ETHENE/NORBORNENE COPOLYMERIZATION WITH (ISODICYCLOPENTADIENYL)TITANIUM COMPLEX–MAO CATALYST

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Dedicated to Dr Karel Mach on the occasion of his 70th birthday in recognition of his important contribution in organometallic chemistry.

Norbornene (NB) homopolymerization and ethene/NB copolymerizations with a silylene-bridged (isodicyclopentadienyl)(*tert*-butylamido)titanium dichloride–methylalumoxane (MAO) catalyst system were investigated. This catalytic system shows no efficiency towards NB homopolymerization but produces poly(ethene-*co*-norbornene)s. An increase in the initial NB feed content leads to a loss of copolymerization activity as well as NB copolymer incorporation. The structure of the isodicyclopentadienyl fragment (IsodiCp) has a strong limiting effect on comonomer incorporation possibilities.

Keywords: Amido-isodicyclopentadienyl ligand; Poly(ethene-*co*-norbornene); Titanium catalysts; Constrained geometry complexes; Copolymerization.

Development of *ansa*-isodicyclopentadienyl-amidotitanium and -zirconium complex technology for ethene copolymerizations makes possible the synthesis of new engineering materials. Bulky α-olefins like oct-1-ene[1–4], styrene[4] and cycloolefins[3,5–10] are known to be able to copolymerize with ethene in the presence of constrained geometry catalysts[11] (CGC). Polyethene-*co*-cycloolefin like norbornene materials are thermoplastics with excellent combination of properties. Norbornene (NB), which is more bulky than ethene (E), is incorporated in the polymer main chains. Depending on the monomer ratios, final copolymer characteristics can be very different. Higher NB ratios provide copolymers with higher glass temperatures and

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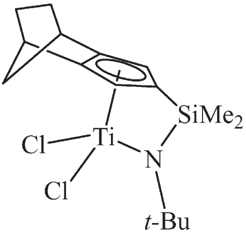
with better mechanical and optical properties. The material microstructure highly depends on the metallocene catalyst design such as the metal[5–8] and the nature of the cyclopentadienyl ligand[5–9] including nitrogen atom substitution[10]. Among all of the studies carried out on cyclopentadienyl fragments, reports involving the use of non-planar cyclopentadienyl examples have been few.

In our previous papers[12–17], it was demonstrated that Group 4 metallocenes and constrained geometry complexes featuring isodicyclopentadienyl ligands (IsodiCp = 4,7-methano-1*H*-indene-4,5,6,7-tetrahydroion(1–)-(9CI)) exhibit interesting results as Ziegler–Natta homogeneous catalysts. Isotactic and syndiotactic polypropylene were obtained with bis(isodicyclopentadienyl)titanium dichloride[15] and with silylene-bridged (isodicyclopentadienyl)fluorenylzirconium dichloride[12], respectively, and *exo*-[Ti{{(*t*-BuN)-Me_2Si}-η^5-isodicyclopentadienyl}Cl_2] (**1**)[17] produces styrene/ethene copolymer with good styrene incorporation.

In the light of positive preliminary polymerization results with *ansa*-isodicyclopentadienyl-amido complexes[13,17], the present paper reports the use of the **1**/MAO system for achieving E/NB copolymer formation.



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EXPERIMENTAL

All manipulations involving air-sensitive products were carried out under argon atmosphere. Toluene was dried and freshly distilled under argon from solution of $NaK_{2.8}$ prior to use. Ethene (N35) was purchased from Air Liquide and methylalumoxane (10 wt.% solution in toluene) from Crompton. NB (Aldrich) was purified by distillation and stored under argon. Complex **1** was synthesized according to the previously reported procedure using butyllithium to deprotonate the ligand, $TiCl_3(thf)_3$ for metallation, and subsequent treatment with CCl_4 [17].

E/NB copolymerizations were conducted in a 250-ml Büchi glass autoclave equipped with a magnetic stirrer. In the autoclave, MAO was added to a solution of 50 ml of dry toluene and the selected amount of NB in 10 ml of toluene solution under argon. The reactor was maintained at the desired temperature and pressurized with ethene (1 bar) for 30 min. A solution of **1** (20–50 mg) in toluene (5 ml) was then added via syringe. After the addition, the autoclave was pressurized with a monomer pressure of 4 bar and the reaction mixture was stirred for several minutes owing to the evolution of its viscosity. During the polymerization, monomer was fed continuously to maintain the desired pressure. Finally, the autoclave was vented, the reaction mixture was quenched with 10% HCl in methanol (30 ml), and stirring was maintained for 1 h. The precipitated polymer was collected by filtration, washed several times with water and methanol to remove Al residues and dried under vacuum for 1 day to a constant weight.

$^{13}C\ \{^{1}H\}$ NMR spectra were recorded with a Bruker DRX500 spectrometer with dilute (<10 mg/ml) polymer solution in 2,4,6-trichlorobenzene/C_6D_6 (4:1) at 343 K.

RESULTS AND DISCUSSION

E/NB copolymerizations were conducted with catalyst **1** at several monomers feed ratios. Reactions were carried out at 70 °C to conform to previously reported ethene/styrene results[17]. The examined catalyst proved to be stable during the polymerization reactions; selected runs are presented in Table I. As described in the literature for cyclopentadienyl-amido (CpA) catalysts[9], activities decrease when the E:NB monomer feed ratio decreases. The **1**/MAO system exhibits a polymerization activity of 390 kg of copolymer/(mol Ti) (mol NB+E) h with a E:NB ratio of 0.27 and the productivity reaches 580 kg of copolymer/(mol Ti) (mol NB+E) h with a higher E:NB ratio of 0.78.

Isodicyclopentadienyl ligand results are thus in the range of activities obtained with $[Ti\{\{(t\text{-}BuN)Me_2Si\}\text{-}\eta^5\text{-indenyl}\}Cl_2]$ (920 kg of copolymer/(mol Ti) (mol NB+E) h) for an E:NB ratio of 3.9 and far from the classical $[Ti\{\{(t\text{-}BuN)Me_2Si\}\text{-}\eta^5\text{-}C_5Me_4\}Cl_2]$ complex (10 500 kg of copolymer/(mol Ti) (mol NB+E) h)[9] with the same E:NB ratio. When NB homopolymerizations are conducted under the same experimental conditions (Table I, run 4), no

TABLE I
E/NB copolymerizations at 70 °C

Run	Al/Ti	Ti µmol	Time min	E:NB mol/mol	Yield %	Activity[a]	NB content[b] %
1	2000	44.8	6	0.78	2.78	580	13
2	2000	31.7	5	0.40	1.86	540	23
3	2000	39.6	7	0.27	3.94	390	11
4[c]	2000	21.5	60		0.00	0.00	
5[d]	2000	21	10		5.35	1530[e]	

[a] kg of copolymer/(mol Ti) (mol NB+E) h. [b] NB incorporation estimated by ^{13}C NMR spectra. [c] NB homopolymerization. [d] E homopolymerization[12]. [e] kg of PE/(mol Ti) h.

polynorbornene formation is observed[9]. Waymouth reported the isolation of a few mg of NB homopolymer with an extended reaction time of 8 days[9]. In that case, CGC complexes are found not to be efficient for homopolymerization.

An example of a spectrum of poly(ethene-*co*-norbornene) generated with our catalyst system (Table I, run 1) is presented in Fig. 1. The ^{13}C NMR NB/E copolymer spectrum contains a multitude of resonance signals depending on the material microstructure. Bridged biscyclopentadienylmetallocene systems[5,6,18–22] are known to produce copolymers containing NB microblocks and CpA catalysts are used more to generate isolated NB units or alternating copolymers[5–9] which give spectra that are easier to interpret. Resonance peak interpretations were made according to the reported literature[19,21,23,24]. ^{13}C NMR signals can be subdivided in four different groups. Resonance peaks at 47.6 and 48.2 ppm correspond to the two norbornene carbons C2 and C3 in the polymer main chains. The two peaks around 42 ppm can be assigned to the resonances of carbons C1 and C4, and C7 gives rise to one signal at 33.3 ppm. The methylene signals centered around 30 ppm are typical of the polyethene main chains and of the ethylene bridge carbons of NB. ^{13}C NMR spectroscopy reveals that no NB·NB or NB·NB·NB sequences are present in the copolymer. No resonance peaks above 48.2 ppm or between 36 and 40 ppm, corresponding to NB blocks, were detected, which is consistent with the CpA catalyst tendency to form isolated NB units or alternating copolymers. The norbornene incorporation

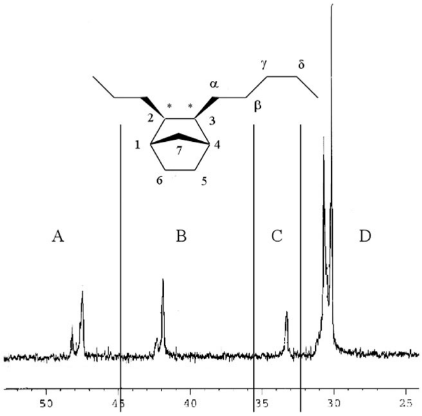

FIG. 1
^{13}C NMR spectrum of poly(ethene-*co*-norbornene) (run 1)

ratio was determined by comparing the intensity of the NB methylene bridge carbon C7 signal to the sum of intensities arising from the main chain methylene peaks. NB incorporation reaches a maximum value of 23% with *exo*-[Ti{{(*t*-BuN)Me_2Si}-η^5-isodicyclopentadienyl}Cl_2] (**1**). The isodicyclopentadienyl steric influence strongly limits norbornene incorporation when compared to its homolog [Ti{{(*t*-BuN)Me_2Si}-η^5-C_5Me_4}Cl_2] (46% max.) or to the bulky [Ti{{(*t*-BuN)Me_2Si}-η^5-*t*-BuC_5H_3}Cl_2] (35%)[9]. Surprisingly, decreasing the E:NB monomer feed ratio drops the NB polymer content. Such an insertion limitation is unexpected because of the open nature of the catalyst which allows insertion of larger monomers. The steric interactions between the inserting NB monomer units at the titanium active centre and the isodicyclopentadienyl ligand norbornane part are not favorable to high NB copolymer content.

CONCLUSION

E/NB materials can be made using the *ansa*-isodicyclopentadienyl-amidotitanium complex **1**. The tested catalyst is not active for NB homopolymerization under our experimental conditions. As a consequence, the resultant copolymers exhibit no NB microblocks; isolated NB units or alternating E/NB units result instead. The natural isodicyclopentadienyl steric hindrance limits both polymerization activities and comonomer incorporation. Additional experiments including other ethene/α-olefin copolymerizations with complex **1** have still to be performed for a more detailed understanding of isodicyclopentadienyl steric effects.

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REFERENCES

1. Pannell R. B., Canich J. A. M., Hlatky G. G. (Exxon): PCT Int. Appl. WO 94/00500 1994; *Chem. Abstr.* **1995**, *122*, 10940.
2. Canich J. A. M. (Exxon): Eur. Pat. Appl. 0 420 436 A1 1991, *Chem. Abstr.* **1991**, *115*, 184145.
3. Canich J. A. M. (Exxon): U.S. 5,096,867 1992, *Chem. Abstr.* **1992**, *118*, 60283.
4. Stevens J. C., Timmers F. J., Wilson D. R., Schmidt G. F., Nickias P. N., Rosen R. K., Knight G. W. (Dow): Eur. Pat. Appl. 0 416 815 A2 1991, *Chem. Abstr.* **1991**, *115*, 93163.
5. Ruchatz D., Fink G.: *Macromolecules* **1998**, *31*, 4669.
6. Ruchatz D., Fink G.: *Macromolecules* **1998**, *31*, 4674.
7. Ruchatz D., Fink G.: *Macromolecules* **1998**, *31*, 4681.

8. Ruchatz D., Fink G.: *Macromolecules* **1998**, *31*, 4684.
9. McKnight A. L., Waymouth R. M.: *Macromolecules* **1999**, *32*, 2816.
10. Harrington B. A., Crowther D. J.: *J. Mol. Catal. A: Chem.* **1998**, *128*, 79.
11. McKnight A. L., Waymouth R. M.: *Chem. Rev.* **1998**, *98*, 2587.
12. Gentil S., Dietz M., Pirio N., Meunier P., Gallucci J. C., Gallou F., Paquette L. A.: *Organometallics* **2002**, *21*, 5162.
13. Gentil S., Pirio N., Meunier P., Gallucci J. C., Schloss J. D., Paquette L. A.: *Organometallics* **2000**, *19*, 4169.
14. Gobley O., Meunier P., Gautheron B., Gallucci J. C., Erker G., Dahlmann M., Schloss J. D., Paquette L. A.: *Organometallics* **1998**, *17*, 4897.
15. Zaegel F., Gallucci J. C., Meunier P., Gautheron B., Bzowej E. I., Paquette L. A.: *Organometallics* **1995**, *14*, 4576.
16. Fritze C., Knickmeier M., Erker G., Zaegel F., Gautheron B., Meunier P., Paquette L. A.: *Organometallics* **1995**, *14*, 5446.
17. Gentil S., Pirio N., Meunier P., Gallou F., Paquette L. A.: *Eur. Polym. J.* **2004**, *40*, 2241.
18. Kaminsky W., Schupfner G.: *Macromol. Symp.* **2002**, *177*, 61.
19. Wendt R. A., Fink G.: *Macromol. Chem. Phys.* **2001**, *202*, 3490.
20. Wendt R. A., Fink G.: *Macromol. Chem. Phys.* **2000**, *201*, 1365.
21. Wendt R. A., Mynott R., Hauschild K., Ruchatz D., Fink G.: *Macromol. Chem. Phys.* **1999**, *200*, 1340.
22. Bergström C. H., Sperlich B. R., Ruotoistenmäki J., Seppälä J.: *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1633.
23. Arnd-Rosenau M., Beulich I.: *Macromolecules* **1999**, *32*, 7335.
24. Provasoli A., Ferro D. R., Tritto I., Boggioni L.: *Macromolecules* **1999**, *32*, 6697.