Macromolecules **2008**, *41*, 5107−5115

Propene−Norbornene Copolymers by C_2-Symmetric Metallocene *rac*-Et(Ind)$_2$ZrCl$_2$: Influence of Reaction Conditions on Reactivity and Copolymer Properties

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Received February 26, 2008; Revised Manuscript Received April 17, 2008

ABSTRACT: The copolymerization of propene and norbornene by catalytic systems composed by C_2 symmetric *rac*-Et(Ind)$_2$ZrCl$_2$ (**1**), methylaluminoxane, and triisobutylaluminum was investigated. Propene−norbornene (P−N) copolymers with about 50 mol % of norbornene are highly alternating at low temperature and pressure. The influence of propene pressure (1−8 bar) and temperature (30−70 °C) on activity, norbornene content, molar masses, and glass transition temperatures of (P−N) copolymers has been assessed. A deeper analysis of the complex ^{13}C NMR spectra of these copolymers has allowed us to evaluate the diad composition, as well as the propene placement in the chain. A great number of 1,3-propene insertions were found, all occurring after an inserted norbornene unit, especially at high temperature and pressure. This indicates that the limiting step in P−N copolymerization is the difficulty to insert a P after N. For the first time, copolymerization parameters were estimated. It was found that P−N copolymers are alternating at temperature as low as 30−40 °C and tend to become random as temperature increases. Chain terminations are likely to occur when the last inserted unit is propene. This along with an increase in k_P would explain the decrease of norbornene content, molar mass, and glass transition temperature, observed at high T and P.

Introduction

Cyclic olefin copolymers are one of the new families of olefinic copolymers made available by metallocene catalysts. Among the copolymers of cyclic olefins such as norbornene the most versatile ones are the ethylene− (E−) norbornene (N) copolymers. In the last 15 years, since their discovery by Kaminsky in 1991,[1] they have been studied in detail by both academic and industrial groups[2–6] for their interesting properties, such as high heat resistance, high glass transition temperatures (T_g) and excellent transparency. They are today commercialized under the trademark of TOPAS by Topas Advanced Polymers (formerly Ticona).[6]

In contrast, only few studies on propene− (P−) norbornene (N) copolymers have been reported in the literature,[7–10] including our papers regarding the synthesis and the first assignments of the main ^{13}C NMR signals of the P−N copolymers prepared with a *rac*-Et(Ind)$_2$ZrCl$_2$-based catalyst at room temperature.[9] Actually, 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 since polypropene (PP) has a higher T_g than polyethylene. 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. Propene concentration and polymerization temperature can influence polypropene tacticity and regioregularity, besides molar mass and polymerization activities.[11] Temperature[12] can also affect the copolymerization parameters: this is very important since norbornene copolymers such as TOPAS[6] are produced by solution polymerizations, which are performed at high temperature in order to exploit all the advantages of this technology. However, in the literature there are no studies on copolymerization parameters and behavior in P−N copolymerization obtained at various temperatures and at different propene pressure.

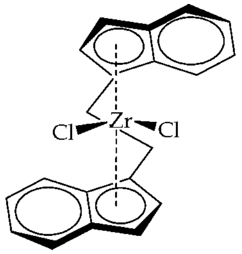

Figure 1. *rac*-Et(Indenyl)$_2$ZrCl$_2$ catalyst.

Thus, the aim of this work is to clarify aspects of the polymerization of P−N copolymers crucial for the development of new materials. Namely, we study the influence of experimental conditions, i.e., pressure, monomer concentration, and temperature on copolymerization activity, comonomer content, norbornene/propene relative reactivity and on their distribution along the macromolecular chain as well as on the propene placement in the copolymer. The prototypical *rac*-Et(Ind)$_2$ZrCl$_2$ (**1**) has been selected as precatalyst for this study before investigating P−N copolymerization with other metallocene catalysts or postmetallocene catalysts. One good reason for selecting catalyst **1,** reported in Figure 1, is that this *ansa*-metallocene catalyst of C_2 symmetry has proven effective for producing prevailingly isotactic and regioregular polypropene[11–13] as well as E−N copolymers with a tendency to alternate monomer units ($r_1r_2 = 0.072$).[14]

Here we present the synthesis of several series of P−N copolymers in a wide range of chemical compositions prepared with methylaluminoxane (MAO) and triisobutylaluminum (TIBA) as cocatalysts under different experimental conditions. Copolymers were examined as carefully as possible through ^{13}C NMR analysis and by GPC and DSC. Relative reactivity and intramolecular distribution of the comonomers were expressed by reactivity ratios r_1 and r_2 and by their product r_1r_2, respectively.

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10.1021/ma8004235 CCC: $40.75

Table 1. Polymerization Conditions and Copolymers Obtained with Propylene−Norbornene Copolymerizations with Catalyst *rac*-Et(Indenyl)$_2$ZrCl$_2$:[a] Mole Percent of Norbornene in the Copolymer, Productivity, Glass Transition Temperature, and Molecular Weight

entry	P, T	[N]/[P]	% N feed	f_N[b]	activity[c]	yield/time (1 g/0.5 h)	T_g (°C)	M_n (g/mol)	M_w/M_n	$\bar{P}_n$[f]
1	8 bar, 70 °C	0.00	0	0.00	3993	22.4		8849	1.6	211
2		0.06	5.3	0.09	2293	12.8	−0.4	3727	2.0	80
3		0.11	9.8	0.13	2455	13.7	n.d.	3827	3.1	78
4		0.15	10.3	0.22	310	1.7	41.9			
5		0.23	18.5	0.32	291	1.6	63.7	5885	1.5	100
6		0.36	26.2	0.32	249	1.4	79.2	7224		123
7	8 bar, 50 °C	0.17	14	0.34	195	1.1	77.1	10383	1.6	174
8		0.24	18.3	0.39	145	0.8	81.7	10920	1.7	175
9		0.26	20.7	0.40	63	0.4	82	12235	1.7	195
10	5 bar, 40 °C	0.00	0	0.00	6137	34.4				
11		0.06	5	n.d.	399	2.2	38.8	3918[e]	1.6	93
12		0.11	10	0.36	165	0.9	80	11100	1.9	183
13		0.22	18	0.42	48	0.3	104	15056	1.9	236
14		0.42	30	0.47	22	0.1	113	13737	1.9	210
15		0.53	35	0.53	9	0.1	121	13536	1.7	205
16	2 bar, 30 °C	0.00	0	0.00	1259	7.1				
17		0.05	4.9		218	1.2	−1.1	7948	1.6	189
18		0.06	5.2	0.18	170	1.0		6600	2.5	128
19		0.11	9.8		119	0.7	62.4	13818	1.4	329
20		0.19	16	0.37	72	0.4	87.2	12390	2.2	202
21		0.28	22	0.42	66	0.4	91.7	38397	1.7	601
22		0.37	27	0.45	41	0.2	105.6	17427	2.0	266
22		0.46	32	0.46	27	0.2	108.1	15838	2.1	240
23	1 bar, 30 °C[d]	0.05	4.8	0.16	164	0.2	19	5504	2.7	109
24		0.07	6	0.25	107	0.1	37	9188	1.2	167
25		0.10	9	0.23	70	0.1	47			
26		0.26	20.8	0.35	56	0.1	119	7681	2.2	127

[a] Polymerization conditions: total volume in toluene = 350 mL, cocatalyst = dried MAO + TIBA, $[Al_{tot}]/[Zr] = 2000$, $[Zr] = 10^{-4}$ mol/L. [b] Fraction of norbornene incorporated in the copolymer calculated from ^{13}C NMR spectra. [c] Activity = (kg of P/mol of Zr × h) calculated assuming constant reaction rate over a period of 3 h. [d] Runs performed at 30 °C in batch, with 2 μmol of catalyst and 4 mmol of dried MAO, in a total toluene volume of 100 mL. [e] Molar mass of the soluble fraction of the sample: a part of the samples is insoluble in *o*-dichlorobenzene also at high temperature. [f] $\bar{P}_n = M_n/(f_n \times PM_n + f_p \times PM_p)$.

The microstructural, molecular, and thermal characterization of the copolymers is presented.

Results and Discussion

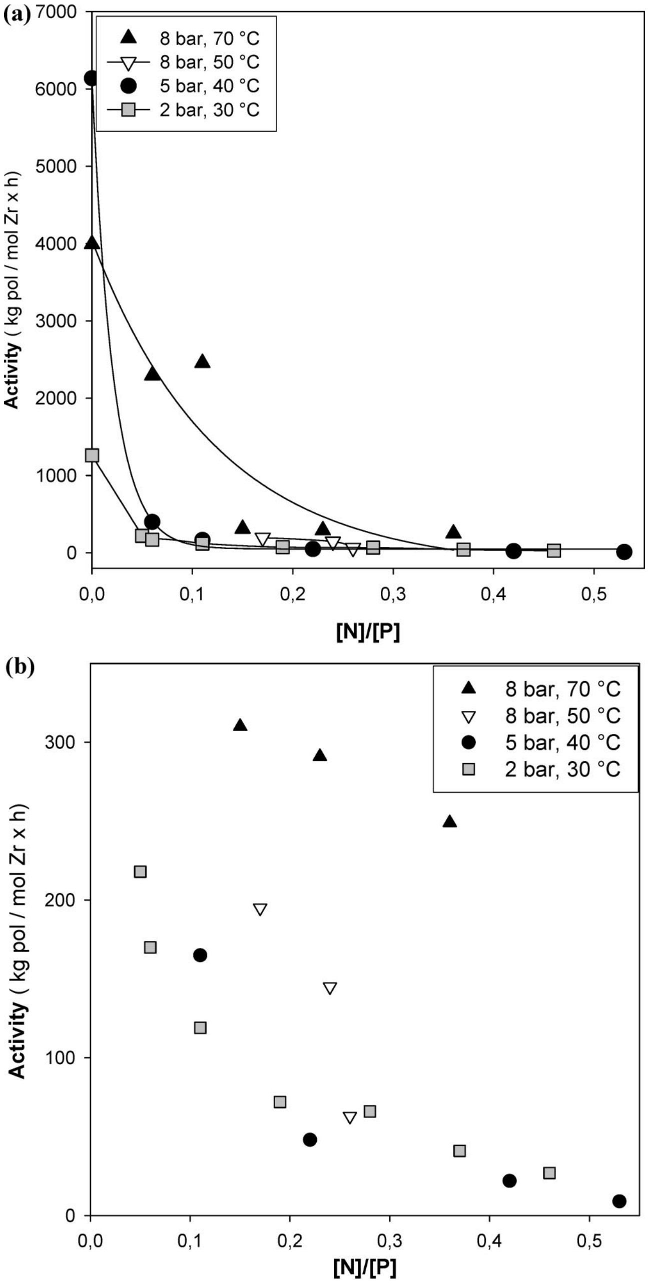
Synthesis and ^{13}C NMR Characterization. As catalyst productivity, norbornene incorporation, and molar masses would be expected to be temperature and pressure dependent, we have carried out copolymerizations in order to have an overview as large as possible of the system behavior. Series of copolymerizations of propene and norbornene were performed with catalyst **1**/MAO + TIBA (MAO = 20 mmol, TIBA = 6 mmol) in toluene over a wide range of comonomer feed ratios, with an [Al]/[Zr] molar ratio of 2000, varying temperature from 30 to 70 °C and propene pressure from 2 to 8 bar in a Büchi 1L autoclave. Use of dried MAO and TIBA together as cocatalysts was expected to have a positive effect on the catalytic activity and to increase chain lengths. Activating effects of TIBA were previously observed in E−N copolymerization by Nì Bhriain et al.[15] and in propene homopolymerization with various *ansa*-zirconocene/MAO catalytic systems.[16] These effects were ascribed to the tendency of MAO and possibly also of other [Al]−Me species present in MAO to react with triisobutylaluminum forming mixed Me$_x$*i*Bu$_{(3-x)}$Al−MAO derived species. The alkyl ligands of these species are probably too bulky to react with catalytically active alkyl zirconocene cations to form heterobinuclear adducts, which are considered resting species. The scavenging of the trimethylaluminum present in MAO and hence the control of catalyst inhibition and/or polymer transfer have been considered the origin, at least in part, of increases in activities and molar masses, observed by additions of TIBA.

Copolymerization data (pressure, temperature, norbornene content in feed, reaction time) are reported in Table 1 along with previous data obtained in batch (1 bar at 30 °C). In the runs performed in batch the cocatalyst was dried MAO, without addition of TIBA. Polymerization tests have been designed to ensure low comonomer conversion and also to yield enough copolymer to be studied by NMR, GPC, and DSC analysis. In general the catalytic activities are quite low compared to those obtained in similar conditions for E−N copolymerizations.[1,5] The catalytic activities obtained under the different polymerization conditions explored are represented in parts a and b of Chart 1 as a function of the [N]/[P] ratio in feed. From the chart, it is clear that the catalytic activities decrease rapidly with the norbornene content in feed, such a decrease being more rapid than in E−N copolymerization. Indeed, while it is possible to obtain copolymers up to a [N]/[E] feed ratio of 24, here the highest [N]/[P] feed ratio is 0.53. Polymerization conditions greatly influence the catalyst activities: an increase of propene pressure and polymerization temperature within the ranges explored leads in fact to a higher activity. In particular, at the same pressure (8 bar) the best results are obtained at the highest temperature (70 °C, points indicated by black triangles).

The structure and carbon numbering of an isotactic P−N copolymer chain are sketched in Figure 2. On the basis of previous studies, 2,3-norbornene insertion is considered to occur into the metal−carbon bond, the exo face being more reactive than the endo face.[17] The two propene consecutive monomer units have the methyls in erythro relationships as in an isotactic polypropene chain.

The ^{13}C NMR spectra of three copolymers obtained in different experimental conditions, with similar [N]/[P] feed ratios, are displayed in Figure 3 along with the main peak assignments, described in detail in ref 8. In summary, the signals of methylenes C6 and C5 appear at 30.10 and 27.34 ppm, respectively; the signal observed at 31.91 ppm arises from the C7 carbon and the signals at 37.17 and 41.32 ppm have been

Chart 1. (a) Plot of activity values obtained under different experimental conditions with *rac*-Et-(Indenyl)$_2$ZrCl$_2$ versus [N]/[P] in feed. (b) Expansion of (a).



assigned to methynes C1 and C4, respectively. The tertiary carbons at 45.40 and 53.32 ppm have been ascribed to C3 and C2, respectively, while the methyl P_β peak appears at 21.24 ppm. The three spectra show the typical signal pattern for a P–N copolymer obtained with the C_2 symmetric catalyst. From spectrum a, of a sample obtained at 8 bar and 70 °C, to spectrum c, referring to a sample obtained at 2 bar and 30 °C, the spectra appearance indeed changes, showing an increase of the intensities of N signals and of the norbornene content. The methyl region of the PP blocks is complex and could be instructive after further studies. It is evident that the widths of signals become wider and minor peaks appear in the region of 2,1-inversion.

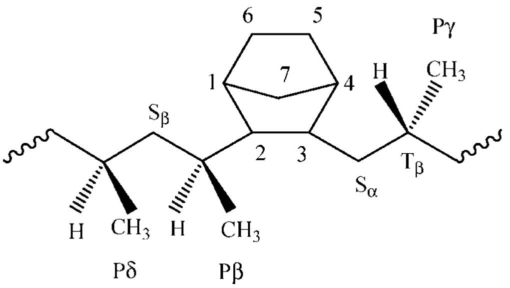


Figure 2. Structure and carbon numbering of an isotactic poly(P-*co*-N). P, S, and T denote primary, secondary, and tertiary propene carbons, respectively. Greek letters denote the distance of a given carbon from the closest tertiary norbornene carbon.

The molar fraction of norbornene incorporated in the prepared copolymers, f_N, was obtained from ^{13}C NMR spectra analysis by means of the following set of equations, as previously reported by us.[8] We take into account all the possible modes of insertion of propene and utilize all the assigned propene and norbornene signals.

$$f(P) = f(P_1) + f(P_{13}) + f(P_3)$$

$$f(N) + f(P) = 1$$

$$\frac{I_{CH_3}}{I_{tot}} = \frac{f(P_1) + f(P_3)}{7f(N) + 3f(P)} \tag{1}$$

$$\frac{I_{CH_2}}{I_{tot}} = \frac{3f(N) + f(P_1) + 3f(P_{13}) + 2f(P_3)}{7f(N) + 3f(P)} \tag{2}$$

$$\frac{I_{CH}}{I_{tot}} = \frac{4f(N) + f(P_1)}{7f(N) + 3f(P)} \tag{3}$$

where I_{CH_3}, I_{CH_2}, and I_{CH} are the peak areas of methyl, methylene, and methyne carbon signals, respectively, and I_{tot} is the total sum of the peak areas; $f(P_1)$ is the molar fraction of 1,2- and 2,1-propene insertions, $f(P_{13})$ is the molar fraction of 1,3-propene insertions, and $f(P_3)$ is the molar fraction of chain terminals.

Results of $f(P_{12})$ and $f(P_{13})$ propene insertions are reported in Table 2. The frequency of 1,3 propene insertions is much higher than in propene homopolymerization with the same catalyst under similar experimental conditions.[13] They are especially high at 8 bar propene pressure and 70 °C, where on average the ratio $f(P_{12})/f(P_{13})$ is about 3. This means that for four propene units, three are 1,2-inserted and one is inserted 1,3. We may anticipate that this is due to the difficulty to insert a propene unit into a Mt–N bond. The molar fractions of 2,1-insertion are often about 100 times less than the 1,2-insertions (Table 2).

The N molar fractions incorporated in the P–N copolymers under the different experimental conditions tested are reported in Chart 2. The effect of temperature on the norbornene incorporated in the copolymers is opposite to that on activity. In fact as the reaction temperature increases, norbornene incorporation drops off, as is often observed in ethylene-norbornene copolymerization. By increasing the propene pressure at similar [N]/[P] molar ratio the highest norbornene incorporation is obtained at 5 bar and 40 °C, with the f_N value of 0.53. Under all polymerization conditions f_N values seem to tend to a plateau for a [N]/[P] value of about 0.5, as visible in the graph.

Structural Analysis at the Diad Level. We have made an analysis of the ^{13}C NMR spectra of P–N copolymers as detailed as possible based on an appropriate partitioning of the molecular chain into fragments, defined according to the assignment level. Scheme 1 illustrates the various types of chain fragments, with all the possible diads defined in the calculation.

In this denomination we consider that during the propagation, the transition metal is bound to the left monomer. For example, according to this nomenclature the NP_{12} diad derives from the 1,2-insertion of propene into a Mt–N bond, while $P_{12}N$ derives from

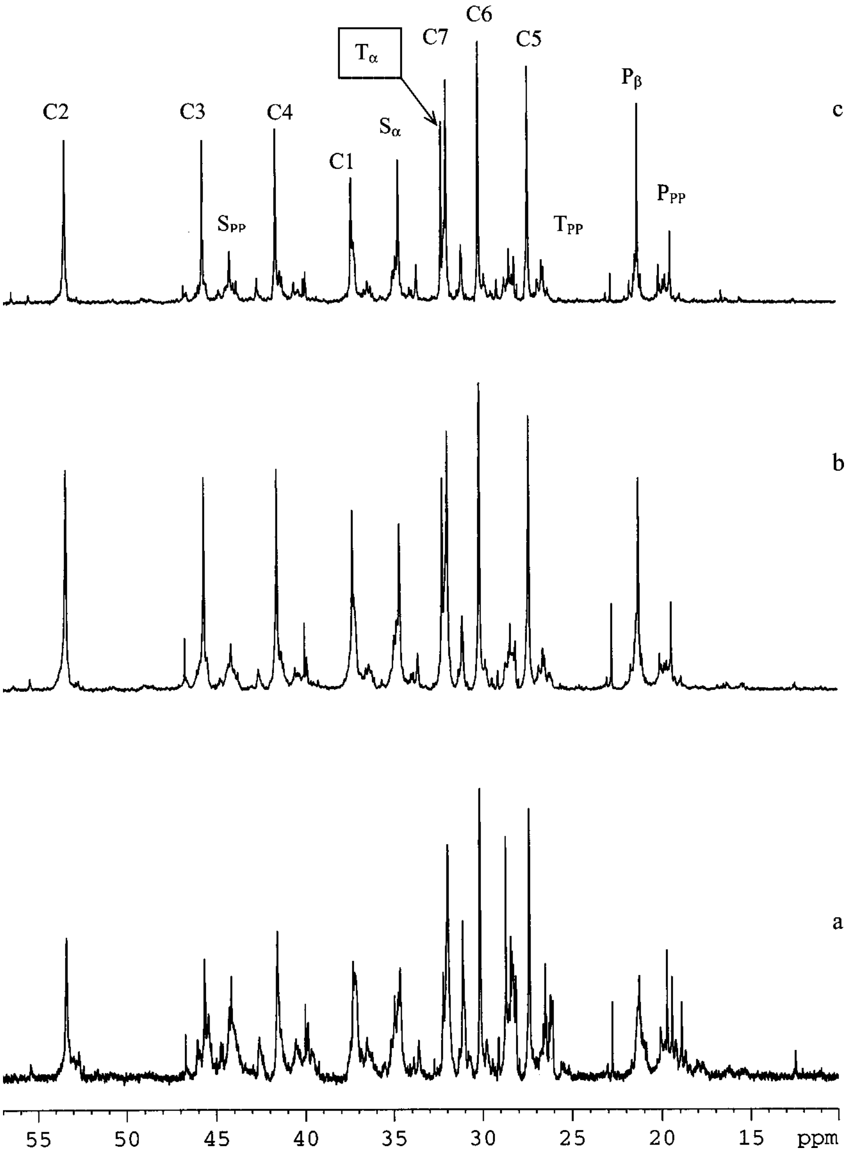


Figure 3. ^{13}C NMR spectra of PN copolymers obtained under different conditions, with similar [N]/[P] in feed. Key: (a) T = 70 °C, P = 8 bar, [N]/[P] = 0.23, f_N = 0.22; (b) T = 50 °C, P = 8 bar, [N]/[P] = 0.24, f_N = 0.39; (c) T = 30 °C, P = 2 bar, [N]/[P] = 0.19, f_N = 0.37.

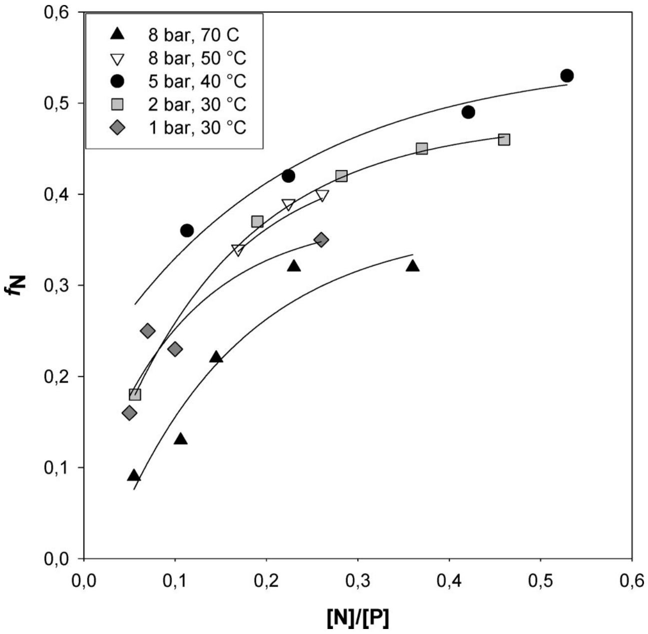
Table 2. Molar Fractions of P and of Possible Insertion Modes of Propene in the P−N Copolymers of Table 1

P, T	[N]/[P]	f_N	f_P	$f(P_{12})$	$f(P_{13})$	$f(P_{12})$/ $f(P_{13})$	$f(P_{21})$
8 bar, 70 °C	0.15	0.22	0.78	0.605	0.175	3.46	0.005
	0.23	0.32	0.68	0.514	0.166	3.09	0.006
	0.36	0.32	0.68	0.458	0.222	2.06	0.012
				av. ***0.526***	***0.187***	***2.87***	***0.008***
8 bar, 50 °C	0.17	0.34	0.66	0.520	0.140	3.71	n.d.
	0.24	0.39	0.61	0.542	0.068	7.97	0.008
	0.26	0.40	0.60	0.529	0.071	7.45	0.011
				av. ***0.530***	***0.093***	***6.37***	***0.010***
5 bar, 40 °C	0.11	0.36	0.64	0.543	0.097	5.60	0.017
	0.22	0.42	0.58	0.503	0.077	6.53	0.007
	0.42	0.47	0.53	0.480	0.050	9.60	n.d.
	0.53	0.53	0.47	0.430	0.040	10.75	n.d.
				av. ***0.489***	***0.066***	***8.12***	***0.012***
2 bar, 30 °C	0.19	0.37	0.63	0.555	0.075	7.34	0.006
	0.28	0.42	0.58	0.493	0.087	5.67	0.007
	0.37	0.45	0.55	0.495	0.055	9.00	0.005
	0.46	0.46	0.54	0.414	0.126	3.29	n.d.
				av. ***0.489***	***0.086***	***6.33***	***0.006***

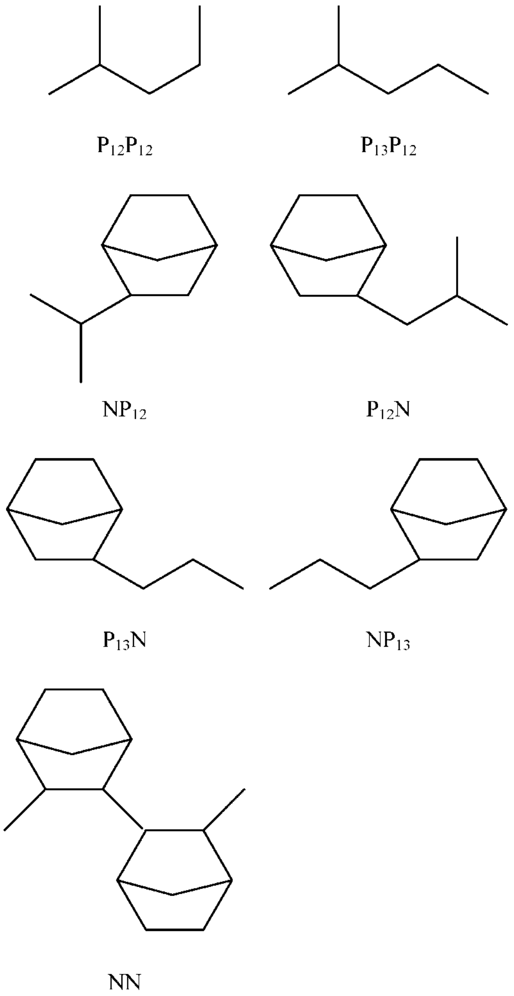
the insertion of N into a Mt−P_{12}, that is a metal bound to a 1,2-inserted propene unit. This distinction would allow us to quantify the modes of insertion of P before or after N. Our purpose is to determine the molar fractions of alternating sequences (NP_{12}, NP_{13}, $P_{12}N$, and $P_{13}N$), as well as blocks of NN and PP diads (distinguishing also between 1,2 and 1,3 insertions). We assume that the $P_{13}P_{13}$ and $P_{12}P_{13}$ diads are absent. Thus, of all the nine possible diads, we have to determine only the seven ones present. For this purpose, it is necessary to extract all the information contained in the spectra, even though not all the signals are interpreted owing to the great complexity of spectra.

We use the peak area of T_α to quantify the NP_{12} diad. In principle the peak area of S_α gives us the $P_{12}N$ diad: unfortunately, it is difficult to accurately evaluate the area of this signal due to the vicinity with other (CH) signals. The peak area of $S_{\alpha\alpha}$ signals between 43.31 and 44.44 ppm corresponds to the $P_{12}P_{12}$ diad. Finally, the area of the methyl P_β peak, which appears at 21.24 ppm, should also correspond to the NP_{12} diad. To accurately determine the above molar fractions, distortionless enhancement by polarization transfer (DEPT) ^{13}C spectra of some representative P−N copolymers have been registered and are displayed in the Supporting Information. DEPT experiments, where the intensities of signals depend on the θ pulse of the sequence applied, allow one to distinguish signals of methyl and methyne carbons from those of methylene carbons. In particular, DEPT experiments of copolymers prepared under

Chart 2. Plot of norbornene content in the copolymers obtained under different experimental conditions with *rac*-Et(Indenyl)$_2$ZrCl$_2$ versus [N]/[P] in feed



Scheme 1. All the Possible Diads Defined in the Calculation



different experimental conditions allow us to correctly quantify the peak areas of T$_\alpha$ and C7, a tertiary and a secondary carbon with quite close chemical shifts at around 32.21 and 31.91 ppm, respectively. The DEPT spectra allow us also to correctly evaluate the areas of all the tertiary C1, C4, C2, and C3 signals and of S$_{\alpha\alpha}$, which corresponds to diad P$_{12}$P$_{12}$, in the region between 37 and 55 ppm. In practice, we have only four experimental data, namely the molar fractions of T$_\alpha$ and S$_{\alpha\alpha}$ in addition to the relative areas of all the methyls, methylenes, and methynes. On the other hand accounting for the stoichiometric relationships the seven diads reduce to four independent variables, which can be determined by solving a system of four equations.

For clarity, we introduce the four variables $a = f(P_{12}P_{12})$, $b = f(P_{13}P_{12})$, $f(NP_{12}) = c$, and $f(NN) = d$, which can be considered as independent variables. Indeed, a and c can be obtained directly from the analysis of spectra since we can determine accurately $f(NP_{12})$ by the peak area of T$_\alpha$. and $f(P_{12}P_{12})$ by the peak area of S$_{\alpha\alpha}$. Variables b and d are derived from eqs 1−3, considering that $f(P_3)$ is irrelevant and that $f(P_{12})$, $f(P_{13})$, and $f(N)$ can be expressed in terms of diads as follows:

$$f(P_{12}) = f(P_{12}P_{12}) + f(P_{13}P_{12}) + f(NP_{12}) = f(P_{12}P_{12}) + f(P_{12}N) \qquad (4)$$

$$f(P_{13}) = f(NP_{13}) = f(P_{13}P_{12}) + f(P_{13}N) \qquad (5)$$

$$f(N) = f(NN) + f(NP_{12}) + f(NP_{13}) = f(NN) + f(P_{12}N) + f(P_{13}N) \qquad (6)$$

Equation 4 is obtained by considering that all P$_{12}$ units arise from the 1,2-propene insertion into Mt−P$_{12}$, Mt−P$_{13}$, and Mt−N bonds and that once P$_{12}$ has been inserted, we can have P$_{12}$ or N insertion into the Mt−P$_{12}$ bond. Similarly we can derive eqs 5 and 6.

Then by substituting $f(P_{12})$ in eqs 1 and 3, we obtain:

$$\frac{I_{CH_3}}{I_{tot}} = f(CH_3) = \frac{f(P_{12})}{4f(N)+3} = \frac{f(P_{12}P_{12}) + f(P_{13}P_{12}) + f(NP_{12})}{4f(N)+3} \qquad (7)$$

$$f(CH) = \frac{f(P_{12}) + 4f(N)}{4f(N)+3} \qquad (8)$$

$$\Delta = f(CH_3) - f(CH) = \frac{f(P_{12})}{4f(N)+3} - \frac{f(P_{12}) + 4f(N)}{4f(N)+3} = \frac{4f(N)}{4f(N)+3} \qquad (9)$$

$$4f(N) = \frac{3\Delta}{(1-\Delta)} \qquad (10)$$

It is possible to calculate $f(P_{13}P_{12}) = b$ by substitution of (10) in (7).

$$f(P_{13}P_{12}) = \frac{3f(CH_3)}{(1-\Delta)} - a - c$$

Hence $d = f(NN) = 2f(N) - 1 + a + b$.

The remaining $f(P_{12}N)$, $f(NP_{13})$, and $f(P_{13}N)$ are dependent variables that can be derived by using eqs 4, 5, and 6.

Then

$$f(P_{12}N) = b + c$$

$$f(NP_{13}) = \frac{1}{2}(1 - a - b - 2c - d)$$

$$f(P_{13}N) = \frac{1}{2}(1 - a - 3b - 2c - d)$$

The molar fractions of P$_{12}$P$_{12}$, P$_{13}$P$_{12}$, NP$_{12}$, P$_{12}$N, NP$_{13}$, P$_{13}$N, and NN diads, resulting from our ^{13}C NMR spectra analysis of P−N copolymers prepared under different polymerization conditions and at a similar [N]/[P] feed ratio, are reported in Table 3. The estimated standard error associated with each diad represents the pure error in the peak area reading.

Table 3. Diad Molar Fractions for Some P–N Copolymers

entry	conditions	[N]/[P]	$f(P_{12}P_{12})$	$f(P_{13}P_{12})$	$f(NP_{12})$	$f(NP_{13})$	$f(P_{12}N)$	$f(P_{13}N)$	$f(NN)$
5	8 bar, 70 °C	0.23	0.25 (±*0.01*)	0.16 (±*0.01*)	0.11 (±*0.003*)	0.16 (±*0.01*)	0.27 (±*0.01*)	0.01 (±*0.01*)	0.04 (±*0.01*)
8	8 bar, 50 °C	0.24	0.20 (±*0.00*)	0.06 (±*0.01*)	0.29 (±*0.01*)	0.06 (±*0.004*)	0.34 (±*0.01*)	0.01 (±*0.002*)	0.04 (±*0.004*)
13	5 bar, 40 °C	0.22	0.18 (±*0.002*)	0.02 (±*0.01*)	0.31 (±*0.01*)	0.07 (±*0.01*)	0.33 (±*0.002*)	0.05 (±*0.01*)	0.04 (±*0.01*)
20	2 bar, 30 °C	0.19	0.21 (±*0.02*)	0.06 (±*0.02*)	0.29 (±*0.01*)	0.07 (±*0.01*)	0.35 (±*0.002*)	0.01 (±*0.01*)	0.01 (±*0.003*)

Table 4. r_1 and r_2 Reactivity Ratios Obtained by Using Diads Calculated in Table 3 and According to Equations 11 and 12

copolymers	entry	condition	[N]/[P]	[N]/[E]	r_1	r_2	$r_1 \times r_2$
P–N	5	8 bar, 70 °C	0.23		0.21 ± 0.04	0.63 ± 0.08	0.14 ± 0.05
	8	8 bar, 50 °C	0.24		0.14 ± 0.01	0.48 ± 0.002	0.07 ± 0.01
	13	5 bar, 40 °C	0.22		0.11 ± 0.02	0.49 ± 0.05	0.05 ± 0.02
	20	2 bar, 30 °C	0.19		0.10 ± 0.02	0.15 ± 0.03	0.02 ± 0.01
E–N		1 bar, 30 °C		2.33[5]	2.6	0.027	0.072
		1 bar, 30 °C		4.00[5]	2.3	0.031	0.072

It is worth noting the great amount of 1,3-inserted units $f(NP_{13})$, which arise when a propene is inserted into a Mt–N bond. This value is particularly high in entry 5 obtained at the highest pressure and temperature, where interestingly $f(NP_{13})$ is even higher than $f(NP_{12})$, which means that the 1,2-propene insertion after N is so difficult that the 1,3-insertion is preferred. In addition, $f(NP_{13})$ is similar to $f(P_{13}P_{12})$. It is also worth noting that $f(P_{12}N)$ is always higher than $f(P_{12}P_{12})$, $f(P_{12}N)$ decreasing and $f(P_{12}P_{12})$ increasing with temperature. This is an indication that norbornene reactivity is higher than that of propene, probably due to the release of cyclic strain after norbornene insertion.

Determination of Reactivity Ratios of Comonomers. The effect of temperature and pressure on norbornene content is reflected by the copolymerization parameters. It is known that when the insertion of a comonomer is influenced by the last inserted unit (ultimate effect) or by the penultimate unit, a first order[18] or a second Markovian statistical model is adopted to determine the reactivity ratios.[19] In the literature, the first order Markovian model has often been used to describe E–P copolymerizations promoted by many different single center catalysts.[12] Nevertheless, some authors reported that metallocene catalysts of the $XInd_2MR_2$ type (X = ethylene, Me_2Si, Me_2C) with either aromatic or hydrogenated C-6 ring fused on the Cp group, promote E–P copolymerizations that can be better described by the second order model.[11,21–24] On the other side in our studies on E–N copolymerizations we have found that when hindered monomers such as norbornene are involved, second order models are needed to describe the copolymerization. However, second Markovian statistical models need detailed information on the copolymer microstructure at least at triad level. The present elucidation of the complex spectra of P–N copolymers does not allow one to evaluate their triad compositions.

From the first Markovian model, the r_1 ($= k_{11}/k_{12}$) and r_2 ($= k_{22}/k_{21}$) reactivity ratios are derived, where k_{ij} is the rate constant of the reaction for the addition of the monomer j to a growing chain bearing the comonomer i as the last inserted one. Here, 1 and 2 indicate propene and norbornene, respectively.

We have used the calculated diads of Table 3 to evaluate the reactivity ratios[18] according to the following equations:

$$r_1 = \frac{2 \times [P_{12}P_{12}]}{([NP_{12}] + [NP_{13}] + [P_{12}N] + [P_{13}N]) \times \frac{P}{N}} \qquad (11)$$

$$r_2 = \frac{2 \times [NN] \times \frac{P}{N}}{[NP_{12}] + [NP_{13}] + [P_{12}N] + [P_{13}N]} \qquad (12)$$

In Table 5, r_1 and r_2 values, obtained for P–N copolymers prepared under different polymerization conditions and at a similar [N]/[P] feed ratio, are collected together with their estimated standard errors. They are compared with those reported in the literature for E–N copolymerizations performed at 30 °C.

We have also calculated the propene/norbornene reactivity ratios by using data of the series of copolymerizations according to the Fineman–Ross and Kelen–Tudos equations for which a terminal copolymerization model has to be valid. The plots are reported in the Supporting Information, and the results of the reactivity ratio calculations from Kelen–Tudos equations are listed in Table 4.

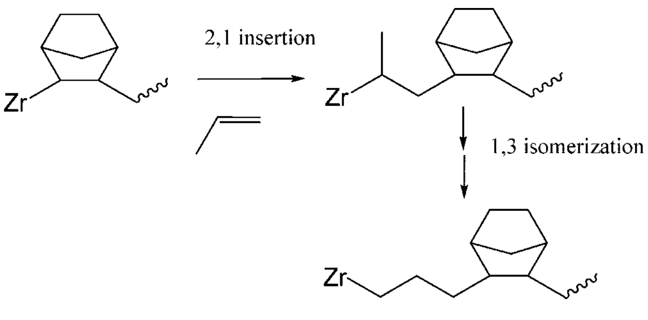
Even though, due to the complexity of the spectra, the errors in these calculations are quite high, the trend in r_1 and r_2 values calculated from the diads are comparable to those obtained by Kelen–Tudos equations. It is worth noting that r_2 is not much lower than r_1, as it was in the case of E–N copolymerizations, thus indicating that norbornene insertions are not less favored than propene insertions (Table 5). This is in agreement with the $f(P_{12}N)$ values higher than $f(P_{12}P_{12})$. In fact, r_1 in P–N copolymerizations is lower than 1, while in E–N copolymerizations is higher than 1. The fact that catalyst productivity decreases with increasing N concentration in the feed, while the f_N content in the copolymer is much higher than the molar fraction of N in the feed before reaching the plateau, indicates that the insertion of N after P is higher than that of P after P, in agreement with the tendency to alternate. The r_2 value, much higher in P–N than in E–N copolymerizations, seems to be due to the difficulty to insert P after N rather than to the facility to insert N after N. Indeed, we obtain copolymers with a maximum of N content of about 53 mol %. In addition, by raising the temperature and the pressure, the copolymers become less alternating. In fact, k_{22}/k_{21} and k_{11}/k_{12} are both low at temperature as low as 30 °C, while in the series performed at 8 bar at 70 °C the k_{22}/k_{21} value is higher than k_{11}/k_{12}, although polymerization activities are higher. In other words the k_{21}/k_{22} values are higher than 1 and tend to decrease by raising the temperature. This is an indication that at higher temperature the difference between the rate of insertion of propene after a norbornene and that of a norbornene after a norbornene becomes greater and thus copolymers at low temperature are more alternating than at high temperature. This is also pointed out by the r_2 r_1 products closer to 0 at lower temperatures. They are all below 1, but become higher at higher temperature, indicating that copolymers become more random and less alternating at higher temperatures.

The tendency of r_2 r_1 products to increase with temperature has been recently demonstrated in the case of E–P copolymerizations with various metallocene catalysts.[12] Especially with the sterically hindered stereorigid isospecific metallocene catalyst *rac*-H_2C-(3-$^tBuInd)_2ZrCl_2$, the high copolymerization temperature was shown to bring about a remarkable increase of reactivity ratios, such as r_p and r_{pp}, that indicate the formation of propene sequences. In P–N copolymers the more sterically

Table 5. r_1 and r_2 Reactivity Ratios Obtained by Kelen and Tudos Plots

conditions	r_1	r_2	$r_1 \times r_2$
8 bar, 70 °C	0.56 ± 0.12	0.88 ± 0.06	0.49 ± 0.13
8 bar, 50 °C	0.25 ± 0.05	0.68 ± 0.03	0.17 ± 0.03
5 bar, 40 °C	0.13 ± 0.01	0.42 ± 0.01	0.05 ± 0.01
2 bar, 30 °C	0.14 ± 0.03	0.16 ± 0.01	0.02 ± 0.02

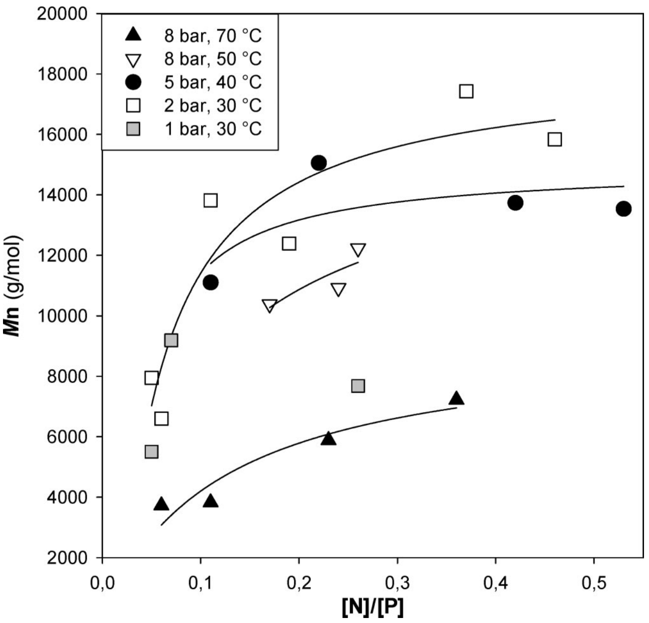
Scheme 2. 2,1-Propene Insertion in the Zr−Norbornene Bond Followed by 1,3-Propene Isomerization



hindered of the two comonomers is norbornene; thus, by analogy, we would expect an increase in NN dyads. A closer inspection of Table 3 reveals this is not the case. It is worth noting that the same catalytic systems allow for the formation of NN diads in E−N copolymerizations and for the synthesis of copolymers with N content up to 65−70 mol %.[5] Thus, these findings could be interpreted by considering that both k_P and k_N increase with temperature, likely k_N increases less than k_P. In particular, the rate of insertion of P after P increases since we observe higher activities, lower N incorporation and an increase of $P_{12}P_{12}$ and $P_{13}P_{12}$ diads at higher temperature. However, the rate of insertion of a propene after a norbornene increases less than that of a norbornene after a norbornene, indeed $f(NP_{12})$ decreases with temperature in contrast to the $f(NP_{13})$ increase. All these data confirm that the limiting step in P−N copolymerization is the difficulty to insert a propene into the Zr−N bond in the 1,2-orientation. Thus, often propene inserts in the 2,1-orientation and immediately isomerizes to the 1,3-placement as shown in Scheme 2.

Molecular and Thermal Characterization of Copolymers. Copolymerization temperature and pressure have a strong influence also on the copolymer molar masses (Table 1). As to the norbornene incorporation, also the molar masses decrease with an enhancement of temperature and pressure, as visible from Chart 3, where M_n values are plotted against the molar ratio between norbornene and propene in feed. Under the different conditions explored, M_n values increase with the norbornene content in feed and in the copolymer. In general, the obtained M_n values are lower than in E−N copolymers. This may be related to the facility to obtain β-hydrogen elimination when the last inserted monomer unit is propene. Concerning the molar masses distribution, almost all the values are below 2, as we could expect for a single site catalyst. Temperature has a greater effect with respect to pressure on molar masses. In fact, from Chart 3, we can see that samples obtained at the same pressure but at different temperatures (8 bar, 70 °C, triangles in black, and 8 bar, 50 °C, triangles in white) have quite different M_n values, the highest values (∼10 000 g/mol) being those referred to samples obtained at the lower temperature (∼5000 g/mol). The M_n variation between samples obtained at very different pressure (5 bar, 40 °C, black balls, and 2 bar, 30 °C, white squares) is instead not too high, and it could be due to the slightly different polymerization temperatures, rather than to the different pressures. The increase of molar masses with the norbornene incorporation seems to be related to the fact that by increasing the [N]/[P] molar ratio in the feed the active sites are more likely to be in a Mt−N state where chain terminations are difficult for steric reasons. The molar masses dependence on the temperature is similar to that of propene polymerization, where chain transfer reactions become more probable at higher temperatures, suggesting that chain transfers occur at propene chain ended, that is, at a Mt−P state. Thus, we can conclude that chain terminations are likely to occur after propene insertion.

Chart 3. Plot of M_n values obtained under different experimental conditions with *rac*-Et(Indenyl)$_2$ZrCl$_2$ versus [N]/[P] in feed



The interest in cycloolefin copolymers derives from the possibility to modulate the glass transition temperature (T_g), which can reach high values. Thus, T_g of P−N copolymers is an important characteristic of these materials and is expected to reach values higher than in E−N copolymers. The glass transition temperature of the P−N copolymers was determined by DSC. T_g values of the copolymer samples obtained under different conditions are plotted against the [N]/[P] molar ratio in the feed and f_N in Charts 4 and 5, respectively. The latter graph shows that for these series of copolymers the dependence of T_g on f_N is rather well represented by a linear relationship considering the data from the different series. Therefore the N content is the dominant factor determining T_g, even though we cannot exclude that the deviation from linearity may be related to differences in molar masses or to the molar fractions of 1,3 insertion.

Indeed, in Chart 4, T_g values tend to a plateau at the [N]/[P] value of 0.5 for all polymerization conditions, as the norbornene incorporation. For samples obtained at the same pressure (8 bar), the T_g values decrease with the rise in polymerization temperature (triangles black, 8 bar, 70 °C, and white, 8 bar, 50 °C), this being due to the lower norbornene incorporation in these samples. Thus, the highest T_g value is of 121 °C, obtained at 5 bar and 40 °C, because the copolymers of this series have higher f_N as shown in Chart 5.

Conclusions

Experimental conditions applied have a great influence on the catalytic behavior and on P−N copolymer properties. Temperature and propene pressure have a positive effect on the polymerization activity (highest activity at 8 bar, 70 °C), while they often have a negative effect on molar masses, norbornene

Chart 4. Plot of T_g values obtained under different experimental conditions with *rac*-Et(Indenyl)$_2$ZrCl$_2$ versus [N]/[P] in feed

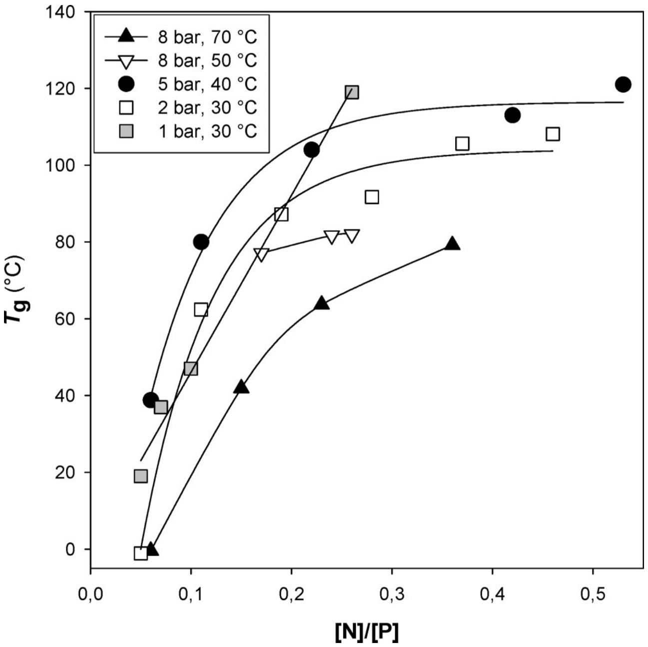
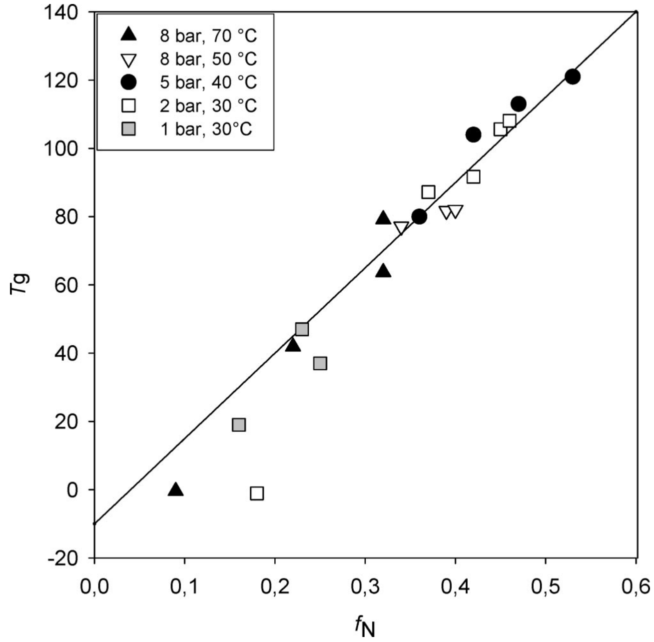


Chart 5. Plot of T_g values obtained under different experimental conditions with *rac*-Et(Indenyl)$_2$ZrCl$_2$ versus f_N



content, and T_g values. The best compromise between chain propagation of the two competing comonomers and chain termination with this catalytic system are 5 bar and 40 °C; indeed, in this case, the activity remains acceptable, and the norbornene incorporation and the T_gs are quite high.

A deeper analysis of the complex ^{13}C NMR spectra of the these copolymers has allowed us to evaluate the diad composition, as well as the propene placement in the copolymers. A great number of 1,3-propene insertions were found, all occurring after an inserted norbornene unit, especially at high temperature and pressure. This is an evidence that the limiting step in P−N copolymerization is the difficulty to insert a propene after N. For the first time copolymerization parameters have been estimated. It was found that P−N copolymers are alternating at temperature as low as 30−40 °C and tend to become more random with the increase in temperature. It is well-known that olefin insertion into a catalytic site is a result of the cooperation of the organometallic complex and of the growing chain. The role of penultimate inserted units can be relevant in some olefin copolymerizations and in the case of norbornene copolymerization, as demonstrated in E−N copolymerizations, penultimate inserted units play for sure an important role. However, a more detailed assignment of the complex of ^{13}C NMR spectra of P−N copolymers is required to draw information about penultimate effects. Surely, all the findings indicate that the ultimate unit plays a very important role in P−N copolymerization.

The molar masses decrease by enhancing the molar ratio between propene and norbornene in the feed and in the copolymers and upon increasing temperature and pressure. Thus, chain terminations are likely to occur when the last unit inserted is propene. This along with an increase in k_P would explain the decrease of norbornene content, molar masses, and glass transition temperature, observed at high T and P.

Experimental Part

All experiments involving air-sensitive compounds were performed using standard glovebox and Schlenk techniques. **1**, **2**, and MAO were obtained from Witco Company. **1** and **2** were used as received, MAO was dried under vacuum and stored as a powder, and 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 (4 Å) and BTS to remove oxygen and water.

Polymerization. Experiments were performed in a Buchi BEP2000 autoclave with a 1 L reactor. Before starting with the polymerization, the reactor was conditioned by means of three N$_2$/vacuum cycles performed at 70 °C; then, in a typical experiment, the reactor was charged with a solution of 26 mmol of cocatalyst and an opportune quantity of norbornene (used as toluene solution) with about 300 mL of dried toluene. After thermal equilibration of the reactor system at the proper temperature (between 30 and 70 °C), propene was continuously added until saturation (at a pressure intermediate between 2 and 8 bar). The equilibrium was reached after 1 h, and then the 25 mL injector was charged with 10 mL of a solution of 10 μmol of catalyst in toluene. The injector with the catalyst solution was pressurized to the proper pressure, higher than that present inside the reactor (between 2.5 and 8.5 bar), and the solution was injected into the reactor. The mixture was stirred for a variable time period (between 5 min and 3 h), depending on the catalytic activity and the norbornene content in feed. The reaction was then terminated by addition of a small amount of acidic ethanol; the polymer was precipitated upon pouring the whole reaction mixture into ethanol (1 L) to which concentrated HCl (10 mL) had been added. The product was at last collected by filtration, washed again with ethanol, and finally dried under vacuum at 70 °C.

^{13}C NMR. For ^{13}C NMR analysis about 100 mg of copolymer was dissolved in C$_2$D$_2$Cl$_4$ in a 10 mm tube. HDMS (hexamethyldisiloxane) was used as internal reference.

The spectra were recorded on a Bruker NMR Advance 400 Spectrometer operating at 100.58 MHz (^{13}C) in the PFT mode working at 103 °C. The applied conditions were the following: 10 mm probe, 90 °C pulse angle; 64 K data points; acquisition time 5.56 s; relaxation delay 20 s; 3−4 K transient. Proton broadband decoupling was achieved with a 1D sequence using bi_waltz_16_32 power-gated decoupling.

DSC. Measurements were performed on a Pyris 1 Perkin-Elmer instrument. The samples (around 8 mg) were heated from 50 to 250 at 20 °C/min, with a nitrogen flow (30 mL/min). A first scan was realized to erase the thermal history of each polymer. T_g was then recorded during a second thermal cycle. In some cases it was necessary to begin with the experiment at a lower temperature; then the instrument could be cooled by means of liquid nitrogen, and the initial point was set at −40 °C.

Molecular Weight Measurement. GPC measurements were performed on about 12 mg of product in o-dichlorobenzene at 105

°C by a GPCV2000 high temperature size exclusion chromatography (SEC) system from Waters (Millford, MA) equipped with two online detectors: a viscometer (DV) and a differential refractometer (DRI). The column set was composed of three mixed TSK-Gel GMHXL-XT columns from Tosohaas. The universal calibration was constructed from 18 narrow MMD polystyrene standards, with the molar mass ranging from 162 to 5.48×10^6 g/mol.

Acknowledgment. We thank Mr. G. Zannoni and Mr A. Giacometti Schieroni for their valuable cooperation in NMR and GPC analysis, respectively.

Supporting Information Available: DEPT spectra of P−N copolymers with different N content and microstructures and Fineman and Ross and Kelen-Tudos plots for all the series of copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA8004235