

Influence of the Polymerization Conditions on the Impact Properties of Metallocene-Catalyzed Copolymers of Ethylene and Aryl-Substituted Norbornenes with Low Exo/Endo Ratios

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ABSTRACT: When testing copolymers of ethylene and aryl-substituted norbornenes with the Charpy impact method it was found that under certain polymerization conditions their impact properties increased with increasing polymerization time. It was also found that this improvement on impact properties was due to increasing exo/endo ratios of the incorporated aryl-substituted norbornene comonomers. This effect is important because impact-resistant copolymers can be made using aryl-substituted norbornene comonomers with low exo/endo ratios, which are more easily synthesized and purified.
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Key words: cyclic olefin copolymers; phenylnorbornene; indanylnorbornene; metallocene catalysts; NMR; impact-resistance

INTRODUCTION

Norbornene-ethylene copolymers are manufactured in the semicommercial scale using metallocene catalysts and methylaluminoxane (MAO) as cocatalyst.^{1–3} Amorphous and heat-resistant cyclic olefin copolymers (COC) are marketed by Ticona⁴ of Frankfurt, Germany (TOPAS) and Mitsui Chemical⁵ of Tokyo, Japan (APEL). Other important features are good opticals, low water take-up and permeability, good electrical properties, and bio-compatibility.^{2,3} The impact properties are, however, not good enough but can be

improved by orientation or blending.² Targeted applications are packaging, blisterpack, and capacitor films (biaxially oriented), syringes, bottles, and vials for medical use, as well as lenses, prisms, and displays.³

By using phenylnorbornene (PN) or indanylnorbornene (IN) instead of or in addition to norbornene the impact properties of COC can be improved and the higher the exo/endo ratio of these comonomers the better the impact properties.^{6,7} However, when synthesizing substituted norbornenes with higher exo/endo ratios higher temperatures are needed in the Diels-Alder reaction, which at the same time tends to increase the amount of impurities.⁸ It is therefore of great importance to be able to use PN or IN that have been synthesized under conditions providing as

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pure comonomers as possible and obtain COC with good impact properties in spite of low exo/endo ratios of the comonomers.

The intention with this study was to find out under what conditions good impact properties can be obtained and what the mechanism is.

EXPERIMENTAL

Apparatus and Polymerization Method

The polymerization was done using a semiflow method and a reactor system described in detail in an earlier paper of our group.⁹ The comonomer was dissolved in toluene and diluted to 100 mL or 200 mL for a 500-mL reactor and 400 mL for a 1000-mL reactor. The solution was dried with molecular sieves overnight and poured into the thermostated stainless steel reactor equipped with a stirrer. After purging with nitrogen and ethylene the ethylene pressure and the temperature of the reactor content were set at the chosen values and ethylene was supplied until the toluene solution was saturated and the ethylene flow stopped. Then half of the MAO was added to the reactor and mixed with the monomer solution for a chosen time (0–120 min) before the pretreated catalyst solution was added and the polymerization started. This catalyst solution contained the metallocene catalyst dissolved in toluene and pretreated for 15 min at room temperature with half of the MAO. The concentrations of metallocene catalyst in the polymerizations were $1.2\text{--}4.9 \times 10^{-5}$ M in the 500-mL reactor and 3.6×10^{-5} M in the 1000-mL reactor. The polymerization was allowed to continue for 15–180 min, the ethylene consumed in the polymerization was constantly replaced, and the pressure and temperature were automatically controlled. No hydrogen or other chain transfer agents were used. After the polymerization the ethylene supply was shut, the reactor vented, and the reactor content poured into ethanol (300 mL). Then hydrochloric acid was added in order to deactivate MAO, and the sample was kept that way until the next day when it was filtered, washed with acetone, filtered again, and dried in a vacuum oven.

Chemicals

The comonomers, PN (5-phenyl-bicyclo-(2,2,1)-hept-2-ene) and IN (1,4-methano-1,4,4a,9a-tetrahydrofluorene) were made in the pilot scale by reacting dicyclopentadiene with styrene and indene, re-

spectively. In order to obtain a pure product this Diels-Alder reaction was done at a rather low temperature, 180°C, by adding dicyclopentadiene gradually to the dienophile during 2 h. Under such conditions the exo/endo ratios of the comonomers are low, but the purification through vacuum distillation is easier.⁸ The purified comonomers were analyzed with ¹H-NMR and the contents of exo-diastereomer were 17% for PN and 19% for IN.¹⁰

The ethylene used was AGA's grade 2.7, which was further purified in columns containing molecular sieves, CuO, and Al₂O₃ before entering the reactor, and the toluene used was Riedel – de Häen's grade RG.

The catalysts were the soluble racemic ansa-metallocene catalysts ethylene bis (indenyl) zirconium dichloride (A; EURECEN 5036 from CK Witco of Greenwich, CT, USA) and dimethylsilyl bis (indenyl) zirconium dichloride (B; TA 02720 from CK Witco of Greenwich, CT, USA). The cocatalyst was 10 wt % MAO in toluene from CK Witco of Greenwich, CT, USA. The Al content of the cocatalyst was 4.5–5.5 wt %.

Polymer Characterization

The concentrations of PN and IN in the copolymers as well as the diastereomer ratios in the comonomers and the copolymers were measured by 600 MHz ¹H-NMR spectroscopy. The spectra were obtained at 100°C with dideutero-1,1,2,2-tetrachloroethane as solvent. A wide spectral width of 15 000 Hz (25 ppm) was used in order to confirm that no folding of possible impurity signals occurs and that no filtering of signals affects the results. A 20° pulse angle, an acquisition time of 1.0 s with 32 000 data points was used to accumulate 32 scans for integration of the signals. In order to obtain the concentrations of comonomer the areas of aromatic hydrogens (6–8 ppm) were measured and related to the areas of paraffinic hydrogens (1–4 ppm) and corrected for the paraffinic hydrogens of the comonomer. The exo/endo ratios were obtained from the areas representing the hydrogens in geminal position to the aromatic groups. For PN exo appears at 2.7 ppm and endo at 3.2 ppm and for IN the equivalent signals appear at 3.1 ppm and 3.6 ppm.¹⁰ Also ¹³C-NMR spectra were made in order to obtain heteronuclear multiple quantum coherence (hmqc) spectra, which provide the ¹H – ¹³C one-bond correlations.

The weight average molecular weights (\bar{M}_w), number average molecular weights (\bar{M}_n), and the molecular weight distributions (\bar{M}_w/\bar{M}_n) were

Table I Influence of Concentration of PN and IN as well as Polymerization Time on Comonomer Incorporation and Glass Transition Temperature of Ethylene Copolymers Polymerized at 50°C and 4 Bar Ethylene Absolute Pressure using Ethylene Bis (Indenyl) Zirconium Dichloride as Catalyst and 3000 Al/Zr as MAO

Run	Comonomer in the Feed		Time (min)	Catalyst (mg)	Yield (g)	Activity (10^6 g/mol Zr h bar)	Comonomer Incorporated (mol %)	Comonomer Conversion (%)	T_g (°C)
	(g/200 mL)	(mol %)							
1	9.1	40 PN	15	2	11.1	2.3	14	60.4	21
2	13.7	50 PN	15	2	10.4	2.2	15	51.9	41
3	13.7	50 PN	60	2	17.7	0.9	17	71.5	40
4	20.5	60 PN	15	2	5.1	1.1	20	15.1	55
5	20.5	60 PN	60	2	17.7	0.9	20	52.2	54
6	32.0	70 PN	15	2	1.3	0.3	22	2.5	77
7	32.0	70 PN	60	2	5.4	0.3	23	10.9	74
8	54.8	80 PN	15	4	0.8	0.04	28	1.1	103
9	54.8	80 PN	60	2	0.4	0.02	29	0.5	101
10	3.6	20 IN	15	1	13.2	5.5	8	88.9	15
11	6.3	30 IN	15	1	4.7	2.0	9	28.6	16
12	9.8	40 IN	15	1	0.4	0.2	12	2.0	37
13	14.7	50 IN	15	2	1.1	0.2	15	4.1	62
14	14.7	50 IN	60	2	16.4	0.9	17	63.9	70
15	21.9	60 IN	15	4	14.2	1.5	22	42.0	99
16	21.9	60 IN	60	4	19.7	0.5	24	60.5	106

measured by gel permeation chromatography (GPC). The equipment used was a Waters 150 ALC equipped with three (Polymer Laboratories) columns (10^3 , 10^5 , and 10^6 Å) and 1,2,4-trichlorobenzene as solvent. The temperature was 140°C and the flow rate 1 mL/min. Because the columns were calibrated universally with narrow molecular weight polystyrenes, the results are not absolute but relative.

The glass transition temperatures (T_g) of the copolymers were measured using a Mettler – Toledo TA 8000 DSC (differential scanning calorimeter). The sample was first heated to 200°C, then cooled to -20°C ($20^\circ\text{C}/\text{min}$), and after that heated again to 200°C ($20^\circ\text{C}/\text{min}$). The data used in this publication were taken from the second heating. No crystalline melting point was observed for any of the copolymers included in this study. The impact resistance of the copolymers was tested according to the unnotched Charpy method (ISO 179) using compression-molded plaques.

RESULTS AND DISCUSSION

Influence of the Concentration of PN and IN on the Glass Transition Temperature

Different amounts of PN and IN were copolymerized with ethylene at 50°C and 4 bar absolute

ethylene pressure for 15 and 60 min using the 500-mL reactor and 200-mL toluene solutions. One to four milligrams ($1.2\text{--}4.9 \times 10^{-5}$ M) of ethylene bis (indenyl) zirconium dichloride was

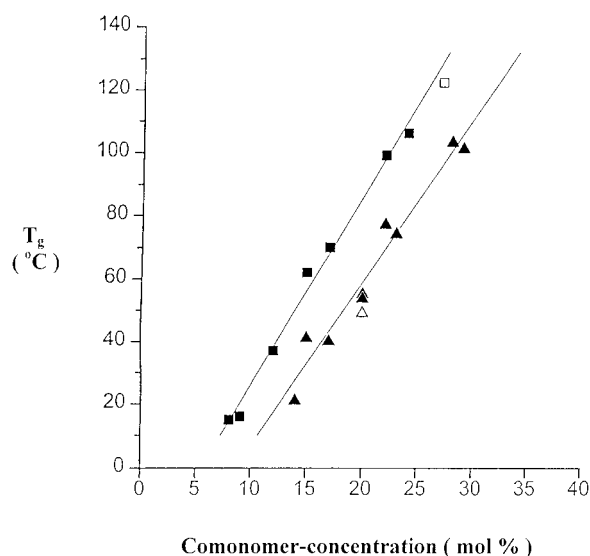


Figure 1 Influence of different aryl-substituted norbornenes on the T_g of their ethylene-copolymers: (■) Indanylnorbornene, 19% exo; (□) Indanylnorbornene, 59% exo; (▲) Phenylnorbornene, 17% exo; (△) Phenylnorbornene, 100% exo.

Table II Influence of Exo/Endo Ratio of IN in the Feed on the Impact Properties of IN-Ethylene Copolymers Polymerized for 15 min using 6.3 g/100 mL IN, 50°C, 2 Bar Ethylene Absolute Pressure, 4.8×10^{-5} M (2 mg) Ethylene Bis (Indenyl) Zirconium Dichloride as Catalyst and 3000 Al/Zr as MAO

Run	IN in the Feed (% exo)	Yield (g)	Activity (10^6 g/mol Zr h bar)	IN in the Copolymer		T_g (°C)	Charpy Impact Unnotched (kJ/m ²)
				(mol %)	(% exo)		
17	9	7.4	3.1	25	10	121	6.2
18	46	2.4	1.0	28	47	122	6.4
19	59	3.4	1.4	27	57	122	6.9

used with 3000 Al/Zr as MAO. The detailed polymerization conditions and results are seen in Table I and T_g vs. comonomer incorporation is presented in Figure 1.

In Figure 1 are also plotted two ethylene copolymers that have been polymerized using comonomers with very high exo/endo ratios. PN composed of 100% exo-diastereomer was synthesized from norbornadiene and iodobenzene¹¹ and IN composed of 59% exo-diastereomer was obtained by separation with a solution crystallization method.¹² The detailed preparation procedures of these comonomers are confidential. The polymerization conditions used for the fractionated IN are presented in Table II.

One can see from Figure 1 that the stiffening effect on the polymer chain (T_g) is stronger for IN than for PN. These same correlations have also been obtained for other metallocene catalysts and other polymerization conditions and the conversion of comonomer does not seem to have any significant effect. What is also surprising is that an increasing exo/endo ratio of the comonomer did not increase the stiffness of the polymer chains that was predicted from molecular modelling of isolated copolymer chains. For corresponding incorporations of comonomer the T_g s were also higher than for norbornene-ethylene copolymers. In the literature, however, very many correlation curves for T_g vs. norbornene incorporation have been presented. To achieve a T_g of 110°C, Kaminsky et al.¹³ needed 57 mol %, Abe et al.¹⁴ 47 mol %, and Benedikt et al.¹⁵ 42 mol %. In our studies we have also found that 42 mol % is enough when the polymerization has been done under conditions that minimize the formation of block and alternating sequences.¹⁰ In cases when a lot of block and alternating sequences have been obtained not more than 32 mol % norbornene incorporation has been needed to reach a T_g of 110°C.^{16,17}

In a previous work the existence of isolated, alternating, and block sequences of norbornene has been demonstrated using the hmqc technique¹⁸ and a dependence on the polymerization conditions has been shown.¹⁷ hmqc spectra of two PN-ethylene copolymers have also been made using the same method and for 34 mol % PN (Run 22, Fig. 2) two new cross-peaks were obtained that could not be found for 7 mol % PN (Fig. 3) that must be considered as random. In our previous work with norbornene-ethylene copolymers only two cross-peaks were obtained from the tertiary carbons of the comonomer in the random copoly-

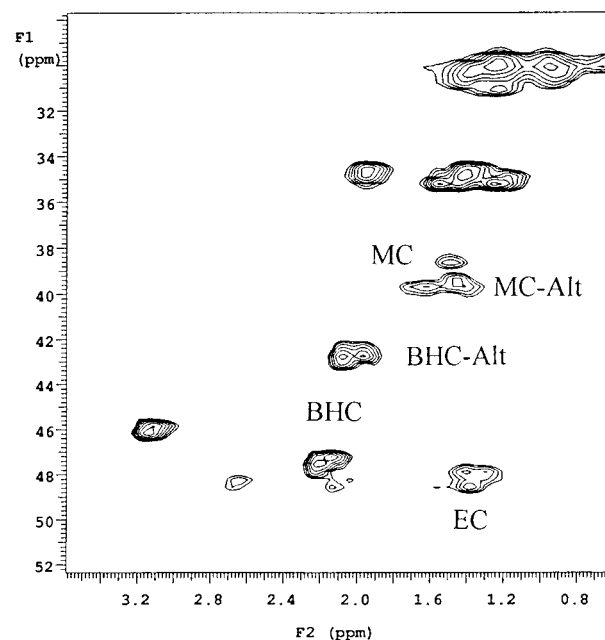


Figure 2 Heteronuclear multiple quantum coherence (hmqc) spectrum for a phenylnorbornene-ethylene copolymer (34 mol %) showing the existence of isolated and alternating sequences (Alt) of phenylnorbornene: BHC, bridgehead carbons; EC, enchained carbons; MC, methylene carbon adjacent to the phenyl group.

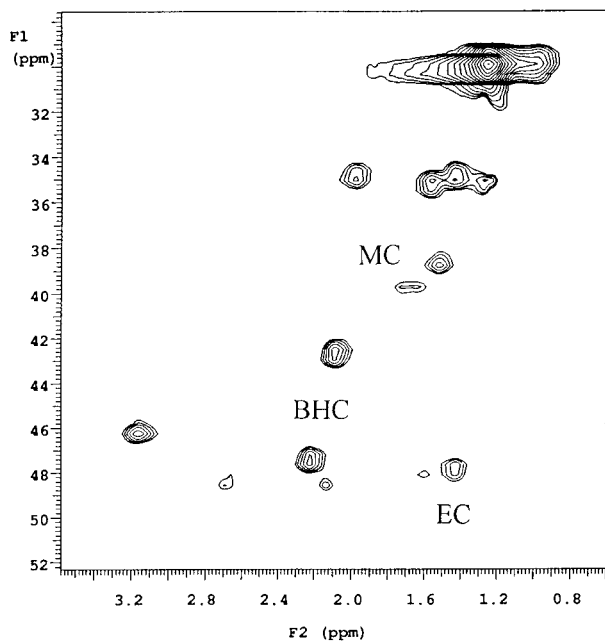


Figure 3 Heteronuclear multiple quantum coherence (hmqc) spectrum for a phenylnorbornene-ethylene copolymer (7 mol %) showing the existence of only isolated sequences of phenylnorbornene: BHC, bridgehead carbons; EC, enchained carbons; MC, methylene carbon adjacent to the phenyl group.

mer. One cross-peak for the bridgehead carbon pairs appeared in the ^{13}C -NMR spectrum at 42 ppm and another cross-peak for the enchained carbon pairs appeared at 47 ppm.¹⁸ For the PN-ethylene random copolymer in Figure 3, however, there were three cross-peaks for the bridgehead carbons (BHC), two cross-peaks for the enchained carbons (EC), and two cross-peaks for the methylene carbons (MC) adjacent to the phenyl group due to the asymmetry of the comonomer and the existence of two diastereomers. The detailed assignments can be seen from a ^1H -NMR-spectrum presented in a previous work.¹⁰ When increasing the incorporation of PN to 34 mol % (Fig. 2) the hmqc spectrum obtained was still rather simple. Clearly one new cross-peak appeared for the bridgehead carbon opposite the phenyl group (BHC-Alt) and another one for the methylene group opposite the phenyl group (MC-Alt). Also, in our previous work on norbornene-ethylene copolymers the alternating sequences created only two new cross-peaks, one for the BHC and one for the EC whereas the block sequences (diads) created four additional cross-peaks. One can also expect that PN diads would create even more cross-peaks than norbornene did because there

are so many theoretically possible combinations of diastereomers as well as regio and stereo configurations. We therefore concluded that no PN diads appeared in Run 22 nor in any other of the PN-ethylene copolymers presented in this study. There are only random and alternating sequences. The very good correlations of T_g vs. comonomer incorporation for PN and IN regardless of polymerization conditions can also be explained from their lack of block sequences. One can also understand that big monomers such as PN and IN are sterically hindered to form block sequences.

Influence of the Exo/Endo Ratio of the IN Comonomer

It has been shown in a previous work that PN-ethylene copolymers with higher exo/endo ratios have better impact properties.⁷ A high exo/endo ratio in the copolymer can be obtained by using a comonomer with a high exo/endo ratio and it can be further increased by optimizing the polymerization conditions. Now we wanted to find out if the exo/endo ratio of IN also have this effect.

Table II presents the results obtained for IN-fractions containing 9, 46, and 59% exo-diastereomer. One hundred milliliters of toluene solutions containing 6.3 g of the IN fractions were made and allowed to polymerize for 15 min at 50°C and 2 bar absolute ethylene pressure. The concentration of ethylene bis (indenyl) zirconium dichloride was 4.9×10^{-5} M (2 mg) and the concentration of MAO was 3000 Al/Zr.

Surprisingly about the same comonomer incorporations and T_g s were obtained for the fractions and they correlate very well with the results obtained when using IN containing 19% exo-diastereomer and presented in Figure 1. However, there was no significant improvement in Charpy impact when the exo/endo ratio in the copolymer increased which is different from what we have seen for PN-ethylene copolymers. In addition, the exo/endo ratio in the copolymer was about the same as in the comonomer, which is also different from the copolymerization of PN with ethylene where the exo-concentration increased.

Influence of Some Polymerization Conditions on the Exo/Endo Ratio and the Properties of PN-Ethylene Copolymers

Because PN with lower exo-concentrations (<20%) are easier and more economical to manufacture in

Table III Influence of Mixing 75 g/400 mL (85 mol %) PN with MAO (1000 Al/Zr) on the Properties of Phenylnorbornene-Ethylene Copolymers Polymerized for 30 min at 50°C and 2 Bar Ethylene Absolute Pressure Using 3.6×10^{-5} M (6 mg) Ethylene Bis (Indenyl) Zirconium Dichloride as Catalyst and 2000 Al/Zr as MAO

Run	Mixing of PN with MAO (min)	Yield (g)	Activity (10^6 g/mol Zr h bar)	PN in the Copolymer		T_g (°C)	Charpy Impact Unnotched (kJ/m ²)
				(mol %)	(% exo)		
20	0	2.6	0.2	31	17	121	5.8
21	15	16.0	1.1	32	19	128	4.5
22	30	21.0	1.5	34	18	130	4.6
23	60	19.6	1.4	33	14	127	4.1
24	120	18.8	1.3	35	12	126	3.0

the commercial scale⁸ and the route via norbornadiene and iodobenzene¹¹ is not a practical production method it is of great interest to study how the impact properties can be improved using PN with a low exo-concentration (17%). Because we have found that the exo/endo ratio increases during the polymerization⁷ it is obvious that the length of one or several of the working steps involved will have an influence on the exo/endo ratio in the copolymer and hence the Charpy impact strength.

The first working step that could have an influence is the mixing of the PN-toluene-ethylene solution with MAO before the polymerization. MAO of course reacts with water and other catalyst poisons but one could also suspect a catalytic effect on the isomerization of PN. In the literature isomerization reactions from endo to exo under the influence of solid acid catalysts have been presented.¹⁹

Table III presents the influence of the mixing time of the monomers with MAO before polymerization. Four hundred milliliters of toluene solutions containing 75 g PN (85 mol %) were made and polymerized for 30 min in the 1000 mL reactor at 50°C and 2 bar absolute ethylene pressure. The concentration of ethylene bis (indenyl) zirconium dichloride was 3.6×10^{-5} M (6.0 mg) and the concentration of MAO 2000 Al/Zr. Half of MAO was mixed with the monomer solution before polymerization and the other half was used for preactivation of the catalyst (15 min). The mixing times were 0, 15, 30, 60, and 120 min. One can see that by mixing MAO with the monomer solution for 30 min before polymerization the yield was increased and the PN concentration and T_g were at their maximum. However, the exo/endo ratio, surprisingly, decreased when mixing

for more than 60 min resulting in decreasing Charpy impact strength.

Using the same conditions as above but treating the monomer solution with MAO for 30 min the influence of different polymerization times was investigated and the results are seen in Table IV. Also 3.6×10^{-5} M (6.3 mg) of dimethylsilyl bis (indenyl) zirconium dichloride was tested at two different polymerization times, 60 and 180 min. It can be clearly seen that the exo/endo ratio of PN and hence the Charpy impact strength increased with increasing polymerization time. This is not expected to be mainly due to a decreasing comonomer concentration leading to copolymer molecules with lower comonomer incorporations and therefore increased chain mobility. One can expect that the increasing concentration of copolymer in the solution at the same time decreased the solubility of ethylene so that the monomer ratio did not change significantly as a function of time. The polymerizations presented in Table I indicated that the conversion of comonomer does not have much influence on the comonomer incorporation. The molecular weight (\bar{M}_w) and its distribution (\bar{M}_w/\bar{M}_n) increased slightly when increasing the polymerization time from 30 to 60 min, after which they remained rather constant. These effects of polymerization time did, however, not appear when using the catalyst dimethylsilyl bis (indenyl) zirconium dichloride (B) and the exo/endo ratios were about the same as in the comonomer. In addition the activities and molecular weights were very low and the molecular weight distributions were somewhat broader.

The observation that when using the catalyst ethylene bis (indenyl) zirconium dichloride (A) the exo/endo ratio actually increased with an increasing polymerization time even if the mixing of

Table IV Influence of Polymerization Time on the Properties of PN-Ethylene Copolymers Polymerized from 75 g/400 mL (85 mol %) PN at 50°C and 2 Bar Ethylene Absolute Pressure Using 3.6×10^{-5} M (6.0 mg) Ethylene Bis (Indenyl) Zirconium Dichloride (A) or 3.6×10^{-5} M (6.3 mg) Dimethylsilyl Bis (Indenyl) Zirconium Dichloride (B) as Catalyst and 2000 Al/Zr as MAO^a

Run	Polymerization				PN in the Copolymer		<i>T_g</i> (°C)	GPC Data			Charpy Impact Unnotched (kJ/m ²)
	Time (min)	Catalyst	Yield (g)	Activity (10 ⁶ g/mol Zr h bar)	(mol %)	(% exo)		\bar{M}_w (10 ³ g/mol)	\bar{M}_n (10 ³ g/mol)	\bar{M}_w/\bar{M}_n	
22	30	A	21.0	1.5	34	18	130	275	162	1.7	4.6
25	60	A	23.0	0.8	32	20	121	463	191	2.4	4.7
26	120	A	39.4	0.7	33	21	124	439	153	2.9	4.9
27	180	A	69.3	0.8	31	24	118	409	174	2.3	6.3
28	60	B	2.4	0.08	31	18	119	38	11	3.5	4.5
29	180	B	4.0	0.05	29	17	118	41	12	3.4	4.4

^a One thousand Al/Zr of MAO was mixed with the monomer solution for 30 min before polymerization.

MAO with the monomers had an opposite effect indicates that it is the catalyst-MAO-complex that is effective. It is proposed that the catalyst-MAO-complex changes over time due to, for instance, an interaction with the aromatic group of the comonomer and favors insertion of the exo-diastereomer.

In order to study the effects of concentration and time of the catalyst-MAO-complex on the polymer properties the experiments presented in Table V were made with a constant polymerization time of 120 min. Run 26 in Table IV was modified so that the activated catalyst was added twice in equal amounts (3.0 mg) at different times. The second addition of activated catalyst took place 90, 60, and 30 min after the first addi-

tion. By doing so the exo/endo ratio and the Charpy impact strength decreased. This indicates that when half of the catalyst-MAO-complex is very fresh and therefore less favorable for insertion of the exo-diastereomer, the concentration of which is lower at the end of the polymerization, the total exo-concentration in the polymer decreases. This would also explain the higher yields for these polymerizations. If there were a catalytic isomerization from endo to exo one would have more of the exo-diastereomer at the end of the polymerization and when adding more catalyst-MAO-complex in this stage the overall exo-concentration would increase. We therefore propose a catalyst-MAO-complex that changes as a function of time and makes the insertion of the

Table V Influence of the Time the Preactivated 3.6×10^{-5} M (6.0 mg) Ethylene Bis (Indenyl) Zirconium Dichloride Catalyst (A) has been in Contact with the Monomer Solution when 75 g/400 mL (85 mol %) PN was Copolymerized with Ethylene for 120 min at 50°C, 2 Bar Ethylene Absolute Pressure, and 2000 Al/Zr as MAO^a

Run	50% of the Catalyst Added (min)	Yield (g)	Activity (10 ⁶ g/mol Zr h bar)	PN in the Copolymer		<i>T_g</i> (°C)	GPC Data			Charpy Impact Unnotched (kJ/m ²)
				(mol %)	(% exo)		\bar{M}_w (10 ³ g/mol)	\bar{M}_n (10 ³ g/mol)	\bar{M}_w/\bar{M}_n	
26	0	39.4	0.7	33	21	124	439	153	2.9	4.9
30	90	56.6	1.0	31	19	116	392	163	2.4	4.2
31	60	39.7	0.7	34	17	131	364	170	2.1	2.7
32	30	46.1	0.8	34	16	127	323	162	2.0	1.9

^a One thousand Al/Zr of MAO was mixed with the monomer solution for 30 min before polymerization.

Table VI Influence of Polymerization Time on the Properties of PN-Ethylene Copolymers Polymerized from 75 g/400 mL (73 mol %) or 150 g/400 mL (85 mol %) PN at 50°C and 4 Bar Ethylene Absolute Pressure using 3.6×10^{-5} M (6.0 mg) Ethylene Bis (Indenyl) Zirconium Dichloride (A) or 3.6×10^{-5} M (6.3 mg) Dimethylsilyl Bis (Indenyl) Zirconium Dichloride (B) as Catalyst and 2000 Al/Zr as MAO^a

Run	Polymerization				PN in the Copolymer		<i>T_g</i> (°C)	GPC Data			Charpy Impact Unnotched (kJ/m ²)	
	Time (min)	PN (g)	Catalyst	Yield (g)	Activity (10 ⁶ g/mol Zr h bar)	(mol %)		(% exo)	\bar{M}_w (10 ³ g/mol)	\bar{M}_n (10 ³ g/mol)		\bar{M}_w/\bar{M}_n
33	30	75	A	82.7	2.9	28	23	97	320	89	3.6	6.1
34	90	75	A	89.6	1.0	27	27	93	1100	195	5.6	9.0
35	90	75	B	3.4	0.04	26	17	92	123	30	4.1	5.3
36	180	75	B	4.1	0.02	25	18	87	131	31	4.2	5.5
37	30	150	A	15.6	0.5	31	23	122	311	97	3.2	5.4
38	90	150	A	71.8	0.8	31	24	116	432	117	3.7	5.6

^a One thousand Al/Zr of MAO was mixed with the monomer solution for 30 min before polymerization.

exo-diastereomer more favorable. When adding fresh catalyst later on during the polymerization the molecular weights decreased slightly and the molecular weight distributions became narrower. However, the differences are so small that it cannot be the reason for the decreasing Charpy impact strengths. On the other hand, it indicates that the longer the catalyst-MAO-complex has been present in the reactor the more stressed are the effects of changing active sites.

In order to further test the theory of changing active sites some polymerizations were also made at 4 bar absolute ethylene pressure but otherwise with the same conditions as in Tables III–V. In Table VI one can see that when 75 g PN (73 mol %) was polymerized the *T_g* level was of course lower due to the higher ethylene concentration. Therefore two polymerizations with 150 g PN (85 mol %) were also made to see the influence of the ethylene pressure when keeping the same *T_g* level. One can see that for both PN concentrations the exo/endo ratio and the Charpy impact strength increased with polymerization time and that the effects were greater compared to the results obtained for 2 bar absolute ethylene pressure. In addition a broadening of the molecular weight distribution was observed when using a higher ethylene pressure and longer polymerization times.

When increasing the ethylene pressure and keeping the catalyst and cocatalyst concentrations (the concentrations of active sites) the same the speed of ethylene insertion and as a conse-

quence the insertion of PN increase, which means that all the effects seen at a lower ethylene pressure are more stressed. The exo-diastereomer is incorporated more rapidly which increases the exo/endo ratio in the polymer and decreases the exo/endo ratio of the unreacted comonomer at a certain polymerization time. This faster change of the monomer composition also seems to change the nature of the active sites more rapidly. The molecular weight distribution becomes very broad already after 90 min polymerization, especially for the lower comonomer concentration (Run 34), the composition of which changes more rapidly than for the corresponding polymerization with a higher comonomer concentration (Run 38). One possibility is that the phenyl groups of PN interact with the zirconium atom of the metallocene catalyst in a similar way as in the polymerization of syndiotactic polystyrene.²⁰ Because these phenyl groups are of two types, endo- and exo-substituents, one can assume two types of active sites whose relative concentrations change as a function of time.

Finally all Charpy impact results of this study were plotted vs. the exo-concentration of the incorporated PN and presented in Figure 4. It can be seen that despite differences in the molecular weight and its distribution as well as the concentration of PN there is a correlation between impact strength and exo-concentration. Generally speaking the PN-ethylene copolymers made at the higher ethylene pressure providing lower *T_g*s had slightly better Charpy

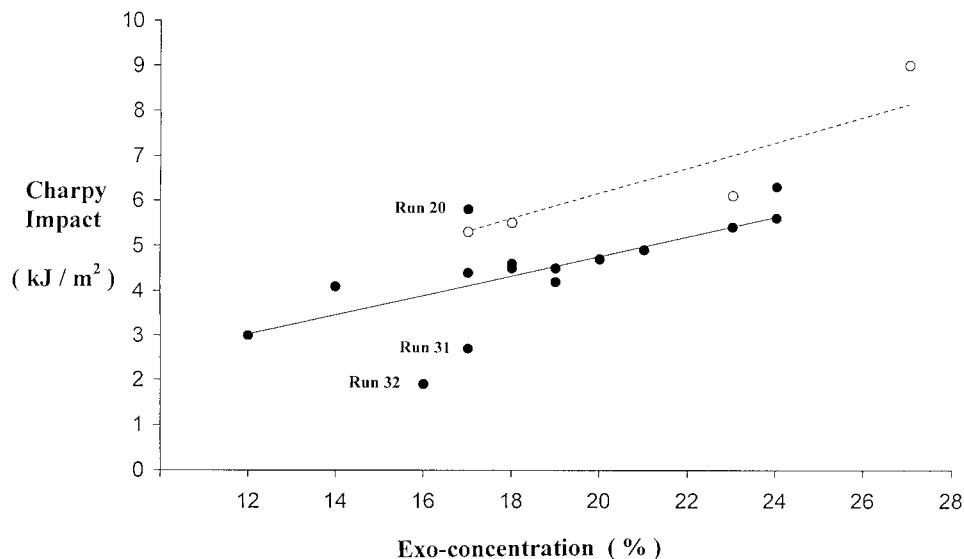


Figure 4 Charpy impact strength vs. exo-concentration of the PN incorporated in phenylnorbornene-ethylene copolymers: (—○—) $T_g = 87^\circ\text{C}–97^\circ\text{C}$; (—●—) $T_g = 116^\circ\text{C}–131^\circ\text{C}$.

impact strengths than were obtained for the higher T_g s. The copolymers that differed most from a correlation were Run 20 (no mixing of the comonomer with MAO) and Runs 31 and 32 (more catalyst added in a later stage) and these polymerizations must be considered to be very special. This same trend has been presented in an earlier work in which the PN comonomer contained 27% exo-diastereomer.⁷

CONCLUSIONS

When copolymerizing PN or IN with ethylene using the metallocene catalysts ethylene bis (indenyl) zirconium dichloride or dimethylsilyl bis (indenyl) zirconium dichloride and MAO, T_g increased linearly with increasing comonomer incorporation. For corresponding molar concentrations of comonomers the T_g for the IN-ethylene copolymers were higher than for the PN-ethylene copolymers, which in turn were higher than most published T_g data for norbornene-ethylene copolymers. These correlations were also independent of the ratio of exo- and endo-diastereomers. In contrast to norbornene-ethylene copolymers, these PN-ethylene and presumably also IN-ethylene copolymers did not indicate any block sequences. When copolymerizing PN with ethylene using ethylene bis (indenyl) zirconium dichloride the exo/endo ratios in the copolymers were higher

than in the monomer and the exo/endo ratios increased with increasing polymerization time and ethylene pressure. When using dimethylsilyl bis (indenyl) zirconium dichloride or IN, however, the exo/endo ratios were about the same in the copolymers as in the comonomers. Because the exo-diastereomer polymerized more rapidly than the endo-diastereomer the monomer composition changed as a function of time which seems to have changed the active sites. This shows up in broader molecular weight distributions, higher exo/endo ratios, and higher Charpy impact strengths for longer polymerization times.

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