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Non-Cp type titanium precatalysts for ethylene/norbornene copolymerization

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Dedicated to Dr. Swaminathan Sivaram on the occasion of his 60th birthday.

Abstract

Ethylene/norbornene monomers were homo- as well as copolymerized using titanium-based non-Cp precatalysts [2-(2,6-dialkylphenylamino)-1-phenylethoxy $TiCl_2$] in the presence of methylaluminoxane. The precatalysts polymerized ethylene with moderate activities that increased with increase in temperature reaching a maximum yield of polyethylene at 70 °C. However, these catalysts showed relatively low activity towards norbornene homopolymerization. Precatalysts **$1ATiCl_2$** and **$3ATiCl_2$** were used for ethylene/norbornene copolymerization. The microstructural analysis of these copolymers suggests that these are alternating copolymers with *meso* (major) and *racemic* (minor) sequences. Higher norbornene incorporation in the copolymer was obtained with precatalyst **$3ATiCl_2$**, which is a more "open" catalyst system. The reactivity ratios for ethylene/norbornene copolymerization suggest that these precatalysts show lesser tendency towards norbornene homopropagation in the copolymerization reactions.
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Keywords: Non-Cp catalyst; Ethylene/norbornene copolymerization; Reactivity ratios

1. Introduction

Vinyl addition polymerization of the cyclic olefins (cyclobutene, cyclopentene, cyclooctene, norbornene, etc.) is possible by both metallocene [1] and non-metallocene catalysts [2−4]. Since polycycloolefins prepared with these catalysts show no melting point and cannot be processed like thermoplastic polymers, they are of no commercial interest. However, copolymerization of cycloolefins with ethylene results in cyclic olefin copolymers (COC's) that show thermoplastic behavior with some interesting optoelectronic properties [5]. COC's are important engineering polymers, which can be prepared by copolymerization of cyclic olefins such as norbornene (NB) with ethylene or α-olefins using various metallocene and non-metallocene catalysts [3−16]. The properties of the copolymer mainly depend on parameters, such as the comonomer composition, the distribution of the comonomer within the chain and also the chain stereoregularity, which are in turn dependent on the structure of the precatalyst. If these copolymers contain more than 15 mol% of cycloolefin then they are amorphous in nature with high mechanical strength, glass transition temperature (T_g) and are stable towards common solvents. Since they contain no aromatic groups or double bonds, their interaction with light waves is modest. Therefore they are well-suited for optoelectronic applications in data transfer and storage. NB also stiffens and strengthens the polymer, and increases its T_g in proportion to its incorporation in the chain.

Depending on the catalyst structure, the microstructure of the copolymers consists of mainly isolated NB units, alternating monomer sequences or short NB microblocks [7]. In literature there are only a few reports on ethylene/norbornene copolymerization using non-metallocene systems. Fujita et al. reported the first non-metallocene catalysts in combination with MAO which initiate living ethylene/norbornene copolymerization to furnish monodisperse COC's with very high

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molecular weights (max. $M_n = 800{,}000$). These catalysts exhibit very high NB incorporation (48.6%), superior to constrained geometry catalysts (31.2%) and its distributions reveal that this pyrrolide-imine chelate ligand based catalyst (PI catalyst) systems show a high propensity to yield alternating copolymers [4]. The sterically open and highly electrophilic nature of the catalysts are probably responsible for the excellent NB incorporation. There are only a few examples of catalysts that copolymerize ethylene and NB in a (quasi) living fashion [4,17–22].

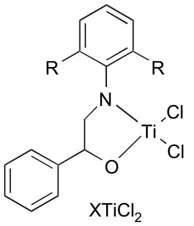
We have synthesized a series of titanium-based non-metallocene precatalysts [2-(2,6-dialkylphenylamino)-1-phenylethoxy $TiCl_2$] by reacting lithium salts of the corresponding amino alcohols with $TiCl_4(THF)_2$ [23]. These precatalysts **1–3ATiCl$_2$** (Scheme 1) were able to polymerize 1-hexene in isotactic manner (up to 90%). The ligand environment around the metal center showed greater influence on catalyst activity. In 1-hexene polymerization reactions, catalyst activity and polymer properties are depended on the steric features in the *ortho* positions of the aniline moiety of the ligands [23].

In this connection here we will discuss the results on the study of homo- and copolymerization of ethylene/norbornene using precatalysts **1ATiCl$_2$** and **3ATiCl$_2$** with MAO as a cocatalyst.

2. Experimental section

2.1. Materials and general considerations

All reactions were carried out under dry and oxygen-free nitrogen or argon using glove box or standard Schlenk techniques. Transfers were performed in a glove box containing inert atmosphere or by standard syringe techniques. Solvents were distilled from sodium/benzophenone ketyl (hexane, toluene and THF) or P_2O_5 (CH_2Cl_2 and chlorobenzene) under nitrogen prior to use. Norbornene was purchased from Sigma–Aldrich, distilled over sodium and was stored under nitrogen. MAO was purchased as 10% by weight solution in toluene from Witco GmbH, Germany and was used after estimating the aluminum content. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using Bruker AV-400 spectrometer or Jeol GSX-400 spectrometer. ^{13}C NMR spectra of the polyethylene and ethylene/norbornene copolymer samples were recorded with short pulse angle and long relaxation delay at 120 °C. These NMR samples were prepared in 10 mm NMR tube as 10% v/v in benzene-d_6 and 1,2,4-trichlorobenzene. Solid-state ^{13}C CPMAS NMR spectra of these polymers were acquired on a Bruker AV-400 spectrometer operating at 100 MHz, in zirconium rotor with a spinning rate of 7000 Hz and a total of 700 scans were collected. DSC measurements were done on Stanton Redcrofts simultaneous thermal analyzer (781 series). Ethylene gas of >95% purity, purchased from Intergas, was used for polymerization.



XTiCl$_2$

R = isopropyl **1ATiCl$_2$**
R = ethyl **2ATiCl$_2$**
R = methyl **3ATiCl$_2$**

Scheme 1. Structures of the precatalysts used in this study.

2.2. Ethylene polymerization

All ethylene polymerization reactions were performed in Buchi Type I high-pressure reactor at different temperatures (0–80 °C). Initially the autoclave was heated to 100 °C with a constant temperature circulation bath for an hour under argon atmosphere. Subsequently, 100 mL of dry toluene/chlorobenzene was transferred into the reactor via a long double tipped needle under argon atmosphere. The autoclave was then cooled to the required temperature under ethylene atmosphere at the required pressure. During the polymerization runs, the ethylene pressure was kept constant using a pressure controller, as the pre-mixed precatalyst and cocatalyst were transferred into the autoclave and stirred for required time. At the end of the reaction time, the polymerization was quenched by the addition of 5 mL of acidified methanol and the obtained polymer was washed with excess of methanol and dried in vacuum at 80 °C for 10 h. The ethylene concentration in the reactor was calculated using Henry-Gesetz equation [24].

2.3. Polymerization of norbornene

Chlorobenzene or toluene (25 mL) was taken in a 100 mL flame-dried round bottom flask. Into this prescribed amount of precatalyst and MAO was added and stirred for 10 min. To this a stock solution of NB in chlorobenzene containing 2.0 g of NB was injected. The reaction mixture was stirred for the required time at the end of which was quenched by pouring this viscous mass into 100 mL of acidified methanol. The precipitated polymer was filtered, washed with methanol and dried in vacuum at 80 °C for 5 h.

2.4. Ethylene/norbornene copolymerization

The autoclave was pre-equilibrated with ethylene atmosphere at the required temperature as mentioned earlier. Prescribed amount of NB was added to the reactor, while keeping the ethylene pressure constant during copolymerization. Polymerization was commenced by introducing the precatalyst and the cocatalyst via syringe. The reaction temperature, pressure and ethylene flow rate were monitored and recorded through Buchi data acquisition system. The polymerization was terminated after a prescribed time by the addition of 5 mL of methanol. The resulting reaction mixture was poured into a stirring solution of acidified methanol (500 mL), the polymer was collected by filtration, washed with methanol

(100 mL × 3) and dried in vacuum at 80 °C until the weight remained constant.

3. Results and discussion

3.1. Homopolymerization of ethylene

Ethylene polymerization reactions were carried out employing precatalysts **1−3ATiCl$_2$** with MAO as cocatalyst against temperature, ethylene pressure, Al/Ti ratio and solvent. Results are shown in Table 1. For attaining optimal catalyst activity we have checked the ethylene polymerization with precatalysts **1−3ATiCl$_2$** at different Al/Ti molar ratios ranging from 100 to 500. At Al/Ti ratio of 300 these precatalysts showed better activity. On the Gibson scale these precatalysts have ‘‘moderate activity’’ for ethylene polymerization [25].

3.1.1. Effect of temperature

Ethylene polymerization reactions were carried out at different temperatures ranging from 5 to 80 °C in two different solvents namely toluene and chlorobenzene at Al/Ti ratio 300. At 5 °C precatalysts **2ATiCl$_2$** and **3ATiCl$_2$** did not show any activity. As the polymerization temperature increased catalyst activity of the three systems towards ethylene polymerization also increased (Fig. 1). This may be due to spontaneous alkylation of the titanium species at moderately high temperatures while it is probably difficult to activate the complex at low temperatures. When we lowered the polymerization temperature to rt and lower, after initiating at 50 °C, polymerization was found to occur with decrease in the activity. At 70 °C maximum yield of polyethylene (PE) and high activity of catalysts were observed. Further increase in temperature (from 70 °C) resulted in decreased activity and this may be due to thermal instability of the active species at higher temperatures. The decrease in activity at 80 °C was especially more for **3ATiCl$_2$** compared with other two systems, indicative of its lower thermal stability compared with other two precatalysts.

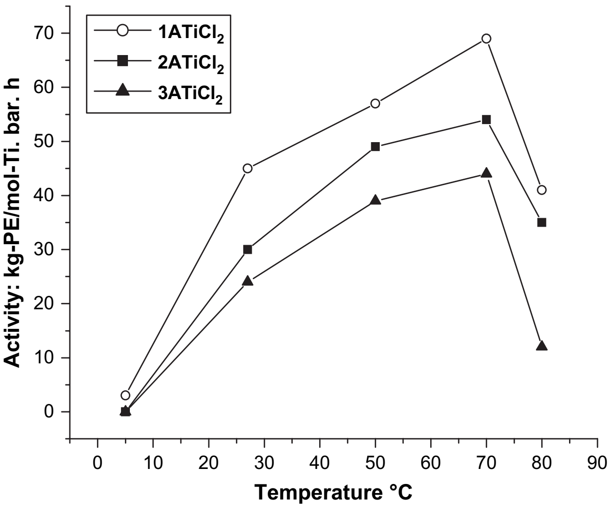


Fig. 1. Temperature vs activity of three different catalyst systems for ethylene polymerization at 2 bar ethylene pressure in chlorobenzene solvent.

3.1.2. Effect of solvent

To understand the effect of solvent on the catalyst activity towards ethylene polymerization, two different solvents (toluene and chlorobenzene) were chosen as reaction medium with **1−3ATiCl$_2$**/MAO catalyst systems while varying the ethylene pressures and polymerization temperatures (Table 1). At different ethylene pressures and polymerization temperatures the catalyst showed higher activity in chlorobenzene than in toluene (Fig. 2). The lower activity in toluene may be due to the

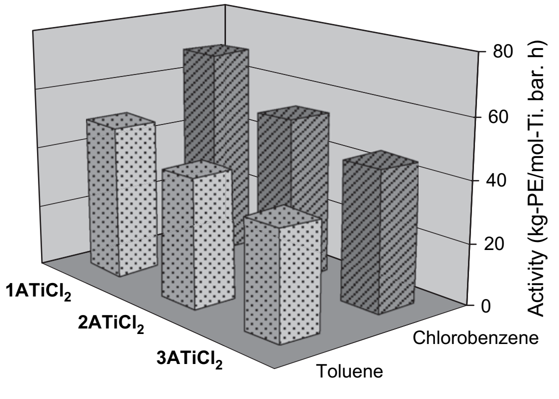


Fig. 2. Activities of **1−3ATiCl$_2$**/MAO catalyst systems towards ethylene polymerization in two different solvents at 70 °C with 2 bar ethylene pressure.

Table 1
Catalyst activities for ethylene polymerization in two different solvents using **1−3ATiCl$_2$**/MAO catalyst systems[a]

S.No	Temperature (°C)	Ethylene pressure (atm)	Activity of **1ATiCl$_2$**[b]		Activity of **2ATiCl$_2$**[b]		Activity of **3ATiCl$_2$**[b]	
			Toluene	Chlorobenzene	Toluene	Chlorobenzene	Toluene	Chlorobenzene
1	5	2	2.5	3	0	0	0	0
2	27	2	40	45	23	30	19	24
3	50	2	50	57	42	49	34	39
4	70	2	65	69	49	54	38	44
5	80	2	35	41	28	35	10	12
6	70	0.5	49	53	16	27	10	22
7	70	1	53	59	27	31	19	29
8	70	1.5	59	62	38	46	25	38
9	70	2	65	69	49	54	38	44
10	70	3	72	78	56	59	45	48

[a] Polymerization conditions: precatalyst = 50 μmol, Al/Ti ratio = 300, solvent = 100 mL toluene/chlorobenzene, polymerization time = 30 min.
[b] Activity = kg-PE/mol-Ti · bar · h.

competitive binding of toluene with metal cationic active species [26]. Also due to the increased polarity of chlorobenzene, charge separation between the cationic metal center and the bulky anion is more favoured. Hence the coordination of the monomer to the metal center is easier, showing increased activity [27].

3.1.3. Microstructure of polyethylene

The polyethylene obtained had good solubility in *o*-dichlorobenzene, 1,2,4-trichlorobenzene at high temperatures (>100 °C). The ^{13}C NMR spectrum (solution and solid) of the PE showed a prominent peak at around 29 ppm (Fig. 3) but no other signals due to branching carbons. The melting and cooling isotherms of the PE samples were obtained by DSC. The samples were first heated rapidly at 30 °C/min from 50 to 200 °C, allowed to cool and the second heating was done at 10 °C/min in the above range. The melting points of the PE sample varied from 131 to 141 °C. The values obtained for all PE samples were indicative of high-density polymers.

3.2. Homopolymerization of norbornene

Precatalysts **1ATiCl$_2$** and **3ATiCl$_2$** on activation with MAO showed moderate activity towards NB homopolymerization (Scheme 2). When Al/Ti ratio is 200 these precatalysts showed maximum activity. NB polymerization was carried out with **1ATiCl$_2$** and **3ATiCl$_2$** at four different temperatures (0, 27, 40 and 50 °C) and at Al/Ti ratio of 200 in toluene. At 0 °C both the catalysts do not show any activity towards NB polymerization. Catalyst activities increased with temperature (Table 2). For **3ATiCl$_2$** precatalyst the activity increased tenfold, when the reaction temperature was increased from 27 to 50 °C.

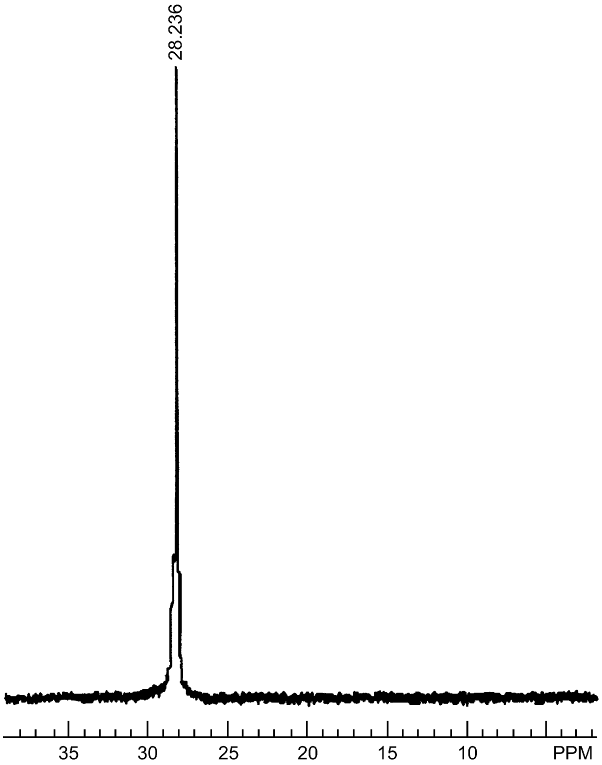
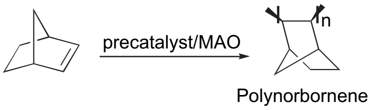


Fig. 3. ^{13}C NMR spectrum of PE obtained with **1ATiCl$_2$**/MAO.



Scheme 2. Homopolymerization of norbornene.

Table 2
Norbornene polymerization at different temperatures[a]

S.No	Temperature (°C)	Activity[b]	
		3ATiCl$_2$	**1ATiCl$_2$**
1	0	–	–
2	27	0.4	14.5
3	40	4.2	25.0
4	50	4.5	26.0

[a] Polymerization conditions: norbornene = 2 g, precatalyst = 50 μmol, Al/Ti ratio = 200, polymerization time = 12 h, solvent = 50 mL toluene.

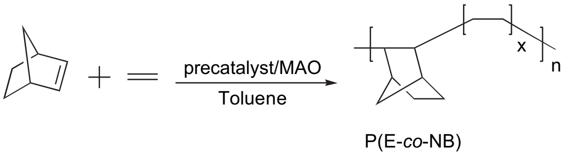
[b] Activity = kg-PNB/mol-Ti·h.

The obtained polynorbornene (PNB) is a white amorphous solid with poor solubility in common organic solvents that precluded its molecular weight determination by GPC. However, the ^{1}H NMR spectrum of the homopolymers at 120 °C in 1,2,4-trichlorobenzene indicated that only vinyl addition had occurred without any ROMP side reactions. The DSC profile of PNB obtained with these precatalysts does not show any evidence for melting endotherm indicative of its amorphous nature.

3.3. Ethylene/norbornene copolymerization

Ethylene/norbornene copolymerization reactions were carried out with precatalysts **1ATiCl$_2$** and **3ATiCl$_2$** using MAO as cocatalyst (Scheme 3) over several feed ratios at 50 °C and the results are shown in Table 3. The reaction times were varied to keep the conversion below 5%. The amount of NB incorporated into the copolymer was calculated from ^{13}C NMR spectra.

Even at lower NB feed concentrations these systems showed better NB incorporation in the copolymer. For **1ATiCl$_2$** precatalyst, as [E]/[NB] feed ratio decreased, NB incorporation in the copolymer increased up to a feed value of 0.068 then reached a plateau value of about 36 mol% NB (Table 3,



Scheme 3. Ethylene/norbornene copolymerization.

Table 3
Ethylene/norbornene copolymerization with **1ATiCl$_2$**/MAO and **3ATiCl$_2$**/MAO catalyst systems[a]

Run	[E][b] (mol/L)	[NB] (mol/L)	$[E]/[NB]_{feed}$	T_g[c] (°C)		NB content[d] (mol%)	
				1ATiCl$_2$	**3ATiCl$_2$**	**1ATiCl$_2$**	**3ATiCl$_2$**
1	0.04	0.14	0.335	31	76	16.5	27
2	0.09	0.14	0.642	20	–	14	25
3	0.14	0.14	1.000	9.9	57	11	22
4	0.19	0.06	3.166	–	40	5.5	18
5	0.09	0.28	0.321	37	–	17.8	–
6	0.04	0.28	0.142	48	92	20	35
7	0.04	0.43	0.093	75	–	28	38
8	0.04	0.58	0.068	95	114	36	43

[a] Reaction conditions: catalyst 50 μmol, Al/Ti ratio = 200, solvent = 100 mL toluene, temperature 50 °C; polymerization periods have been varied to keep NB conversion below 5%.

[b] Ethylene concentrations in toluene were calculated according to Henry-Gesetz expression.

[c] By DSC.

[d] By ^{13}C NMR.

run 8). But the **3ATiCl$_2$** precatalyst showed better NB incorporation (43 mol%) at 0.068 [E]/[NB] feed ratio (Table 3, run 8).

Although **3ATiCl$_2$**/MAO displayed lower activity for the polymerization, it produced the copolymer with higher NB incorporation. We speculate that, this may be due to sterically less demanding ligand in **3ATiCl$_2$** catalyst. Generally, the degree of incorporation of NB depends on the catalyst activity and in general, catalysts that incorporate NB well are less active [11].

The DSC traces of copolymers prepared with these two catalysts do not show any evidence of melting endotherms. The T_g values of copolymers prepared from the precatalyst **1ATiCl$_2$** vary from 10 to 95 °C. The copolymer with 14 mol% NB had T_g of 20 °C and it increased to 95 °C when the NB content in the copolymer increased to 36 mol%. Fig. 4 shows T_g as a function of molar percent of NB in the copolymer prepared from **1ATiCl$_2$**/MAO at different [E]/[NB] feed ratios. As the NB incorporation increases in the copolymers, T_g values also increased as expected. A linear relationship between NB content (mol%) and T_g (°C) of the copolymers is an indicative of alternative nature of the copolymer. Copolymers prepared from **3ATiCl$_2$**/MAO also followed the same trend. Generally, deviation from the linear correlation is due to the presence of branches in the methylene chain as well as NB blocks [28,29].

3.3.1. Reactivity ratios

Ethylene/norbornene reactivity ratios (r_E and r_N) for the precatalysts **1ATiCl$_2$** and **3ATiCl$_2$** were calculated using Fineman–Ross method [30]. Fineman–Ross plots for **1ATiCl$_2$** and **3ATiCl$_2$** are shown in Fig. 5. The r_N values were found to be very less and approach zero indicating that these catalysts do not encourage NB homopropagation. Precatalyst **1ATiCl$_2$** with bulky isopropyl group in the *ortho* position of the aniline moiety in the ligand, has a greater r_E value of 4.9 compared to 2.4 for **3ATiCl$_2$** precatalyst, having methyl groups in the *ortho* position. This may be due to nonbonding

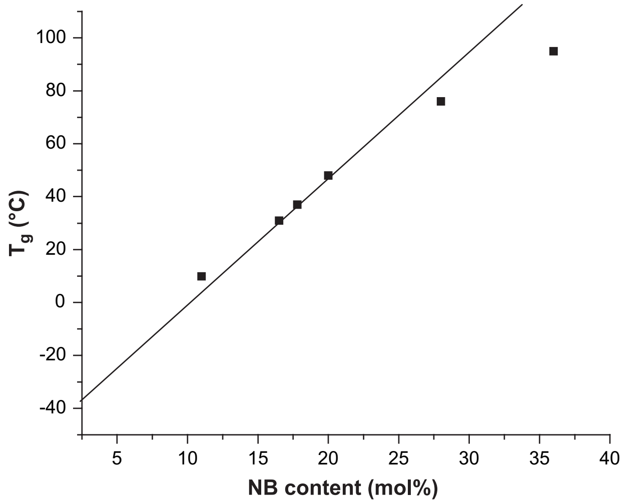


Fig. 4. Plot of T_g vs NB content in P(E-*co*-NB) prepared from **1ATiCl$_2$**/MAO at different [E]/[NB] feed ratios.

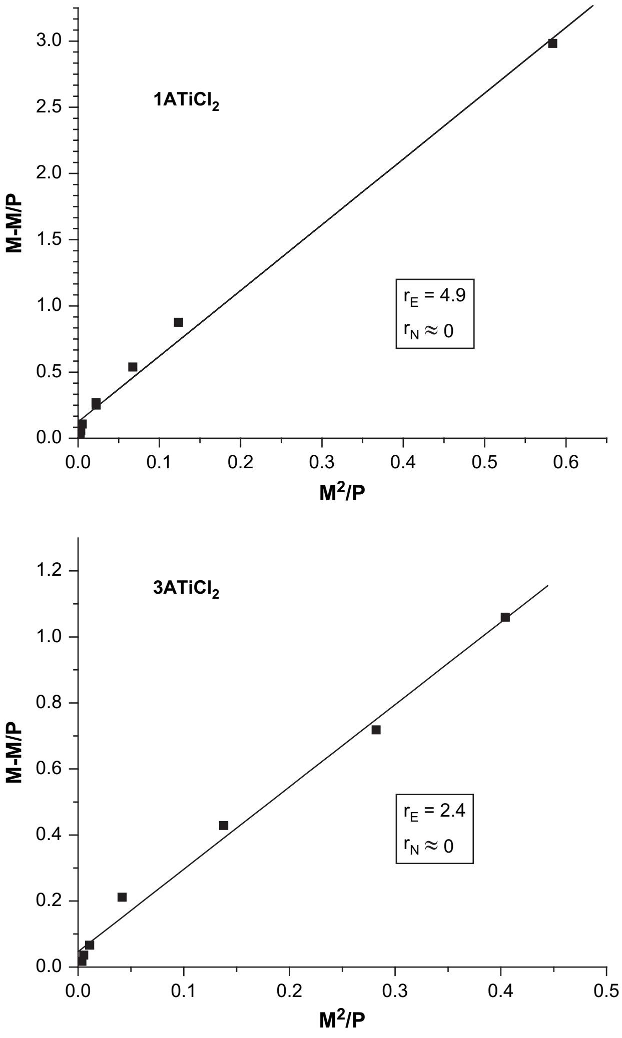


Fig. 5. Fineman–Ross plot for P(E-*co*-NB) with **1ATiCl$_2$** and **3ATiCl$_2$**.

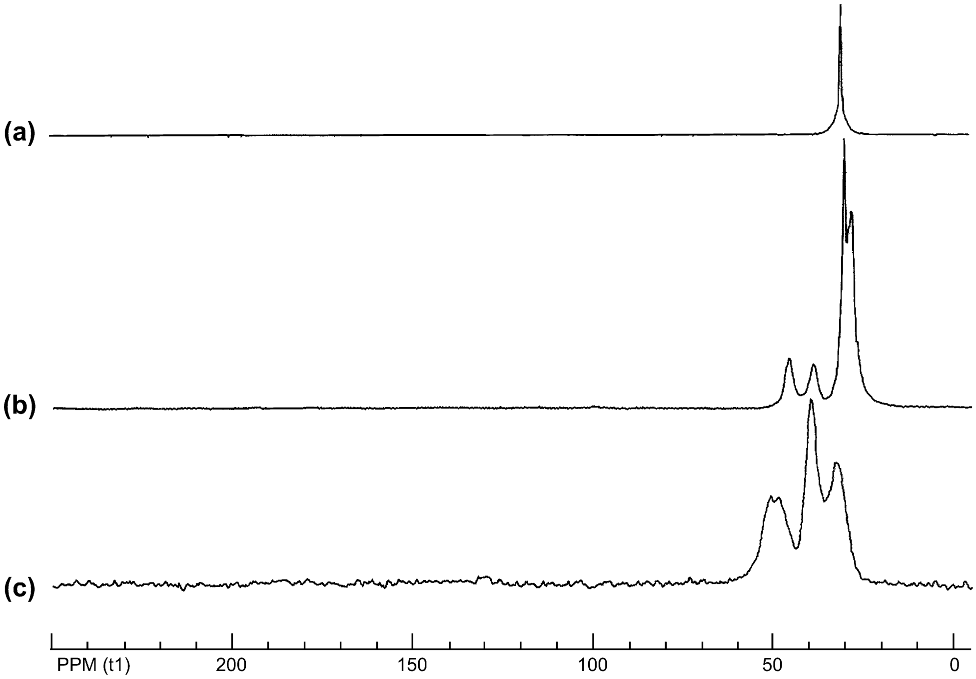


Fig. 6. ^{13}C CPMAS NMR stack spectra of (a) PE, (b) P(E-*co*-NB) and (c) PNB obtained with **3ATiCl$_2$**/MAO.

interaction between the ligand and the large cyclic olefin (NB). The product of reactivity ratios for both the catalysts is very low indicative of alternative copolymerization.

3.3.2. Microstructure analysis of P(E-co-NB)

The copolymer microstructure was analyzed by DSC, TGA and ^{13}C NMR (solution and solid state) spectroscopic techniques. The polymers obtained are insoluble in common organic solvents but they are freely soluble in 1,2,4-trichlorobenzene at higher temperatures (>100 °C). Fig. 6 shows the ^{13}C CPMAS NMR stack spectra of PE, PNB and P(E-*co*-NB) prepared from **3ATiCl$_2$**/MAO. Since PE is crystalline in nature it gave sharp peaks in the ^{13}C CPMAS NMR, whereas PNB gave broad signals due to its amorphous nature. The formation of copolymer can be clearly seen from ^{13}C CPMAS NMR with sharp signals indicative of the presence of a copolymer and not a mixture of homopolymers.

The carbon NMR spectra of the copolymer samples were recorded with short pulse angle and long relaxation delay at 120 °C. Peak assignments were performed based on a comparison of the observed chemical shifts with the literature data [31]. The amount of NB incorporated into the copolymer can be calculated from ^{13}C NMR using Eq. (1).

$$\%\mathrm{NB} = \frac{100(I_{\mathrm{C2,3}} + I_{\mathrm{C1,4}})}{2(I_{\mathrm{C5,6}} + I_{\mathrm{E}})} \qquad (1)$$

The ^{13}C NMR spectrum of the alternating P(E-*co*-NB)s is less complex which is caused by the absence of NB microblocks and the high symmetry of the NB-E-NB-E-NB and E-NB-E-NB-E pentads. In the case of a perfectly alternating structure only five resonances are expected. The five major signals correspond to the perfectly alternating sequence (E-NB-E-NB-E) while carbons of alternating units adjacent to different sequences (NB-E-NB-NB, NB-E-NB-E-E) give rise to slightly shifted signals [21]. The reason for the complexity of the NMR spectra includes different monomer sequences, varying lengths of the NB microblocks, *meso* or *racemic* connection of the NB units, and pentad sensitivity.

Fig. 7 shows the ^{13}C NMR spectrum of the copolymer prepared with **1ATiCl$_2$**/MAO presenting alternating *meso* and *racemic* NB-E-NB sequences, with predominantly *meso* signals. The signals of the carbon atoms of a *racemic* alternating NB-E-NB sequence are characterized by an upfield shift with respect to those of a *meso* alternating sequence [21]. For instance, C2 and C3 carbons in *racemic* NB-E-NB sequence resonates at 48.25 ppm and those of the *meso* NB-E-NB sequence and that of the isolated C2 and C3 carbons of NB adjacent to ethylene blocks, resonated at an upfield 47.52 ppm [4,17]. The ratio of the peaks at 48.25 and 47.54 ppm is constant, 1:5.5 and 1:3 for the copolymers with different NB content prepared from precatalysts **1ATiCl$_2$** and **3ATiCl$_2$**, respectively. As a specific example, the ^{13}C NMR of a homomixture of PE and PNB (Fig. 8) is very much complicated with featureless signals and is entirely different from that of the five major peaks seen in the spectra of the copolymers (Figs. 7 and 9) prepared from these precatalysts. NMR and thermal analyses suggest that there is no homopolymer (PE or PB) in the copolymer systems.

Furthermore, the presence of NB blocks can be excluded owing to the absence of resonances ranging below 29.9 ppm and between 35 and 41 ppm, which are characteristic of NB dimers and trimers. The microstructure of the resulting P(E-*co*-NB) reveals that it does not have NB blocks in the copolymer.

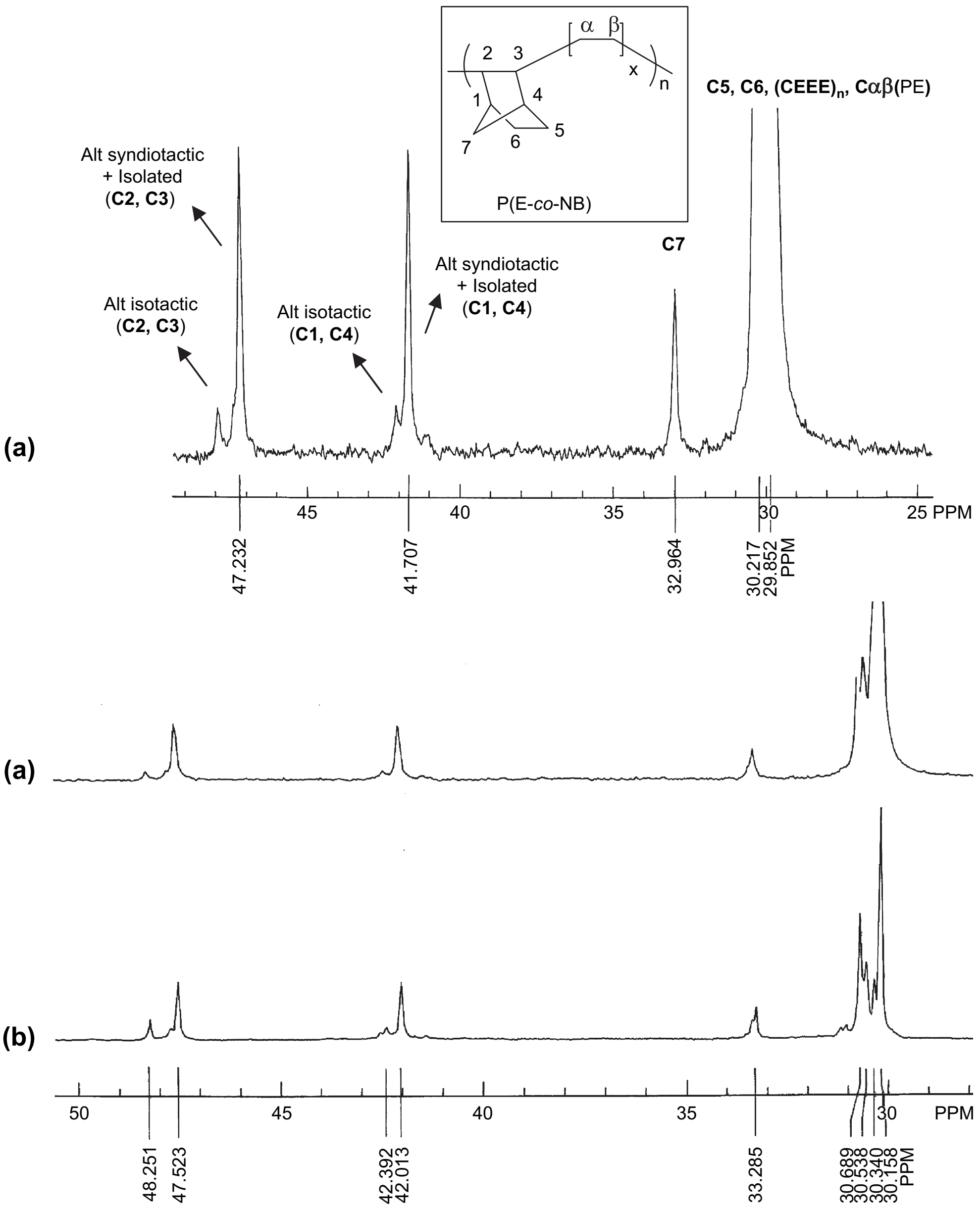


Fig. 7. ^{13}C NMR spectra of P(E-*co*-NB) with (a) 5.5% and (b) 20% NB mole ratio synthesized using **1ATiCl$_2$**/MAO.

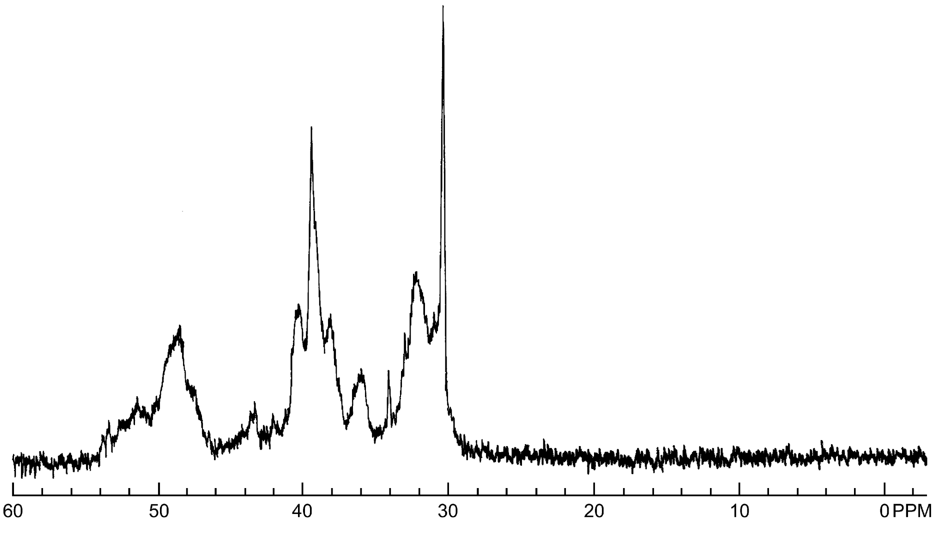


Fig. 8. ^{13} C NMR spectrum of a homomixture of PE and PNB prepared from **1ATiCl$_2$**/MAO.

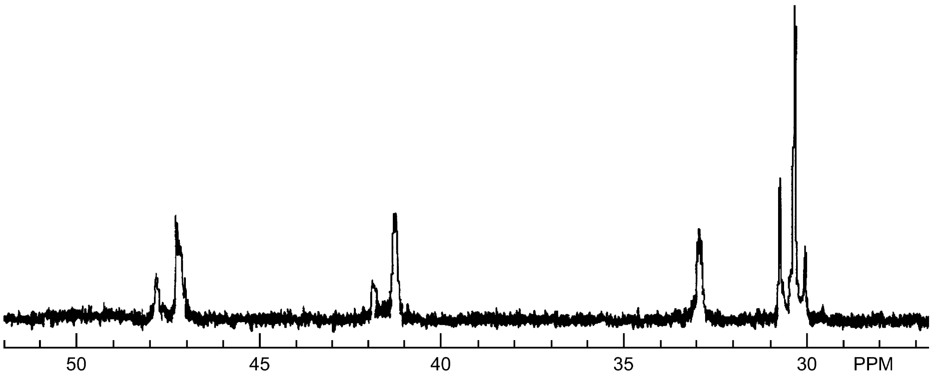


Fig. 9. ^{13}C NMR spectra of P(E-*co*-NB) with 43% NBE mole ratio synthesized using **3ATiCl$_2$**/MAO.

4. Conclusion

On the basis of the obtained results, it could be concluded that the copolymers generated with precatalysts **1ATiCl$_2$** and **3ATiCl$_2$** are alternating copolymers with ethylene blocks. Results have shown that the NB content in P(E-*co*-NB) depends on the feed ratio. Higher norbornene incorporation was obtained with **3ATiCl$_2$**, which is a more "open" catalyst system. The r_N values for precatalysts **1ATiCl$_2$** and **3ATiCl$_2$** were found to be very less and approach zero indicating that these catalysts do not encourage NB homopropagation.

Acknowledgements

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