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REVIEW PAPER

Propene-cycloolefin polymerization

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ABSTRACT

Highly active metallocenes and other single site catalysts have opened up the possibility of polymerizing cycloolefins such as norbornene (N) or of their copolymerization with ethene (E) or propene (P). The polymers obtained show exciting structures and properties. E-N copolymers are industrially produced materials, with variable and high glass transitions depending on the wide range of their microstructures. By realizing the possibility in great variety of stereoregularity of propene and norbornene units and the difference in comonomer distribution, P-N copolymers were expected to have fine tuned microstructures and properties. Moreover, P-N copolymers should be characterized by higher Tg-values than E-N copolymers with the same norbornene content and molar mass. A review of the state of the art of P-N copolymerization by *ansa*-metallocenes of C_2 symmetry, namely *rac*-$Et(Ind)_2ZrCl_2$ (I-I) and *rac*-$Me_2Si(Ind)_2ZrCl_2$ (I-II), and *rac*-$Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ (I-III), and of catalysts of Cs symmetry, namely $(tBuNSiMe_2Flu)TiMe_2$ (IV-I) and derivatives, is given here. Special emphasis is given to microstructural studies of P-N copolymers, including stereo- and regioregularity of propene units as well as of comonomer distribution, stereoregularity of norbornene units, and the structure of chain end-groups. This information allows us to find a rationale for the catalytic activities and the copolymer properties. **Polyolefins J (2014) 1:61-75**

Keywords: propene, norbornene, metallocene catalysts, cycloolefin copolymers, microstructure

CONTENT

INTRODUCTION

The discovery of homogeneous *ansa* metallocene/methylaluminoxane (MAO) catalysts for α-olefin polymerization is considered a major breakthrough in this industrially important field [1-4]. The ligand structure of *ansa* metallocenes can be rationally modified, allowing one to have a high degree of control over polymer stereoregularity, comonomer distribution, molar masses, and molar mass distribution

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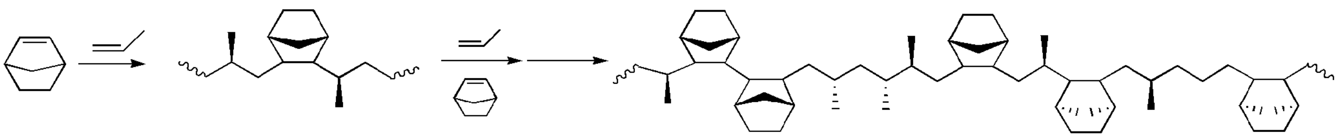
and thus over their thermal and mechanical properties. Hundreds of metallocene catalysts having C_1, C_2, C_{2v}, and C_s symmetry are developed. The best studied metallocene catalysts are the chiral, C_2-symmetric *ansa*-zirconocenes, which because of their symmetry produce mainly isotactic polypropenes. Since a large number of insertion, isomerization, and chain release reactions have been documented in the polymerization of propene with C_2-symmetric *ansa*-zirconocenes, the produced polypropenes (PP) have isotacticity indices spanning from almost atactic to perfectly isotactic, an often incomplete regioregularity, and a random distribution of stereo- and regioerrors in the polymer chain. In addition, polypropenes from metallocenes, due to facile β-hydride transfer reactions, are characterized by narrower and often lower molecular weights, than PP obtained by Ti-based heterogeneous catalysts. The development of C_s-symmetric fluorenyl-containing metallocenes of the type Me_2C-$(C_5H_4)(C_{13}H_8)MCl_2$ (e.g., M=Zr) by Ewen and Razavi [3, 5,6], activated with methylaluminoxane (MAO), offered the possibility of synthesizing syndiotactic polypropene (sPP). These systems, endowed with two enantiomorphic sites, are interesting as they offer the possibility of testing theories on the origin of polypropene syndiotacticity [7-9]. The success of metallocenes has stimulated research on homogeneous organometallic catalysts, and a variety of single-site catalysts has been developed, including half-sandwich and cyclopentadienyl-free group 4 metal catalysts.

Among the most interesting copolymers achievable with *ansa*-metallocene/MAO catalysts, those with cyclic olefins are the most interesting. Sartori et al. [10] were the first researchers who investigated the polymerization of norbornene (N) by $TiCl_4/(i\text{-}Bu)_3Al$ (Ti/Al=1:2) catalyst. The homopolymerization of norbornene using early transition metal catalysts drew more attention from Kaminsky [11,12] who first report on cycloolefin polymerization via addition without ring-opening metathesis polymerization (ROMP) by metallocene/MAO. This led to a great interest in these polymers. Indeed, while cycloolefin homopolymers synthesized by metallocene polymerizations are not processable because of their low solubility in organic solvents and their high melting points [13], copolymers of cycloolefins, namely of norbornene with ethene, are usually amorphous. The fine-tuning of ligand substituents of group 4 metallocene catalysts allows us to control the copolymer structures, from random to alternating, and consequently copolymer properties [14-20]. Ethene-norbornene (E–N) copolymers display a wide range of glass transition temperatures (T_g), from room temperature to about 220°C. They are characterized by high chemical resistance as well as by good processability, and show excellent transparency and high refractive index, owing to their high carbon/hydrogen ratio. These properties make them suitable for optical applications such as coatings for high-capacity CDs and DVDs, for lenses, medical equipment, blisters, toner binder, and packaging. E–N copolymers have been developed into commercial products such as TOPAS by Ticona [20]. The industrially produced copolymers have norbornene contents between 30 and 60 mol %.

In case of propene-norbornene (P–N) copolymers; by realizing the possible great variety of stereo- and regioregularity of propene units, as well as of comonomer distribution and stereoregularity of the bicyclic units they were expected to have fine tuned microstructure and properties. Moreover, P–N copolymers were anticipated to be characterized by T_g-values higher than E–N copolymers with the same norbornene content and molar mass, since polypropene has a higher T_g-value than polyethene. Nevertheless, compared to E–N copolymers, reports regarding P–N copolymers are quite limited [21-30]. A review on the state of the art of P–N copolymerization is given here. Special emphasis is dedicated to microstructural studies of P–N copolymers (Scheme 1).

Propene-norbornene copolymer synthesis

In comparison with E–N copolymers, much less attention has been paid to P–N copolymers. Arnold was the first to report on amorphous P–N copolymers with a norbornene incorporation up to 98 mol % with the *rac*-$Me_2Si(Ind)_2ZrCl_2$ (**I-II**) (Figure 1) activated with MAO, that is, a catalytic system which allows for the synthesis of isotactic polypropene [21]. In contrast



Scheme 1. Typical random P-N copolymer chain

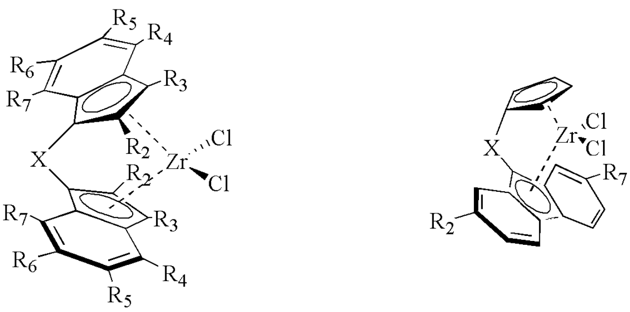


Figure 1. Structures of the C_2 and Cs Zr based *ansa*-metallocenes for propene-norbornene copolymerization

to the low polymerization activity, surprisingly a system of high norbornene incorporation was reported, but T_g values of P–N copolymers were lower than those of E–N copolymers, probably because of their low molecular weight. Copolymer composition was reported to be determined from NMR signals, without any spectroscopic detail.

Then, Tritto et al. [22-24], given the great general interest in norbornene copolymers and having in mind that difficulties in understanding the complex P–N copolymer spectra may have limited the studies on these copolymers, have undertaken a study of P–N copolymerization with specific regard to the elucidation of their microstructure.

Initially, two *ansa*-metallocenes of C_2 symmetry, *rac*-Et(Ind)$_2$ZrCl$_2$ (**I-I**) and *rac*-Me$_2$Si(Ind)$_2$ZrCl$_2$ (**I-II**), already proven effective for producing prevailingly isotactic and regioregular polypropene as well as E–N copolymers with a tendency to alternate, were selected for this study [17]. Copolymerization activities and copolymer properties obtained with **I-I** and **I-II** at 30°C are compared in Table 1. The polymerization activities of **I-I** and **I-II** were found to be quite low, especially when compared to those obtained for E–N copolymerization under analogous experimental

Table 1. P−N copolymerization by C_2 metallocene catalysts:activities and properties

Catalyst symmetry		Activity ^{a}	[N]/[P]	P (bar)	T (°C)	N_{cop}.mol %	T_g (T_m)	M_n (10^{-3}g/mol) Ref.	
C_2	I-I	567 ^{b}	0.25	0.7	30	40.0	82	6.4 ^{g}	[25]
		271 ^{b}	0.66	0.7	30	61.0	107	6.5 ^{g}	[25]
		82 ^{b}	1.5	0.7	30	76.0	135	4.0 ^{g}	[25]
		56 ^{c}	0.26	1	30	35.0	119	7.7	[22]
		33 ^{c}	0.67	1	30	33.0	139	20.4	[22]
		9 ^{c}	1.00	1	30	41.0	129	19.5	[22]
		48 ^{d}	0.22	5	40	42.0	104	15.1	[27]
		22 ^{d}	0.42	5	40	47.0	113	13.7	[27]
		9 ^{d}	0.53	5	40	53.0	121	13.5	[27]
		195 ^{d}	0.17	8	50	34.0	77	10.4	[27]
		145 ^{d}	0.24	8	50	39.0	82	10.9	[27]
		63 ^{d}	0.26	8	50	40.0	82	12.2	[27]
		310 ^{d}	0.15	8	70	22.0	42	/	[27]
		291 ^{d}	0.23	8	70	32.0	64	5.9	[27]
		249 ^{d}	0.36	8	70	32.0	79	7.2	[27]
	I-II	38 ^{c}	0.25	1	30	29.0	87	7.7	[22]
		8 ^{c}	0.67	1	30	32.0	108	14.6	[22]
		4 ^{c}	1.00	1	30	n.d.	115	12.3	[22]
		140 ^{e}	0.33	1.5	60	33.0	83	5.8	[21]
		100 ^{e}	0.67	1.0	60	40.0	101	5.6	[21]
		60 ^{e}	1.00	1.0	60	56.0	140	1.9	[21]
	I-III	180 ^{d}	0.10	5	40	16.0	12	7.1	[27]
		60 ^{d}	0.13	5	40	15.0	10	7.4	[27]
		30 ^{d}	0.29	5	40	16.0	22	5.0	[27]
		4200 ^{f}	0.003	2	55	2.4	n.d (136)	37.0 ^{h}	[30]
		2400 ^{f}	0.007	2	55	3.4	n.d (126)	32.0 ^{h}	[30]
		600 ^{f}	0.013	2	55	7.3	n.d (120)	27.0 ^{h}	[30]

Polymerization conditions:
(a) (kg pol/mol Zr×h),
(b) MAO/Zr = 349, [Zr] = 1×10^{-5} mol/L
(c) MAO/Zr = 2000, [Zr] = 2×10^{-6} mol/L;
(d) MAO/Zr = 2000, [Zr] =$\times10^{-4}$ mol/L;
(e) MAO/Zr = 370, [Zr] = 1.5×10^{-5} mol/L
(f) MAO/Zr = 2000, [Zr] = 3×10^{-6} mol/L
(g) M_η (g/mol) viscosity molecular weight
(h) M_w (10^{-3} kg/mol)

conditions. It was confirmed that it is possible to obtain P–N copolymers, which are relatively richer in norbornene than the E–N copolymers prepared under similar conditions, because norbornene competes more easily with propene than with ethene. However, the M_w values as well as T_g values of P–N copolymers were quite low in comparison to those of E–N copolymers. The initial elucidation of the NMR spectra revealed the possibility of propene 2,1- and 1,3-misinsertions into the Mt-N carbon bond, especially at higher norbornene/olefin feed ratios, causing the low polymerization activities, molecular masses, and T_g. The results revealed that a different bridge in **I-I** and **I-II** has only a small influence on

Table 2. P-N copolymerization with C_1 and C_s metallocene catalysts:activities and properties

Catalyst symmetry		Activity ^{a}	[N]/[P]	P (bar)	T (°C)	$N_{cop.}$ (mol %)	T_g (T_m)	M_n (10^{-3}g/mol)	Ref.
C_s	II-I	145 ^{b}	0.25	0.7	30	36	n.d.	0.99 ^{f}	[25]
		140 ^{b}	0.67	0.7	30	57	n.d.	0.73 ^{f}	[25]
		101 ^{b}	1.50	0.7	30	71	n.d.	0.82 ^{f}	[25]
		72 ^{b}	4.00	0.7	30	81	n.d.		[25]
		1040 ^{c}	0.01	2.0	0	3	1.4 (134)	13.8	[35]
		780 ^{c}	0.02	2.0	0	5	4.2 (127)	9.2	[35]
		570 ^{c}	0.03	2.0	0	7	10.8 (118)	7.4	[35]
		2830 ^{c}	0.01	4.0	20	6	11.3 (124)	14.5	[35]
		2320 ^{c}	0.02	4.0	20	9	18.1 (118)	11.4	[35]
		2090 ^{c}	0.05	4.0	20	13	26.3 (110)	8.2	[35]
		2540 ^{c}	0.05	4.0	50	53	78.2 (-)	1.3	[35]
		4672 ^{c}	0.01	8.0	20	5	3.1(128)	31.2	[36]
		3358 ^{c}	0.02	8.0	20	8	12.3(122)	21.6	[36]
		2196 ^{c}	0.03	8.0	20	12	23.9(113)	14.2	[36]
		2010 ^{c}	0.05	8.0	20	17	30.4 (-)	8.6	[36]
	II-II	7400 ^{d}	0.01	2.0	55	1.3	-0.017 (124)	n.d.	[30]
		4400 ^{d}	0.02	2.0	55	4.0	0.76 (108)	n.d.	[30]
		3800 ^{d}	0.03	2.0	55	6.9	1.39 (102)	n.d.	[30]
		4000 ^{d}	0.04	2.0	55	7.9	1.98 (98)	n.d.	[30]
		2800 ^{d}	0.05	2.0	55	8.0		n.d.	[30]
	II-III	4011 ^{b}	0.11	1.5	30	16	23	n.d	[25]
		2976 ^{b}	0.25	1.5	30	29	40	n.d	[25]
		2142 ^{b}	0.43	1.5	30	37	48	n.d	[25]
		1194 ^{b}	1.00	1.5	30	50	52	n.d	[25]
		705 ^{b}	2.33	1.5	30	61	59	n.d	[25]
		429 ^{b}	4.00	1.5	30	68	80	n.d	[25]
		204 ^{b}	9.00	1.5	30	72	82	n.d	[25]
		51 ^{b}	19.00	1.5	30	84	101	n.d	[25]
	IV-I	1580 ^{e}	0.60	1.0	20	36	112	94.9	[31]
		866 ^{e}	1.13	1.0	20	58	198	137.9	[31]
		895 ^{e}	2.00	1.0	20	71	249	155.9	[31]
	IV-II	3000 ^{e}	0.73	1.0	20	81	291	167.0	[32]
	IV-III	4920 ^{e}	0.73	1.0	20	76	285	159.0	[32]
	IV-IV	17100 ^{e}	0.73	1.0	20	71	250	232.0	[32]
C_1	V-I	153 ^{b}	0.11	1.5	30	20	37	n.d	[25]
		105 ^{b}	0.25	1.5	30	29	56	n.d	[25]
		66 ^{b}	0.66	1.5	30	35	72	n.d	[25]
		51 ^{b}	1.50	1.5	30	39	84	n.d	[25]
		18 ^{b}	4.00	1.5	30	54	94	n.d	[25]
		12 ^{b}	9.00	1.5	30	64	107	n.d	[25]
		6 ^{b}	19.00	1.5	30	77	105	n.d	[25]

(a) (kg pol/mol Zr×h)

(b) MAO/Zr = 349, [Zr] = 1 10^{-5} mol/L

(c) MAO/Zr = 2000, [Zr] = $1\cdot10^{-4}$ mol/L

(d) MAO/Zr = 2000, [Zr] = $3\cdot10^{-6}$ mol/L

(e) MAO/Ti = 400, [Ti] = 6.67 10^{-4} mol/L

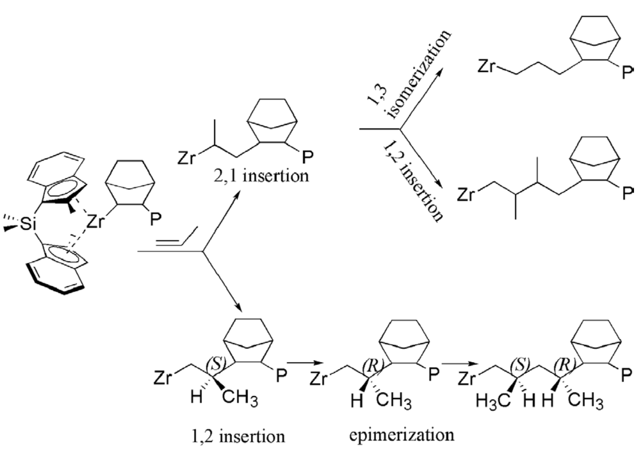
(f) M_η (g/mol) viscosity molecular weight catalytic activity, comonomer molar fractions, T_g, and M_n values.

The influence of propene pressure and temperature on activity, norbornene content, M_w, and T_g of P-N copolymers was assessed by **I-I** [27]. A decrease of norbornene content, M_w, and T_g, was observed at high T and P. In particular, it was found that T_g values of copolymer samples obtained under different conditions, when plotted against [N]/[P] molar ratio in the feed and f_N, tend to a plateau at the [N]/[P] value of 0.5 for all polymerization conditions. For samples obtained at the same pressure (8 bar), the T_g values decrease with the rise in polymerization temperature which being due to the lower norbornene incorporation in these samples. The highest T_g value is of 121°C, obtained at 5 bar and 40°C because the copolymers of this series have higher $f_{N.}$ The plot of T_g values from the different series versus f_N shows a linear relationship. Therefore, the N content is the dominant factor determining T_g, even though some deviation from linearity may be related to differences in molar masses or to the molar fractions of 1,3 insertion. Indeed, a great number of 1,3 propene insertion was found, especially at high temperature and pressure: 1,3 propene insertion occurs after an inserted norbornene unit, confirming that the limiting step in P–N copolymerization is the difficulty of inserting a P after N. Moreover, chain transfer reactions are likely to occur more often at a P-last inserted-Mt bond: indeed, chain transfer reactions at a Mt-N bond are rather difficult because the β-H transfer would violate Bredt's rule, that is, the coplanarity of Zr–C(α)–C(β)–H. The M_w values of the P–N copolymers are quite low in comparison to those of E–N copolymers. The highest molar masses obtained at room temperature were in the range of 40,000 g/mol.

Since the 2-alkyl indenyl substitutions of C_2-symmetric zirconocenes are the key to increase considerably the molar masses of the produced polypropenes [1,2], Tritto et al. investigated the synthesis of P–N copolymers with *rac*-$Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ (**I-III**) for obtaining P–N copolymers with high norbornene content and high molar masses [27]. Methyl-2 substitution on the indenyl ligand in **I-III** had an unexpected and strong influence on the catalyst behaviour in P–N copolymerization, causing a great decrease in catalytic activity, molar fractions f_N, T_g, and M_n values (Table 1). P-N copolymers with maximum 16 mol % of norbornene were obtained by **I-III** in contrast to those highly alternating obtained by **I-I**.

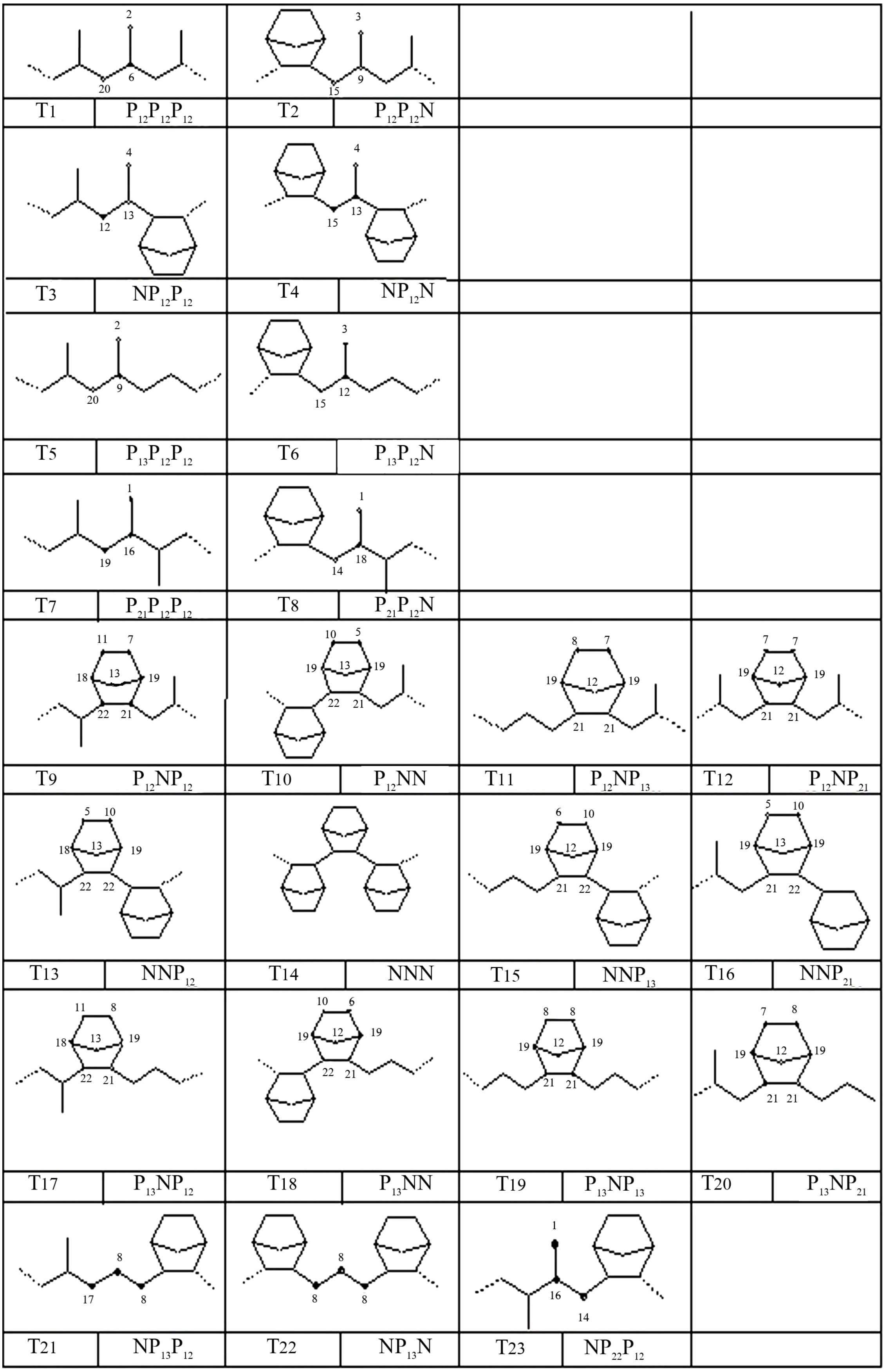
The microstructural analysis by ^{13}C NMR of the copolymers gave evidence of the tendency of **I-I** to alternate P and norbornene comonomers and of **I-III** not alternating the comonomers, as well as information on the probability of insertion of norbornene and of the possible forms of P insertion (P_{12}, P_{13}, and P_{21}), as shown below. An interesting piece of information is regarding the unexpected amount of triads containing propene misinsertions or regioerrors, which are greater in the series from **I-III** than from **I-I**. Regarding the 1,3 enchained units, it is worth noting the relevant amount of $NP_{13}P_{12}$ (Chart 1 for definition) in the series from **I-III** and of $NP_{13}N$ in the series from **I-I**, reflecting the different tendency to alternate the comonomers of the two catalysts and the important penultimate effects with **I-III**. A great decrease in the tacticity of the PP blocks was found in the copolymers prepared with **I-III** by increasing the norbornene content in the feed, which was explained by the difficulty of this catalyst in accommodating a norbornene into $Mt\text{-}P_{12}N$, which increases the probability in unimolecular epimerization events (Scheme 2).

Kaminsky et al. studied P–N copolymerizations with two C_s-symmetric $Me_2C(Cp)(Flu)ZrCl_2$/MAO (**II-I**) and $Ph_2C(Cp)(2,7\text{-}t\text{BuFlu})ZrCl_2$ (**II-III**) systems and with the constrained-geometry catalyst **V-I**, which were compared to those with the C_2-symmetric **I-II** (Table 2). In the middle range of the molar fraction of norbornene in the feed, incorporation rates are comparatively low for the catalysts **II-III** and **V-I.** The copolymers obtained with the metallocene **II-III** show clear glass transition temperatures, which



Scheme 2. 2,1 and 1,3 insertions and chain epimerization occurring with catalyst I-III

Chart 1. Possible triads of a random P-N copolymer chain. Each triad $M_1M_2M_3$ is depicted as $M_3M_2M_1$, i.e., running from right to left (the catalyst metal ideally being bound to the extreme left side of the chain)



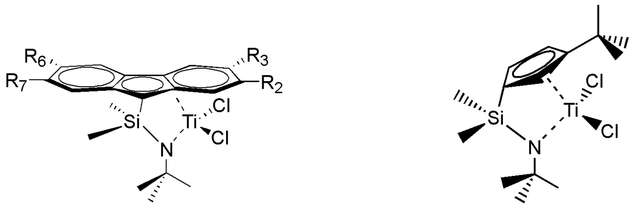


Figure 2. Structures of the Cs and C1 Ti based constrained geometry catalysts for propene-norbornene copolymerizations.

linearly increase from 23°C, for a polymer with 16 mol% incorporated norbornene, up to 101°C. Authors report up to 84 mol% norbornene content for these copolymers. However, it should be noted that calculation of N content in these copolymers is overestimated, as it is evident in the section on NMR analysis. In the case of polymers obtained with catalyst precursor **V-I**, an incorporation of approximately 60 mol% and a glass transition temperatures increase up to about 105°C are reported. A plateau in the glass transition temperatures of the copolymers is reached. In comparison to catalyst **V-I**, the reactivity of norbornene with catalysts **I-I** and **II-I** is significantly higher than that of propene. These studies confirmed that high reactivity of the cyclic monomer makes P–N copolymers with higher norbornene incorporation accessible, but with lower molar masses than E–N copolymers [25, 27, 29].

P–N copolymerizations with low norbornene molar fractions by **I-III** and **II-II** were reported recently by Galland [30]. The trends which had already been established in previous studies were confirmed. In addition, they found that norbornene concentration had a significant impact on the physical properties, since low norbornene content in the polymer produced an increase in elongation-at-break in polymers from both systems. A substantial increase was found in the case of the polymer synthesized by $Ph_2C(Flu)(Cp)ZrCl_2$ system.

Shiono et al. succeeded in the synthesis of P–N copolymers with high norbornene content up to 71 mol% with catalyst $(^{t}BuNSiMe_2Flu)TiMe_2$ (**IV-I**) (Figure 2) activated by Me_3Al-free methylaluminoxane (dried MAO) [26]. They had previously reported that this metallocene, when activated with dried MAO, yielded living propene and norbornene homopolymerization [31]. The use of dried modified methylaluminoxane (*d*-MMAO) facilitated the living polymerization of propene in heptane. This solvent, among all the solvents employed, permitted the synthesis of PP with the highest syndiotacticity.

P–N copolymerizations were carried out at 20°C under atmospheric pressure of propene. Dimethylmetallocene **IV-I** was activated by dried MAO, modified methylaluminoxane (MMAO) and $Ph_3CB(C_6F_5)_4/Oct_3Al$. The system activated by $Ph_3CB(C_6F_5)_4/Oct_3Al$ was the most active one and yielded the copolymer with the lowest molecular weight and broadest molecular weight distribution. Dried MAO yielded the copolymer with the narrowest polydispersity (MWD). The norbornene content in the copolymer was almost proportional to [N]/[P] feed ratio. T_g of the P–N copolymers increased linearly against the norbornene content in the copolymers, from 53°C to 249°C. The **IV-I**/*d*-MAO system also produced P–N copolymers with high molecular weight and narrow MWDs. The alkyl substituent on the fluorenyl group of **IV-I** affected not only the activity but also the stereospecificity during propene polymerization. The catalytic systems promoted random copolymerizations in a living manner regardless of the titanium complex used. The activity increased with the introduction of the ^{t}Bu groups on the Flu ligand, and **IV-IV** gave the highest activity and copolymers with norbornene content up to 70 mol% and high T_g values (250°C). All the catalytic systems gave copolymers with high norbornene content, which is slightly dependent on the complex used. All the

Table 3. Synthesis of syn-PP-block-poly(propene-ran-norbornene) with catalyst IV-III and d-MMAO [34]

NB (g)	Yield (g)	M_n (10^{-4} g/mol)	M_w/M_n	T_m (°C)	T_g (°C)
0	0.48[a]	10.8	1.36	135	-
2.77 [b]	0.92	20.8	1.21	135	311
2.07 [b]	1.12	22.4	1.30	133	231
1.38 [b]	1.09	22.6	1.32	133	93

Polymerization conditions:

(a) Prepolymer:propene = 1 atm, toluene = 30 ml, Ti = 10 μmol, Al =2.0 mmol, T = -20°C, time = 5 min

(b) T = 25°C, time = 6 min

135°C) and T_g (93-311°C) values that corresponded to those of the crystalline syndiotactic PP sequence and amorphous poly(propene-*ran*-norbornene) sequence, respectively. The T_g values were controlled by the amount of norbornene added. These results suggested the formation of the expected block copolymers and the phase separation of the copolymers.

Microstructure of propene-norbornene copolymers

Figure 3 displays the ^{13}C NMR spectrum of a P–N copolymer prepared with **I-I** /MAO, at [N]/[P] feed ratio of 0.22, along with the final signal assignment and the structure and carbon numbering of an isotactic P–N copolymer. *Cis*-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. A first assignment of the main ^{13}C NMR signals of P–N copolymers with norbornene content up to 35 mol % was obtained on the basis of distortionless enhancement by polarization transfer (DEPT) ^{13}C spectra, comparison made with isotactic polypropene (*i*-PP) and E–N copolymer spectra, and *ab initio* theoretical ^{13}C NMR chemical shifts. These were computed for the most relevant conformers of model compounds and averaged using the rotational isomeric state (RIS) conformer populations estimated for an isotactic chain $(P_4\text{–}N)_x$ [22-24]. Such assignments were used to estimate the norbornene copolymer content and showed the presence of 1,3-propene misinsertions, which were formed in significant amounts when increasing the [N]/[P] ratio of the feed.

Recently, a general scheme for describing the microstructure of P–N copolymers at triad level from ^{13}C NMR spectra was proposed by Boggioni et al. [29]. This scheme included: (i) definition of the possible triads composing the copolymer chain, (ii) use of NMR techniques for assigning new signals; and (iii) a best-fitting procedure to determine the copolymer microstructure [29]. This procedure, which allows for a quantitative analysis of copolymer sequences as accurate as possible, has been applied to the analysis of ^{13}C NMR spectra of a number of P–N copolymers prepared with catalyst precursors *rac*-$[Et(Ind)_2]ZrCl_2$ (**I-I**) and *rac*-$[Me_2Si(2\text{-}Me\text{-}Ind)_2]ZrCl_2$ (**I-III**). A complete description of the microstructure at triad level, including 1,3 and 2,1 propene insertions, has been attempted. The possible triads of a random P–N copolymer chain are displayed in Chart 1, while in Table 4 the current assignments of ^{13}C NMR spectra of random P–N copolymers are reported. New signals have been assigned (Chart 2). Some examples are the signals of: (i) the carbons of propene in the alternating triad $NP_{12}N$ and of norbornene in tetrad $NP_{12}N\ P_{12}$; (ii) P_β methyls in triad $NP_{12}P_{12}$ adjacent to a variable number of P_{12} units all in isotactic relationship; (iii) the $S_{\alpha\gamma}$ methine of a 1,3 propene inserted units

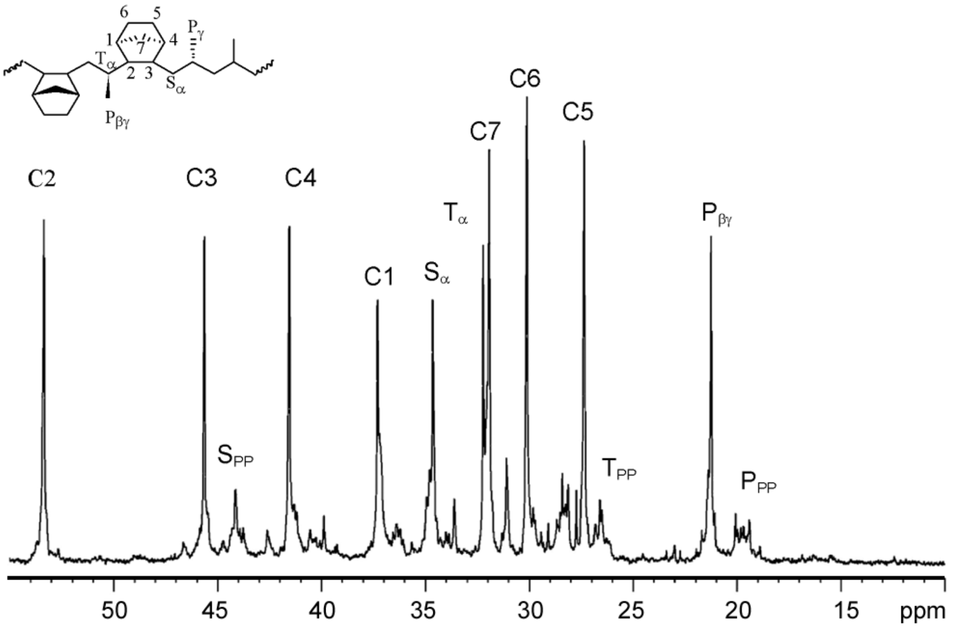


Figure 3. ^{13}C NMR spectrum of a P-N copolymer obtained by I-I ([N]/[P] = 0.22, f_N = 0.42).

Table **4**. Current assignments of ^{13}C NMR spectra of random P-N copolymers

Signal code from chart 1	Range (ppm)$^{(a)}$	Carbon	Triads
1	15.45 – 16.80	P	T7, T8, T23
2	17.80 – 19.83	P	T1, T5
3	20.08	P	T2,T6
4	20.08 – 21.70	P	T3, T4
5	25.95	C5	T10, T13, T16
6	26.15 - 26.77	T	T1
		C5	T15, T18
7	26.80 - 27.45	C5	T9, T11, T12, T20
8	28.12 - 28.41	S	T21
		C5	T11
		C6	T17, T19, T20, T22
9	28.68	T	T2
		$T_{\beta\delta}$	T5
10	29.30 - 29.70	C6	T10, T13, T15, T16, T18
11	29.72 - 30.20	C6	T9, T17
12	30.20 - 31.31	C7	T11, T12, T15, T18, T19, T20
		S	T3, T6
13	31.93 - 32.21	T	T3
		$T_{\alpha\beta}$	T4
		C7	T9, T10, T13, T16, T17
14	33.60 - 33.90	$S_{\alpha\alpha}$	T8, T23
15	34.64 - 35.12	S	T2, T4, T6
16	34.91	T	T7, T23
17	35.70	$S_{\alpha\gamma}$	T21
18	36.80 – 38.00	C1	T9, T8, T13, T17
19	39.20 - 42.60	C4	T9, T10, T11, T12, T13, T15, T16, T19, T20, T7
		S	
20	43.65 - 44.63	S	T1, T5
21	45.44 - 46.20	C3	T9, T10, T11, T12, T15, T16, T17, T19, T20
22	49.00 - 55.70	C3	T13, T15, T18,
		C2	T9, T10, T13, T16 T17

(a) HDMS (hexamethyldisiloxane) was used as internal reference

copolymers were amorphous with high T_g values, which indicated the formation of random copolymers irrespective of the titanium complex.

These living systems were utilized by Shiono to synthesize syndiotactic PP-*block*-poly(propene-*ran*-norbornene) with **IV-III**–*d*-MMAO. As an example, results of these syntheses are summarized in Table 3. The PP obtained in the first step showed an M_n value of 108,000 with an M_w/M_n of 1.36 and a melting point of 135°C. After the copolymerization, the yields increased, as did M_n values (208,000-226,000); however, the M_w/M_n values decreased (1.21-1.32) regardless of the amount of norbornene added. The block copolymers showed T_m (133-

Table 5. Molar fraction of tactic triads of PP blocks and molar fractions of 1-butenyl and vinylidene end groups obtained by the ^{1}H NMR spectra of P-N copolymers.

Cat.	[N]/[P]	f_n	M_n (10^{-3}g/mol)	$f_{(vinyl)}$ x 10^3	$f_{(2\text{-butenyl})}$ x 10^3	mm	mr	rr
I-I	0.11	0.34	11.1	0.80	3.17			
I-I	0.22	0.41	15.1	0.62	2.70			
I-I	0.42	0.45	13.7	0.00	2.03			
I-I	0.53	0.45	13.5	0.29	2.00			
I-III	0.05	0.12	15.5	0.59	0.13	0.90	0.06	0.04
I-III	0.10	0.16	7.1	1.88	1.03	0.66	0.19	0.15
I-III	0.13	0.15	7.4	0.83	0.08	0.60	0.17	0.23
I-III	0.29	0.16	5.0	3.96	5.61	0.44	0.31	0.25

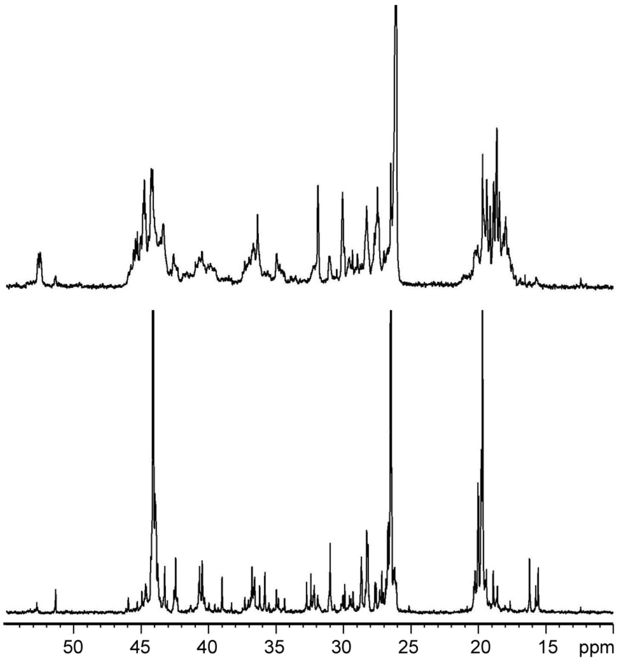


Figure 4. ^{13}C NMR spectra of P-N copolymers produced with I-III at 5 bar, 40°; a) [N]/[P] = 0.05 and f_N = 0.12; b) [N]/[P] = 0.29 and f_N = 0.16

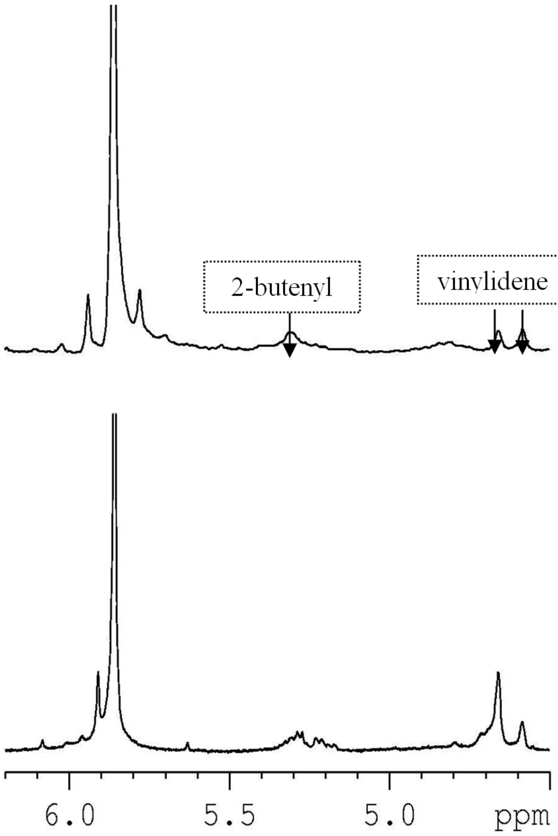
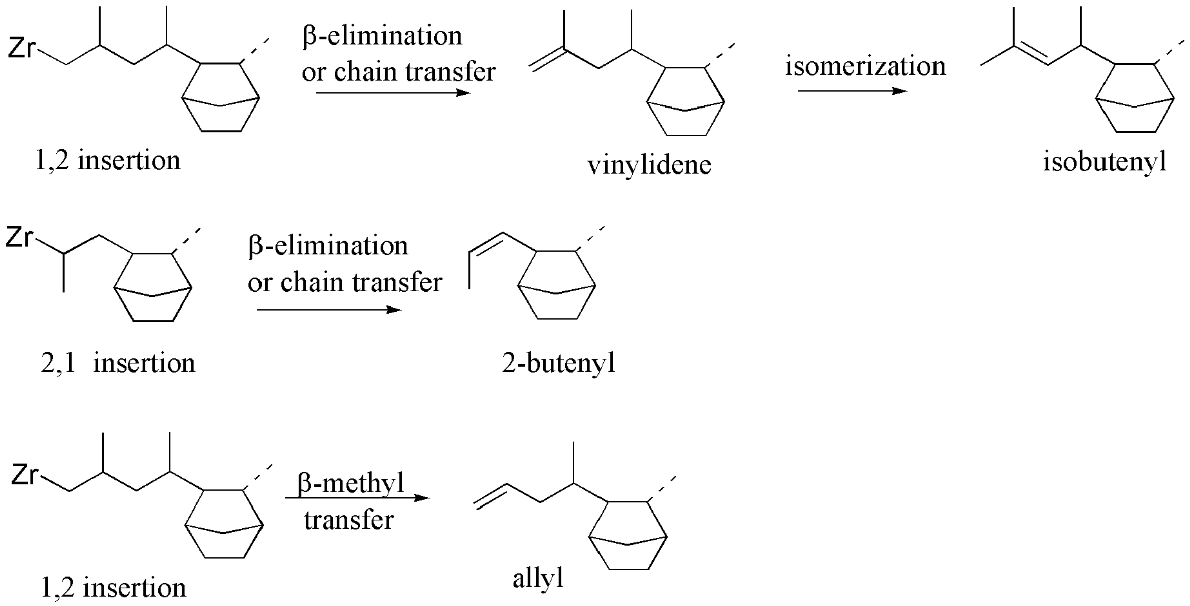


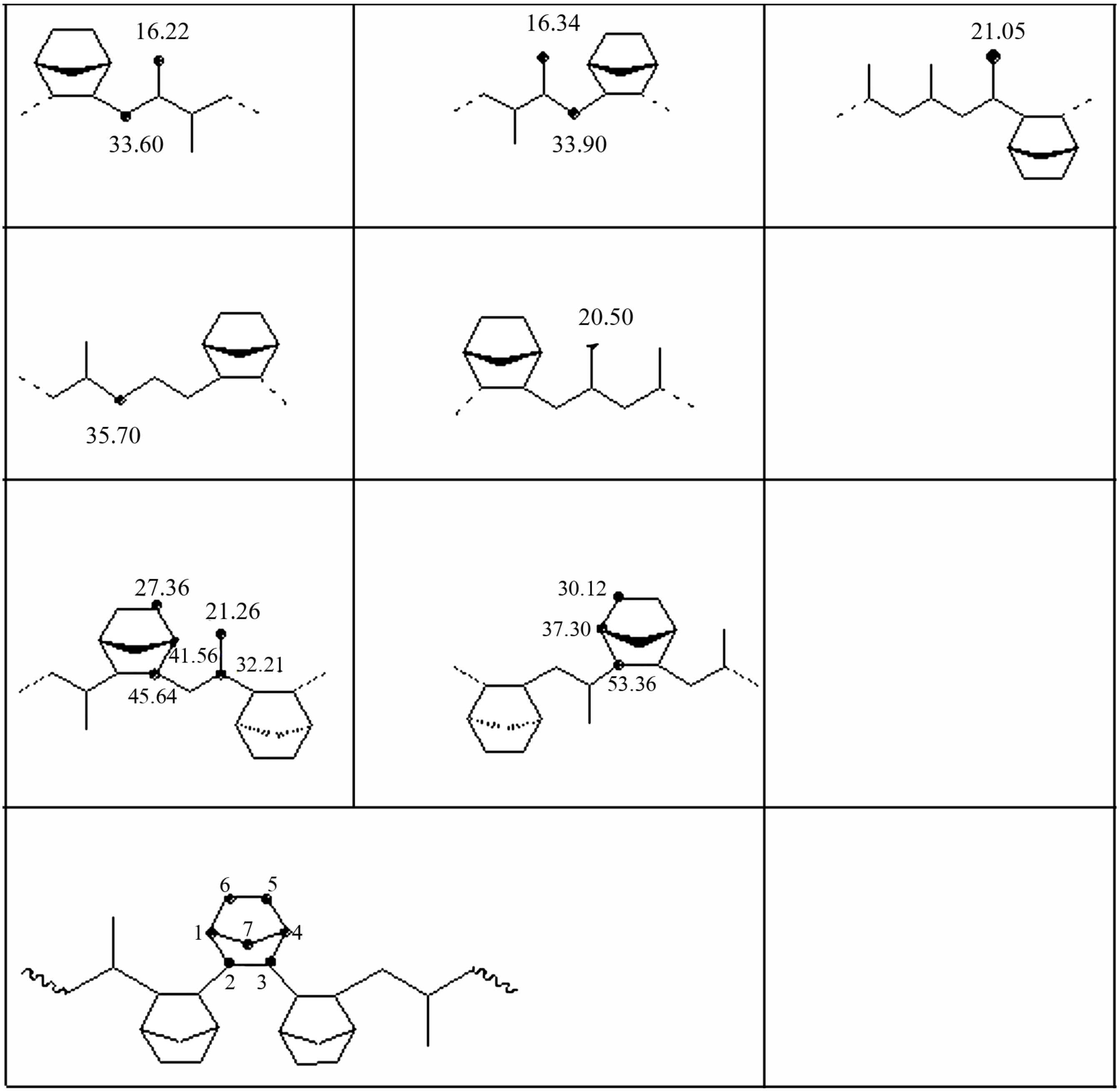
Figure 5. 2-Butenyl and vinylidene end groups signals in ^{1}H NMR spectraof P-N copolymers produced with I-III at 5 bar, 40°C ; (a) [N]/[P] =0.10 and f_N =0.16; (b) [N]/[P] =0.13 and f_N = 0.15

in the $NP_{13}P_{12}$; and (iv) the methyl carbon atom of central monomer in $P_{21}P_{12}N$ and $NP_{21}P_{12}$. Although determination of all the triads has not been achieved, an estimate of the molar fractions of the major sequences with a standard deviation in the order of 2-4% has been obtained. The expansions of the methyl region of two ^{13}C NMR spectra of P-N copolymers obtained by **I-III** at low and high [N]/[P] revealed a great difference in the tacticity of the PP blocks (Figure 4). The tacticity at triad level was quantified in order to evaluate the effect of [N]/[P] feed ratio on the microstructure of PP blocks. Molar fractions of tactic triads of PP blocks



Scheme 3. Processes involved in the formation of most interesting termination chain-end groups.

Chart 2. Main novel assignments



C5/C6	(27.3-31.3 ppm)
C7	(32.8-36.3 ppm)
C1/4	(36.3-41.8 ppm)
C2/3	(45.3-52.8 ppm)

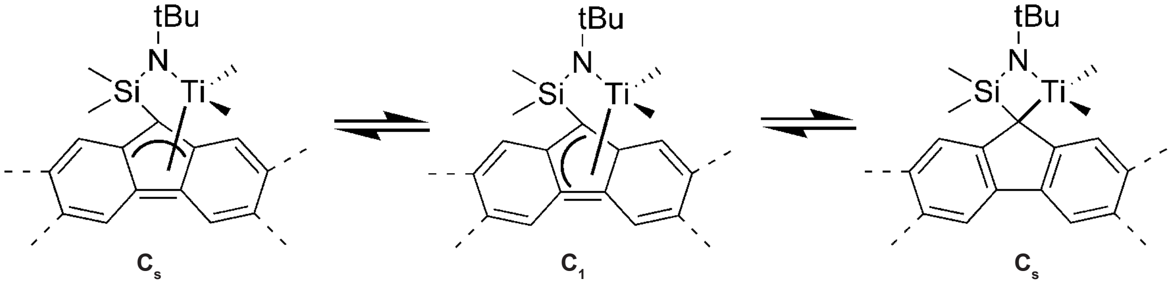


Figure 7. Isomerization mechanism of IV [34]

Table 6. Reactivity ratios calculated from triads molar fractions

Cat.	f_N	[N]/[P]	r_{11}	r_{21}	r_{31}	r_{41}	r_{23}
I-I	0.34	0.11	0.36	0.03	0.00	0.22	0.11
I-I	0.41	0.22	0.57	0.03	0.05	0.33	0.27
I-I	0.45	0.42	0.84	0.04	1.16	0.59	0.13
I-I	0.45	0.53	1.40	0.03	9.00	0.74	0.18
I-III	0.12	0.05	0.52	>10	0.06	0.32	0.82
I-III	0.16	0.10	0.63	0.57	0.03	0.53	2.88
I-III	0.15	0.13	1.08	0.15	0.36	0.67	22.62
I-III	0.16	0.29	1.44	>10		1.31	

$r_{11} = (k_{P12\,P12\,P12}/k_{P12\,P12\,N})$
$r_{21} = (k_{N\,P12\,P12}/k_{N\,P12\,N})$
$r_{31} = (k_{P13P12P12}/k_{P13P12N})$
$r_{41} = (k_{P21P12P12}/k_{P21P12N})$
$r_{23} = (k_{NP13P12}/k_{NP13N})$

in P-N copolymers produced with **I-III -MAO** are reported in Table 5, where the molar fractions of chain end-groups are shown as well.

Chain end-group analysis by ^{13}C and ^{1}H NMR spectra of polymers gives important information on the reactions involved in chain transfers and terminations [28]. Scheme 3 displays the processes which could lead to the most interesting termination chain-end groups, which derive only from chain transfer after primary or secondary inserted propene units, since chain transfers after an inserted norbornene unit are unlikely to occur.

The molar fractions of 2-butenyl and vinylidene end-groups, based on analysis of the integrated signals of the ^{1}H NMR spectra of the polymers (Figure 5), are reported in Table 5. In general, a greater amount of 2-butenyl end groups arising from termination at Mt-P_{21} rather than vinylidene arising from termination at Mt-P_{12} is observed. This is the opposite of what has been observed in P homopolymerization with **I-I-MAO** and **I-III-MAO** [33]. Moreover, the amount of 2-butenyl end groups is greater for the samples with lower molar fractions of triads containing the P_{21} unit. Thus, 2-butenyl end groups are greater for samples obtained with **I-I-MAO** than with **I-III-MAO,** except for the sample obtained at the highest norbornene concentration in feed with **I-III-MAO**, that is, the one in which we observed the lowest molar fractions of triads containing P_{21} units. This is an additional evidence that the limiting step in P–N copolymerization is the difficulty of inserting a propene after N, which causes 2,1 insertions with subsequent isomerization to 1,3 propene insertions as well as chain epimerization.

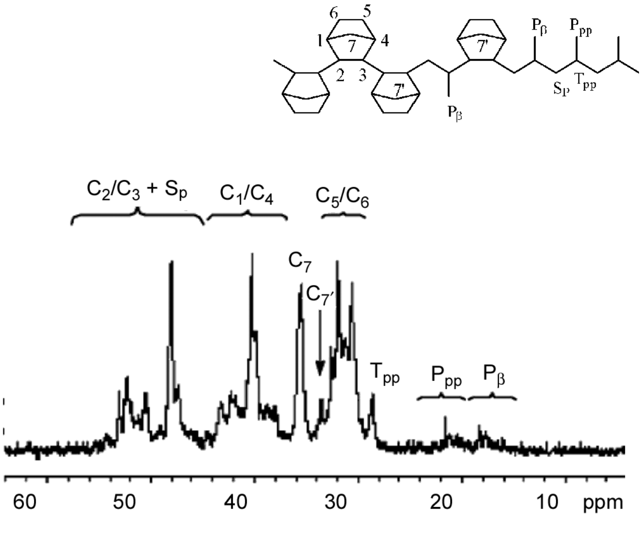


Figure 6. ^{13}C NMR spectrum of a P-N copolymer obtained with IV-I and d-MMAO

Thus, 2-methyl substitution of the indenyl ligand of **I-III-MAO** makes the insertion of N into the Mt-P_{12}N bond so difficult that *R*-*S* isomerization of the last inserted propene unit is possible, at relatively high [N]/[P] ratios, i.e., under starved propene conditions. Moreover, with this catalyst, which does not tend to chain transfer to the monomer in P homopolymerization, a $P_{2,1}$ insertion can compete with a $P_{1,2}$ insertion: as a consequence the molar fractions of triads containing $P_{2,1}$ are relatively high, while with catalyst **I-I -MAO** the $P_{2,1}$ insertions tend to terminate giving more 2-butenyl chain end groups. The isomerization to 1,3 insertions is similar in the copolymers prepared with both catalysts (Scheme 2).

In Figure 6 the ^{13}C NMR spectrum along with structure and assignments of a P–N copolymer produced with catalyst dimethyl **IV-1** [26] by Shiono is reported. Several signals for each carbon due to the different comonomer sequences and stereoisomers of the norbornene unit were observed. The signals around 26-30.4 and 30.26-35.42 ppm were tentatively assigned to carbons C5/C6 and C7, respectively. In particular, a broad resonance with several peaks at

31.2-32.1 ppm, which disappeared in the spectrum of polynorbornene, could be assigned to the C7 carbon of the norbornene unit in alternating and/or norbornene diad sequences. The signals at 33.3-35.4 ppm, visible also in the spectrum of polynorbornene, were assigned to NNN triads. The signals at about 36.4-41.4 ppm and 43-53 ppm were therefore tentatively assigned to C1/C4 and C2/C3 carbons, respectively. Signals between 48-53 ppm were assigned to C2/C3 carbons of NNN triads. Moreover, the signals between 12.0 and 17.0 ppm, which appear at high norbornene content, were assigned to a methyl of propene unit connected to norbornene. Thus, the microstructure of these copolymers with a high norbornene content is of a random type.

The isomerization of (tBuNSiMe$_2$Flu)TiMe$_2$ during the polymerization (Figure 7) was hypothesized to justify the considerable amount of *mmmm* and *mmmr* sequences contained in the PP obtained with this catalyst and the possible presence of isotactic blocks in the syndiotactic sequence. The isotactic block might be produced by the C$_1$-symmetric Ti species formed by the isomerization. Probably, at least under the conditions used for P–N copolymerization with this catalyst, that is, low temperature and propene pressure, the C$_1$-symmetric Ti species formed by the isomerization may facilitate the insertion of a propene after N as well as a second norbornene unit at high [N]/[P] molar ratios.

Reactivity ratios of propene-norbornene copolymerizations and mechanisms

The microstructural analysis by ^{13}C NMR of the copolymers at triad level allowed us to determine the reactivity ratios r_i and r_{ij} obtained from diads and triads (Table 6) [27]. The highly alternating nature of the copolymerization with **I-I** is evidenced by the high value of $NP_{12}N$ triads and by the low r_1 (= k_{P12P12} / k_{P12N}) and r_3 (= k_{P13P12} / k_{P13N}) values, as well as by the low r_{21} (= $k_{NP12P12}$ / k_{NP12N}) and r_{23} (= $k_{NP13P12}$ / k_{NP13N}) values, all close to zero.

The difficulty of catalyst **I-III** in inserting a norbornene into a Mt-P$_{12}$N bond appears from the particularly low content of NP$_{12}$N triads and from the r_1 values greater than for **I-I**, but lower than in E–N copolymerizations. Thus, also for this catalyst norbornene insertions compete with propene insertions, but less than for **I-I**. The higher r_{11} and r_{21} values for **I-III** with respect to **I-I** are a clear indication of the different tendency to give alternating or random copolymers of the two catalysts. The r_2 values for **I-III**, greater than for **I-I**, and higher than r_1 values testify the difficulty to insert P after N.

The $r_{2''}$ (= k_{NN} / k_{NP21}) values higher than $r_{2'}$ (= k_{NN} / k_{NP13}) confirm the tendency of 2,1 propene insertion to isomerize to 1,3 especially in P–N copolymerizations with **I-I**. Interestingly, the r_2, $r_{2'}$, and $r_{2''}$ values, which are quite similar in copolymers from **I-III,** show that the last norbornene inserted unit slows down P$_{12}$ insertions so that all the possible forms of P insertions (P$_{12}$, P$_{13}$, and P$_{21}$) have a similar probability of insertion. The high r_{23} values indicate that **I-III** does not allow a norbornene insertion even into a Mt-P$_{13}$N bond, demonstrating a penultimate effect.

CONCLUSION

The microstructure of the norbornene homo- and copolymers can be greately influenced by the symmetry and structure of the ligands on the transition metal complexes. In comparison to the successful E–N copolymerization, copolymerizations of norbornene with higher α-olefins such as propene still give low activity, and often low comonomer incorporation and molar masses.

The low activity of P-N copolymerization by C$_2$ symmetric *ansa* metallocenes was demonstrated to result from the difficulty of inserting a propene into the Mt–tertiary carbon bond formed after the norbornene insertion (Mt-N), which is even more sterically crowded than the sites formed after a propene (2,1) regioirregular insertion, which is less reactive than the sites with a primary growing polypropene chain. Despite the relatively lower polymerization activity, at low norbornene/olefin ratio it is possible to obtain P–N copolymers that are relatively richer in norbornene than the E–N copolymers prepared in similar conditions. However, at higher norbornene/olefin feed ratios the great amount of 1,3 propene misinsertions clearly revealed that the steric hindrance of the Mt–tertiary carbon bond when norbornene is the last inserted unit makes the next propene insertion difficult causing low polymerization activities, molecular masses, and T$_g$. The P–N copolymers with high N content and high T$_g$ obtained with (^{t}BuNSiMe$_2$Flu)TiMe$_2$ at low temperature and propene pressure and high [N]/[P] molar ratios may probably arise from an isomerization of the catalyst: the C_1-symmetric Ti species formed by the isomerization may facilitate the insertion of a propene after N as well as of a second norbornene unit at high [N]/[P] molar ratios.

Thus, there is now a question raised that whether it is possible to synthesize new organometallic complexes in high yields with appropriate structures that allow for the synthesis of propene-norbornene copolymers with controlled microstructure, high molar masses and with desired physical, mechanical and optical properties?

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- Modeling and simulation
- Structure-property relationship
- Polyolefins degradation
- Other related subjects

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