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ORIGINAL PAPER

Copolymerization of ethylene and norbornene by zirconium complexes containing symmetrically tuned trianionic ligands

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Abstract Homo and copolymerization of ethylene and cyclic olefins were carried out using C_3 symmetric $N[CH_2CH(Ph)O]_3ZrCl$ (**1**-ZrCl) and also pseudo-C_s symmetric $N[CH_2CH(Ph)O]_3ZrCl$ (**2**-ZrCl) catalyst systems upon activation with MAO. Incorporation of comonomer into the polyethylene back bone was mainly governed by catalyst symmetry. Norbornene (NB) incorporation was as high as 40% in the ethylene–norbornene copolymer (ENC) using C_3 symmetric **1**-ZrCl/MAO catalyst system and 25% in the case of the pseudo-C_s symmetric analogue **2**-ZrCl. Unlike the more efficient titanium analogues, the copolymerization of ethylene and NB showed a marginal decrease in catalyst activity and NB incorporation on switching over to the Zr analogues. The aluminum to metal ratio required for catalyst activation was higher for the Zr catalysts compared to that of its Ti analogues. ^{13}C NMR spectral studies on the copolymer clearly indicated the incorporation of NB in an alternating manner.

Keywords Non-metallocene · Copolymerization · Cyclic olefin · Ethylene–norbornene copolymer · Zirconium

Introduction

In recent years, selected metallocene and non-metallocene complexes have been effectively used for the homopolymerization of ethylene and copolymerization of ethylene with a variety of α-olefins and cyclic olefins [1–4]. Some of the non-metallocene catalysts have been found to polymerize ethylene and higher α-olefins

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in a living manner. The anionic donor ligands whose environment can be tuned by simple modifications have drawn much attention because of their ability to tune the steric and electronic environment around the metal center and thus make the metal active and adoptive for comonomer insertion [5–12].

Homopolymers and copolymers of strained cyclic olefins such as norbornene (NB) constitute an important class of materials because of their high glass transition temperature and improved heat resistance in comparison to polyethylene [13]. Their high temperature resistance makes them suitable for making molded articles having utility in thermally stressed applications. The metallocene- and non-metallocene-based transition metal complexes are able to polymerize cyclic olefins in a vinyl addition pathway in quantitative yields [14–18]. Processing of homopolymers constituting cyclic olefins is not easy because they do not exhibit sharp melt characteristics like other thermoplastic materials. Hence the use of such polymers is very limited. In contrast, the copolymers of cyclic olefins with ethylene exhibit sharp melt characteristics like any other thermoplastic material and hence find application in optoelectronic devices [13].

Cyclic olefin copolymers are important engineering polymers, which can be prepared by copolymerization of cyclic olefins such as NB with ethylene or α-olefins using various metallocene and non-metallocene catalysts [17–35]. The catalyst structure determines the microstructure of the copolymers which are mainly isolated, alternating monomer sequences or short monomer blocks [20–23]. 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 stereo-regularity, which are in turn dependent on the structure of the catalysts. If these copolymers contain more than 15 mol% of cyclic olefin then they are amorphous in nature with high mechanical strength, glass transition temperature (T_g) and are stable toward common solvents. Not only the ligand environment but also the type of metal used in the system plays a major role in the catalyst activity. For example, Kol and coworkers [36] prepared C_2 symmetric Ti and Zr complexes using diamine bis(phenolate) ligands and used for 1-hexene polymerization. They observed low molecular weight atactic polymer in case of Zr-based catalyst and when they replaced Zr with Ti, ultra-high molecular weight isotactic polyhexene was observed. In the same line, Fujita and coworkers [37] reported that Ti-based FI catalyst produced ultra-high molecular weight atactic polypropylene (PP), whereas its Zr and Hf analogues gave high molecular weight isotactic PP via site-control mechanism.

We have already reported that C_3 symmetric $N[CH_2CH(Ph)O]_3TiCl$ and/or pseudo-C_s symmetric $N[CH_2CH(Ph)O]_3TiCl$ upon activation with MAO was able to homopolymerize ethylene, α-olefins, cyclic olefins in a controlled manner [38–40]. The catalyst symmetry had a greater influence over the obtained polymer characteristics. This is true in the case of ethylene and NB copolymerization, where in the catalyst symmetry had a good dependency over the percentage of NB incorporated. The % NB incorporation in ethylene–NB copolymerization is 42 and 33% for C_3 and pseudo-C_s symmetric aminotriolate-based titanium catalysts, respectively [41]. As an extension it was proposed to study the effect of the C_3 and pseudo-C_s symmetric zirconium analogues for the homo- and copolymerization of NB with ethylene.

Experimental section

General considerations

Precatalyst preparation and polymerization reactions were carried out under dry and oxygen free nitrogen atmosphere. Transfers were performed in nitrogen-filled glove bag or by standard syringe addition techniques. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using BRUKER 400 MHz spectrometer. ^{13}C NMR of the polymer samples were recorded under quantitative conditions with pulse angle 25°, pulse width 1.3 μs, acquisition time = 1 s, relaxation time = 10 s, and number of scans = 3000 at 130 °C in 1,2,4-trichlorobenzene. DSC of polymer samples was recorded in Perkin-Elmer thermal analysis instrument. MAO was purchased as 10% by weight solution (in toluene) from Witco GmbH, Germany and was used after estimating the aluminum content. NB, cyclopentene (CPE), and cyclooctene (COE) were purchased from Merck-Schuchardt and were used as such.

Preparation of the precatalyst

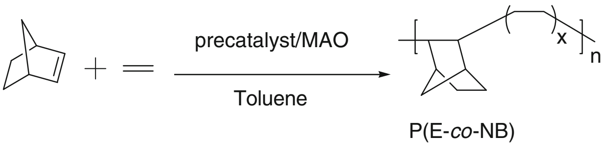
Precatalysts **1**-ZrCl and **2**-ZrCl were prepared as per reported literature procedure [40].

Homopolymerization of cyclic olefins

To a 50 mL flame dried Schlenk flask equipped with Teflon coated magnetic stirrer was added 15 mL of dry toluene, 10 mg precatalyst, and the required amount of monomer (3 g of NB or 2 mL for CPE or 2 mL COE) under inert conditions. Polymerization was started by adding required amount of MAO to the above reaction mixture maintaining the required temperature and agitation speed. The reaction was stopped after appropriate time by quenching with acidic methanol.

Polymerization of ethylene

Ethylene polymerization reactions were performed in Buchi Type I high-pressure reactor equipped with BDS (Buchi Database System). Initially the autoclave was heated to 120 °C with a constant temperature circulation bath for an hour under nitrogen atmosphere. 200 mL of dry toluene was transferred to the reactor via a double tipped needle under nitrogen atmosphere. The autoclave was cooled to the required temperature under ethylene atmosphere at required pressure. Required amount of catalyst and cocatalyst were mixed in toluene (50 mL) in a separate flask and the contents were stirred for 15 min and transferred into the autoclave. This was stirred for required period while feeding the reactor with ethylene gas at the end of which the monomer supply was stopped and the reaction mixture quenched with



Scheme 1 Ethylene/norbornene copolymerization

300 mL of acidic methanol. The polymer obtained was washed with methanol and dried in vacuum.

Copolymerization of ethylene and NB

The autoclave was preequilibrated 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. Required amount of preactivated catalyst solution (precatalyst and cocatalyst were mixed in toluene (50 mL) in a separate flask and the contents were stirred for 15 min) was transferred into the autoclave to initiate the polymerization (Scheme 1). The reaction temperature, pressure, and ethylene flow rate were monitored and recorded through Buchi data acquisition system. Reaction times were kept low in order to keep the NB conversion below 10%. The reactions were quenched with acidic methanol and the polymers obtained were washed with methanol and dried in vacuum.

Calculation of percentage of NB incorporated in ENC

From the ^{13}C NMR spectra of ethylene–norbornene copolymer (ENC), the percentage of NB incorporated was calculated using Eq. 1. Peak assignments were performed based on a comparison of the observed chemical shifts with the literature data [20–23, 41].

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

Results and discussion

The aminotriolate-based zirconium chloride precatalysts (C_3-symmetric **1**-ZrCl and pseudo-C_s-symmetric **2**-ZrCl) were prepared from corresponding tri-sodium salt of aminotriol by reacting it with $ZrCl_4$ in ether as per our earlier reports (Fig. 1) [38–41]. These catalysts upon activation with MAO were able to polymerize 1-hexene in moderate yields [38–40]. These catalysts were found to be less active toward homopolymerization of cyclic olefins compared to that of the titanium analogues [41]. The polymerization reactions were carried out at different Al/Zr ratios and the results are shown in Table 1. Among cyclic olefins, homopolymerization NB got converted to polynorbornene (PNB) in quantitative yields. The other

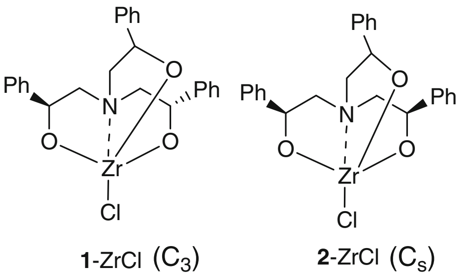


Fig. 1 Catalysts used for this study

Table 1 Homopolymerization of cyclic olefins

Monomer	Al/Zr	**1**-ZrCl		**2**-ZrCl	
		Yield (g)	Activity[a]	Yield (g)	Activity[a]
NB	100	0.915	45.7	1.02	51.0
NB	250	2.814	140.7	2.71	165.5
NB	400	0.735	36.7	0.81	40.5
CPE	250	0.210	10.5	0.18	9.0
COE	250	0.180	9.0	0.12	6.0

Reaction conditions: catalyst = 0.02 mmol, cocatalyst = MAO in toluene, solvent = 15 mL toluene, monomer = 3 g of NB/2 mL of cyclopentene/2 mL of cyclooctene, polymerization temperature = 30 °C, polymerization time = 12 h

[a] Activity in kg of polymer/mol catalyst/h

cyclic monomers namely CPE and COE also gave satisfying results (Table 1). The obtained PNB has poor solubility in common organic solvents that preclude molecular weight determination by GPC. However, the ^{1}H-NMR spectrum of the homopolymers at 100 °C in 1,2,4-trichlorobenzene indicated that only vinyl addition had occurred without any ROMP side reactions.

Polymerization of ethylene was carried out under varying conditions of pressure and temperature and the results are shown in Table 2. The catalyst activity had a direct bearing on the ethylene pressure. The trend observed was as expected since the concentration of the monomer in the reaction increases with increasing pressure. Polymerization carried out at different temperatures namely 0, 30, 45, and 60 °C gave comparable yield revealing the thermal stability of the catalytic species (Table 2). In all these reactions, the active species was generated separately and added to the reactor maintained at the desired temperature. The increase in activity at lower temperature (0 °C) could be due to relative increase in solubility of the ethylene at lower temperatures.

The polyethylene (PE) samples were subjected to DSC studies and the melting points were observed to be in the range of 130–135 °C indicating the formation of high density polyethylene (HDPE). The ^{13}C NMR of the PE showed only one peak at 28 ppm confirming the absence of any branches in the polymer produced.

Table 2 Ethylene polymerization at different temperature and pressure

Catalyst	T (°C)	PC_2 (bar)	Yield (g)	Activity[a]	M_η[b] ($\times 10^{-4}$)
1-ZrCl	30	1	0.21	10.5	98
	30	2	0.50	25.0	–
	30	2.5	1.10	55.0	–
	30	3	2.0	100.0	–
	0	2	0.64	32.5	92
	45	2	0.45	22.0	79
	60	2	0.38	19.2	70
2-ZrCl	30	1	0.32	16.5	72
	30	2	0.64	32.2	–
	30	2.5	1.2	60.1	–
	30	3	2.4	120.0	–

Reaction conditions: catalyst = 0.02 mmol, Al/Zr = 400, polymerization time 1 h

[a] Activity in kg of PE/mol catalyst/h

[b] Viscosity-based molecular weight at 135 °C using decaline as a solvent

Copolymerization of ethylene with NB

We have already established that **1**-TiCl and **2**-TiCl exhibited good catalytic activity in the presence of MAO, for the copolymerization of ethylene/NB. The amount of NB incorporated was calculated from the ^{13}C NMR spectra of the copolymer. In the case of precatalyst **1**-TiCl, in 10 min the percentage of NB incorporated in the copolymer is about 42% and with time the percentage of NB content in the copolymer decreased. In the case of precatalyst **2**-TiCl, in 10 min the amount of NB incorporated was 33% [41]. We have previously observed such a role in symmetry of the catalysts which influences the stereo-regularity of the polymers obtained in 1-hexene polymerization [38–40]. Here in we have extended our studies with the Zr analogues for the copolymerization of ethylene and NB. Since NB was fed with specified quantity and ethylene with continuous flow, in order to keep the monomer feed ratio constant and the conversions below 10%, the polymerization reactions were quenched in short periods. The resultant copolymers were analyzed by the standard techniques.

As seen from the Table 3, **1**-ZrCl showed an activity of 260 kg of polymer/mol of catalyst/h as compared to 360 kg of polymer/mol of catalyst/h for **1**-TiCl. Similarly the pseudo-C_s analogue **2**-ZrCl also showed less activity compared to that of **2**-TiCl clearly indicating the decrease in activity when we changed the metal from Ti to Zr in the precatalyst.

In the case of precatalyst **1**-ZrCl, in 15 min the percentage of NB incorporated in the copolymer is about 40% and with time the percentage of NB content in the copolymer decreased. The copolymer obtained after 20 min contained 34% of NB units. In the case of precatalyst **2**-ZrCl, in 15 min the amount of NB incorporated was 25% (Fig. 2). Although both the catalysts differs only by symmetric environment and not by electronic environment the difference in % NB incorporation clearly indicates

Table 3 Ethylene/NB copolymerization

Catalyst	Time (min)	Yield (g)	NB[a] (mol/L)	Activity[b]	% NB[c] (mol%)	NB conversion	T_g[d] (°C)
1-ZrCl	15	0.60	5.0	260	40.0	12.3	98
	15	0.50	2.5	210	16.0	4.1	29
	15	0.32	1.0	165	04.5	0.7	nd
	20	0.60	5.0	282	34.0	10.4	92
2-ZrCl	15	0.71	5.0	295	25.0	9.1	76
	15	0.65	2.5	262	15.0	4.5	nd
	15	0.56	1.0	244	04.0	1.1	nd
	20	0.71	5.0	309	22.0	8.0	59

Reaction conditions: catalyst = 0.02 mmol, Al/Zr = 400, polymerization temperature 30 °C, ethylene 2 bar

nd not determined

[a] NBE concentration charged (mol/L)

[b] Activity in kg of PE/mol catalyst/h

[c] Determined from ^{13}C NMR spectra

[d] Determined from DSC analysis

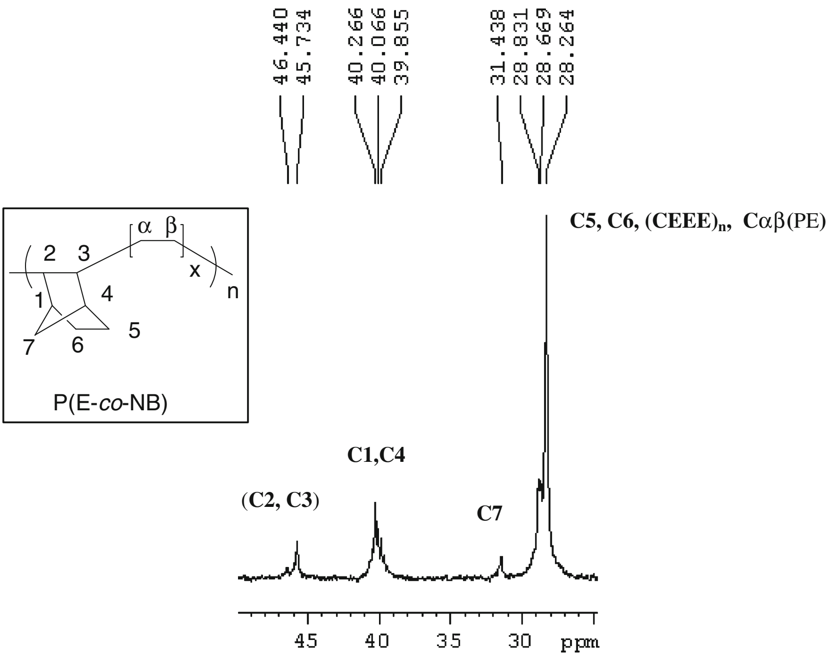


Fig. 2 ^{13}C NMR spectra of ethylene norbornene copolymer with 16% NB mole ratio, synthesized using **1**-ZrCl/MAO

the effect of steric environment provided by the symmetry of the catalysts does dictates the amount of NB incorporation in the copolymer obtained. In the case of C_3-symmetric **1**-ZrCl upon activation with MAO one of the alkoxo arms got cleaved and produces pseudo-C_2 symmetric species as proposed by us for 1-hexene polymerization [39] and by Nomura et al. [30] for ethylene polymerization. In pseudo-C_s symmetric **2**-ZrCl, detaching one arm from the metal center by MAO can create two different species in different propositions namely pseudo-C_2 and pseudo-C_s symmetric catalysts. Hence the percentage of NB incorporation in the case of **2**-ZrCl depended on the performance of both the catalyst species. C_2-symmetric species formed from **1**-ZrCl showed higher incorporation of NB whereas the catalyst species produced from **2**-ZrCl showed comparatively less NB incorporation suggesting the pseudo-C_s species produced from **2**-ZrCl is responsible for bringing down the percentage of NB incorporation. Hence it is clear that symmetric environment around the metal center in these types of catalysts is highly desirable for uniform and higher NB incorporation. Thermal analyses and ^{13}C NMR studies suggest that there is no homopolymer (PE or PNB) in copolymer produced. ^{13}C NMR spectra of ENCs prepared from these catalyst systems are less complex and a representative ^{13}C NMR spectrum is shown in Fig. 2. In ^{13}C NMR spectra, absence of signals below 29.9 ppm and between 35 and 41 ppm (which are characteristic of NB dimers and trimers) confirms the absence of NB micro-blocks and the less complex nature of these spectra suggests an alternating copolymers. We have calculated the glass transition temperature (T_g) for these copolymers using DSC analysis. As the NB content in the copolymer increased, an increase in T_g was observed (Table 3). For instance, the T_g value of copolymer increased from 29 to 98 °C when the NB content was increased from 16 to 40 mol%. Figure 3 shows the DSC trace of ethylene NB copolymer with

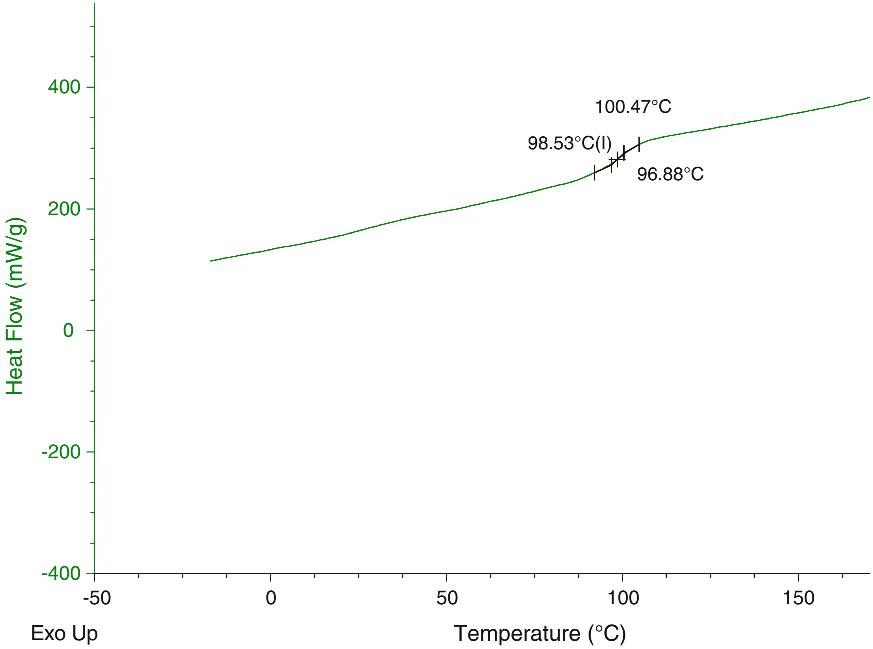


Fig. 3 DSC trace of ethylene norbornene copolymer with 40 mol % of NB, having T_g 98 °C, prepared from **1-ZrCl**/MAO

40 mol% of NB, having T_g 98 °C, prepared from **1**-ZrCl/MAO. Presence of one glass transition temperature for these copolymers further confirms their alternating behavior with uniform composition. It is very encouraging to know that effective incorporation of NB was feasible by using zirconium analogue of the titanium catalysts which also gave similar results.

Summary

The zirconium catalysts were moderately active for the homo and copolymerization of NB and ethylene. The catalyst activity in the case of ethylene polymerization was having a direct bearing with pressure and was comparable over the temperature range of 0–60 °C revealing the thermal stability also. The polymer produced was of HDPE type as evidenced from thermal and spectral studies. Copolymerization of ethylene and NB by using these catalysts was encouraging since it gave quantitative incorporation of the comonomer in the polyethylene back bone. The extent of comonomer incorporation was governed by the catalyst symmetry.

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