-44.70
	(44.19)	*(44.10)*
	Norbornene	
	P–N	E–N
C5 / C6	27.33	28.33
C5 / C6	30.09	28.33
C7	31.90	30.90
C1 / C4	37.17	39.50
C1 / C4	41.32	39.50
C2 / C3	45.40	45.03
C2 / C3	53.32	45.03

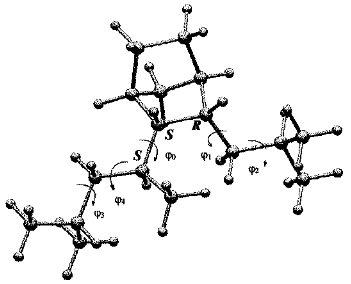

Figure 6. Model compound **PSLP** representing a segment of an isotactic poly(P-*co*-N) chain.

Moreover, the conformational characteristics of an ideal P–N chain were investigated by means of molecular mechanics calculations. The model compound **PSLP** (Figure 6) has been utilized to gain indications for the assignment of the complex spectra of mid-low N-content copolymers.

The conformations and the relative energies of the most stable conformers of **PSLP** have been computed with the quantum-mechanical method B3LYP/6-31G**.[3] The relative energies *via* molecular mechanics with force fields MM2 and MM3 were obtained and the conformer populations for the PSLP moiety of the *isotactic* $(P_4\text{–}N)_x$ copolymer, using the RIS statistics of the chain based on MM2, were computed and the statistics was also corrected for the deviations from the *ab initio* computations. The theoretical ^{13}C NMR chemical shifts for the most relevant conformers of selected model compounds were obtained according to the GIAO method using a large base set and Adamo and Barone's functional.[8] The theoretical chemical shifts have been averaged over the RIS populations. The third column of Table 2 shows the *expected* chemical shift values for the norbornene carbons, obtained by shifting the *MM2corr* average by the difference between the chemical shift of an *isolated* N unit observed in E–N copolymers and the value computed for the *all-trans* conformer of 2,3 di-*n*-propyl-norbornane, which we have taken as a model for the *isolated* N unit of an E–N copolymer:

Eq. 1 $\nu_{expect} = \nu_{average} + \nu_{exptl}(\text{E-N}_{copol}) - \nu_{calc}(\text{di-}n\text{-propyl-N})$ (+ correction)

Such an equation is needed for applying the computed results to the interpretation of the ^{13}C NMR spectra of P–N copolymers as we do not rely on absolute theoretical chemical shift values. In some cases further corrections are required as described in ref. 3b.

The results of the calculations presented in Table 2 along with DEPT experiments and comparison with spectra of *i*-PP and E–N copolymer provides the first detailed assignment of P–N spectra obtained with catalysts **1** and **2**.

Table 2. Chemical shifts (ppm) expected for some carbons of isotactic P–N copolymers on the basis of *ab initio* differences between corrected MM2 statistical averages and reference model values (see eq. 1).

Atom	Average (*MM2*)	Average (*MM2corr*)	Expected (*MM2corr*)	Observed
C2	57.50	57.82	52.5 / 53.0	53.33
C1	43.18	43.13	37.1	37.28
C7	37.13	36.89	31.98	31.91
C6	34.94	34.93	29.79	30.10
C5	32.47	32.38	27.24	27.34
C4	47.16	46.93	40.8	41.54
C3	49.45	49.17	43.8 / 44.3	45.61
Pβ	21.99	22.02	20.9	21.24

The molar fractions of norbornene (f_N) and propene (f_P) incorporated in the P–N copolymers can be calculated from the propene methyl signals or from norbornene signals by using the two following equations:

Eq. 2A $\frac{f_P}{7f_N+3f_P}=\frac{I_{CH_3}}{I_{tot}}$ Eq.2B $\frac{f_P}{7f_N+3f_P}=\frac{I_{CH3}}{I_{tot}}$ $\frac{f_N}{7f_N+3f_P}=\frac{1}{7}\frac{I_{C5,C6,C1,C4,C7,C2,C3}}{I_{tot}}$

where $f_P+f_N=1$, I_{CH3} is the observed peak area for propene methyl signals, $I_{C5,C6,C1,C4,C7,C2,C3}$ is the sum of the areas of norbornene signals, and I_{tot} is the sum of the areas of all peaks, i.e. the main signals listed in Table 1 as well as the unassigned smaller ones. The two equations should give similar results. However, the calculations, performed for a number of samples, show a great discrepancy between the values of comonomer content derived from the two equations: the value of f_N obtained from the areas of norbornene signals being much smaller than the one calculated from the propene methyl signals in the region between 15 and 22 ppm. Inspection of the ratios between the CH and CH_2 peak areas suggested that eq. 2A could overestimate the norbornene amount. Indeed, the total CH_2 peak area is in excess with respect to the expected stoichiometric value. Such a CH_2 excess induced us to consider the existence of propene 1,3 misinsertions in the Mt–N bond as a possible source of the observed discrepancy (see Figure 3). The total propene molar fraction could arise from the contribution of propene units in three different situations:

Eq. 3 $f_P=f_{P1}+f_{P2}+f_{P3}$

where f_{P1} is the molar fraction of 1,2- or 2,1-inserted propene which yields one methyl, one methylene, and one methine within the polymer chain; f_{P2} is the molar fraction of 1,3 misinserted propene yielding three methylenes; and f_{P3} is the molar fraction of P units present as chain-ends which give rise to one methyl and two methylenes as polymer chain ends.

The peak areas of all methyl (I_{CH3}), methylene (I_{CH2}) and methine (I_{CH}) signals are:

Eq. 4 $$\frac{I_{CH3}}{I_{tot}} = \frac{f_{P1} + f_{P3}}{7f_N + 3f_P} = \frac{f_{P1} + f_{P3}}{7 - 4f_P}$$

Eq. 5 $$\frac{I_{CH2}}{I_{tot}} = \frac{3f_N + f_{P1} + 3f_{P2} + 2f_{P3}}{7f_N + 3f_P} = \frac{3f_N + f_{P1} + 3f_{P2} + 2f_{P3}}{7 - 4f_P}$$

Eq. 6 $$\frac{I_{CH}}{I_{tot}} = \frac{4f_N + f_{P1}}{7f_N + 3f_P} = \frac{4f_N + f_{P1}}{7 - 4f_P}$$

By using equations 3-6, with the help of DEPT spectra we obtain a *N content value which is the most accurate estimate at the present level of assignments.*[9] This value is higher than the one obtained from eq. 2A and smaller than the one obtained from eq. 2B. Indeed, it seems reasonable that by using eq. 2B on the basis of the present assignments, one would underestimate the N content since the contributions from minor peaks are neglected. In Figure 7 (left) the plots of the f_N value calculated with eqs 3-6 *vs* feed ratio are shown. It is worth noting that the M_W values of the P–N copolymers are quite low in comparison to those of E–N copolymers.[2],[3] Most P–N copolymer samples have polydispersity values close to a Schulz-Flory distribution ($M_w/M_n \approx 2$). The MM (g/mol) values, from 11.000 to 45.600, are of the order of magnitude of those reported in the literature.[10] Variations of T_g values of selected P–N copolymer samples *versus* [N]/[P] feed ratio are displayed in Figure 7 (right). Such plots indicate that the values of both f_N and T_g for the P–N copolymers obtained with **1**/MAO and **2**/MAO increase quite sharply and seem to reach a plateau at a rather low [N]/[P]. In general T_g values are rather low; this could be due to the low molar mass of the polymer samples, as well as to a significant amount of propene 1,3-misinsertions.

Our results confirm that, in the presence of the catalysts selected, despite the relatively lower polymerization activity, at low norbornene/olefin ratios it is possible to obtain P–N copolymers which are relatively richer in norbornene than the E–N copolymers prepared in similar conditions. It is conceivable that this could arise from the fact that norbornene competes more easily with propene than with ethene.

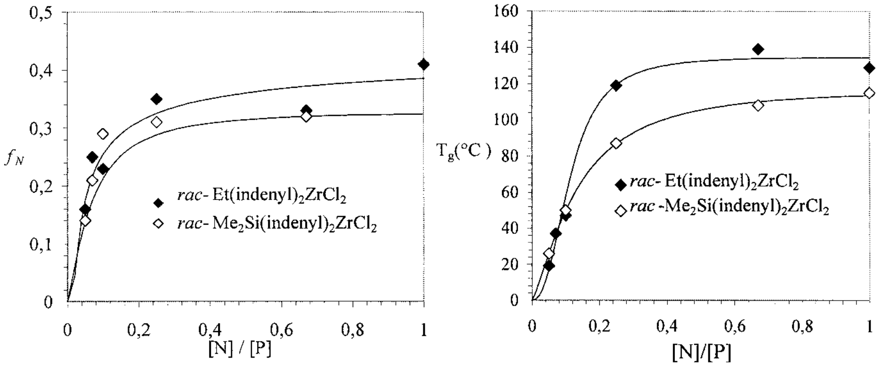

Figure 7. Plots f_N (left) and T_g (right) *vs* [N]/[P] feed ratio.

Microstrucure of propene-norbornene copolymers with a C_s symmetric catalyst

The spectra of P–N copolymers obtained with catalysts **3** (Figure 8) are very complex and show a multitude of signals with low intensities. With the help of DEPT spectra we are able to distinguish between methyl, methine, and methylene signals. The comparison with chemical shifts of syndiotactic polypropene (*s*-PP)[6] shows that the major signals of the spectrum represent long syndiotactic polypropene sequences. These signals are indicated as S_{PP}, T_{PP}, and P_{PP} for methylene, methine and methyl carbons, respectively. Furthermore, comparison with spectra of P–N copolymers obtained with C_2 catalysts, allows one to reasonably distinguish four areas of the spectrum (from 35 to 56 ppm) with similar normalized peak areas corresponding to carbon C2, C3, C1, and C4 of norbornene. In the region of the spectrum at higher field (from 12 to 23 pmm) only methyl (P_p) carbon atoms of polypropene are present. Thus, it is reasonable to conclude that the carbon atoms corresponding to T_p and S_p of polypropene and the C5/C6 and C7 carbon atoms of norbornene appear in the region between 23 to 35 ppm.

At present the complexity of the spectra of these copolymers prevents from drawing safe conclusions on the tacticity of these copolymers and on regioregularity of propene insertion in the vicinity of the norbornene unit. However, this limited assignment of the spectra allows us to evaluate the norbornene content. The f_N has been calculated in three different ways: from methyl carbon signals of propene (eq. 2A), from the intensities of the signals of C2, C3, C1,

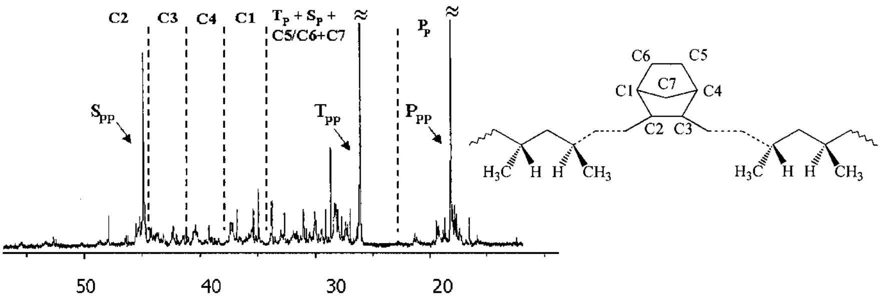

Figure 8. ^{13}C NMR spectrum of P–N copolymers prepared in the presence of **3**/MAO at [N]/[P] feed ratio of 0.10.

and C4 carbon atoms of norbornene (eq. 2B) and from a set of equations similar to that discussed in the previous section (eqs 3-6). The f_N calculated with the three different ways are very similar with a difference on the order of 1-2%. The discrepancy between the values of norbornene content obtained from the areas of the major signals assigned to norbornene carbons and from the propene methyl signals was not found and so we can say that 1,3 misinsertions are very low in P–N copolymerization with catalyst **3**. Instructive is the comparison between norbornene (f_N) and propene (f_{p1}, f_{p2}, and f_{p3}) molar fractions of P–N copolymers obtained with the two C_2 symmetric zirconocenes **1** and **2** and with the C_s symmetric zirconocene **3** reported in Table 3. Under similar polymerization conditions, **3** allows for a lower N incorporation

Table 3. Norbornene f_N and propene f_{p1}, f_{p2} and f_{p3} molar fraction of poly(P-*co*-N) obtained with catalysts **1**, **2**, and **3** as a function of [N]/[P] molar ratio in the feed.

Catalyst	[N]/[P]	f_N	f_{P1}	f_{P2}	f_{P3}
1	0.05	0.16	0.71	0.11	0.02
1	0.07	0.25	0.58	0.16	0.01
1	0.10	0.23	0.57	0.19	0.01
2	0.05	0.14	0.78	0.08	0.00
2	0.10	0.21	0.63	0.13	0.00
3	0.025	0.02	0.98	/	/
3	0.05	0.10	0.90	/	0.00
3	0.10	0.22	0.74	0.04	0.00

Polymerization conditions: 30°C, PP:= 1,01 atm, MAO (4 mmol) catalyst (2 μmol), 100 mL toluene.

than catalysts **1** and **2**. These results are in keeping with results on ethylene/2-butene copolymerization with the same C_2 symmetric metallocene **2** and C_s symmetric metallocene **3**.[11] C_2 symmetric metallocenes scarcely insert 25% of *Z*-butene, and only 2% of *E*-butene, in contrast the C_s symmetric metallocene **3** inserts 14% of *E*-butene, and less than 2% of *Z*-butene. This experimental result was predicted from QM/MM calculations.[11] *Z*-butene is disfavored in the insertion into Mt-isopropyl bond of a C_s symmetric metallocene since both methyls of *Z*-butene are located close to the two six-membered rings of the fluorenyl ligand in the transition state. If we consider *Z*-butene as a simplified model for norbornene our results are easily understood. In addition, Table 3 clearly reveals that, with a similar N molar content of about 22 mol%, catalysts **1** and **2** allow for 19 and 13 mol% of 1-3 misinsertions, respectively (see Figure 3), while catalyst **3** allows for only 4 mol% of 1-3 misinsertions. This is in agreement with the higher regioselectivity in propene polymerization found with syndiospecific catalytic systems based on C_s symmetric metallocenes than with the isospecific C_2 symmetric metallocenes.[6] Finally, the finding that the P–N copolymerization activity of **3** is low even when only 2% of N is inserted into the copolymer chain confirms that the coordinating ability of N present in solution is responsible for slowing down the polymerization activity.

[1] a) W.Kaminsky, A. Bark, A., M. Arndt, *Macromol. Chem. Macromol. Symp,*. **1991**, *47*, 83; b) H. Cherdron, M.-J. Brekner, F. Osan, *Angew. Makromol. Chemie*, **1994**, *223*, 121; c) M. Arndt, W. Kaminsky, *Macromol. Symp.*, **1995**, *97*, 225; d) M. Arndt, R. Engehausen, W. Kaminsky, K. Zoumis, *J. Mol. Catalysis A: Chem,*. **1995**, *101*, 171; e) M. Arndt, I. Beulich, *Macromolecules*, **1999**, *32*, 7335; f) D. Ruchatz, G. Fink, *Macromolecules*, **1998**, *31*, 4674; h) D. Ruchatz, G. Fink, R. A. Wendt, R. Mynott, K. Hauschild, *Macromol. Chem. Phys.*, **1999**, *200*, 1340; i) B. A Harringhton, D. J. Crowther *J. Mol. Catal., A: Chem.*, **1998**, *128*, 79.

[2] a) I. Tritto, L. Boggioni, M. C. Sacchi, P. Locatelli, *J. Mol. Catalysis A: Chem.*, **1998**, *133*, 139; b) A. Provasoli, D.R. Ferro, I. Tritto, L. Boggioni, *Macromolecules*, **1999**, *32*, 6697; c) I. Tritto, C. Marestin, L. Boggioni, L. Zetta, A. Provasoli, D. R. Ferro *Macromolecules*, **2000**, *33*, 8931; d) I. Tritto, C. Marestin, L. Boggioni, H.H Brintzinger, D. R. Ferro *Macromolecules*, **2001**, *34*, 5770; e) I. Tritto, L. Boggioni, J.C. Jansen, K. Thorshaugh, M. C. Sacchi, D. R. Ferro, *Macromolecules*, **2002**, *3*, 616.

[3] a) L. Boggioni, F. Bertini, G. Zannoni, I. Tritto, P. Carbone, M. Ragazzi, D. R. Ferro, *Macromolecules*, **2003**, 36, 882; b) P. Carbone, M. Ragazzi, I. Tritto, L. Boggioni, D. R. Ferro, *Macromolecules*, **2003**, *36*, 891.

[4] Y. Brun, R. Nielson, R. Tacconi, *Proc. Int. GPC Symp.* '98, Phoenix AZ USA, **1998**, 415.

[5] A Carvill, I. Tritto, P. Locatelli, M. C. Sacchi, *Macromolecules* **1997**, *30*, 7056.

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

[7] S.K. Sahoo, T .Zhang, D.V. Reddy, P L. Rinaldi, L.H. McIntosh, R.P. Quirk, *Macromolecules*, **2003**, *36*, 4017.

[8] V.Barone, C. Adamo, *J. Chem. Phys,*. **1998**, *108*, 664.

[9] 2D HMQC or HMBC and modern 3D techniques are powerful tools for assigning ^{13}C NMR spectra. However, 3D techniques in particular require high field instrumentation.

[10] O.Henschke, F. Köller, M. Arnold, *Makromol. Rapid Commun,*. **1997**, *18*, 617

[11] G. Guerra, P. Longo, P. Corradini, L. Cavallo, *J. Am. Chem. Soc.*, **1999**, *121*, 8651.